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VOLUME 3

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A Specialist Periodical Report

Inorganic Reaction Mechanisms

Volume 3

A Review of the Literature Published
between December 1971 and June 1973

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Foreword

The format, coverage, and approach of this third volume dealing with Inorganic Reaction Mechanisms are similar to those for the previous volumes. In view of the appearance of the Specialist Periodical Reports on Organometallic Chemistry, we have been much more selective in our choice of references in this area. We have concentrated on references in which kinetics or reaction mechanisms form the principal interest, rather than attempting, as in the first two volumes, to cite all references with some mention of kinetics or mechanism. Solvent effects on reactivities and mechanisms of inorganic reactions, which were somewhat neglected in Volume 2, are considered in a separate chapter in this volume.

The nominal period for coverage of the literature is December 1971 to July 1973, inclusive. However, the boundaries at both ends of this period are somewhat vague. Some pre-December 1971 references, omitted from Volume 2 because of late arrival of journals, are included in the present volume. Conversely many references later than July 1973, some from issues dated as late as October 1973, have been included. The hazy end-of-coverage date merely reflects the differences between the dating habits and distribution efficiencies of the various journals.

Material which is derived from *Chemical Abstracts* rather than directly from the original source is indicated by the inclusion of a *Chemical Abstracts* citation in the reference quoted. References to Russian journals which give a transliteration of the Russian title of the journal give the page number of the Russian original, and have been derived from *Chemical Abstracts*; references which give the title of the English translation quote the page number from the translation. Mention of review articles is generally restricted to those which are readily accessible to most readers.

We have usually reported kinetic results in the form (E_a plus log A *versus* $\Delta H^{\neq}$ plus $\Delta S^{\neq}$) or units (SI or other) used in the original publication, though some conversions have been effected to make comparisons easier, particularly within tables.

The Reporters are grateful to many of their colleagues for suggestions and comments. In particular we would like to express our appreciation of the valuable help rendered by Drs J. S. Coe, D. R. Rosseinsky, G. Stedman, and A. G. Sykes in reading sections of the manuscript. Without their assistance the number of errors and infelicities in this volume would have been much greater.

J. B.

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Abbreviations for Ligands and Solvents

Abbreviations which appear only once in the text are generally defined at their point of use; those which appear more than once are defined below.

General

R	alkyl, aryl
L	unidentate ligand
LL	bidentate ligand
LLL	terdentate ligand
LLLL	quadridentate ligand
X	halide (except where otherwise stated)

Specific

acac	acetylacetonate
ADP	adenosine-5′-diphosphate
2′-AMP	adenosine-2′-monophosphate
3′-AMP	adenosine-3′-monophosphate
5′-AMP	adenosine-5′-monophosphate
asp	aspartate
ATP	adenosine-5′-triphosphate
big	biguanide
bipy	2,2′-bipyridyl
bzac	benzoylacetonate
cal	calmagite [1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonate]
CDP	cytosine-5′-diphosphate
cod	cyclo-octadiene
Cp	cyclopentadienyl
CTP	cytosine-5′-triphosphate
cyclam	1,4,8,11-tetra-azacyclotetradecane
cydta	cyclohexane-1,2-diaminetetra-acetate
diars	*o*-phenylenebisdimethylarsine
dien	diethylenetriamine
dien − H	diethylenetriamine minus one nitrogen proton
dimetn	*NN*′-dimethylpropane-1,3-diamine
diphos	1,2-bisdiphenylphosphinoethane
DMF	dimethylformamide
dmg	dimethylglyoximate
DMSO	dimethyl sulphoxide
DNA	deoxyribonucleic acid
dpt	dipropylenetriamine

dtc	dithiocarbamate
dto	dithio-oxalate
dtp	diethyldithiophosphate
dtpa	diethylenetriaminepenta-acetate
edda	ethylenediaminediacetate
eddda	ethylenediaminediacetatedipropionate
edds	*NN'*-ethylenediaminedisuccinate
edma	ethylenediaminemonoacetate
edta	ethylenediaminetetra-acetate
edtra	ethylenediaminetriacetatoacetate (*i.e.* quinquedentate edta)
egta	ethylene glycol bis-(2-aminoethyl ether)-tetra-acetate
en	ethylenediamine
Et$_4$dien	*NN''N''*-tetraethyldiethylenetriamine
gedta	2,2'-ethylenedioxybis(ethyleneiminodiacetate)
glu	glutamate
gly	glycinate
hedta	*N*-(2-hydroxyethyl)ethylenediaminetetra-acetate
hfac	hexafluoroacetylacetone
his	histidine
hm	histamine
ida	iminodiacetate
ind	indenyl
mal	malonate
Me$_4$dien − H	*NN''N''*-tetramethyldiethylenetriamine minus the nitrogen proton
Me mal	methylmalonate anion
Me$_6$tren	2,2',2''-tris-(*NN*-dimethylamino)triethylamine
mida	*N*-methyliminodiacetate
mnt	maleonitriledithiolate
mq	2-methyl-8-quinolinate
NADH	nicotinamide adenine dinucleotide (reduced form)
niox	nioxime
nta	nitrilotriacetate
ox	oxalate
pdta	propylenediaminetetra-acetate
phen	1,10-phenanthroline
pn	propylenediamine
py	pyridine
salen	*NN'*-bis(salicylaldehydo)ethylenediamine
tar	tartrate
tcne	tetracyanoethylene
terpy	2,2',2''-terpyridyl
tet-*a*, tet-*b*	5,7,7,12,14,14-hexamethyl-1,4,8,11-cyclotetra-azatetradecane
tetren	tetraethylenepentamine
tfac	1,1,1-trifluoroacetylacetone

thiox	monothio-oxalate
tmd	trimethylenediamine
tmeda	*NNN′N′*-tetramethylethylenediamine
TP	tripolyphosphate
trans-14-diene	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene
tren	triaminotriethylamine
trien	triethylenetetramine
trigly	triglycine
ttha	triethylenetetraminehexa-acetate
tu	thiourea
xyl	xylenol orange

Part I

ELECTRON TRANSFER PROCESSES

By

A. McAULEY

Introduction

BY A. McAULEY

The format of this Part follows closely that of the previous volumes in this series. Although some degree of selection has had to be imposed owing to the large number of papers involving electron-transfer processes, an attempt has been made to cover comprehensively all the areas in which studies are currently being undertaken. As in the previous volumes, compilations of data have been assembled to allow more direct comparison of rate constants and thermodynamic parameters of reactions of a similar type.

Differing aspects of the subject have been dealt with in several publications. A very readable account of the present 'state of the art' in inorganic mechanisms has been published by Tobe[1] in which there are chapters dealing with redox systems involving both interactions between two metal-ion complexes and also reactions where ligands are oxidized or reduced. A series of review articles on this subject has appeared in a volume edited by Edwards,[2] including an account of chromium(VI) oxidations of inorganic substrates,[3] where both one-electron and two-electron systems are discussed, together with the role of Cr^V and the fate of Cr^{IV} in these reactions.

Electron-transfer processes between two metal ions continue to be investigated and in several papers the importance of medium effects has been noted. In a re-examination of the role of co-ordinated water as a bridging ligand in the Cr^{II} reduction of penta-amminecobalt(III) complexes, the use of lithium perchlorate yields data[4] which are consistent with a single-term rate law instead of the two-term law noted previously in solutions where sodium perchlorate was used as the supporting electrolyte. Similar effects have also been observed in the corresponding reaction of the cobalt(III)–malonato-complexes.[5] The metal-ion reduction of cobalt(III) complexes containing co-ordinated sulphur donor atoms has been studied with interesting differences in reactivity when compared with the corresponding N- or O-donor systems.[6,7] Radical intermediates of sufficiently long life for spectrophotometric identification have been observed in the chromium(II) reduction of the corresponding carboxylato-

---

[1] M. L. Tobe, 'Inorganic Reaction Mechanisms', Nelson, London, 1972.
[2] *Progr. Inorg. Chem.*, ed. J. O. Edwards, Wiley, New York, Vol. 17, Part II, 1972.
[3] J. K. Beattie and G. P. Haight, ref. 2, p. 93.
[4] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.
[5] C. Lavalee and E. Deutsch, *Inorg. Chem.*, 1972, **11**, 3133.
[6] M. Gilroy, F. A. Sedor, and L. E. Bennett, *J.C.S. Chem. Comm.*, 1972, 181.
[7] J. H. Worrell, R. A. Goddard, E. M. Gupton, and T. A. Jackman, *Inorg. Chem.*, 1972, **11**, 2734.

penta-ammine complex ions.[8] A review has also been written[9] in which comparison has been made between vanadium(IV) and iron(II) as reductants in aqueous electron-transfer processes.

The plenary lectures at the 14th I.C.C.C. Meeting at Toronto have been published,[10] as have the papers presented at the Bressanone Conference.[11] Several other useful reviews of reactions involving metal ions have been published. The oxidation–reduction of the cobalt centre in vitamin B_{12} has been discussed[12] and recent developments in the bioinorganic chemistry of this complex have also been described.[13,14] Electron-transfer catalysts involving metalloenzyme systems have also been reviewed by Williams.[15] The role of transition metals in homogeneous catalysis has been described[16] and homolytic oxidation and reduction reactions of organic compounds by metallic ions have been reviewed.[17]

---

[8] E. S. Gould, *J. Amer. Chem. Soc.*, 1972, **94**, 4360.

[9] D. R. Rosseinsky, *Chem. Rev.*, 1972, **72**, 215.

[10] *Pure Appl. Chem.*, 1973, **33**, No. 4.

[11] *Coordination Chem. Rev.*, 1972, **8**, Nos. 1 and 2.

[12] J. M. Pratt, 'The Inorganic Chemistry of Vitamin B_{12}'. Academic Press, London, 1972.

[13] R. H. Prince and D. A. Stotter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 321; J. Lewis, R. H. Prince, and D. A. Stotter, *ibid.*, p. 341.

[14] G. N. Schrauzer, *Pure Appl. Chem.*, 1973, **33**, 545.

[15] R. J. P. Williams, *Inorg. Chim. Acta, Rev.*, 1971, **5**, 137.

[16] R. G. Linck, 'Transition Metals in Homogeneous Catalysis', ed. G. N. Schrauzer, Marcel Dekker, New York, 1971, p. 297.

[17] J. S. Littler, 'M.T.P. International Review of Science', Organic Chemistry, Series 1, Vol. 10, ed. W. A. Waters, Butterworths, London, 1973, p. 237.

1

Reactions Between Two Metal Complexes

BY A. McAULEY

1 Reducing Agents

Chromium(II).—Quantitative data for this and for the other reducing species are tabulated in Tables 1 and 2 on pp. 17 and 24.

Many reactions have been studied using this reagent, especially those involving the inert ammine complexes of cobalt(III), and in the case of organic derivatives of these complexes a wide variety of reactivity patterns has emerged which has not yet been encountered with any other reducing centre. Electron transfer through organic structural units has been investigated in the case of the alkenecarboxylatopenta-amminecobalt(III) species,[18] in which there is a double bond lying between the $-CO_2Co(NH_3)_5$ unit and an aromatic ring. An interesting feature of these reactions is that some retardation of the reduction rate is observed at high hydrogen-ion concentrations which is not observed (over a sixty-fold range) in the case of the corresponding benzoato- and *p*-hydroxybenzoato-species.[19a] The reaction products for the systems involving the *o*-hydroxycinnamato- and acetylenecarboxylato-complexes are the corresponding carboxylatochromium(III) species, confirming the expected inner-sphere paths for these reactions. Specific rates for the reduction of $\alpha\beta$-unsaturated complexes of this type are significantly higher than those obtained for aromatic and straight-chain derivatives, and the decrease in reaction rate at high acidity appears to be a general effect for these species, the observed retardations being too large to be attributable to medium effects. The rate law may be described as

$$\text{Rate} = \left\{\frac{k_1 + k_2K_B[H^+]}{1 + K_B[H^+]}\right\}[Cr^{II}][Co^{III}]$$

where the rate constants k_1 and k_2 are associated with the reactivity of the unprotonated and protonated forms of the cobalt(III) complex, K_B being the protonation equilibrium constant. Comparison of the data for the protonated acetato-complex (in which the site of protonation is considered to be the carbonyl oxygen) with those of the unsaturated systems where the hydrogen ion may be associated at the double (or triple) bond suggests that the strong

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[18] A. Liang and E. S. Gould, *Inorg. Chem.*, 1973, **12**, 12.

[19a] A. Liang and E. S. Gould, *J. Amer. Chem. Soc.*, 1970, **92**, 6791.

base-strengthening action of the $-Co(NH_3)_5$ group (when substituted for a hydrogen atom or alkyl group) is transmitted through the conjugated systems, giving rise to the acid dependences observed. In the reaction with the *p*-formylbenzoatopenta-amminecobalt(III) ion with Cr^{II},[19b] however, the observed rate is strongly dependent on acidity, the rate law being expressed in the form

$$\frac{-d[Co^{III}]}{dt} = \left\{k_0 + k_1[H^+]\right\}[Cr^{II}][Co^{III}]$$

The rate constant for the acid-independent term is much larger than that for the corresponding benzoato-complex, which may be due to attack by the reducing agent at the remote carbonyl of the group. Stopped-flow experiments confirm the existence of an intermediate complex of structure $[(p\text{-}HO_2C\cdot C_6H_4\cdot CHO)Cr(H_2O)_5]^{3+}$, in which the absorption maximum is ascribed to a π–π^* transition, the band being shifted by interaction of the carbonyl group with the Cr^{III} to 290 nm from the free-ligand position of 254 nm. The intermediate decays to yield $[Cr(H_2O)_6]^{3+}$ and the free ligand in a unimolecular reaction independent of $[H^+]$ and of Cr^{II} at low concentrations. In the corresponding reaction with the *m*-formylbenzoato-complex, whereas 55% of the ligand in the cobalt complex is released, the remainder being bound to the chromium(III) as a carboxylato-complex, there is no evidence of rate promotion by hydrogen ions. The overall rate constant for this acid-independent route is about 170 times smaller than that for the *p*-formylbenzoato-species but only a factor of two different from that of the unsubstituted benzoato-species. From values of product distribution as a function of temperature, the rate constants for both the reaction of the adjacent carboxyl leading to formation of a *m*-formylbenzoato intermediate and for the path leading to ligand release have been evaluated. In the reduction of *m*-formylbenzoic acid by chromium(II), however, the rates are a factor of 10^4 lower.

Co-ordination of a $(NH_3)_5Co^{III}$ unit to glycine lowers the pK_a by about 1.3 units and the reaction of substituted glycinato-complexes with Cr^{II} has been investigated[20] to study the possibility of steric crowding as alkyl substitution on the ammonium nitrogen increases such that attack at the adjacent carboxy-group would be hindered. For the complex $[(H_3N)_5CoO_2C\cdot CH_2NH_3]^{3+}$ there is no acid dependence on the rate constant within the range $[H^+] = 0.019$—$0.54M$, the reaction proceeding *via* an inner-sphere mechanism. Increased substitution of H by methyl groups causes a decrease in the reaction rate; however, the factor of four decrease in rate for the trimethylglycinato-complex compared with the glycinato-species is reflected in only a small (3 cal deg^{-1} mol^{-1}) change in $\Delta S^{\ddagger}$. The reductions of malonatopenta-amminecobalt(III) and the corresponding dimethylmalonato-species by Cr^{II} have been re-investigated,[5] the acidity dependence observed previously for the malonato-

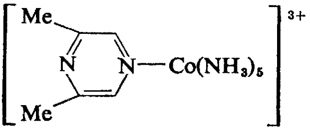
---

[19b] A. Zanella and H. Taube, *J. Amer. Chem. Soc.*, 1972, **94**, 6403.

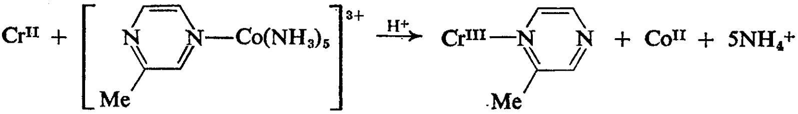
[20] R. Holwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, 1972, **11**, 1965.

complex in sodium perchlorate media being shown to be a medium effect. Whereas over the range $[H^+]$ = 1.0—3.95M (I = 4.0M) with $NaClO_4$ as supporting electrolyte the observed rate constant increases from 2.64 to 3.94 $l\ mol^{-1}\ s^{-1}$, no such variation in rate is seen in $LiClO_4$ solutions, the value being 4.05 ± 0.14 $l\ mol^{-1}\ s^{-1}$. A similar effect is seen for the dialkylated species.

The outer-sphere reductions of penta-ammine pyridine and alkyl-substituted pyridine complexes have been investigated[21] and have been compared with similar reactions involving Eu^{2+} as reductant. For the Cr^{II} reactions, the rate constants are in the range 10^{-3}—10^{-2} $l\ mol^{-1}\ s^{-1}$. In the reactions with the 4-ethoxycarbonylpyridine, 2-methylpyrazine, and 2,6-dimethylpyrazine (1) complexes, where there is a site for inner-sphere reduction and electron transfer through the conjugated system, the rates are appreciably greater, especially for the pyrazine complexes where the Cr^{III} products are not the hexa-aquated ion but involve a metal ion–nitrogen bond. A probable pathway may be written as in Scheme 1. In the reduction of the pyrazinecarboxylatopenta-amminecobalt(III) ion (2) with Cr^{II}, however, physical evidence has



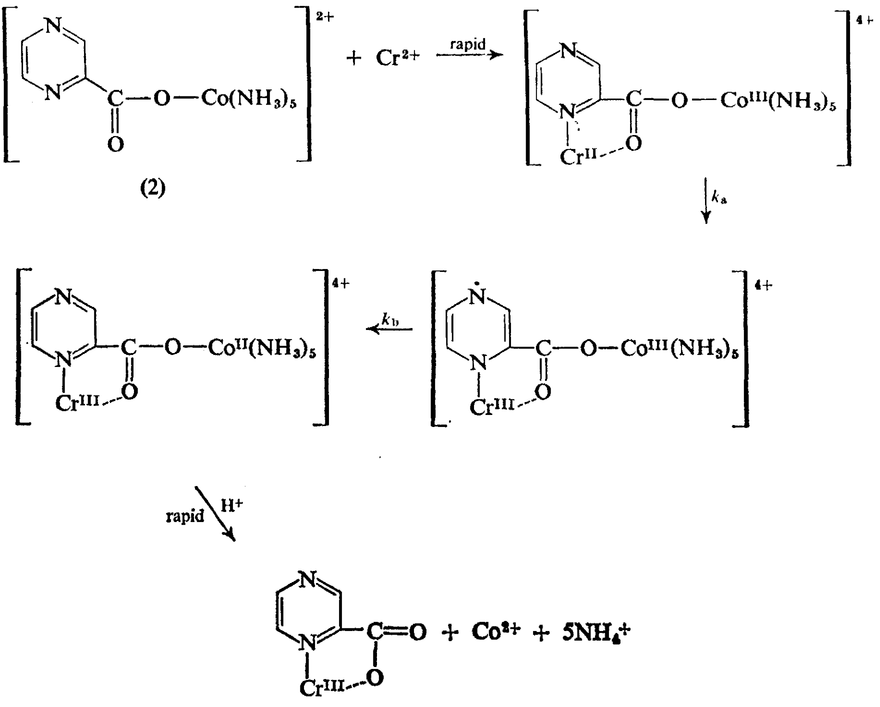
(1)



Scheme 1

been presented for a radical cation intermediate in the course of the reaction.[8] Addition of excess Cr^{II} to oxidant (2) results in a marked increase in absorbance in the range 400—600 nm within 10 ms of mixing, followed by a slower decay to yield cobalt(II) and the chromium(III) product. Both reactions are first-order, the maximum concentration of absorbing species and its formation and decomposition rates being independent of the Cr^{II} added. The data are interpreted in terms of a reaction scheme (Scheme 2) where there is a precursor complex formed which undergoes an intramolecular electron transfer to yield the radical cation (k_a = 263 s^{-1}) with a subsequent slower transformation (k_b = 2.4 s^{-1}) to the successor complex, which then aquates rapidly in the

[21] E. R. Dockal and E. S. Gould, *J. Amer. Chem. Soc.*, 1972, 94, 6673.



Scheme 2

acid media to yield the products. The corresponding reaction with the 4-cinnolinecarboxylato-derivative (3) again exhibits behaviour of this type, but in this case both formation and disappearance (k_c) of the intermediate are first-order dependent on Cr^{II}, a mechanism of the type shown in Scheme 3 being invoked.

In the reduction of aromatic nitrile complexes of cobalt by chromium(II), second-order rate behaviour is observed.[22] In the case of terephthalonitrile as ligand, no detectable ligand transfer occurs and in the case of complexes of 3- or 4-cyanophenol the reaction proceeds with only 10—15% of the bridging ligand attached to the chromium(III) product. These reactions are of interest from the point of view that the reducing agent cannot attack at the atom or group directly attached to the cobalt since there are no free electron pairs available for bonding to the reducing agent. Although at first sight it would appear that the data could be described by an outer-sphere mechanism, a consideration of the rate and activation parameters would require some modi-

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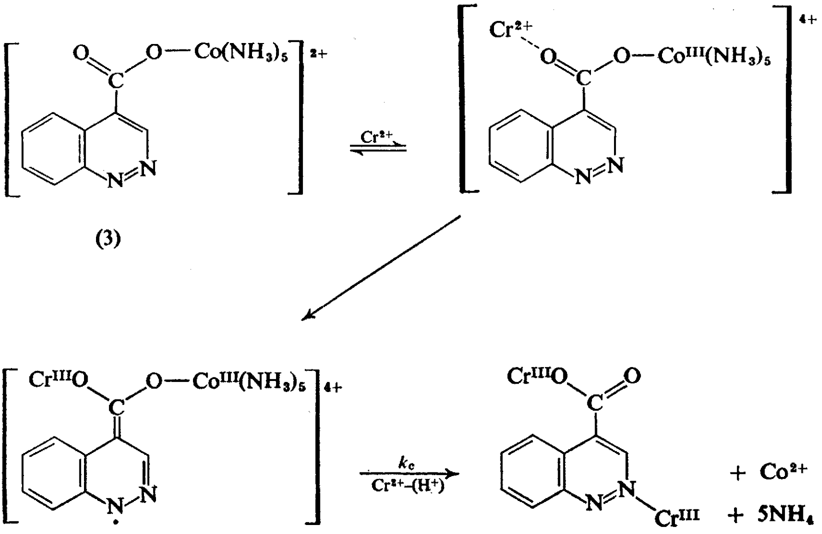
[22] R. J. Balahura, G. B. Wright, and R. B. Jordan, *J. Amer. Chem. Soc.*, 1973, **95**, 1173.



(3)

Scheme 3

fication of this view. For a simple outer-sphere route, little difference would be expected in the rates of reduction of the 3- and 4-cyano-substituted complexes whereas in fact they differ by ~30% and the terephthalonitrile species reacts about 30 times still faster. The mechanism postulated involves an outer-sphere reduction of the nitrile ligand where the electron is transferred to the ligand without co-ordination of a remote group to the chromium(II). A route of this type would be favoured by an easily reducible ligand containing a remote substituent which was not very basic towards Cr^{II}. In support of this view a correlation has been shown between the rate of reduction and Hammett σ constants, which themselves have been shown to be a measure of the polarographic half-wave reduction potentials of the uncomplexed aromatic nitriles.

The role of co-ordinated water as a bridging ligand in redox systems has been discussed,[4] the data for the reaction

$$Cr^{II} + [Co(NH_3)_5OH_2]^{3+} \xrightarrow{5H^+} 5NH_4^+ + Cr^{7+} + Co^{2+}$$

in lithium perchlorate media being consistent with a single-term rate law. The hydrogen-ion-independent pathway is considered too insignificant to be measured directly and it is postulated that for all reactions of Cr^{II} with complexes containing water as the only bridging ligand any hydrogen-ion-independent pathway proceeds *via* an outer-sphere mechanism.

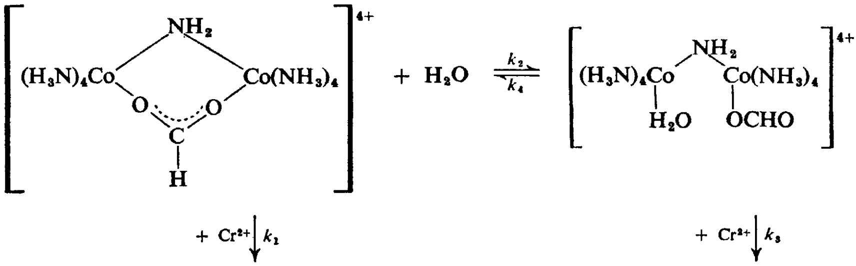
The reduction of thioether and carboxylate chelates of cobalt(III) by Cr^{II} has been investigated.[6] The complexes $[(en)_2Co(NH_2CH_2CO_2)]^{2+}$ and

$[(\mathrm{en})_2\mathrm{Co}(\mathrm{O_2CCH_2SMe})]^{2+}$ react *via* an inner-sphere mechanism with carboxylate bridging, whereas the species $[(\mathrm{en})_2\mathrm{Co}(\mathrm{NH_2CH_2CH_2SMe})]^{3+}$ interacts in an outer-sphere manner. The rate for $[(\mathrm{en})_2\mathrm{Co}(\mathrm{O_2CCH_2SMe})]^{2+}$ is very high and may be due to the *cis* non-bridging influence of the thioether function. Symmetry rules have been applied to electron-transfer reactions of $\mathrm{Cr^{II}}$ (and $\mathrm{V^{II}}$) with complexes of the penta-amminecobalt(III) type including a bridging ligand,[23] the reactivity of the co-ordination compounds increasing with decreasing symmetry.

The reductions of di- and tetra-nuclear cobalt(III) complexes have been studied by Sykes and his co-workers. In the reaction with μ-amido-μ-formato-bis[tetra-amminecobalt(III)][24] the only observable stage in the reaction may be represented by the rate law

$$\frac{-\mathrm{d}\ln[(\mathrm{Co^{III}})_2]}{\mathrm{d}t} = k_1[\mathrm{Cr^{2+}}] + \frac{k_2k_3[\mathrm{Cr^{2+}}]}{k_4 + k_3[\mathrm{Cr^{2+}}]} \tag{1}$$

when the reductant is present in large excess. No dependence on hydrogen ion was detected in the range $[\mathrm{H^+}] = 0.04$—$0.98\mathrm{M}$. The observed rate law has been interpreted by assuming an equilibrium between the μ-formato-species and an aquoformato-complex, both of which react with the chromium(II), *e.g.* as shown in Scheme 4. The reaction was also found to be strongly catalysed by chloride ions. In the corresponding reaction of the μ-acetato-complex, however, there is no evidence for the second term in equation (1), the observed rate constants being a factor of four lower than for the former system. The reaction of the μ-amido-μ-oxalato-complex (4) shows two reduction stages with the formation of an intermediate.[25] In this case, the reaction is much faster than those previously described and probably proceeds *via* an inner-sphere mechanism. The first two stages of the reduction of the superoxo-



Scheme 4

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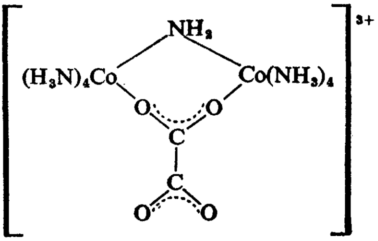
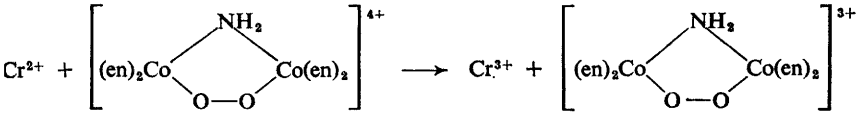
[23] K. B. Yatsimirskii, *Teor. i eksp. Khim.*, 1972, **8**, 617 (*Chem. Abs.*, 1973, **78**, 34 381a).
[24] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.
[25] M. R. Hyde, K. L. Scott, and A. G. Sykes, ref. 8, p. 121.



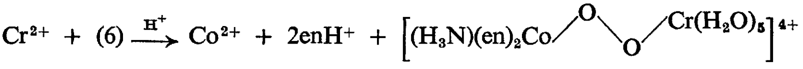
(4)

complex $[(en)_2Co \cdot \mu\text{-}(NH_2,O_2) \cdot Co(en)_2]^{4+}$ (5) have been described,[26] the reaction product being the μ-peroxo-species (6).



(5) (6)

The second redox reaction involves one cobalt(III) centre, but the second cobalt(III) site reacts only after the peroxo-bridge has been reduced. The Cr^{2+} reduction of (5) is too rapid for detection by flow techniques, but the $[Cr(H_2O)_6]^{3+}$ product is indicative of an outer-sphere route. The reduction of (6) is also fast and here the reaction product is not a mononuclear chromium(III) species but the first example of a μ-peroxo-complex involving different metal atoms,



$$Cr^{2+} + (6) \xrightarrow{H^+} Co^{2+} + 2enH^+ + \left[(H_3N)(en)_2Co{-}O{-}O{-}Cr(H_2O)_5\right]^{4+}$$

confirming an inner-sphere pathway for this reaction.

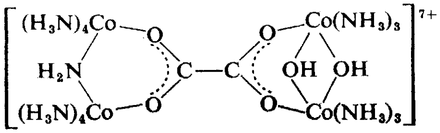
In the case of the trinuclear μ-oxalato-complexes,[27] parallel inner- and outer-sphere routes have been observed. It is interesting to note, however, that whereas the reaction of the species $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)]^{5+}$ follows second-order kinetics, reaction of the corresponding complex $[Co_3(NH_3)_{11}(OH)_2(C_2O_4)]^{5+}$ is more complicated and at least two stages are observed in the chromium(II) reduction. The reactions of three tetranuclear μ-oxalato-cobalt(III) complexes have been reported[28] where in a 40—400-fold excess of reductant all four Co^{III} centres undergo reduction, the first stage of the reaction in each case being rate determining. The rate of reduction of μ_4-oxalato-[di-μ-hydroxo-bis{triamminecobalt(III)}]-[μ-amido-bis{tetraamminecobalt(III)}] (7) is found to be independent of hydrogen-ion

[26] M. R. Hyde and A. G. Sykes, *J.C.S. Chem. Comm.*, 1972, 1340.
[27] K. L. Scott, K. Wieghardt, and A. G. Sykes, *Inorg. Chem.*, 1973, **12**, 655.
[28] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1973, 736.

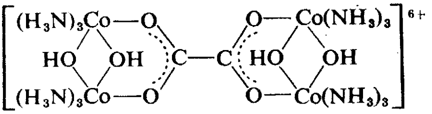
concentration over the range 0.1—0.9M, the rate law being

$$-\mathrm{d}\ln[\{\mathrm{Co^{III}}\}_4]/\mathrm{d}t = k_1[\mathrm{Cr}^{2+}]$$

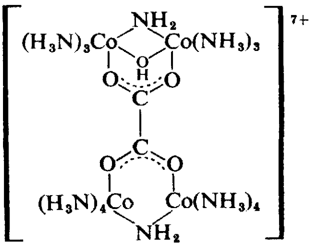
A similar rate law was observed for the 6+ ion μ_4-oxalato-bis[di-μ-hydroxo-bis{triamminecobalt(III)}] (8) and for the 7+ species μ_4-oxalato-[μ-amido-μ-hydroxo-bis{triamminecobalt(III)}]-[μ-amido-bis{tetra-amminecobalt(III)}] (9).



(7)



(8)



(9)

In these systems no rate-determining hydroxo-bridge cleavage was encountered and the mechanism of reduction in each case is outer-sphere. It is considered that the secondary and tertiary redox stages involving tri- and di-nuclear μ-oxalato-complexes are fast, since in these species there are possible sites for attack *via* an inner-sphere route.

The reaction between the strongly oxidizing hexa-aquocobalt(III) ion and $\mathrm{Cr^{II}}$ has been investigated[29] using stopped-flow spectrophotometry. The rate law is of the form

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = \{k_1 + k_2/[\mathrm{H}^+]\}[\mathrm{Co^{III}}][\mathrm{Cr^{II}}]$$

where k_1 corresponds to the reaction of Cr^{2+}_{aq} and Co^{+}_{aq}, the reaction taking place *via* an outer-sphere pathway. The hydrogen-ion-dependent path involves Cr^{2+} and CoOH^{2+} as reactants and may be inner-sphere in character. The reaction is catalysed by chloride ion, and two chloride-ion-dependent paths have been identified involving the terms $k_3[\mathrm{Cr}^{2+}][\mathrm{CoCl}^{2+}]$ and $k_4[\mathrm{Cr}^{2+}][\mathrm{Co}^{3+}][\mathrm{Cl}^-]$

Kinetic studies have been made on the reduction of the tantalum cluster ion $[\mathrm{Ta_6Br_{12}}]^{3+}$ by chromium(II).[30] The rate is greatly increased by relatively low

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[29] M. R. Hyde, R. Davies, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1838.

[30] J. H. Espenson and T. R. Webb, *Inorg. Chem.*, 1972, **11**, 1909.

concentrations of ions such as Cl^-, Br^-, I^-, and NCS^-, the overall rate law in the presence of such ions (X^-) being

$$-d[(Ta_6Br_{12})^{3+}]/dt = \{k_1 + k_2[X^-]\}[(Ta_6Br_{12})^{3+}][Cr^{II}]$$

The small decrease in rate with acidity which is also observed may be due to medium effects. In perchlorate media, the product is $[Cr(H_2O)_6]^{3+}$, whereas in the presence of other anions a mixture of Cr^{3+} and CrX^{2+} is obtained. The mechanism consistent with these findings may be represented as

$$\begin{tikzcd}
& {[Ta_6Br_{12}]^{2+} + Cr^{3+}} \\
{[Ta_6Br_{12}]^{3+} + Cr^{2+}} \arrow[ur, "k_1"] \arrow[dr, "k_2", "+ X^-"'] & \\
& {[Ta_6Br_{12}]^{2+} + CrX^{2+}}
\end{tikzcd}$$

In the thiocyanate reaction, however, both linkage isomers $[CrNCS]^{2+}$ and the less stable $[CrSCN]^{2+}$ appear to be produced and it may be that an ion pair of the type $[Ta_6Br_{12}]^{3+} NCS^-$ is formed where the thiocyanate ion could act as a bridging ligand, leading to the formation of the S-bonded Cr^{III} product.

The reaction between $[UO_2]^{2+}$ and Cr^{2+} has been monitored using flow techniques and results in the formation of a dinuclear $[U^V \cdot Cr^{III}]$ complex.[31] The rate law is first order with respect to both U^{VI} and Cr^{II} with no hydrogen-ion dependence in the concentration range 0.3—2.0M. A possible mechanism postulated involves the rate-controlling transfer of an electron after the rapid formation of an inner-sphere complex (Scheme 5).

$$\begin{tikzcd}
{[Cr^{2+}(H_2O)_6]\cdot UO_2^{2+}} \arrow[r, shift left] & {[(H_2O)_5Cr^{2+}\cdot UO_2^{2+}] + H_2O} \arrow[l, shift left, "K_1"] \arrow[d, "\text{slow}"] \\
& {[(H_2O)_5Cr^{III}\cdot U^V]}
\end{tikzcd}$$

Scheme 5

The inner-sphere reduction of tetraphenylporphineiron(III) chloride has been studied in benzene,[32] and using ^{36}Cl it has been shown that 96% of the radioactivity is transferred to the chromium centre. No significant role of the delocalized porphyrin ring system as a route for enhancement of electron transfer was detected in this system. The reaction with horse-heart ferricytochrome *c* has been investigated[33] using a stopped-flow device over the pH range 1—7. The rate passes through a maximum at pH ~ 3.7 (Figure 1) and the reduction is catalysed by iodide, azide, and thiocyanate ions. The rate law shows no direct proportionality to the Cr^{II} concentration, a limiting rate being observed at high Cr^{II} values. A mechanism consistent with these observations

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[31] A. Ekstrom and Y. Farrar, *Inorg. Chem.*, 1972, **11**, 2610.

[32] I. A. Cohen, C. Jung, and T. Governo, *J. Amer. Chem. Soc.*, 1972, **94**, 3003.

[33] D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, 1972, **11**, 2361.

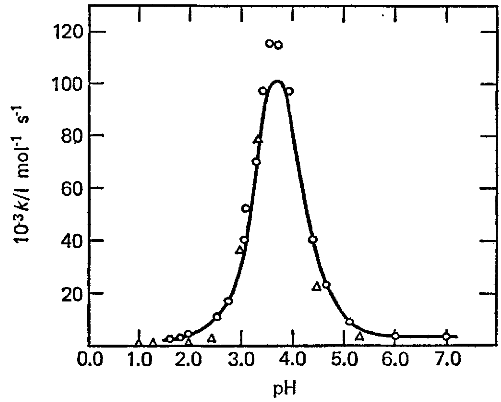

Figure 1 *Plot of rate constant against pH for the reaction of chromium*(II) *with ferri-cytochrome* c *in chloride media: circles,* I = 1.0M; *triangles,* I = 0.15M (Reproduced by permission from *J. Amer. Chem. Soc.*, 1973, **95**, 1133)

may be written as

$$\text{Ferricyt } c \xrightleftharpoons[k_1]{k_{-1}} \text{Ferricyt* } c$$

$$\text{Ferricyt* } c + \text{Cr}^{\text{II}} \xrightleftharpoons[k_2]{} \text{Cr}^{\text{III}} + \text{Ferrocyt } c$$

Values of k_1 and k_1k_2/k_{-1} may be obtained from a plot of $1/k_{\text{obs}}$ against $[\text{Cr}^{\text{II}}]^{-1}$ [equation (2)]:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2[\text{Cr}^{\text{II}}]} \qquad (2)$$

The effects of anions in these systems may be considered to derive from binding between the anion and the iron centre by displacing a methionine sulphur atom from the co-ordinating position, and a value of 60 s^{-1} has been estimated for the rate of rupture of the Fe—S bond in the pH range 6.1—7.0. The anions may now act as bridging ligands in the inner-sphere reduction where a transition state involving the grouping —Fe—X—Cr— may be envisaged. The pH dependence may be described using a curve of the form

$$k = \frac{a/[\text{H}^+] + ac/d[\text{H}^+]^2}{1 + a/d[\text{H}^+]} \qquad (3)$$

where the fit is especially good at the extreme pH values. A dependence of this type has been described in terms of the reaction of various protonated forms of the oxidant,

$$\text{H}_2\text{Ferricyt } c \xrightleftharpoons[K_1]{} \text{H}^+ + \text{HFerricyt } c$$

$$\text{HFerricyt } c \xrightleftharpoons[K_2]{} \text{H}^+ + \text{Ferricyt } c$$

$$\mathrm{H_2Ferricyt}\ c + \mathrm{Cr^{II}} \xrightarrow[k_a]{}$$

$$\mathrm{HFerricyt}\ c + \mathrm{Cr^{II}} \xrightarrow[k_b]{}$$

$$\mathrm{Ferricyt}\ c + \mathrm{Cr^{II}} \xrightarrow[k_c]{}$$

and provided the protonation equilibria involved are rapid, this scheme leads to an expression of the form

$$k = \frac{k_a + k_b K_1/[\mathrm{H^+}] + k_c K_1 K_2/[\mathrm{H^+}]^2}{1 + K_1/[\mathrm{H^+}] + K_1 K_2/[\mathrm{H^+}]^2}$$

which is identical to that above [equation (3)] when the first term in the numerator and the second in the denominator are neglected. It is found that $K_2 > K_1$ and hence the concentration of the singly protonated species never builds up to significant levels. From a kinetic analysis of the catalytic effects of the anions, it is considered that whereas the chloride ion is involved in an adjacent attack of the $\mathrm{Cr^{II}}$ on the $\mathrm{iron^{III}}$ centre, in the case of the azide and thiocyanate ions there is evidence of remote attack, where use is made of an electron-transfer site possibly on the edge of the porphyrin ring system.

The outer-sphere reduction of several *trans*-$[\mathrm{Co(N_4)(NH_3)_2}]^{3+}$ complexes has been examined, where $\mathrm{N_4}$ represents a quadridentate macrocyclic ligand. In the case of tetra-amine and tetraimine ligands, the observed rate constants are fairly similar, but when allowance is made for the variations in reduction potential of the cobalt(III) complexes, the rate constant increases by a factor of 10^2 on going from a tetra-amine to a tetraimine. The rate law is second-order overall in these reactions with some autocatalysis observed in the tetraimine systems. From free energy considerations, it would seem that in reductions of complexes of this type the reorganizational parameters depend more strongly on the reducing agent and less on the cobalt(III) than would be predicted.

The reaction of $[\mathrm{Cr(CN)_6}]^{4-}$ with $[\mathrm{Co(CN)_5Br}]^{3-}$ in the presence of cyanide ions takes place in two stages,[34] the first step leading to the formation of $[\mathrm{Co(CN)_6}]^{3-}$, $[\mathrm{Co(CN)_5}]^{3-}$, and $\mathrm{Br^-}$ with the rate law

$$-\mathrm{d}[\mathrm{Cr(CN)_6^{4-}}]/\mathrm{d}t = k_1[\mathrm{Cr(CN)_6^{4-}}][\mathrm{Co(CN)_5Br^{3-}}]$$

the rate being independent of $[\mathrm{CN^-}]$ in the range 0.20—0.98M and of hydroxide ion concentration between 0.02 and 0.20M. The second stage is the reaction between the product $[\mathrm{Co(CN)_5}]^{3-}$ and $[\mathrm{Cr(CN)_6}]^{4-}$ and is of importance when a large excess of the reductant is present. Again the overall reaction is second order. An interesting aspect of the coupled reactions is that they provide a means of carrying out the catalytic hydrogenation of $\alpha\beta$-unsaturated compounds without molecular hydrogen in that $[\mathrm{Cr(CN)_6}]^{4-}$ may serve as a reducing agent to liberate hydrogen from water *via* the intermediate hydrogenating agent $[\mathrm{Co(CN)_5H}]^{3-}$:

$$[\mathrm{Cr(CN)_6}]^{4-} + [\mathrm{Co(CN)_5}]^{3-} + \mathrm{H_2O} \longrightarrow [\mathrm{Cr(CN)_6}]^{3-} + [\mathrm{Co(CN)_5H}]^{3-} + \mathrm{OH^-}$$

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[34] J. H. Espenson and D. A. Holm, *J. Amer. Chem. Soc.*, 1972, **94**, 5709.

Vanadium(II).—A substantial amount of work has been undertaken using this reductant, especially in comparison of systems where Cr^{II} has also been used as a reducing agent in order to identify possible reaction pathways. A number of kinetic data have been interpreted in terms of an inner-sphere mechanism with the rate of substitution of co-ordinated water on the metal ion as rate determining. In the reaction with azido-ammine complexes of cobalt(III),[35]

$$V^{II} + [CoL_5N_3]^{n+} + H^+ \longrightarrow V^{3+} + Co^{II} + HN_3 + 5L^{(n-2)+}$$

the mechanism is inner-sphere and in the case of the complex ion $[Co(NH_3)_5N_3]^{2+}$ the formation of VN_3^{2+} as an unstable intermediate has been observed. From a comparison of the data, it is considered that non-bridging ligand effects on the reduction rate are quenched by the solvent-exchange rate on the V^{II}. A similar mechanism is proposed in the reaction of *cis*- and *trans*-diformatobis(ethylenediamine)cobalt(III).[36] In the case of the *trans*-complex, the second-order rate constant is independent of $[H^+]$ in the range 0.11—0.91M whereas for the *cis* species the rate decreases with increasing hydrogen-ion concentration. In this system, protonation of the complex is important,

$$cis\text{-}[Co(en)_2(HCO_2)_2]^+ + H^+ \underset{K}{\rightleftharpoons} cis\text{-}[Co(en)_2(HCO_2)_2H]^{2+}$$

the reducing agent reacting with the non-protonated diformato-complex (k_{cis}) in accordance with the rate law (k_2 = observed second-order rate constant)

$$k_2 = \frac{k_{cis}}{1 + K_{cis}[H^+]}$$

Protonation of the *trans*-form appears to be negligible. When compared with the corresponding data with Cr^{II} as reductant, it is apparent that in the latter systems the nature of the ligand *trans* to the bridging group is important, since it changes the energy of the acceptor orbital and thus determines the reactivity, whereas for the former (V^{2+}) reagent the dissociative character of the rate-determining substitutions dominates the reaction. The rate constants for the reduction of *p*- and *m*-formylbenzoatopenta-amminecobalt(III) ions have been reported,[19] the values being a factor of ten lower than for the cobalt(III) systems reported above.

A comparison has been made of vanadium(II) and chromium(II) reactions which occur *via* outer-sphere pathways and for reactions occurring by this mechanism the ratio $k(Cr^{II})/k(V^{II}) \approx 0.02$ has been derived (Table 1) for

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[35] K. W. Hicks, D. L. Toppen, and R. G. Linck, *Inorg. Chem.*, 1972, **11**, 310.
[36] T. J. Przystas and A. Haim, *Inorg. Chem.*, 1972, **11**, 1016.
[37] P. Dodel and H. Taube, *Z. phys. Chem. (Frankfurt)*, 1965, **44**, 92.
[38] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, **86**, 1019.
[39] F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 1163.
[40] J. Doyle and A. G. Sykes, *J. Chem. Soc. (A)*, 1968, 2836.
[41] R. G. Gaunde and H. Taube, *Inorg. Chem.*, 1970, **9**, 2627.
[42] A. B. Hoffmann and H. Taube, *Inorg. Chem.*, 1968, **7**, 1971.
[43] P. K. Zia, R. B. Fisher, and W. K. Wilmarth, *Abs. Amer. Chem. Soc.*, 161st Meeting, Los Angeles, 1971, Inorg. 027.

Table 1 *Comparison of outer-sphere reduction rates of* Cr^{II} *and* V^{II}

Oxidant	$k(Cr^{II})$/l mol^{-1} s^{-1}	$k(V^{II})$/l mol^{-1} s^{-1}	$k(Cr^{II})/k(V^{II})$	*Ref.*
$[Co(NH_3)_6]^{3+}$	8.9×10^{-5}	3.7×10^{-3}	0.024	37
$[Co(en)_3]^{3+}$	2×10^{-5}	2×10^{-4}	0.1	38
$[Co(NH_3)_5py]^{3+}$	4.3×10^{-3}	2.4×10^{-1}	0.018	39, 4
$[\{Co(NH_3)_5\}_2NH_2]^{5+}$	3.1×10^{-3}	1.5×10^{-1}	0.021	40
$[Ru(NH_3)_5py]^{3+}$	3.4×10^{3}	1.2×10^{5}	0.028	41
$[(H_3N)_5Co\cdot O_2\cdot Co(NH_3)_5]^{5+}$	2.3×10^{3}	9.6×10^{4}	0.023	42
$[(trenen)Co\cdot O_2\cdot Co\cdot(trenen)]^{5+}$	8.4×10^{3}	4.3×10^{5}	0.020	43[a]
$[(H_3N)_4Co\cdot\mu\text{-}(NH_2,O_2CH)\cdot Co(NH_3)_4]^{4+}$	1.68×10^{-3}	6.0×10^{-2}	0.028	24
$[(H_3N)_4Co\cdot\mu\text{-}(NH_2,O_2CMe)\cdot Co(NH_3)_4]^{4+}$	4.7×10^{-4}	2.2×10^{-2}	0.021	24
$[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)]^{7+}$	8.1×10^{-3}	0.363	0.022	27[b]
$[Co_4(NH_3)_{12}(OH)_4(C_2O_4)]^{6+}$	3.6×10^{-3}	0.21	0.017	27[c]
$[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)]^{7+}$	4.4×10^{-3}	0.217	0.020	27[d]
$[Co(H_2O)_6]^{3+}$	1.25×10^{4}	8.8×10^{5}	0.017	29
$[Co(tet\text{-}a)(NH_3)_2]^{3+}$	4.8×10^{-3}	0.17	0.028	33[e]
$[Co(trans\text{-}14\text{-}diene)(NH_3)_2]^{3+}$	4.0×10^{-3}	0.098	0.040	33[e]
$[Co(tim)(NH_3)_2]^{3+}$	1.2×10^{-2}	0.41	0.029	33[e]

[a] trenen = 4-aminoethyl-1,4,7,10-tetra-azadecane. [b] Tetranuclear cobalt(III) complex (7); see p. 12. [c] Tetranuclear complex (8); see p. 12 [d] Tetranuclear complex (9); see p. 12. [e] For details of quadridentate ligands and ionic strength variations see Table 2.

systems where the rate constants for V^{II} reduction vary by nine orders of magnitude. The reduction of the dinuclear μ-amido-cobalt–ammine complexes with μ-formato- and μ-acetato-bridges has been described[24] and the suggestion that the lack of a co-ordination site imposes an outer-sphere mechanism on the system is consistent with the observed ratios of the rates of Cr^{II} and V^{II} reduction. The corresponding V^{II} reactions on the tetranuclear bridged oxalato-complexes show strict adherence to second-order kinetics,[28] the first reduction stage of the overall four-electron change being rate determining. The reaction with the hexa-aquocobalt(III) ion is too rapid for direct measurement by stopped-flow techniques.[29] The reaction rate was determined, however, by a competitive method in which Cr^{II} and V^{II} were allowed to react with the cobalt(III), the Cr^{II} being in large (30-fold) excess. By monitoring transmittance changes for the slower Cr^{II}–V^{III} reaction, it was possible to show that 66% of the cobalt(III) was reduced by the V^{II}, and from a knowledge of the $Cr^{II}{}_{aq}$–$Co^{III}{}_{aq}$ reaction rate that of the $V^{II}{}_{aq}$–$Co^{III}{}_{aq}$ reaction could be derived. The reaction is of the outer-sphere type, as is the rapid reduction[44] of $[Co(bipy)_3]^{3+}$, where the observed subsequent reactions are due to acid dissociation reactions of the $[Co(bipy)_3]^{2+}$ product.

The overall reaction for the reduction of chromium(VI) by vanadium(II) in acidic media may be represented[45] as

$$3V^{2+} + Cr^{VI} \xrightarrow{H^+} 3V^{3+} + Cr^{3+}$$

The rate law for this reaction with the reductant present in excess is

$$-d[Cr^{VI}]/dt = \{k_1 + k_2[H^+] + k_3[V^{II}]\}[HCrO_4^-][V^{II}]$$

the first step in the reaction resulting in the direct formation of vanadium(III) by means of a one-electron transfer. There is no direct formation of V^{IV} in the reaction. The pathway k_1 may be represented as

$$HCrO_4^- + V^{II} \xrightarrow{k_1} Cr^V + V^{III}$$

and accounts for >70% of the reaction. The hydrogen-ion dependence is considered to derive from the reactions

$$HCrO_4^- + H^+ \underset{K_a}{\rightleftharpoons} H_2CrO_4$$

$$H_2CrO_4 + V^{II} \xrightarrow{k_2'} \text{products}$$

where $k_2 = k_2'K_a$. A possible mechanism for the vanadium(II)-dependent term involves the formation of a dinuclear complex which is present in steady-state concentrations and which undergoes reduction. There is no evidence for any effect of vanadium(III) on the reaction rate. The one-equivalent reduction of titanium(IV) by vanadium(II) has been shown[46] to be

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[44] R. Davies, M. Green, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1171.
[45] K. L. Bridges, S. K. Mukherjee, and G. Gordon, *Inorg. Chem.*, 1972, **11**, 2494.
[46] J. D. Ellis and A. G. Sykes, *J.C.S. Dalton*, 1973, 537.

independent of hydrogen ions in the concentration range 0.35—1.85M; the rate equation is of the form

$$-\mathrm{d}[\mathrm{V^{II}}]/\mathrm{d}t = \mathrm{d}[\mathrm{Ti^{III}}]/\mathrm{d}t = k[\mathrm{V^{II}}][\mathrm{Ti^{IV}}]$$

the value for k being in the range consistent with a substitution-controlled rate-determining step.

Several approaches have been made to identify free energy correlations in the outer-sphere reactions of vanadium(II).[33,47,48] Electrochemical data have been used to provide information on the standard redox potentials of cobalt(II)–cobalt(III) couples involving a variety of ligands, and the standard free energies have been calculated. The correlation between activation free energy and overall free energy may be described[48] in terms of an expression

$$\Delta G^{\neq} = a + b\Delta G^{\circ} + \ldots$$

for the outer-sphere reactions of vanadium(II), the value of b being slightly greater than the predicted Marcus value of 0.5 (0.56 ± 0.08). The parameter a is only slightly dependent on the nature of the cobalt(III) complex being reduced and it is suggested that there is a smaller dependence on reorganizational parameters with the oxidant than would be predicted on the basis of the Marcus theory, changes in the axial ligands in $[\mathrm{Co^{III}N_4L_2}]$ complexes showing only small variations in reaction rate. A modification of the simple Marcus cross-reaction relationship which explicitly utilizes fractional b values differing from 0.5 has been shown to agree with experimentally derived values for two redox series.[47]

Iron(II).—An excellent review of electron-transfer (inner- and outer-sphere) reactions involving vanadium(IV) as compared with iron(II) as a reductant for both cationic and anionic species has been published.[9] The rate constants for oxidations of iron(II) are almost invariably greater than those for vanadium(IV), the difference being smaller when there is evidence for an inner-sphere oxidation. For outer-sphere reactions, on the other hand, the rates may differ by several hundred-fold.

The kinetics of the electron-transfer reactions between oxalatocobalt(III) complexes and iron(II) have been described.[49] For cationic complexes, the rates decrease in the order (ox = oxalate) $[\mathrm{Co(ox)(phen)_2}]^+ > [\mathrm{Co(ox)(bipy)_2}]^+ > [\mathrm{Co(ox)(NH_3)_4}]^+ > [\mathrm{Co(ox)(en)_2}]^+ > [\mathrm{Co(ox)(trien)}]^+$; the variation in reactivity is attributed to changes in the enthalpy of activation, a linear relationship being observed between $\Delta H^{\neq}$ and $\log k$ (k = observed rate constant). The much faster reactions of the phenanthroline and bipyridyl complexes are also considered to derive from the efficiency of these ligands as electron mediators in reactions of this type. A relationship has also been observed between $\log k$ and the half-wave potential of the polarographic reduction of the cobalt(III)

[47] D. R. Rosseinsky, *J.C.S. Chem. Comm.*, 1972, 225.

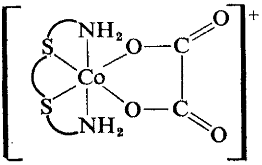
[48] D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, 1972, **94**, 394.

[49] K. Ohashi, *Bull. Chem. Soc. Japan*, 1972, **45**, 3093.

centre. In the corresponding reduction of the *s-cis*-oxalato-(1,8-diamino-3,6-dithiaoctane)cobalt(III) ion (10), $[CoN_2S_2(ox)]^+$, the rate enhancement over the tetra-ammine analogue is very marked (3.9×10^3 greater) and is probably due to the influence of the co-ordinated sulphur of the thioether groups. The observed rate law may be represented by the expression

$$-d[Co^{III}(N_2S_2)(ox)^+]/dt = k_2[Co^{III}][Fe^{II}]$$

no significant hydrogen-ion dependence being observed in lithium perchlorate media. Medium effects have been shown to be very significant in these reductions and whereas in $LiClO_4$–$HClO_4$ solutions over the range 0.20—0.95M $[H^+]$ the average value for the second-order rate constant $k_2 = 1.65 \pm 0.05$ l mol^{-1} s^{-1} it is seen from Figure 2 that over a comparable acidity range in $NaClO_4$–$HClO_4$ a 36% increase in k_2 is observed, suggesting that the data derived from the former media are more readily interpretable than those in sodium perchlorate solutions. The reaction mechanism is considered to involve a bridged activated complex, and experiments with $[Co(N_2S_2)(phen)]^+$ and $[Co(N_2S_2)(acac)]^+$, which were essentially unreactive on the time-scale of reduction of the oxalate complex, would tend to rule out the possibility of a sulphur bridge. It is suggested that the extent to which the bond to the sulphur



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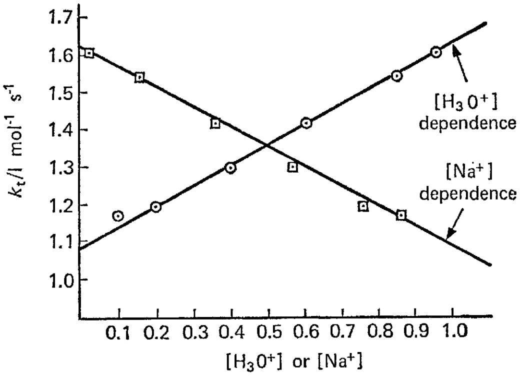

Figure 2 *Effect of* $[H_3O^+]$ *or* $[Na^+]$ *on the rate of the iron*(II)–$[Co(N_2S_2)(ox)]^+$ (10) *reaction in sodium perchlorate–perchloric acid media*
(Reproduced by permission from *Inorg. Chem.*, 1972, **11**, 2735)

atom *trans* to the bridge can be stretched may be responsible for rate enhancement.

Complexing of the reductant also induces rate enhancement of cobalt(III) complexes.[50] The rate constant for reduction of $[Co(NH_3)_5OAc]^{2+}$ by iron(II) has been given a lower limit of 5×10^{-5} l mol^{-1} s^{-1} whereas when the reductant is complexed to *N*-methyliminodiacetate (L^{2-}) in glycine buffer the corresponding value is 1.52×10^{-3} l mol^{-1} s^{-1}. The rate law derived is

$$-d[Co^{III}]/dt = k_2[Co^{III}(NH_3)_5OAc^{2+}][FeL]$$

with little effect of the complex $[FeL_2]^{2-}$ on the reaction rate. It may be that whereas the reactions of Fe^{2+} and FeL proceed *via* one pathway (*e.g.* inner-sphere with acetate bridging) that of $[FeL_2]^{2-}$ would take place by an outer-sphere mechanism.

The reduction of cobalt(III) complexes containing polymeric ligands, *e.g.* *cis*-$[Co(en)_2(PVP)X]^{2+}$ (X = Cl^-, Br^-, or N_3^- and PVP = poly-4-vinylpyridine), have been reported,[51, 52] the rate data being compared with those for the corresponding mono-pyridine species. The polymeric complexes are less reactive than the simpler species, probably as a result of the higher energy of rearrangement. The effects of bridging and non-bridging ligands are, however, similar for both types of complex ion.

In an investigation of the non-complementary redox process

$$\textit{cis-}\text{ or }\textit{trans-}[PtL_2X_2] + 2Fe^{3+} + 2X^- \underset{k_f}{\overset{k_r}{\leftrightharpoons}} \textit{cis-}\text{ or }\textit{trans-}[PtL_2X_4] + 2Fe^{2+}$$

(L = NH_3, NH_2Me, NH_2Et, NH_2Pr, or $\frac{1}{2}$en, X = Cl or Br) it has been shown[53] that, whereas the forward reactions involve the reaction of iron(III)–halide complexes, the reverse reaction when studied in at least a thirty-fold excess of reductant exhibits second-order kinetics, with the rate law

$$\text{Rate} = k_r[Pt^{IV}][Fe^{II}]$$

The reduction rate constants of the platinum(IV) complexes possessing the same geometric configuration and bonded halide depend to some extent on the ligand co-ordinated, the reactivity sequence being en < NH_3 < NH_2Me < NH_2Et < NH_2Pr, and a linear free energy relationship has been shown to exist between the activation free energy, $\Delta G^{\ddagger}_{red}$, and the overall free energy change ΔG_{red} for the above reaction (k_r). The slopes are slightly greater than 0.5, which may indicate an outer-sphere mechanism.

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[50] D. R. Cannon and J. Gardiner, *J.C.S. Dalton*, 1972, 887.

[51] Y. Kurimura and E. Tsuchida, *Nuova Cim.*, 1973, **49**, 64 (*Chem. Abs.*, 1973, **78**, 102 435y).

[52] E. Tsuchida, Y. Karino, H. Takahashi, and Y. Kurimura, *Nippon Kagaku Kaishi*, 1972, **12**, 2420 (*Chem. Abs.*, 1973, **78**, 62 760s).

[53] A. Peloso and M. Basato, *J.C.S. Dalton*, 1972, 2040.

In the flash photolysis of $[PtCl_6]^{2-}$, an absorption spectrum has been derived corresponding to the production of Pt^{III} as a transient which disproportionates in a second-order process.[54] The reaction with iron(II),

$$Pt^{III} + Fe^{2+} \longrightarrow Pt^{II} + Fe^{3+}$$

has been studied and, using the ionic strength dependence relationship based on this reaction, the charge of the reacting platinum species has been shown to be -1, consistent with a formulation of the ion as $[PtCl_4]^-$. The thallium(I)–thallium(III) exchange has been shown to be catalysed by iron(II),[55] the induced exchange being due to the reactions

$$Tl^{III} + Fe^{II} \rightleftharpoons Tl^{II} + Fe^{III}$$
$$Tl^{II} + Fe^{II} \rightleftharpoons Tl^{I} + Fe^{III}$$

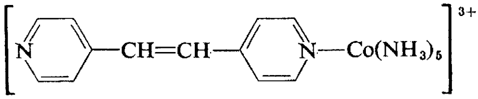
in which thallium(II) is produced as an intermediate.

The reductions of vanadium(V) by cyanobipyridyl complexes of iron(II) are considered[56] to be inner-sphere processes, with iron(III)–vanadium(IV) species as intermediates. In the reactions with $[Fe(CN)_4(bipy)]^{2-}$ and $[Fe(CN)_2(bipy)_2]$ the rates are close to the limits of detection by stopped-flow methods, the rate law being

$$\text{Rate} = k_{ox}[V^{V}][Fe^{II}]$$

Evidence for the inner-sphere mechanism is derived from comparison with cerium(IV) reactions, which have a substantially different rate ratio, with $[Fe(bipy)_3]^{2+}$ which would proceed *via* an outer-sphere process.

Lanthanide(II) Ions.—The europium(II) reductions of penta-amminecobalt(III) complexes with heterocyclic bases have been studied,[21] the reaction rates being shown to be independent of hydrogen-ion concentration. In the cases of the 4-ethoxycarbonylpyridine derivative and of the *trans*-1,2-bis-(4-pyridyl)-ethylene species (11) strong autocatalysis is observed, a reactive radical or radical cation being suggested as an intermediate. In the reaction involving the ethoxycarbonyl complex, it is suggested that the radical formed is of the form (12) and is produced on the one-electron reduction of the free ligand which in turn is liberated on conversion of the cobalt(III) oxidant into the substitution-labile cobalt(II) species, *e.g.* Scheme 6 (co-ordinated ammonia omitted). In the presence of $[Co(NH_3)(pyridine)]^{3+}$, which is not considered



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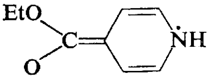

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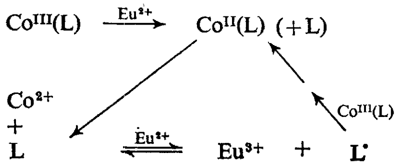
[54] R. C. Wright and G. S. Laurence, *J.C.S. Chem. Comm.*, 1972, 132.
[55] B. Warnqvist and R. W. Dodson, *Inorg. Chem.*, 1971, **10**, 2624.
[56] J. P. Birk and S. V. Weaver, *Inorg. Chem.*, 1972, **11**, 95.



Scheme 6

likely to react *via* an inner-sphere process, this complex is also reduced, suggesting that the autocatalysed reduction of the ester takes place *via* an outer-sphere mechanism.

The europium(II) reduction of *p*-formylbenzoatopenta-amminecobalt(III) has been investigated,[19b] a small acidity variation being observed. The dependence on hydrogen ion is slight, however, and may be due to medium effects.

Two studies have been reported on the reactions of ytterbium(II) as a reductant. There is some disagreement on the stability of this strongly reducing species in aqueous media. Espenson and co-workers[57] have generated the ion using electrochemical techniques in dilute aqueous perchloric acid and found that although solvent reduction occurred within 10—30 min in the absence of dissolved oxygen, the reagent was sufficiently stable to enable stopped-flow measurements to be made with typical reaction concentrations of Yb^{2+} of ~ 1—6×10^{-4}M. In the reactions with cobalt(III) and chromium(III) complexes, a one-electron transfer occurs. It is of interest that in the reaction with $[Co(en)_3]^{3+}$, with ionic strength maintained constant with $LiClO_4$, the second-order rate constant decreased from 548 to 451 l mol^{-1} s^{-1} on increasing the oxidant concentration {as $[Co(en)_3(ClO_4)_3]$} from 2.3 to 15×10^{-3}M. This may be due to medium effects where the rate for a reaction involving cations is dependent on the anion concentration. For the cobalt(III) species, no hydrogen-ion dependence was observed. For the complex $[Cr(H_2O)_6]^{3+}$, however, the rate law

$$-\mathrm{d}[Cr^{3+}]/\mathrm{d}t = k[Cr(H_2O)_6^{3+}][Yb^{2+}]/[H^+]$$

may be interpreted according to the reaction scheme

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [(H_2O)_5CrOH]^{2+} + H^+$$
$$[(H_2O)_5Cr(OH)]^{2+} + Yb^{3+} \longrightarrow Cr^{2+} + Yb^{3+}$$

The reactions are catalysed by chloride ions, which probably react *via* ion-pair formation with the oxidant.

The reactions of cobalt(III) and ruthenium(III) ammine complexes with Yb^{II}, Eu^{II}, and Sm^{II} have been investigated using a pulse radiolysis technique.[58] Whereas the reaction rates for Eu^{II} are similar to those of previous workers, the data for Yb^{2+} are in marked contrast to those described above. A previous

[57] R. J. Christensen, J. H. Espenson, and A. B. Butcher, *Inorg. Chem.*, 1973, **12**, 564.
[58] M. Faraggi and A. Feder, *Inorg. Chem.*, 1973, **12**, 236.

Table 2 *Rate constants and thermodynamic parameters for reduction reactions involving two metal-ion complexes. Second-order rate constants are quoted in* $\mathrm{l\ mol^{-1}\ s^{-1}}$ *unless stated, and* $T = 25$ °C. *The units of* $\Delta H^{\ddagger}$ *and* $\Delta S^{\ddagger}$ *are* $\mathrm{kcal\ mol^{-1}}$ *and* $\mathrm{cal\ deg^{-1}\ mol^{-1}}$ *respectively*

Oxidant	*k* (25 °C)	*I*/M	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Reductant = chromium(II)					
$[Co(NH_3)_5(p\text{-form bz})]^{2+}$	53	1.10	2.7	−42	19*b*[a]
$[Co(NH_3)_5(p\text{-form bz})]^{2+}$	38	1.10	0.3	−46	19*b*[b,c]
$[Co(NH_3)_5(m\text{-form bz})]^{2+}$	0.14	1.10	8.3	−38	19*b*[d,e]
$[Co(NH_3)_5(m\text{-form bz})]^{2+}$	0.17	1.10	2.2	−56	19*b*[d,f]
$[Co(NH_3)_5(benz)]^{2+}$	0.15	1.0	9.0	−33	19*b*[g]
$[Co(NH_3)_5(acrylato)]^{2+}$	0.62	1.20	—	—	18
$[Co(NH_3)_5(acetylenecarboxylato)]^{2+}$	1.46	1.20	—	—	18
$[Co(NH_3)_5(trans\text{-cinnamato})]^{2+}$	1.15	1.20	—	—	18
$[Co(NH_3)_5(sorbato)]^{2+}$	1.25	1.20	—	—	18
$[Co(NH_3)_5(sorbato)]^{3+}$	0.49	1.20	—	—	18[b]
$[Co(NH_3)_5(2\text{-furanacrylato})]^{2+}$	1.36	1.20	—	—	18
$[Co(NH_3)_5(2\text{-furanacrylato})]^{3+}$	0.78	1.20	—	—	18[b]
$[Co(NH_3)_5(o\text{-hydroxycinnamato})]^{2+}$	1.30	1.20	—	—	18
$[Co(NH_3)_5(o\text{-hydroxycinnamato})]^{3+}$	0.44	1.20	—	—	18[b]
$[Co(NH_3)_5(m\text{-methoxycinnamato})]^{2+}$	1.26	1.20	—	—	18
$[Co(NH_3)_5(m\text{-methoxycinnamato})]^{3+}$	0.60	1.20	—	—	18[b]
$[Co(NH_3)_5(p\text{-hydroxycinnamato})]^{2+}$	1.12	1.20	—	—	18
$[Co(NH_3)_5(phenylpropiolato)]^{2+}$	1.40	1.20	—	—	18
$[Co(NH_3)_5(m\text{-hydroxycinnamato})]^{2+}$	1.14	1.20	—	—	18
$[Co(NH_3)_5(2\text{-thiophenacrylato})]^{2+}$	1.36	1.20	—	—	18
$[Co(NH_3)_5(3\text{-pyridineacrylato})]^{2+}$	1.20	1.20	—	—	18
$[Co(NH_3)_5(malonato)]^{2+}$	4.05	4.00	—	—	5
$[Co(NH_3)_5(dimethylmalonato)]^{2+}$	0.312	4.00	—	—	5
$[Co(NH_3)_5(glycinato)]^{3+}$	0.064	1.0	7.7	−38	20
$[Co(NH_3)_5(Me\text{-glycinato})]^{3+}$	0.044	1.0	8.0	−38	20
$[Co(NH_3)_5(Me_2\text{-glycinato})]^{3+}$	0.038	1.0	7.5	−40	20

$[Co(NH_3)_5(Me_3\text{-glycinato})]^{3+}$	0.016	1.0	7.7	−41	20
$[Co(NH_3)_5(\text{benzonitrile})]^{3+}$	0.047	1.0	—	—	22
$[Co(NH_3)_5(\text{3-cyanophenol})]^{3+}$	0.042	1.0	9.4	−34	22
$[Co(NH_3)_5(\text{4-cyanophenol})]^{3+}$	0.030	1.0	11.1	−28	22
$[Co(NH_3)_5(\text{terephthalonitrile})]^{3+}$	0.92	1.0	5.5	−40	22
$[Co(NH_3)_5OH_2]^{3+}$	3.12	1.0	—	—	4[b]
$[(NH_3)_4Co\cdot\mu\text{-}(NH_2,HCHO)\cdot Co(NH_3)_4]^{4+}$	1.68×10^{-3}	1.0	13.9	−24.5	24
$[(H_2O)(NH_3)_4Co\cdot\mu\text{-}(NH_2)\cdot Co(NH_3)_4(OCHO)]^{4+}$	9.2×10^{-6}	1.0	10.6	−46	24
$[(NH_3)_4Co\cdot\mu\text{-}(NH_2,\text{acetato})\cdot Co(NH_3)_4]^{4+}$	4.7×10^{-4}	1.0	11.5	−35	24
$[(en)_2Co\cdot\mu\text{-}(NH_2,O_2)\cdot Co(en)_2]^{4+}$	$>1.4\times10^{5}$	2.0	—	—	26[h]
$[(en)_2Co\cdot\mu\text{-}(NH_2,O_2)\cdot Co(en)_2]^{3+}$	2.1×10^{3}	2.0	7.75	−17.5	26
$[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)]^{5+}$	3.4×10^{-3}	0.2	—	—	27
$[Co_3(NH_3)_{11}(OH)_2(C_2O_4)]^{5+}$	$>3\times10^{-2}$	0.2	—	—	27[h]
Tetranuclear species (7) (p. 12)	8.1×10^{-3}	1.0	10.9	−31.6	28[i]
Tetranuclear species (8) (p. 12)	3.6×10^{-3}	0.2	8.2	−42.1	28[i]
Tetranuclear species (9) (p. 12)	4.4×10^{-3}	1.0	—	—	28[i]
$[Co(H_2O)_6]^{3+}$	1.25×10^{4}	3.0	9.5	−7.8	29
$[Co(OH)]^{2+}$	6.59×10^{3}	3.0	12.7	1.7	29[j]
$[Co(en)_2(MeSCH_2CO_2)]^{2+}$	2.74×10^{2}	1.0	8.5	−19	6
$[Co(en)_2(NH_2CH_2CO_2)]^{2+}$	2.2	1.0	8.8	−27	6
$[Co(en)_2(MeSCH_2CH_2NH_2)]^{3+}$	0.38	1.0	5.4	−42	6
$[Ta_6Br_{12}]^{3+}$	2.7×10^{5}	0.10	0	−30	30
UO_2^{2+}	1.47×10^{4}	2.00	0.79	−36.8	31
$[Co(\text{tet-}a)(NH_3)_2]^{3+}$	4.8	0.37	—	—	33
$[Co(\textit{trans}\text{-14-diene})(NH_3)_2]^{3+}$	4.0	0.65	8.8	−40	33
$[Co(\text{tim})(NH_3)_2]^{3+}$	12.0	0.65	—	—	33[k]
$[Co(CN)_5Br]^{3-}$	1.14×10^{5}	1.00	—	—	34[l]
$[Co(CN)_5]^{3-}$	2.4×10^{4}	1.00	—	—	34[l]
Reductant = *vanadium*(II)					
cis-$[Co(en)_2(NH_3)N_3]^{2+}$	10.3	1.0	12.6	−11.6	35
trans-$[Co(en)_2(N_3)_2]^{+}$	26.6	1.0	12.2	−11.2	35
trans-$[Co(en)_2(H_2O)N_3]^{2+}$	18.1	1.0	11.0	−16.0	35

Table 2 (*continued*)

Oxidant	k (25 °C)	I/M	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
cis-$[Co(NH_3)_4(H_2O)N_3]^{2+}$	16.6	1.0	12.1	−12.5	35
cis-$[Co(en)_2(HCO_2)_2]^+$	7.4	2.0	10.9	−17	36
cis-$[Co(en)_2(H_2O)(HCO_2)]^{2+}$	8.4	2.0	—	—	36
trans-$[Co(en)_2(HCO_2)_2]^+$	6.5	2.0	11.0	−20	36
$[Co(bipy)_3]^{3+}$	1.11×10^3	2.0	3.6	−32.6	44
$[(H_3N)_4Co\cdot\mu\text{-}(NH_2,O_2CH)\cdot Co(NH_3)_4]^{4+}$	6.0×10^{-2}	1.0	—	—	24
$[(H_3N)_4Co\cdot\mu\text{-}(NH_2,O_2CMe)\cdot Co(NH_3)_4]^{4+}$	2.2×10^{-2}	1.0	—	—	24
$[Co_4(NH_3)_{14}(NH_2)(OH)_2C_2O_4)]^{7+}$	0.363	1.0	—	—	27^m
$[Co_4(NH_3)_{12}(OH)_4(C_2O_4)]^{6+}$	0.21	0.2	—	—	27^n
$[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)]^{7+}$	0.217	1.0	—	—	27^o
$HCrO_4^-$	1.02×10^5	1.0	—	—	45^p
H_2CrO_4	3.3×10^5	1.0	—	—	45^p
Ti^{IV}	1.95	2.0	12.7	−14.6	46
$[Co(tet\text{-}a)(NH_3)_2]^{3+}$	0.17	0.14	7.0	−39	33
$[Co(trans\text{-}14\text{-}diene)(NH_3)_2]^{3+}$	9.8×10^{-2}	0.14	7.4	−38	33
$[Co(tim)(NH_3)_2]^{3+}$	0.41	0.14	7.6	−35	33^k
$Co(edta)^-$	7.9×10^2	0.12	—	—	48
$[Co(C_2O_4)_3]^{3-}$	3.1×10^4	0.12	—	—	48
$[Co(tet\text{-}a)Cl_2]^+$	1.56×10^3	0.57	—	—	48
$[Co(tet\text{-}a)Br_2]^+$	3.4×10^4	0.57	—	—	48
$[Co(trans\text{-}14\text{-}diene)Cl_2]^+$	6×10^3	0.10	—	—	48
$[Co(trans\text{-}14\text{-}diene)Br_2]^+$	2.3×10^4	0.12	—	—	48
Reductant = *iron*(II)					
$[Co(C_2O_4)(NH_3)_4]^+$	7.45×10^{-4}	1.5	16.7	−16.7	49^q
$[Co(C_2O_4)(en)_2]^+$	2.28×10^{-5}	1.5	19.1	−15.6	49^q
$[Co(C_2O_4)(trien)]^+$	1.67×10^{-5}	1.5	19.6	−14.8	49^q
$[Co(C_2O_4)(bipy)_2]^+$	1.24	1.5	10.8	−19.1	49^q
$[Co(C_2O_4)(phen)_2]^+$	3.55	1.5	9.5	−24.0	49^q
$[Co(C_2O_4)_2(NH_3)_2]^-$	4.8×10^{-2}	1.0	14.3	−16.5	49

$[Co(C_2O_4)_2(en)]^-$	3.7×10^{-3}	1.0	16.1	−15.6	49
$[Co(N_2S_2)(C_2O_4)]^+$	1.65	1.0	10.7	−21.5	7^r
$[Co(NH_3)_5(OAc)]^{2+}$	1.52×10^{-3}	1.0	21.7	1.7	50^s
trans-$[Pt(NH_3)_2Br_4]$	2.9×10^{-4}	1.0	17.0	−18.7	53^t
cis-$[Pt(NH_3)_2Br_4]$	1.46×10^{-4}	1.0	16.3	−22.5	53
trans-$[Pt(NH_2Me)_2Br_4]$	6.4×10^{-4}	1.0	17.2	−16.0	53
cis-$[Pt(NH_2Me)_2Br_4]$	2.45×10^{-4}	1.0	16.3	−28.6	53^t
trans-$[Pt(NH_2Et)_2Br_4]$	1.15×10^{-3}	1.0	17.2	−15.1	53^t
cis-$[Pt(NH_2Et)_2Br_4]$	4.12×10^{-4}	1.0	16.7	−18.9	53^t
trans-$[Pt(NH_2Pr)_2Br_4]$	1.45×10^{-3}	1.0	16.3	−17.9	53^t
cis-$[Pt(en)Br_4]$	4.5×10^{-5}	1.0	15.8	−26.4	53^t
trans-$[Pt(NH_2Pr)_2Cl_4]$	9.7×10^{-3}	1.0	13.9	−22.0	53^t
trans-$[Pt(NH_3)_2Cl_4]$	5.4×10^{-3}	1.0	14.3	−21.5	53^t
trans-$[Pt(NH_2Et)_2Cl_4]$	8.0×10^{-3}	1.0	14.8	−19.1	53^t
trans-$[Pt(NH_2Me)_2Cl_4]$	5.1×10^{-2}	1.0	15.3	−18.7	53^t
V^V	2.4×10^{6}	0.5	—	—	56^u
V^V	8.3×10^{5}	0.5	—	—	56^v
Reductant = *Europium*(II)					
$[(H_3N)_5Co(pyridine)]^{3+}$	0.083	1.3	—	—	21
$[(H_3N)_5Co(3\text{-}Me\text{-}pyridine)]^{3+}$	0.038	1.3	—	—	21
$[(H_3N)_5Co(4\text{-}Me\text{-}pyridine)]^{3+}$	0.039	1.3	—	—	21
$[(H_3N)_5Co(3\text{-}Et\text{-}pyridine)]^{3+}$	0.067	1.3	—	—	21
$[(H_3N)_5Co(4\text{-}Et\text{-}pyridine)]^{3+}$	0.056	1.3	—	—	21
$[(H_3N)_5Co(pyrazole)]^{3+}$	0.034	1.3	—	—	21
$[(H_3N)_5Co(isoquinoline)]^{3+}$	0.14	1.3	—	—	21
$[(H_3N)_5Co(3\text{-}methoxycarbonylpyridine)]^{3+}$	0.21	1.3	—	—	21
$[(H_3N)_5Co(p\text{-}form\ bz)]^{2+}$	1.08	1.1	—	—	$19b^a$
$[(H_3N)_5CoF]^{2+}$	1.5×10^{4}	1.0	—	—	58
$[(H_3N)_5CoCl]^{2+}$	4.7×10^{2}	1.0	—	—	58
$[(H_3N)_5CoN_3]^{2+}$	$\leqslant 30$	0.06	—	—	58
$[(H_3N)_5CoCN]^{2+}$	< 30	0.06	—	—	58

Table 2 (*continued*)

Oxidant	k (25 °C)	I/M	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Reductant = Ytterbium(II)					
$[Co(en)_3]^{3+}$	445	0.2	1.3	−42.1	57
$[Co(NH_3)_6]^{3+}$	2230	0.2	1.3	−38.9	57
$[Co(NH_3)_5H_2O]^{3+}$	3.14×10^4	0.2	—	—	57
$[(H_3N)_5CrF]^{2+}$	55	0.2	5.2	−33.2	57
$[(H_3N)_5CrCl]^{2+}$	13.5	0.2	5.7	−34.4	57
$[(H_2O)_5CrF]^{2+}$	1.95×10^3	0.2	—	—	57
$[(H_2O)_5CrCl]^{2+}$	1.00×10^3	0.2	—	—	57
$[(H_2O)_5CrBr]^{2+}$	1.65×10^3	0.2	—	—	57
$[(H_2O)_5CrN_3]^{2+}$	4.46×10^3	0.2	—	—	57
$[(H_2O)_5CrOH]^{2+}$	780	0.2	—	—	57
$(Co(en)_3]^{3+}$	$<5\times10^3$	1.0	—	—	58
$[Co(NH_3)_6]^{3+}$	$<5\times10^3$	0.06	—	—	58
$[(H_3N)_5Co(OH_2)]^{3+}$	6.4×10^5	1.0	—	—	58
$[(H_3N)_5CoN_3]^{2+}$	2.6×10^7	0.5	—	—	58
$[(H_3N)_5CoBr]^{2+}$	3.0×10^6	0.06	—	—	58
$[(H_3N)_5CoCl]^{2+}$	4.3×10^6	0.06	—	—	58
$[(H_3N)_5CoF]^{2+}$	1.1×10^7	0.06	—	—	58
$[Ru(NH_3)_6]^{3+}$	5.0×10^6	0.06	—	—	58
$[(H_3N)_5Ru(OH_2)]^{3+}$	1.0×10^7	0.06	—	—	58
$[(H_3N)_5RuCl]^{2+}$	1.5×10^7	0.06	—	—	58
$[(H_3N)_5RuBr]^{2+}$	3.3×10^7	0.06	—	—	58
$[(H_3N)_5RuI]^{2+}$	$\sim10^8$	0.06	—	—	58

[a] (p-form bz) = p-formylbenzoato. [b] Acid-dependent pathway. [c] Units are $l^2\,mol^{-2}\,s^{-1}$. [d] (m-form bz) = m-formylbenzoato. [e] Adjacent attack. [f] Path leading to ligand release. [g] benz = benzoato. [h] $[H^+]$ = 0.1M. [i] See text for formulae of tetranuclear complexes. [j] Composite kinetic term involving K_h (hydrolysis constant for Co^{3+}_{aq}). [k] tim = quadridentate macrocycle, 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene. [l] Reductant is $[Cr(CN)_6]^{4-}$. [m] Tetranuclear complex (7); see p. 12. [n] Tetranuclear complex (8); see p. 12. [o] Tetranuclear complex (9); see p. 12. [p] T = 10 °C, but little variation of rate with temperature observed. [q] Sulphate media, $[H_2SO_4]$ = 0.55M. [r] N_2S_2 ligand = 1,8-diamino-3,6-dithiaoctane. [s] Reductant = iron(II)-N-methyliminodiacetate complex. [t] T = 30 °C, $[H^+]$ = 0.5M. [u] T = 10 °C, reductant is $[Fe(CN)_4(bipy)]^{2-}$. [v] T = 10 °C, reductant is $[Fe(CN)_2(bipy)_2]$.

study on the stability of this reductant[59] indicates a half-time of at most one second, markedly less than that for the species generated electrochemically. It is possible that there may be enhancement of the decay owing to the presence of hydrogen peroxide produced during the radiolysis, and it may be necessary to adopt modified procedures for more satisfactory evaluation of data for this strongly reducing species. Comparison of the rates for the three lanthanide ions suggests that in the reactions with cobalt(III) complexes, an inner-sphere mechanism is adopted, although with the rate for Sm^{II} one order of magnitude lower than for Yb^{II} there may be some outer-sphere contribution. With the halogenopenta-ammine complexes the 'normal' reactivity order ($F < Cl < Br < I$) is found for Sm^{II} whereas the 'inverse' order holds for Eu^{II} and Yb^{II}. In the case of the ruthenium(III) complexes, catalysis by Cl^- of the outer-sphere reactions with $[Ru(NH_3)_6]^{3+}$ is observed with Sm^{II} and Yb^{II}.

2 Oxidizing Agents

Cerium(IV).—The oxidation of vanadium(IV) by cerium(IV) has been studied in 1—2M perchloric acid,[60] the reaction being first-order with respect to each reactant. Under the experimental conditions prevailing, the predominant oxidizing species is $CeOH^{3+}$, the reaction being

$$CeOH^{3+} + VO^{2+} \xrightarrow{k_2} Ce^{III} + VO_2^+ + H^+$$

The dependence of the rate on $[H^+]$, which in a previous study[61] suggested an increase with increasing hydrogen-ion concentration, has been shown to be anomalous, the variation being expressed in the form

$$k_2 + k_0 + k_1[H^+]^{-1}$$

although it is not conclusive that the k_0 term is an additional pathway since medium effects may be important. The oxidation of neptunium(V) has been investigated in perchloric acid using stopped-flow techniques.[62] The rate of disappearance of Ce^{IV} is first-order with respect to both $[Ce^{IV}]$ and $[Np^V]$ and is essentially first-order with respect to hydrogen-ion concentration. In a treatment different from that described above, the authors have chosen to include the contribution of a small amount of $[Ce(OH)_2]^{2+}$ which might be present in their reaction media. They have found that the kinetically important reaction is

$$NpO_2^+ + Ce^{4+} \longrightarrow NpO_2^{2+} + Ce^{III}$$

with little observed variation of rate with temperature. It is of interest to note that the corresponding reaction with hexa-aquocobalt(III) is relatively slow. In the few reactions of MO_2^+ species studied it appears that oxidations by

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[59] M. Faraggi and Y. Tendler, *J. Chem. Phys.*, 1972, **56**, 3287.
[60] N. A. Daugherty and R. L. Taylor, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1756.
[61] G. N. Rao, *Current Sci.*, 1969, **22**, 541.
[62] A. Ekstrom and A. McLaren, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2015.

Fe^{III} or V^{IV} show either small positive or no acid dependences, whereas those involving cerium(IV) have an inverse hydrogen-ion dependence which is taken to imply participation in the reaction of hydrolysed metal ions and an inner-sphere mechanism.

The cerium(IV) oxidation of ferrocene-1,1′-disulphonic acid in sulphate media has been described,[63] kinetic data being derived from potential–time curves. Three moles of oxidant are consumed with breakdown of the sandwich structure ($X = C_5H_4SO_3H$):

$$FeX_2 + 3Ce^{IV} \longrightarrow Fe^{3+} + 2X + 3Ce^{III}$$

Redox systems of the hexamethylbenzene cluster compounds of niobium and tantalum have been investigated,[64] and reactions of the type

$$[(Me_6C_6)_3M_3X_6]_2^{2+} + 2Ce^{IV} \longrightarrow [(Me_6C_6)_3M_3X_6]_2^{4+} + 2Ce^{III}$$

have been shown to occur readily (M = Nb or Ta, X = Cl or Br). These systems are analogous to the metal–chloro cluster ions $[M_6Cl_{12}]^{2+}$ previously studied. The reaction

$$4[Ru(NH_3)_6]^{2+} + 14H^+ + 6Cl^- \longrightarrow 2[Ru_2Cl_3(NH_3)_6]^{2+} + H_2 + 12NH_4^+$$

yields a blue cationic complex with ruthenium in mixed oxidation states[65] which is unstable in oxygen. It is suggested that there are three chlorine bridges between the ruthenium atoms, and evidence for both Ru^{II} and Ru^{III} has been derived from oxidation by cerium(IV). The oxidation of mercury(I) dimer by cerium(IV) in sulphate media is catalysed by ruthenium(IV). A linear dependence on Ru^{IV} is observed[66] and a possible mechanism involves intermediate formation of ruthenium(V):

$$Ru^{IV} + Ce^{IV} \longrightarrow Ru^{V} + Ce^{III}$$
$$Ru^{V} + Hg^{I} \longrightarrow Ru^{IV} + Hg^{II}$$

At high concentrations of mercury(I), however, all the ruthenium(IV) is reduced to ruthenium(III). In the photochemical oxidation of Hg^{I} by Ce^{IV} in acid perchlorate media it has been suggested[67] that the oxidant species is the one involved in the primary photochemical process. In aqueous solution, or even in the presence of excess cerium(IV), there is no indication of the oxidation of free carbon monoxide. When bound to ruthenium in the cation $[Ru(NH_3)_5CO]^{2+}$, however,[68] the CO is readily oxidized (in a ten-fold excess of oxidant) to bound CO_2. The activation of the bound ligand is considered to derive from its binding to the $(H_3N)_5Ru^{2+}$ centre, but the presence of excess

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[63] J. Holecek, K. Handlin, and I. Pavlik, *Coll. Czech. Chem. Comm.*, 1972, **37**, 1085.

[64] R. B. King, D. M. Braitsch, and P. N. Kapoor, *J.C.S. Chem. Comm.*, 1972, 1072.

[65] E. E. Mercer and L. W. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 6426.

[66] K. B. Yatsimirskii, L. P. Tikhonova, L. N. Zakrevskaya, and I. P. Svarovskaya, *Zhur. neorg. Khim.*, 1972, **17**, 3206.

[67] A. Nuyt and M. Zador, *Canad. J. Chem.*, 1972, **50**, 2413.

[68] G. D. Watt, *J. Amer. Chem. Soc.*, 1972, **94**, 7351.

cerium(IV) may also be important since a stable intermediate is formed when $Ce^{IV}] : [Ru(NH_3)_5CO^{2+}]$ is <3.

The uranium(IV)–cerium(IV) reaction has been investigated in tributyl phosphate–chloroform solutions.[69] The reaction is second-order overall and in 20—30% Bu_3PO_4 the rate constant is about two orders of magnitude lower than for the corresponding aqueous reaction at the same temperature. As in the aqueous system, the rate is inversely dependent on hydrogen-ion concentration. The activation energy is also similar to that in water and is independent of tributyl phosphate concentration and pH.

Chromium(VI).—The oxidation of ferrocene has been studied[70] in water–acetone solvent mixtures (1 : 1 v/v) with a mole fraction of the acetone in the solvent of 0.195. The stoicheiometry may be represented by the equation

$$3[Fe(C_5H_5)_2] + HCrO_4^- + 7H^+ \longrightarrow 3[Fe(C_5H_5)_2]^+ + Cr^{3+} + 4H_2O$$

The side reactions, the oxidation of acetone by Cr^{VI}, which occurs if the medium is acidic, and the slow decomposition of ferrocene in acidified solutions of acetone, were overcome by reaction of a solution containing both Cr^{VI} and ferrocene but no perchloric acid in one reservoir of the stopped-flow apparatus with a solution of perchloric acid in aqueous acetone. The above reaction takes place much more rapidly than either of the side reactions. The oxidation rate is dependent on hydrogen-ion concentration, and allowance has been made for the small amount of H_2CrO_4 present in the solutions:

$$H_2CrO_4 \underset{H^+}{\rightleftharpoons} + HCrO_4^- \qquad K_a$$

The rate law may be expressed as

$$\frac{-\,d[Cr^{VI}]}{dt} = \frac{-d[Fe(C_5H_5)_2]}{3dt} = \frac{k_1[H^+]K_a}{[H^+] + K_a}[Fe(C_5H_5)_2][Cr^{VI}]_{tot}$$

The reactive chromium(VI) species is considered to be $HCrO_4^-$ and the activated complex may be formulated as $[Fe(C_5H_5)_2H_2CrO_4]$, the rate-determining process being

$$[Fe(C_5H_5)_2] + HCrO^- + H^+ \longrightarrow [Fe(C_5H_5)_2]^+ + H_2CrO_4^-$$

with two subsequent rapid electron-transfer reactions involving Cr^V and Cr^{IV} to yield the hexa-aquochromium(III) ion.

The association reactions of Cr^{VI} with Np^{IV}, Th^{IV}, and Fe^{III} have been investigated spectrophotometrically.[71] In the case of the reaction with Np^{IV}, a redox reaction occurs at a rate much lower than that for complex formation, the products being Np^V, $[Cr(H_2O)_6]^{3+}$, and a Np^V–Cr^{III} complex which may result from the importance of Cr^{IV} as an intermediate. The corresponding

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[69] L. M. Frovola, V. S. Lakaev, G. A. Timofeev, and A. G. Rykov, *Radiokhimiya*, 1972, **14**, 763 (*Chem. Abs.*, 1973, **78**, 62 779e).

[70] J. R. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, 1972, **11**, 3136.

[71] M. J. Burkhart and R. C. Thompson, *J. Amer. Chem. Soc.*, 1972, **94**, 2999.

reaction with Pu^{IV} has been used to prepare the Cr^{III}–Pu^{V} complex,[72] which has been isolated by ion-exchange techniques. Several redox reactions with this dinuclear species have been investigated and it is found that 'complexing' the PuO_2^+ to the inert Cr^{III} centre slows down the rate of oxidation of the Pu^{V} by Ce^{IV} and Np^{VI}. The stoicheiometry of the reaction with cerium(IV), however, is dependent on whether or not the oxidant is in excess.

The oxidation of uranium(IV) by Cr^{VI} proceeds[73] quantitatively to yield UO_2^{2+} and $[Cr(H_2O)_6]^{3+}$, the rate being inversely dependent on the hydrogen-ion concentration. The rate law may be expressed as

$$-d[Cr^{VI}]/dt = \{k_1 + k_2[H^+]^{-1}\}[U^{IV}][HCrO_4^-]$$

where a small but significant acid-independent pathway is observed which may, however, be due to medium effects. The mechanism may be described as

$$U^{IV} + Cr^{VI} \longrightarrow U^{VI} + Cr^{IV}$$
$$Cr^{IV} + Cr^{VI} \xrightarrow{\text{fast}} 2Cr^{V}$$
$$Cr^{V} + U^{IV} \xrightarrow{\text{fast}} Cr^{III} + U^{VI}$$

Evidence for the formation of Cr^{V} as an intermediate has been derived using the induced oxidation of iodide ions, which may act as a scavenger in the competing reactions:

$$Cr^{V} + I^- + H^+ \longrightarrow Cr^{III} + HOI$$
$$HOI + I^- \longrightarrow I_2$$

The yield of iodine, which has also been evaluated as a function of $[I^-] : [U^{IV}]$ concentrations and $[H^+]$, indicates that no uranium(V) is produced. Support for the absence of any species of this type is also given from the effects of iron(III) on the rate, the rate constants being identical to within experimental error with those where Fe^{III} is absent. It is of interest to note that [as in the case of cerium(IV) oxidations] although in general the reactions of Cr^{VI} with metal ions have either a small positive or no hydrogen-ion dependences, exceptions are provided in the cases of U^{IV}, Np^{IV}, and Pu^{IV}. The effect is considered to arise largely because an aquo-ion (*e.g.* U^{4+}) is oxidized directly to an oxo-cation (UO_2^{2+}) in the reaction

$$U^{4+} + HCrO_4^- + 4H_2O \longrightarrow UO_2^{2+} + [Cr(OH)_4(H_2O)_2] + H^+$$

where the hydrogen ion produced is removed from one reactant prior to the formation of the transition state.

Iron(III).—The reactions of iron(III) with platinum(II) ammine complexes in the presence of halide ions have been described:[53]

$$[PtL_2X_2] + 2Fe^{3+} + 2X^- \rightleftharpoons \textit{cis-}\text{ or }\textit{trans-}[PtL_2X_4] + 2Fe^{2+}$$

[72] T. W. Newton and M. J. Burkhart, *Inorg. Chem.*, 1971, **10**, 2323.
[73] J. H. Espenson and R. T. Wang, *Inorg. Chem.*, 1972, **11**, 955.

The rate law for the oxidation of the platinum(II) bromo-complexes when no iron(II) is added to the reaction mixture may be expressed as

$$\text{Rate} = k_1[\text{Pt}^{\text{II}}][\text{Fe}^{3+}][\text{Br}^-] + k_2[\text{Pt}^{\text{II}}][\text{Fe}^{3+}][\text{Br}^-]^2$$

In an excess of iron(II), however, the forward reaction does not go to completion. Under these conditions, the rate of approach to equilibrium is still of the pseudo-first-order type and is consistent with a reversible process. In the case of the bromo-complexes, the mechanism postulated involves a five-co-ordinate intermediate of platinum(II), *e.g.* (amine ligands omitted)

$$\text{Fe}^{3+} + \text{Br}^- \underset{K_1}{\rightleftharpoons} \text{FeBr}^{2+}$$

$$\text{Pt}^{\text{II}} + \text{Br}^- \rightleftharpoons \text{Pt}^{\text{II}}\text{Br}^-$$

$$\text{Pt}^{\text{II}}\text{Br}^- + \text{FeBr}^{2+} \rightleftharpoons \text{Pt}^{\text{III}}\text{Br} + \text{Fe}^{2+} + \text{Br}^-$$

A further rapid one-electron oxidation of the intermediate platinum(III) complex by iron(III) is then postulated.

The kinetics of the oxidation of uranium(IV) by HNO_2 in the presence of iron(III) have been studied spectrophotometrically[74] in nitrate media. The reaction is first-order with respect to iron(III) and uranium(IV) and zero-order in nitrous acid, the rate being inversely proportional to the concentration of hydrogen ion. The mechanism is considered to involve the non-complementary formation of uranium(VI) with rapid reduction of the nitrous acid:

$$\text{U}^{\text{IV}} + 2\text{Fe}^{\text{III}} \xrightarrow{\text{slow}} \text{U}^{\text{VI}} + 2\text{Fe}^{\text{II}}$$

$$\text{Fe}^{\text{II}} + \text{HNO}_2 \xrightarrow{\text{fast}} \text{Fe}^{\text{III}} + \text{NO}$$

The products of the reaction of $[\text{Fe(CN)}_6]^{3-}$ with the cobalt(I) carbonyl complex $[\text{Co(CN)}_2(\text{PEt}_3)_2(\text{CO})]^-$ (13) are dependent on acidity conditions.[75] In aqueous alkaline media in excess of the oxidant, there is a quantitative reaction to yield the adduct $[(\text{NC})_5\text{Fe}^{\text{II}}(\text{CN})\text{Co}^{\text{III}}(\text{CN})_2(\text{PEt}_3)_2(\text{H}_2\text{O})]^{3-}$. In neutral conditions, however, addition of oxidant results in a rapid reaction with stoicheiometry $[\text{Fe(CN)}_6]^{3-}$: (13) = 2.0 : 1, in which the product is the

$$[(\text{NC})_5\text{Fe}^{\text{II}}(\text{CN})\text{Co}^{\text{III}}(\text{CN})_2(\text{PEt}_3)_2\text{CO}_2\text{H}]^{4-}$$

(14)

adduct (14). It is of interest that the complex (14) could not be generated by oxidation of (13) by non-bridging outer-sphere oxidants such as $[\text{Co}^{\text{III}}(\text{edta})]^-$, where the reaction with (14) did not proceed beyond the 1 : 1 stage with the formation of the cobalt(II) complex $[\text{Co(CN)}_2(\text{PEt}_3)\text{CO}]$. Adduct formation also takes place[76] at high pH in the corresponding reaction with

[74] V. S. Koltunov and V. I. Marchenko, *Zhur. fiz. Khim.*, 1972, **46**, 1465.

[75] J. E. Bercaw, L. Y. Goh, and J. Halpern, *J. Amer. Chem. Soc.*, 1972, **94**, 6534.

[76] J. Halpern and M. Pribanic, *Inorg. Chem.*, 1972, **11**, 658.

hydridopentacyanocobaltate(III):

$$[(NC)_5CoH]^{3-} + 2[Fe(CN)_6]^{3-} + OH^- \longrightarrow [(NC)_5Fe^{II}(CN)Co^{III}(CN)_5]^{6-} + [Fe(CN)_6]^{4-} + H_2O$$

The rate was observed to be independent of oxidant concentration, the mechanism being consistent with the rate-determining formation of a cobalt(I) complex (Scheme 7). The subsequent rapid electron-transfer reactions may be

$$[Co(CN)_5H]^{3-} + OH^- \longrightarrow [Co(CN)_5]^{4-} + H_2O$$

$$\begin{tikzcd}
{[Co(CN)_5]^{4-} + [Fe(CN)_6]^{3-}} \arrow[r] \arrow[d] & {[(NC)_5Fe(CN)Co(CN)_5]^{7-}} \arrow[d, "{[Fe(CN)_6]^{3-}}"] \\
{[Fe(CN)_6]^{4-} + [Co(CN)_5]^{3-}} \arrow[r, "{[Fe(CN)_6]^{3-}}"] & {[(NC)_5Fe(CN)Co(CN)_5]^{6-} + [Fe(CN)_6]^{4-}}
\end{tikzcd}$$

Scheme 7

described in two pathways which are kinetically indistinguishable. The conclusion drawn from this is that the reaction between $[Co(CN)_5]^{4-}$ and $[Fe(CN)_6]^{3-}$ has a rate constant which is close to that for diffusion-controlled reactions. In the reaction[77] of diaquocobal(II)oxime with $[Fe(CN)_6]^{3-}$, the complex formed may be written as $[(NC)_5Fe(CN)Co(dmgH)_2H_2O]^{3-}$ (dmgH = dimethylglyoxime) the rate constant being $\geqslant 3 \times 10^7\ l\ mol^{-1}\ s^{-1}$. The reaction is seen to be rapid when it is considered that the cobaloxime complex is in the low-spin configuration and that the electron is transferred into the e_g orbital.

The redox kinetics of the hexacyanoferrate(III) reaction with uranium(IV) have been reported,[78] the rate being dependent on $[H^+]^{-1}$ with the hydrolysed complex, UOH^{3+}, as the reactive species. The rate law is of the form

$$\text{Rate} = \frac{2k_0K_h[Fe(CN)_6^{3-}][U^{IV}]}{[H^+] + K_h}$$

An intermediate complex possibly involving uranium(V) is postulated and the reaction is considered to involve two one-electron steps. The oxidation in alkaline media of copper(II) by $[Fe(CN)_6]^{3-}$ (and MnO_4^-) has been described, the copper(III) product being stabilized as the tellurato-complex.[79]

The reaction of vanadium(IV) with tris-(2,2′-bipyridyl)iron(III), $[Fe(bipy)_3]^{3+}$ has been investigated,[80] the Guggenheim method being used to treat the data since aquation of $[Fe(bipy)_3]^{2+}$ caused interference in the later parts of the reaction. The order is unity for both reagents and the rate law may be written

$$-d[Fe(bipy)_3^{3+}]/dt = (k_a + k_b[H^+]^{-1})[V^{IV}][Fe(bipy)_3^{3+}]$$

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[77] A. Adin and J. H. Espenson, *Inorg. Chem.*, 1972, **11**, 686.

[78] L. Adamcikova and L. Treindl, *Coll. Czech. Chem. Comm.*, 1972, **37**, 762.

[79] G. I. Rosovskii, A. K. Misyavichyus, and A. Yu. Prokopchik, *Zhur. neorg. Khim.*, 1972, **17**, 420.

[80] J. P. Birk and S. V. Weaver, *Inorg. Chem.*, 1972, **11**, 95.

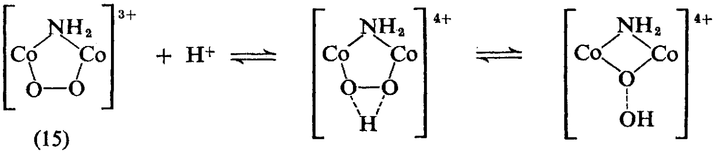
The hydrogen-ion dependence is consistent with the mechanism

$$VO^{2+} + H_2O \rightleftharpoons VO(OH)^+ + H^+ \qquad K_a$$

$$VO(OH)^+ + [Fe(bipy)_3]^{3+} \rightleftharpoons VO_2^+ + H^+ + [Fe(bipy)_3]^{2+}$$

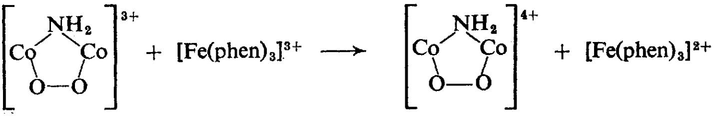
$$VO^{2+} + H_2O + [Fe(bipy)_3]^{3+} \rightleftharpoons VO_2^+ + 2H^+ + [Fe(bipy)_3]^{2+}$$

The results are in qualitative agreement with the corresponding reactions involving $[Fe(phen)_3]^{3+}$ as oxidant. The reaction with $[Fe(phen)_3]^{3+}$ has also been used to obtain information on the reactivity of the differing forms of the μ-amido-μ-peroxo-bis[bis(ethylenediamine)cobalt(III)] complex,[81] which is known to exist in three configurations (15)—(17) (amine ligands omitted).



(15) (16) (17)

The overall stoicheiometry of the reaction in the presence of excess of the peroxo-species is 1 : 1,



the reaction rate approaching the limit for detection by the stopped-flow apparatus. On the basis of a comparison of data derived from runs in which acid was present in the cobalt(III) solutions (*i.e.* sufficient time was allowed to elapse such that there was equilibration among the three forms) and from runs where the peroxo-complex was made up in water with no acid originally present [in this case on mixing there was insufficient time during the reaction for isomerization to species (17) to occur], it is suggested that only the complex (15) contributes to the reaction rate. In this regard, the behaviour is similar to that for the oxidation of the μ-peroxo-complex by four superoxo-complexes.

3 Miscellaneous Redox Reactions

Quantitative rate data for reactions discussed in this section are given in Table 3. Several systems involving the reductant $[Ru(NH_3)_6]^{2+}$, which, unless oxidation is slow compared with the loss of NH_3, is constrained to react *via* an outer-sphere mechanism. A test for mechanisms of this type has recently been described in a cross-section correlation[47] which accommodates deviations of α from 0.5 in the Marcus expression, and in the case of the oxidation of

[81] D. P. Keeton and A. G. Sykes, *J.C.S. Dalton*, 1972, 2530.

Table 3 *Oxidation–reduction reactions between two metal ions (symbols and units are as for Table 2)*

Reaction	k (25 °C)	I/M	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$CeOH^{3+} + V^{IV}$	41	2.0	16.8	5.8	60[a]
$Ce^{4+} + NpO_2^+$	2.6×10^6	2.0	~0	—	62
$HCrO_4^- + Fe(C_5H_5)_2$	1.01×10^4	1.0	—	—	70[b]
$Cr^{VI} + Pu^{IV}$	0.29	2.0	—	—	72[c]
$Cr^{VI} + [Cr^{III}\cdot Pu^{V}]$	6×10^{-6}	2.0	—	—	72[d]
$[Fe(CN)_6]^{3-} + [Co(dmgH)_2(H_2O)_2]$	$\geqslant 3\times10^7$	—	—	—	77[e]
$[Fe(CN)_6]^{3-} + UOH^{3+}$	80	1.5	5.08	-32.9	78
$[Fe(bipy)_3]^{3+} + [Co(NH_2)(O_2)Co]$	8×10^5	0.245	-1.1	-35.1	81[f]

[a] T = 20 °C, reactant species is $CeOH^{3+}$. [b] Reaction in aqueous acetone; third-order rate constant involves term in H^+. [c] $[H^+]$ = 0.1M. [d] T = 23 °C, $[H^+]$ = 1.9M. [e] $[Co(dmgH)_2(H_2O)_2]$ = diaquocobal(II)oxime. [f] Reductant is $[(en)_2Co\cdot\mu\text{-}(NH_2,O_2)\cdot Co(en)_2]^{3+}$.

$[Ru(NH_3)_6]^{2+}$ by cobalt(III) ammine complexes the larger values of the equilibrium constants have been allowed for in $\alpha = 0.415$, which yields values close to the experimentally observed relationships. An assessment of the linear free energy relationships derived in the corresponding reactions[48] with cobalt(III) macrocyclic complexes has also been made. A plot of $\log k_{12}$ against the standard free energy of reaction ΔG°_{12} for all the appropriate data for the reduction of cobalt(III) centres by $[Ru(NH_3)_6]^{2+}$ shows remarkedly good linearity over the range $0 \leqslant \Delta G^\circ_{12} \leqslant 18$ kcal mol^{-1}. In using the simple relationship of this type, the value of α is slightly larger (0.58) than the theoretical value of 0.5. In the reduction of *p*-formylbenzoatopenta-amminecobalt(III), however,[19b] the kinetic behaviour is complex, the values of the rate constant increasing with time. This acceleration of the rate may be the result of the acid-induced aquation of the ruthenium complex. Whereas no thermal reaction takes place between $[(H_3N)_5CoX]^{2+}$ (X = halogen) and $[Ru(bipy)_3]^{2+}$, on exposure of a solution mixture to radiation at 410 nm a rapid reduction of the cobalt(III) complex takes place[82] owing to the action of an excited (triplet) state of the ruthenium(II) species as an electron-transfer reductant.

Equilibrium and kinetic studies have been made[83] on the reactions between Np^{III} and the complexes $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5(OH_2)]^{3+}$. No hydrogen-ion dependences have been observed and the reactions were carried out in trifluoromethanesulphonate media which as a counter ion excludes complex formation and also eliminates any side effects due to the Ru^{II}–ClO_4^- reaction. Rate parameters for the forward reactions (X = NH_3 or H_2O),

$$Np^{3+} + [(H_3N)_5RuX]^{3+} \rightleftharpoons Np^{4+} + [Ru(NH_3)_5]^{2+}$$

are similar (see Table 4, p. 43) and, although for the hexa-ammine complex the classical inner-sphere pathway is excluded, it may be that these systems involve a transition state in which one of the oxygen atoms bound to the reducing agent attacks an octahedral face of the ruthenium complex, thus expanding the co-ordination number of the ruthenium to seven. The high negative entropy of activation (~ -47 cal deg^{-1} mol^{-1}) is seen to be consistent with the attainment of an unorthodox transition state, for the reaction of these highly charged cations.

The reaction of the dinuclear complex $[Cr^{III}\cdot Pu^{V}]$ with Pu^{III},

$$Pu^{3+} + [Cr\cdot PuO_2]^{4+} + 4H^+ \longrightarrow 2Pu^{4+} + Cr^{3+} + 2H_2O$$

has been described,[84] the rate law in perchlorate media being

$$d[Pu^{IV}]/dt = 2k_a[Pu^{III}][Cr^{III}\cdot Pu^{V}]$$

Studies were made with both lithium and sodium perchlorate as counter ions; the rates were sensitive to the nature of the cation present, being lower in

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[82] H. D. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, 1972, **94**, 8238.

[83] D. K. Lavallee, C. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 570.

[84] C. Lavallee and T. W. Newton, *Inorg. Chem.*, 1972, **11**, 2616.

$NaClO_4$ than in $LiClO_4$, probably owing to medium effects. Such effects are also observed in the hydrogen-ion dependence, which may be described in the form

$$k_a = k_0 + k_1[H^+]$$

where $k_1/k_0 = 0.3\ l\ mol^{-1}$ in $NaClO_4$ solutions and 0 in $LiClO_4$ media.

The reduction of vanadium(v) by titanium(III) in acidic perchlorate (or chloride) media occurs in three steps,[85] two of which are important in the presence of excess reductant. Solutions of titanium(III) were prepared in chloride media owing to the reduction of ClO_4^-. The reaction

$$Ti^{3+} + VO_2^+ \longrightarrow TiO^{2+} + VO^{2+}$$

was found to predominate although in excess Ti^{3+} a slower secondary reduction, $VO^{2+} \rightarrow V^{3+}$, may take place. Under conditions of acidity, where no interference from Ti^{III} dimer formation would be expected, and in excess of Ti^{III}, two distinct optical density changes were observed, both independent of chloride-ion concentration. The first step (k_1) corresponds to the formation of a V^V–Ti^{IV} dinuclear complex which then undergoes dissociation (k_2)

$$Ti^{3+} + H_2O \rightleftharpoons TiOH^{2+} + H^+ \qquad K_a$$

$$TiOH^{2+} + VO_2^+ \underset{k_f}{\overset{k_r}{\rightleftharpoons}} [Ti(OH)VO_2]^{3+}$$

whence

$$k_1 = k_r + \frac{k_f K_a[Ti^{III}]}{[H^+] + K_a}$$

The second stage, which is also dependent on hydrogen-ion concentration, may be described as

$$[Ti(OH)VO_2]^{3+} \rightleftharpoons [TiOVO_2]^{2+} + H^+ \qquad K_b$$

$$[TiOVO_2]^{2+} \xrightarrow{k} Ti^{IV} + V^{IV}$$

and

$$k_2 = \frac{kK_aK_bk_f[Ti^{III}]}{k_r(K_a[H^+] + [H^+]^2)(1 + K[Ti^{III}])}$$

with

$$K = \frac{k_fK_a}{k_r(K_a + [H^+])}$$

In the presence of excess vanadium(v), the third process may be identified as the formation of the dinuclear complex $[Ti^{IV}\cdot V^V]$, the rate again being directly dependent on hydrogen-ion concentration. Studies have been reported on the reduction of cyanocobalamin (B_{12}) by titanium(III) in HCl–KCl media,[86] the rate being pseudo-first-order in the presence of excess reductant.

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[85] J. P. Birk and T. P. Logan, *Inorg. Chem.*, 1973, **12**, 580.

[86] K. Pan and M.-T. Hsu, *J. Chin. Chem. Soc.* (*Taipei*), 1972, **19**, 153 (*Chem. Abs.*, 1973, **78**, 89 036x).

The redox reaction between hexachloroiridate(IV) and organo(dimethylglyoximinato)cobalt(III) complexes $[\mathrm{Co(dmgH)_2(H_2O)R}]$ (R = $\mathrm{PhCH_2}$),

$$[\mathrm{Co(dmgH)_2(H_2O)(R)}] + 2[\mathrm{IrCl_6}]^{2-} + 2\mathrm{H_2O} \longrightarrow [\mathrm{Co(dmgH)_2(H_2O)_2}]^+ + 2[\mathrm{IrCl_6}]^{3-} + \mathrm{ROH} + \mathrm{H^+}$$

has been investigated,[87] the reaction being rapid in the presence of excess oxidant. Two one-electron transfer steps are considered to be involved, the rate-determining first reaction being

$$[\mathrm{Co(dmgH)_2(H_2O)R}] + [\mathrm{IrCl_6}]^{2-} \xrightarrow{k_2} [\mathrm{Co(dmgH)_2(H_2O)R}]^+ + [\mathrm{IrCl_6}]^{3-}$$

with subsequent rapid reaction of the intermediate, possibly *via* a radical mechanism. In an excess of cobalt complex, however, a different reaction takes place (quantitatively):

$$[\mathrm{Co(dmgH)_2(H_2O)R}] + [\mathrm{IrCl_6}]^{2-} + \mathrm{H^+} \longrightarrow [\mathrm{IrCl_6}]^{3-} + \mathrm{Co^{II}} + \mathrm{H_2O} + \mathrm{dmgH_2} + \mathrm{HON{=}CMe{-}CMe{=}\overset{+}{N}RO^-}$$

Similar reactions are observed for *para*-substituted analogues of R, the reactivities increasing with increasing electron-donating properties of the substituent groups.

Studies have been made on the complementary reaction between thallium(III) and arsenic(III) in perchloric acid,[88] the empirical rate law being of the form

$$-\mathrm{d}[\mathrm{Tl^{III}}]/\mathrm{d}t = k[\mathrm{Tl^{III}}][\mathrm{As^{III}}]/[\mathrm{H^+}]$$

The rate was also shown to increase in the presence of chloride ions. A mechanism consistent with the data involves the hydroxothallium(III) complex as the reactive species,

$$\mathrm{Tl^{III}} + \mathrm{H_2O} \longrightarrow \mathrm{TlOH^{2+}} + \mathrm{H^+} \qquad K_\mathrm{h}$$

$$\mathrm{TlOH^{2+}} + \mathrm{HAsO_2} \xrightarrow{+\mathrm{H_2O}} \mathrm{Tl^I} + \mathrm{H_2AsO_4} + \mathrm{H^+}$$

although it is possible that an alternative scheme involving the prior formation of a thallium(III) complex might be considered. The catalytic effect of $\mathrm{Cl^-}$ is due to the formation of thallium(III)–chloro-complexes and, although not conclusively confirmed, a two-step process, each step involving a single-electron transfer, is preferred to an overall two-electron path. The corresponding reaction with antimony(III) in acid perchlorate has been investigated[89] using conventional techniques, the overall stoicheiometry of 1 : 1 being confirmed by product studies. In this case, however, unlike the reaction with $\mathrm{As^{III}}$, two transition states are involved, the mechanism postulated involving

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[87] P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, 1972, **94**, 661.

[88] P. D. Sharma and Y. K. Gupta, *J.C.S. Dalton*, 1972, 52.

[89] P. D. Sharma and Y. K. Gupta, *J.C.S. Dalton*, 1973, 789.

hydrolysis both of the thallium(III) and of the antimony(III),

$$Tl^{3+} + H_2O \rightleftharpoons TlOH^{2+} + H^+ \qquad K_h$$

$$SbO^+ + H_2O \rightleftharpoons HSbO_2 + H^+ \qquad K_a$$

$$TlOH^{2+} + HSbO_2 \xrightarrow{k_1} \text{products}$$

$$Tl^{3+} + HSbO_2 \xrightarrow{k_2} \text{products}$$

and it is suggested that the pathway k_1 contributes $\sim 85\%$ to the overall reaction. A comparison of the rate data for the reactions of As^{III} and Sb^{III} shows that the rate of oxidation of the latter is lower in spite of a lower activation energy, a larger entropy change more than compensating for the decrease in E_a.

In contrast to cobalt(III), manganese(III) shows no reaction with thallium(I) except when chloride ions (or MnO_2) are present. This chloride-ion catalysis has recently been investigated,[90] the mechanism postulated being consistent with the prior formation of a manganese(III)–chloro-complex which reacts with chloride ion to yield the oxidizing species Cl_2^-:

$$Mn^{III} + Cl^- \underset{\text{fast}}{\rightleftharpoons} MnCl^{2+} \qquad K_1$$

$$MnCl^{2+} + Cl^- \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Mn^{2+} + Cl_2^-$$

$$Tl^I + Cl_2^- \xrightarrow{k_3} Tl^{II} + 2Cl^-$$

$$Tl^{II} + Cl_2^- \xrightarrow{\text{fast}} Tl^{III} + 2Cl^-$$

$$Tl^{III} + 4Cl^- \xrightarrow{\text{fast}} TlCl_4^-$$

The intermediate formation of Tl^{II} is assumed and, invoking the steady state of both this species and the intermediate Cl_2^-, the rate law

$$\frac{-d[Mn^{III}]}{dt} = k_1K[Mn^{III}][Cl^-]^2\left\{1 - \frac{k_2[Mn^{II}]}{2k_3[Tl^I] + k_2[Mn^{II}]}\right\}$$

may be derived, the ratio k_3/k_2 being ~ 15. It is noteworthy that the mechanism differs from that of the corresponding chloride-ion-catalysed oxidation using cerium(IV), where the rate is independent of thallium(I) concentration.

The stoicheiometry and kinetics of the oxidation of vanadium(IV) by $[Mn^{III}(edta)]^-$ and $[Mn^{III}(cydta)]^-$ (cydta = *trans*-1,2-diaminocyclohexanetetra-acetate) in acid media have been reported,[91] the rate law being of the form

$$-d[Mn^{III}L]/dt = \{k_0 + k_1/[H^+]\}[Mn^{III}L^-][V^{IV}]$$

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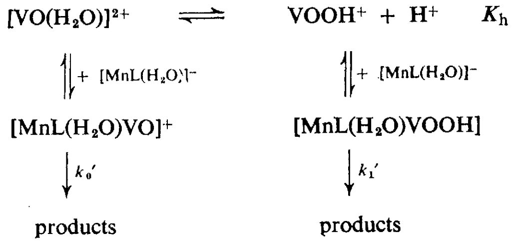
[90] D. R. Rosseinsky and R. J. Hill, *J.C.S. Dalton*, 1972, 715.

[91] D. J. Boone, R. E. Hamm, and J. P. Hunt, *Inorg. Chem.*, 1972, **11**, 1060.

for both complex ions. The mechanism suggested (Scheme 8) involves the rapid formation of a complex with subsequent slow decomposition. In this



Scheme 8

Scheme $k_0' = k_0K_1$ and $k' = k_1K_2K_h$, where K_1 and K_2 are the equilibrium constants for the formation of the intermediate complexes of VO^{2+} and $VOOH^+$ respectively. Under the hydrogen-ion concentrations used, however, some hydrolysis of the $[Mn^{III}edta(H_2O)]^-$ complex cannot be completely discounted and a possible hydroxo pathway from this source would also have to be taken into consideration.

The four-step reduction of 12-molybdophosphoric acid by stannous chloride has been reported,[92] one mole of Sn^{II} being involved in each case. It is suggested that the molybdophosphate anion can accept up to eight electrons without decomposition and that in this ion eight of the twelve molybdenum atoms originally in the +6 oxidation state have been reduced to the +5 state.

The reductions of platinum(IV) complexes by ferrocene,[93]

$$trans\text{-}[PtL_2X_4] + 2Fe(C_5H_5)_2 \longrightarrow trans\text{-}[PtL_2X_2] + 2[Fe(C_5H_5)_2]^+ + 2X^-$$

($L = AsEt_3$, PPr_3, PEt_3, or SEt_2, $X = Cl$ or Br) have been studied in hydroxylic solvents such as methanol, ethanol, and n-propanol. The rates of the reactions, which are outer-sphere in nature, are strongly solvent dependent, the rate law being consistent with a two-step redox process in which a platinum(III) species is formed as an intermediate:

$$Pt^{IV} + Fe(C_5H_5)_2 \longrightarrow Pt^{III} + [Fe(C_5H_5)_2]^+$$
$$Pt^{III} + Fe(C_5H_5)_2 \longrightarrow Pt^{II} + [Fe(C_5H_5)_2]^+$$

There is no information about the formulation of the intermediate but it may be similar in structure to those formed in other non-complementary reactions of platinum(IV) with iron(II).[53] The metal–metal-bonded complex bis-(π-cyclopentadienyldicarbonyliron), $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, is rapidly oxidized by $[Ru(bipy)_2Cl_2]^+$ and by the tetrahedral cluster ion $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ in acetonitrile solutions.[94] For both reactions, the rate law is first-order with

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[92] H. K. El-Shamy and M. F. Iskander, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1227.
[93] A. Peloso and M. Basato, *Coordination Chem. Rev.*, 1972, **8**, 111.
[94] J. N. Braddock and T. J. Meyer, *Inorg. Chem.*, 1973, **12**, 723.

respect to both oxidant and reductant, the rates being sensitive to added electrolyte, $Bu^n_4N^+PF_6^-$. From product studies it is apparent that the metal–metal bond is the source of electrons in the net electron transfer, the rate-determining step involving the transfer of an electron from the iron dimer to the oxidant to yield the intermediate $[(\pi\text{-}C_5H_5)Fe(CO)_2]^+$, which then undergoes reaction by a variety of pathways.

4 Electron Exchange Reactions

Quantitative data for this section are in Table 4.

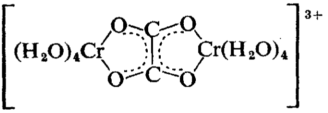
The chromium(II) reductions of oxalatotetra-ammine- and maleatopenta-ammine-chromium(III) have been investigated,[95] the rate law for the oxalato-complex having the form

$$-\mathrm{d}\ln[(NH_3)_4Cr(ox)^+]/\mathrm{d}t = k_2[Cr^{II}]$$

whereas in the case of the maleato-species it is necessary to take into account reaction of both the protonated (k_0) and deprotonated (k_1) forms of the complex, $[(H_3N)_5CrO_2C\cdot CH{=}CH\cdot CO_2H]^+$ and $[(H_3N)_5CrO_2C\cdot CH{=}CH\cdot CO_2]^{2+}$ (K_a = dissociation constant), the hydrogen-ion dependence of the observed first-order rate constant being expressed as

$$k_{obs} = k_0 + k_1K_a/[H^+]$$

The reduction of the deprotonated complex has unusually low activation parameters when compared with other reactions of this type and the possibility exists of a radical mechanism in this instance. ^{51}Cr Labelling has been used[96] in the study of the corresponding reduction of $[Cr(H_2O)_4(ox)]^+$ in which there is no dependence on hydrogen-ion concentration up to $2M\text{-}H^+$, unlike the corresponding reaction of *cis*-$[Cr(ox)_2(H_2O)_2]^-$, which exhibits an inverse hydrogen-ion term. The electron transfer is accompanied by the exchange of a single oxalate group, the inner-sphere reaction taking place *via* a completely symmetrical transition state (18).



(18)

In the Cr^{II}-catalysed aquation of $[(H_2O)_5Cr(py)]^{3+}$ a hydroxy-bridged mechanism for electron transfer is proposed,[97] the rate law being expressed as

$$-\mathrm{d}[Cr^{III}]/\mathrm{d}t = k_0[(H_2O)_5Cr(py)^{3+}][Cr^{II}][H^+]^{-1}$$

No contribution from an acid-independent pathway was observed and attempts to derive the pK_a for the pyridine complex proved unsuccessful.

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[95] R. Davies and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 2432.
[96] T. Spinner and G. M. Harris, *Inorg. Chem.*, 1972, **11**, 1067.
[97] M. Orhanovic and V. Butkovic, *Inorg. Chim. Acta*, 1972, **6**, 652.

Table 4 *Rate constants and thermodynamic parameters for redox reactions* (*symbols and units as for Table* 2)

Reaction	*k* (25 °C)	*I*/M	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Np^{3+} + $[(H_3N)_5Ru(OH_2)]^{3+}$	0.27	1.00	4.2	−46.9	83
Np^{3+} + $[(H_3N)_6Ru]^{3+}$	0.30	0.50	3.9	−45.4	83
Np^{4+} + $[Ru(NH_3)_5(OH)_2]^{2+}$	4.37	1.00	12.9	−12.1	83
Np^{4+} + $[Ru(NH_3)_6]^{2+}$	9.8	0.50	15.4	3.0	83
[Co(*trans*-14-diene)$(NH_3)_2]^{3+}$ + $[Ru(NH_3)_6]^{2+}$	3.0	1.0	—	—	48
[Co(tim)$(NH_3)_2]^{3+}$ + $[Ru(NH_3)_6]^{2+}$	3.7	1.0	—	—	48[a]
[Co(*trans*-14-diene)$(NO_2)_2]^{+}$ + $[Ru(NH_3)_6]^{2+}$	0.57	0.15	—	—	48
[Co(*trans*-14-diene)$(H_2O)_2]^{3+}$ + $[Ru(NH_3)_6]^{2+}$	8×10^{2}	0.1	—	—	48
[Co(tim)$(H_2O)_2]$ + $[Ru(NH_3)_6]^{2+}$	1.9×10^{4}	0.055	—	—	48
[Co(tet-*a*)$(H_2O)_2]^{3+}$ + $[Ru(NH_3)_6]^{2+}$	3×10^{3}	0.1	—	—	48
$[Co(C_2O_4)_3]^{3-}$ + $[Ru(NH_3)_6]^{2+}$	2.2×10^{5}	0.055	—	—	48
[Co(tet-*a*)$Cl_2]^{+}$ + $[Ru(NH_3)_6]^{2+}$	7.5×10^{4}	0.50	—	—	48
[Co(tet-*a*)$Br_2]^{+}$ + $[Ru(NH_3)_6]^{2+}$	1×10^{6}	0.57	—	—	48
Pu^{III} + $[Cr\cdot PuO_2]^{4+}$	122	2.00	4.58	−33.6	84[b]
$TiOH^{2+}$ + VO_2^{+}	~5.3×10^{5}	0.50	—	—	85
Ti^{III} + cyanocobalamin	~1.0	0.2—0.5	—	—	86

[a] See text for formulation of ligand. [b] Results in $LiClO_4$–$HClO_4$ media; see text.

Several studies have been made on electron-transfer reactions involving iron in various oxidation states. The iron(II)–(III) isotope exchange has been investigated in acetonitrile solutions of different solvent compositions;[98] the rate of exchange is a function of the nature of the solvent, the effect of water in the primary co-ordination sphere having been displaced by MeCN at high mole fractions being important. In anhydrous acetonitrile, the electron transfer occurred within the time of observation. In anhydrous formamide solution, however, Mössbauer data[99] are consistent with no electron exchange at 20 °C, but in a solution containing 8% water, where the ions may have primary co-ordination spheres of mixed solvent composition, the second-order rate constant for the iron(II)–(III) exchange is greater than $2\ \text{l mol}^{-1}\ \text{s}^{-1}$. Enthalpies of activation of the iron(II)–(III) redox reaction at platinum and palladium electrodes have been measured in both sulphate and chloride media.[100] In the former case the values obtained are dependent on the nature of the electrode whereas in 6M-HCl no such dependence is observed.

The mechanism of electron-transfer reactions of ferrocenes has been investigated[101] in 1 : 1 $\text{Pr}^n\text{OH–H}_2\text{O}$ solutions at an ionic strength of 0.05M. The reactions between ferrocene and the ferrocinium ions occurred too rapidly to be followed using pseudo-first-order kinetics, the following kinetic scheme being observed (Fe_1 and Fe_2^+ = ferrocene and ferrocinium ions, respectively):

$$\text{Fe}_1 + \text{Fe}_2^+ \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{Fe}_1^+ + \text{Fe}_2 \qquad K_{\text{eq}} = k_1/k_{-1}$$

and

$$-\text{d}[\text{Fe}_1]/\text{d}t = k_1[\text{Fe}_1][\text{Fe}_2^+] - k_{-1}[\text{Fe}_1^+][\text{Fe}_2]$$

Under the experimental conditions prevailing, an integrated form of the rate law was required, use being made of K_{eq} values derived potentiometrically. Eight ferrocene derivatives were studied, the corresponding ions (all of which have identical spectra) being generated using iron(III) [or cerium(IV)] in dilute perchloric acid. Using the substrates, twenty-eight 'cross reactions' were possible, of which twenty-two were investigated and described in terms of the Marcus outer-sphere electron-transfer model. By numbering the ferrocene derivatives (and the corresponding ferrocinium ion) as described in Table 5, a nomenclature may be designated in which the second-order rate constant for reaction of ferrocene (*i*) with ferrocinium (*j*) is k_{ij}. Quantitative data for these reactions are given in Table 6 (p. 46).

Table 5 *Ferrocene compounds studied in electron-transfer reactions*

(19)	$\text{Fe(C}_5\text{H}_4\text{Me)}_2$	(23)	$\text{Fe(C}_5\text{H}_5\text{)(C}_5\text{H}_4\text{HgCl)}$
(20)	$\text{Fe(C}_5\text{H}_4\text{Bu}^n\text{)}_2$	(24)	$\text{Fe(C}_5\text{H}_5\text{)(C}_5\text{H}_4\text{CH}_2\text{OH)}$
(21)	$\text{Fe(C}_5\text{H}_5\text{)(C}_5\text{H}_4\text{Bu}^n\text{)}$	(25)	$\text{Fe(C}_5\text{H}_5\text{)(C}_5\text{H}_4\text{Ph)}$
(22)	$\text{Fe(C}_5\text{H}_5\text{)}_2$	(26)	$\text{Fe(C}_5\text{H}_5\text{)(C}_5\text{H}_4\text{I)}$

[98] T. G. Stavros and W. L. Reynolds, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3579.

[99] A. Vertes and M. Suba, *Acta Chim. Acad. Sci. Hung.*, 1972, **74**, 439 (*Chem. Abs.*, 1973, **78**, 48 479a).

[100] F. R. Smith and C. S. Su, *J.C.S. Chem. Comm.*, 1972, 159.

[101] J. R. Pladziewicz and J. H. Espenson, *J. Amer. Chem. Soc.*, 1973, **95**, 56.

Using self-exchange rate constants for the Fe$_1$/Fe$_1^+$ couples, calculated values of the rate constants k_{ij} were compared with the experimental values, the agreement being extremely good. The reaction of the ferrocenes with iron(III) was investigated in 1 : 1 v/v H_2O–THF (mole fraction THF = 0.180) with ionic strength 1.00M, the order being unity with respect to each reagent. No hydrogen-ion dependence was observed in the range 0.1—1.0M. The corresponding reaction with a carbollyl derivative was also investigated, the rate being about two orders of magnitude greater than for the ferrocinium ions. The electron-exchange reactions between ferricinium ions and the carbollyl complexes were, however, too rapid for measurement.

The rapid reductions of cobalt(III) complexes of the type $[(H_3N)_5CoX]^{2+}$ by $[Co(dmgH)_2(H_2O)_2]$ [diaquocobal(II)oxime] have been studied[77] by products $[Co(dmgH)_2(H_2O)(X)]$ resulting from the transfer of the bridging group. Aqueous solutions of the reductant are stable in the absence of hydrogen ion and oxygen, decomposition being arrested by the use of buffers. The reaction rates vary considerably with the ligand X, the order of effectiveness of halide ions as bridging groups being in the order $Br^- > Cl^- \gg F^-$. The cobalt(II)-catalysed ligand exchange of *trans*-chloro(triphenylphosphine)bis(dimethylglyoximinato)cobalt(III) has also been reported.[102] Self-exchange rates for the couples $[Co(N_4)(OH_2)_2]^{3+/2+}$, where N_4 represents a quadridentate macrocyclic ligand, have been shown[103] to vary by a factor of 10^{10} depending on the nature of the macrocycle, the observed difference amounting to about 14 kcal mol^{-1} in free energy of activation. Using n.m.r. line-broadening, the rate of $\sim 10^3$ l mol^{-1} s^{-1} for the vitamin $B_{12a/12r}$ exchange has been shown to be the highest yet observed for a cobalt(II)–(III) couple.

The effects of organic molecules on the rate of the thallium(I)–thallium(III) exchange reaction have been described.[104] With α,α-bipyridyl, the substantial decrease in the exchange rate is probably the result of the formation of an unreactive Tl^{III} complex. With oxalic acid, some decrease is again observed but in this system an internal redox reaction of Tl^{III} oxalate is a complicating factor. It is suggested that for acceleration of the reaction fairly strong bonding is needed to both the oxidized and reduced species. The exchange between Tl^I and complex addition compounds of the type $[HTlBr_4,py]$, where py = pyridine or a methyl-substituted pyridine, has been described;[105] the exchange rates followed the order of adducts py < Me-py < 2,4-diMe-py < 2,4,6-triMe-py and is consistent with an increased distance between the positively charged organic nucleus and the $TlBr_4^-$ complex. The kinetics of the exchange of Tl^I and Tl^{III} diethylthiocarbamates in chloroform have been reported,[106] the value for the bimolecular reaction rate constant (1.7×10^3

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[102] L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, 1972, **11**, 2050.

[103] D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *J.C.S. Chem. Comm.*, 1972, 495.

[104] O. Farrer, *Acta Chem. Scand.*, 1972, **26**, 534.

[105] A. Cecal and I. A. Schneider, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1565.

[106] E. Hradilova and J. Stary, *Radiochem. Radioanalyt. Letters*, 1972, **11**, 343.

Table 6 *Electron-exchange reactions (for units see Table 2)*

Reaction	k (25 °C)	I/M	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Cr^{II} + $[(H_3N)_4Cr(ox)]^+$	6.37×10^{-3}	1.0	12.6	−26.7	95
Cr^{II} + $[(H_3N)_5Cr(malH)]^{2+}$	1.79×10^{-2}	1.0	10.4	−32.0	95[a]
Cr^{II} + $[(H_3N)_5Cr(mal)]^+$	0.795	1.0	3.4	−48	95[a]
Cr^{II} + $[(H_2O)_4Cr(ox)]^+$	0.13	2.0	11.0	−26	96
Cr^{II} + *cis*-$[Cr(ox)_2(H_2O)_2]^-$	0.04	2.0	12.0	−24	96[b]
Cr^{II} + $[Cr(H_2O)_5py]^{3+}$	~3	1.0	—	—	97
(19) + (21)	3.3×10^7	0.05	—	—	101[c]
(19) + (22)	2.3×10^7	0.05	3.0	−15	101
(19) + (23)	2.6×10^7	0.05	—	—	101
(19) + (24)	3.8×10^7	0.05	—	—	101
(19) + (25)	1.07×10^8	0.05	—	—	101
(19) + (26)	$>1.5 \times 10^8$	0.05	—	—	101
(20) + (21)	8.9×10^6	0.05	—	—	101
(20) + (22)	1.28×10^7	0.05	—	—	101
(20) + (23)	1.4×10^7	0.05	—	—	101
(20) + (24)	1.18×10^7	0.05	—	—	101
(20) + (25)	6.7×10^7	0.05	—	—	101
(21) + (22)	7.3×10^6	0.05	—	—	101
(21) + (23)	8.3×10^6	0.05	—	—	101
(21) + (25)	3.9×10^7	0.05	—	—	101
(22) + (23)	8.2×10^6	0.05	—	—	101
(22) + (24)	6.0×10^6	0.05	—	—	101
(22) + (25)	2.8×10^7	0.05	3.0	−14.4	101
(22) + (26)	1.45×10^8	0.05	—	—	101
(23) + (24)	4.2×10^6	0.05	—	—	101
(23) + (25)	2.9×10^7	0.05	—	—	101
(24) + (25)	2.0×10^7	0.05	—	—	101
(24) + (26)	9.5×10^7	0.05	—	—	101
(25) + (26)	1.09×10^8	0.05	—	—	101
Fe^{3+} + (19)	3.2×10^4	1.00	—	—	101

Fe^{3+} + (20)	1.43×10^4	1.00	—	—	101
Fe^{3+} + (21)	1.50×10^4	1.00	—	—	101
Fe^{3+} + (22)	1.05×10^4	1.00	—	—	101
Fe^{3+} + (24)	1.79×10^4	1.00	—	—	101
Fe^{3+} + (25)	5.0×10^3	1.00	—	—	101
Fe^{3+} + (26)	5.5×10^2	1.00	—	—	101
Fe^{3+} + $[Fe(C_5H_5)(C_2B_9H_{11})]^-$	4.9×10^6	1.00	—	—	101
Cob(II) + $[(H_3N)_5CoBr]^{2+}$	3.2×10^5	0.10	—	—	77[d]
Cob(II) + $[(H_3N)_5CoCl]^{2+}$	1.4×10^4	0.10	—	—	77[d]
Cob(II) + $[(H_3N)_5CoN_3]^{2+}$	6.4×10^3	0.10	—	—	77[d]
Cob(II) + $[(H_3N)_5CoNCS]^{2+}$	2.5×10^2	0.10	—	—	77[d]
Cob(II) + $[(H_3N)_5CoOH]^{2+}$	7.7×10^2	0.10	—	—	77[d]
Cob(II) + $[(H_3N)_5CoF]^{2+}$	10.5	0.10	—	—	77[d]
$[Co(hmtad)(H_2O)_2]^{2+/3+}$	$\sim10^{-7}$	1.0	—	—	103[e]
$[Co(tmtat)(H_2O)_2]^{2+/3+}$	$\sim10^2$	1.0	—	—	103[f]
Vitamin B_{12a}/Vitamin B_{12r}	$\sim2\times10^3$	0.1	—	—	103[g]

[a] malH = protonated form of maleato-complex (see text). [b] Pathway involves protonated ligand. [c] Designation of ferrocene and ferrocinium ions as in Table 5. [d] Cob(II) = diaquocobal(II)oxime; reactions in 0.1M-HOAc–OAc^- buffer. [e] hmtad = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene; pH ≈ 1, T = 70 °C. [f] tmtat = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene. [g] T = 35 °C, pH = 1—5.

C

$l\ mol^{-1}\ s^{-1}$) being significantly different from that in aqueous media.

The rate law for the Pu^{III}–Pu^{V} exchange,[84]

$$Pu^{3+} + PuO_2^{+} + 4H^{+} \longrightarrow 2Pu^{4+} + 2H_2O$$

has been established with

$$\text{Rate} = k_0[Pu^{III}][Pu^{V}][H^{+}]$$

the rate being substantially lower than for the corresponding reduction of the Cr^{III}–Pu^{V} complex described previously. The exchange between Np^{VI} and Np^{VII} in 0.3—0.5M sodium hydroxide is complete within ~3—4 min[107] with solutions of $\sim 10^{-3}$M-Np^{VII} and $\sim 10^{-4}$M-Np^{VI}.

The autocatalytic reduction of the bis-dimethylglyoxime (dmgH) complex $[Rh^{III}(dmgH)(dmgH_2)Cl_2]$ in alkaline aqueous ethanol has been reported,[108a] the product in an inert atmosphere being the rhodium(I) species. The kinetic data are consistent with a rate law of the form

$$d[Rh^{I}]/dt = k[Rh^{III}][Rh^{I}][OH]^{-4}$$

the rate being independent of chloride ion but strongly decreased by hydroxide ions. The results are interpreted in terms of the reaction of $[Rh^{III}(dmgH)_2Cl_2]^{-}$ with the complex $[Rh^{I}(dmgH)_2]^{-}$, which is considered to be rapidly formed in solution. Addition of free dimethylglyoxime markedly slows the reaction. A similar reaction was observed with the complex $[Rh^{III}(\alpha,\alpha\text{-bipy})_2Cl_2]^{+}$, giving $[Rh^{I}(\alpha,\alpha\text{-bipy})_2]^{+}$,[108] but in this instance the rate law, although still indicating a dependence on hydroxide ions, involves a squared term in the oxidant concentration.

The palladium(II)-catalysed interconversion of *trans*-$[Pd^{IV}(en)_2Cl_2]^{2+}$ and *trans*-$[Pd^{IV}(en)_2Br_2]^{2+}$,

$$[\textit{trans}\text{-}Pd(en)_2Cl_2]^{2+} + 2Br^{-} \rightleftharpoons \textit{trans}\text{-}[Pd(en)_2Br_2]^{2+} + 2Cl^{-}$$

has been investigated using stopped-flow techniques,[109] a two-term rate law being observed. Spectrophotometric evidence is provided for ion-pair formation between *trans*-$[Pd(en)_2Br_2]^{2+}$ and Br^{-}, the mechanism postulated being described (amine ligands omitted) as

$$\begin{aligned} Pd^{2+} + Br^{-} &\rightleftharpoons PdBr^{+} \\ PdBr^{+} + Cl\text{—}Pd\text{—}Cl^{2+} &\rightleftharpoons [Cl\text{—}Pd\text{—}Cl\text{—}Pd\text{—}Br]^{3+} \\ Cl^{-} + Pd^{2+} &\rightleftharpoons Cl\text{—}Pd^{+} + Cl\text{—}Pd\text{—}Br^{2+} \end{aligned}$$

the process being repeated for the second ligand.

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[107] V. F. Peretrukhin, N. N. Krot, and A. D. Gel'man, *Radiokhimiya*, 1972, **14**, 628 (*Chem. Abs.*, 1973, **78**, 48 484y).

[108a] J. D. Miller and F. D. Oliver, *J.C.S. Dalton*, 1972, 2469.

[108b] J. D. Miller and F. D. Oliver, *J.C.S. Dalton*, 1972, 2473.

[109] W. R. Mason, *Inorg. Chem.*, 1973, **12**, 20.

2

Metal Ion–Ligand Redox Reactions

BY A. McAULEY

Two reviews[17,18] have recently been published on homolytic redox processes of this type.

Quantitative data for metal ion–ligand redox reactions are collected in Table 1 on p. 50.

1 Chromium(VI)

The mechanism of formation of the intermediate complex in the oxidation of hydrogen thiosulphate by Cr^{VI} has been described,[110] the equilibrium constant K (1.1×10^4 l mol^{-1}) for the reaction

$$HS_2O_3^- + HCrO_4^- \rightleftharpoons O_3CrSSO_3^{2-} + H_2O$$

being ~ 100 times greater than for other complexes of $HCrO_4^-$. This complex is relatively stable to intramolecular redox reaction, although this reaction is only ~ 50% faster than the hydrolysis of the intermediate. In the corresponding oxidation of hypophosphorous and phosphorous acids (P),[111] the presence of intermediate species has been inferred from a Michaelis–Menten kinetic treatment, the rate law having the form

$$\frac{-\mathrm{d}[Cr^{VI}]}{\mathrm{d}t} = \frac{k_0K[Cr^{VI}][P]}{1 + K[P]}$$

with K values of the order of unity. The mechanism is considered to involve a two-electron transfer with the formation of a phosphonium ion which reacts rapidly with water to yield products (R = H or OH) as in the Scheme on p. 51. In the presence of acrylamide, no polymerization was observed, a factor which is presented to indicate a lack of evidence for the formation of an $R\dot{P}O_2H$ radical. The oxidation of phosphine by chromium(VI) in aqueous sulphuric acid is greatly accelerated by halide ions,[112]

$$Cr_2O_7^{2-} + 3PH_3 \xrightarrow{H^+} H_3PO_4 + Cr^{III}$$

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[110] K. A. Muirhead, G. P. Haight, and J. K. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 3006.

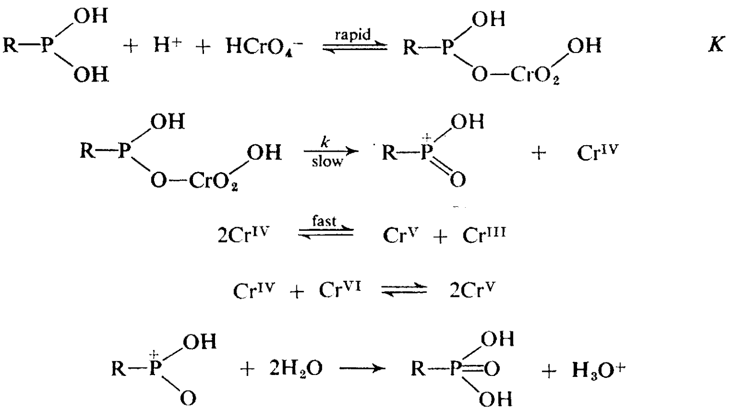
[111] K. K. Sengupta, J. K. Chakladar, and A. K. Chatterjee, *J. Inorg. Nuclear Chem.*, 1973, **35**, 901.

[112] D. V. Sokolskii, Ya. A. Dorfman, and G. S. Utegenova, *Zhur. fiz. Khim.*, 1972, **46**, 507.

Table 1 *Metal-ion–ligand redox reactions*

Reaction	$k_{25\,°C}$/ l mol^{-1} s^{-1}	I/ mol l^{-1}	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal deg^{-1} mol^{-1}	*Ref.*
$Mn^{3+} + [(NH_2)_2CSH]^+$	2.6×10^4	4.0	9.1	−6	133
$MnOH^{2+} + [(NH_2)_2CSH]^+$	3.6×10^4	4.0	10.9	0.4	133
$Mn^{3+} + [(MeNH)_2CSH]^+$	$\leqslant1.6\times10^3$	4.0	—	—	133
$MnOH^{2+} + [(MeNH)_2CSH]^+$	3.25×10^4	4.0	10.3	−1.4	133
$Mn^{3+} + [(EtNH)_2CSH]^+$	$\leqslant6\times10^2$	4.0	—	—	133
$MnOH^{2+} + [(EtNH)_2CSH]^+$	2.3×10^4	4.0	6.6	−10.6	133
$Mn^{3+} + [(CH_2NH)_2CSH]^+$	$\leqslant2\times10^3$	4.0	—	—	133
$MnOH^{2+} + [(CH_2NH)_2CSH]^+$	8.3×10^4	4.0	9.5	2.3	133
$Mn^{3+} + SCN^-$	$\sim10^6$	4.0	—	—	133
$Fe^{3+} + I^-$	16.0	1.0	—	—	139[a]
$Fe^{3+} + H_2A$	30	1.0	—	—	140[b]
$[Fe(phen)_3]^{3+} + HSO_3^-$	20	1.0	9.7	−20	143
$[Fe(phen)_3]^{3+} + SO_3^-$	4.2	1.0	7.4	−31	143
$[Fe(phen)_3]^{3+} + S_2O_5^{2-}$	7.2×10^3	1.0	14.0	6	143
$[Fe(phen)_3]^{3+} + OH^-$	193	1.0	—	—	144[c]
$[Fe(bipy)_3]^{3+} + OH^-$	13.6	1.0	—	—	144[d]
$V^V + NH_3OH^+$	5.2×10^{-3}	1.0	—	—	165
$V^V + N_2H_6^{2+}$	0.157	1.0	12.9	−21.3	166
$[U(OH)_2]^{2+} + Cl_2$	4.2	2.5	—	—	168[e]
$UOH^{3+} + HOCl$	0.84	2.5	—	—	168[e]
$[U(OH)_2]^{2+} + Br_2$	0.106	1.0	—	—	173
$[U(OH)_2]^{2+} + I_2$	0.178	1.0	—	—	173[f]
$UOH^{3+} + HOI$	2.9×10^7	1.0	—	—	173[f]
Cl_2 + phenol	2.3×10^4	1.00	—	—	169
Cl_2 + isopropyl alcohol	1.45×10^{-2}	0.2	—	—	170
Br_2 + isopropyl alcohol	1.2×10^{-2}	3.0	18	−8	171
$[Au(CN)_2]^- + I_2$	2.8×10^4	0.1	7.4	−13.5	176
$[Au(CN)_2]^- + I^-$	4.4×10^6	0.1	5.3	−10.5	176
$VO^{2+} + Cl_2$	7×10^{-3}	1.0	—	—	175
$VO^{2+} + HOCl$	5.6	1.0	—	—	175
$VO^{2+} + ClO_3^-$	1.3×10^{-2}	1.0	—	—	178
$AgOH^+ + NH_3OMe^+$	2×10^4	5.33	—	—	221[g]
$Ag^{2+} + NH_3OMe^+$	$<10^3$	5.33	—	—	221[g]
$AgOH^+ + NH_3OH^+$	1.4×10^6	5.95	—	—	221[g]
$Ag^{2+} + NH_3OH^+$	$<10^4$	5.95	—	—	221[g]
$AgOH^+ + MeNH_2OH^+$	$\sim1.6\times10^5$	2.56	—	—	221[g]
$Np^{VII} + HCO_2H$	0.40	1.0	7.0	—	225
$Np^{VII} + HCO_2H$	5.38	1.0	11.1	—	225[h]
$V^{II} + HN_3$	2.8×10^{-2}	1.0	14.4	−17	226
$Cr^{II} + HN_3$	18	1.0	7.1	−29	226

[a] Third-order rate constant (second-order term in reductant). [b] H_2A = ascorbic acid, T = 0 °C, initial reaction assuming rate first-order in oxidant and reductant. [c] 1.0M-NaCl, T = 14.9 °C. [d] 1.0M-NaCl. [e] T = 30 °C. [f] T = 40 °C. [g] T = 22 °C, assumption that $K_h = 0.32\pm0.14$ mol l^{-1}. [h] First-order rate constant, no allowance made for dissociation constant of HCO_2H.



the involvement of chromium(VI)–bromide complexes of the type $[CrO(OH)Br_2]^+$ being suggested as a complementary pathway.

The reaction of a mixture of oxalic acid and isopropyl alcohol with chromium(VI) occurs at a rate much greater than that for either of the two substrates alone,[113] both substrates undergoing oxidation. In the presence of free-radical scavengers, the products are a 1 : 1 ratio of acetone and CO_2, indicating a two-electron oxidation of the alcohol and a one-electron transfer for the oxalic acid. In the absence of acrylonitrile, however, the yields of these products are not compatible with a simple mechanism. The suggested mechanism is considered to involve a one-step, three-electron oxidation with the change in the chromium reactant from $Cr^{VI} \rightarrow Cr^{III}$. Over a wide concentration range, the rate may be described by the rate law

$$\text{Rate} = k_1[HCrO_4^-][ROH][H^+]^2 + k_2[HCrO_4^-][(CO_2H)_2][ROH] + k_3[HCrO_4^-][(CO_2H)_2]^2$$

(where ROH = alcohol), the undissociated oxalic acid being the kinetically reactive species. The second term in the rate law predominates and a mechanism consistent with the formation of a 'mixed' transition state is postulated to involve an ester-type intermediate with the rate-determining fission of a C—H bond in the alcohol molecule (see below), the free-radical anion undergoing further oxidation with chromium(VI) to yield CO_2 and (probably) chromium(V), which decomposes. It is suggested that a possible driving force for the reaction lies in the fact that whereas oxidation of a single component, *e.g.* the isopropyl alcohol, leads to an unstable and very reactive Cr^{IV} species, the presence of the second substrate affords the possibility of the direct reduction of the stable Cr^{III} ion, thus avoiding the formation of the energetically unfavourable Cr^{IV} complex.

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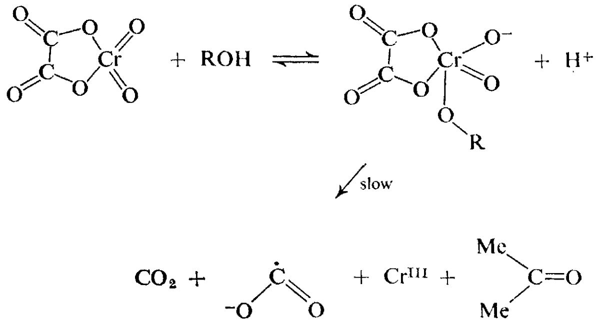
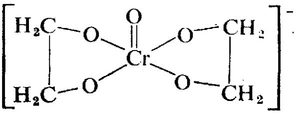
[113] F. Hasan and J. Rocek, *J. Amer. Chem. Soc.*, 1972, **94**, 3181.

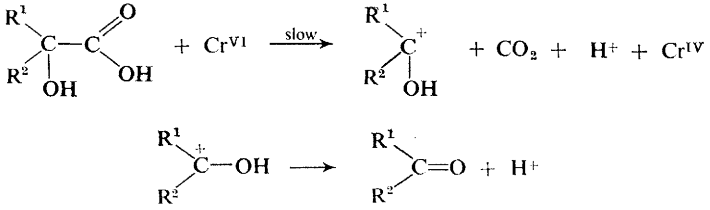


The oxidation of ethylene glycol[114] has been shown by e.s.r. techniques to involve the formation of intermediate Cr^{V} species. Kinetic data suggest that the intermediate is formed by the reaction of Cr^{IV} and Cr^{VI}. Addition of water to the reaction medium affects the stability of the complex, which has a structure (1) consistent with eight equivalent protons in the e.s.r. spectrum.



(1)

Maximum concentrations of the species were obtained when the reaction was carried out at low pressure with removal of the water formed in the course of the reaction. In this way the Cr^{V} species stabilized by ethylene glycol was stable at room temperature for several days. When the reaction was studied in dioxan,[115] a variety of hydroxy-carboxylic acids were shown to give rise to Cr^{V} signals whereas oxalic acid and mercapto-carboxylic acids do not. The kinetics of the oxidation of α-hydroxybutyric and other α-hydroxy-acids in water have been investigated,[116] with no evidence for intermediate complex formation. Failure to detect any reduction of $HgCl_2$ has been attributed to the absence of free radicals, the authors considering the rate-determining process to involve the formation of a carbonium ion which yields the ketone product by release of a proton,



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[114] P. R. Boutchev, A. Malinovski, M. Mitewa, and K. Kabassonov, *Inorg. Chim. Acta*, 1972, **6**, 499.

[115] M. Mitewa, P. R. Boutchev, and V. Bojinov, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 51.

[116] K. K. Sengupta, A. K. Chatterjee, and J. K. Chakladar, *Indian J. Chem.*, 1972, **10**, 493.

In the corresponding reaction with hydroxylamine in sulphuric acid, the mechanism and stoicheiometry are dependent on hydrogen ion.[117]

2 Cerium(IV)

The oxidation of hydrogen peroxide in perchloric acid has been reinvestigated.[118] In conditions where the cerium(IV) is generated electrochemically from cerium(III) there is no evidence for the complex formation described previously.[119] It is suggested that solutions of the oxidant prepared from precipitation with ammonium hydroxide and acidification with perchloric acid contain polymeric species which yield orange intermediates. E.s.r. evidence for the production of the radical $HO_2^{\cdot}$ was found. In view of the differing reacting species involved, the kinetic treatment suggested in the earlier paper must be reconsidered. The oxidation of hydrazine in acid perchlorate media has been described,[120] the stoicheiometry of the reaction being

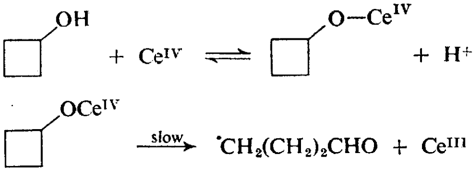
$$Ce^{IV} + N_2H_5^+ \longrightarrow Ce^{III} + NH_4^+ + \tfrac{1}{2}N_2$$

under conditions where the mole ratio $N_2H_4 : Ce^{IV} \geqslant 3$. Use of the stopped-flow technique indicates that $CeOH^{3+}$ reacts more rapidly than Ce^{4+} with the substrate, the second-order rate law being dependent on hydrogen-ion concentration but independent of cerium(III). $CeOH^{3+}$ is also considered to be the reactive species in the oxidation of malonic acid,[121]

$$H_2C(CO_2H)_2 + 6Ce(OH)^{3+} \longrightarrow 2CO_2 + HCO_2H + 6Ce^{III}$$

the reaction being second-order overall. Acrylic acid polymerization has confirmed the existence of radical intermediates during the course of the reaction. No such species have been detected, however, in the corresponding reaction with formaldehyde, the oxidation taking place *via* an outer-sphere process.[122]

Cerium(IV) reacts with cyclobutanol $\sim 10^3$—10^5 times faster than with cyclopentanol, the reaction taking place within the 'time of mixing' in aqueous solutions or in 1M-perchloric acid.[123] The products are derived from the ring-opened free-radical intermediate $^{\cdot}CH_2(CH_2)_2CHO$, suggesting the mechanism



The high reactivity of the cerium(IV) toward cyclobutanol is consistent with the reaction of one-electron oxidants which yield open-chain products, the two-

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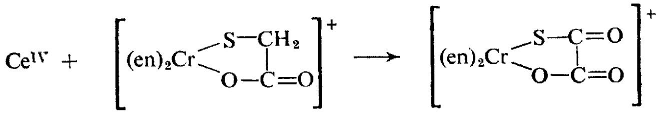
[117] G. A. Rao, H. C. Mishra, and B. P. Gyani, *Indian J. Chem.*, 1972, **10**, 489.
[118] A. Samuni and G. Czapski, *J.C.S. Dalton*, 1973, 487.
[119] C. F. Wells and M. Husain, *J. Chem. Soc.* (*A*), 1970, 1913.
[120] J. I. Morrow and G. W. Sheeres, *Inorg. Chem.*, 1972, **11**, 2606.
[121] M. Ignaczak, *Soc. Sci. Lodz Acta Chim.*, 1972, **17**, 135 (*Chem. Abs.*, 1973, **78**, 34 427v).
[122] P. S. Shankla and R. N. Mehrotra, *Indian J. Chem.*, 1972, **10**, 1081.
[123] K. Meyer and J. Rocek, *J. Amer. Chem. Soc.*, 1972, **94**, 1209.

electron process to produce cyclobutanone taking place much more slowly. In acetonitrile solutions, using cerium(IV) ammonium nitrate as oxidant, however, the open-chain radical reacts with the oxidizing complex, to yield γ-nitrobutyraldehyde:

$$^{\bullet}CH_2(CH_2)_2CHO + ONO_2Ce^{IV} \longrightarrow CHO(CH_2)_3ONO_2 + Ce^{III}$$

This reaction is suppressed in the presence of molecular oxygen, and succinaldehyde is produced. The corresponding reactions with 1-methylcyclobutanol are similar and the high reactivity of these species towards one-electron oxidants provides for their possible use in the classification of one- and two-electron-transfer reagents. In the oxidation of cyclopentanone and cyclohexanone,[124] where the nitrato-complex of the oxidant is used, nitrato-carboxylic acids are produced. Several studies have been made in sulphate media. In the reaction with malic acid,[125] the reactive species has been confirmed as $CeSO_4^{2+}$, with a contributing pathway involving $Ce(SO_4)_2$, the oxidation being considered to take place *via* an intermediate complex. In the oxidation of formaldehyde,[126] a solvent effect $k(H_2O)/k(D_2O) = 1.70$ has been evaluated, with the reaction rate inversely proportional to hydrogen-ion concentration. In the reactions of propane-1,3- and butane-1,4-diols, however,[127] the rate is accelerated by hydrogen ions at constant HSO_4^- concentrations. The oxidation of arsenic(III) is catalysed by iron(III) but inhibited by cerium(III),[128] arsenite complexes of both reagents being detected in the reaction media.

The oxidation of co-ordinated thiol at carbon rather than at sulphur has been reported[129] in the reaction of cerium(IV) [and neptunium(VI)] with (mercaptoacetato-*OS*)bisethylenediaminechromium(III),



to yield the first example of a monothio-oxalato-complex. Four moles of oxidant are required for reaction, which is complete within the time of manual mixing. Oxidations of this type may provide a model for the functioning of enzymes such as hepatic aldehyde dehydrogenase and xanthine oxidase which are capable of catalysing the dehydrogenation of aldehydes to carboxylic acids. In the reaction of cerium(IV) perchlorate with $[Cr(H_2O)_4(C_2O_4)]^+$,[130] approximately 65% of the reductant is consumed within ~30 s at low temperature (~0 °C), all of the oxygen in the carbon dioxide evolved originating

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[124] P. Soucy, T. L. Ho, and P. Deslongchamps, *Canad. J. Chem.*, 1972, **50**, 2047.

[125] R. Dayal and G. V. Bakore, *Indian J. Chem.*, 1972, **10**, 1165.

[126] P. S. Sankhla and R. N. Mehrotra, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3781.

[127] P. S. Sankhla and R. N. Mehrotra, *J. Inorg. Nuclear Chem.*, 1973, **35**, 891.

[128] A. D. Miller and Y. I. Grosse, *Kinetika i Kataliz*, 1972, **13**, 859 (*Chem. Abs.*, 1973, **78**, 62 859f).

[129] C. J. Weschler, J. C. Sullivan, and E. Deutsch, *J. Amer. Chem. Soc.*, 1973, **95**, 2720.

[130] S. G. Gourley and R. M. Milburn, *Inorg. Chem.*, 1972, **11**, 2262.

from the co-ordinated oxalate, thus eliminating any possibility of a carbon–oxygen bond fission:

$$[(H_2O)_4Cr^{III}(C_2O_4)]^+ \xrightarrow[+Ce^{IV}]{slow} [(H_2O)_4Cr(C_2O_4)]^{2+} + Ce^{III}$$

$$[(H_2O)_4Cr(C_2O_4)]^{2+} \xrightarrow[+Ce^{IV}]{rapid} [(H_2O)_6Cr]^{3+} + 2CO_2$$

An interesting example of oscillation in a chemical system has been described in the bromate–cerium(IV)–malonic acid reactions in sulphuric acid media.[131] In a stirred acidic solution containing initially $KBrO_3$, malonic acid, and cerium(IV) sulphate, the concentrations of the cerium(IV) and of bromide ion produced may be monitored potentiometrically using a tungsten and a bromide-ion-sensitive electrode, respectively, and have been shown to undergo marked repeated oscillations. A mechanism has been postulated in which both the overall chemical reactions and those responsible for the oscillations have been identified. In the conditions of malonic acid (0.1—0.5 mol l^{-1}), BrO_3^- ($\sim$0.06 mol l^{-1}), and Ce^{IV} ($\sim 10^{-3}$ mol l^{-1}) in 0.8M-sulphuric acid, there are three overall reactions,

$$BrO_3^- + Br^- + 3CH_2(CO_2H)_2 \xrightarrow{H^+} 3BrCH(CO_2H)_2 + 3H_2O$$

$$BrO_3^- + 4Ce^{3+} + CH_2(CO_2H)_2 \xrightarrow{H^+} BrCH(CO_2H)_2 + 4Ce^{III} + 3H_2O$$

$$4Ce^{4+} + BrCH(CO_2H)_2 + 2H_2O \longrightarrow Br^- + 4Ce^{III} + HCO_2H + 2CO_2 + 5H^+$$

leading to the formation of bromomalonic acid. Product analysis shows no evidence for di- or tri-bromo-derivatives. For the oscillation processes ten reactions have been identified, involving the reduction of bromate ion to bromine by successive two-equivalent redox reactions (oxygen atom transfer) and the bromomalonic acid is produced *via* an enolization reaction:

$$BrO_3^- + Br^- + 2H^+ \longrightarrow HBrO_2 + HOBr$$

$$HBrO_2 + Br^- + H^+ \longrightarrow 2HOBr$$

$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$$

$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^{\cdot} + H_2O$$

$$BrO_2^{\cdot} + Ce^{IV} + H_2O \longrightarrow BrO_3^- + Ce^{III} + 2H^+$$

$$BrO_2^{\cdot} + Ce^{III} + H^+ \rightleftharpoons HBrO_2 + Ce^{IV}$$

$$Br_2 + CH_2(CO_2H)_2 \longrightarrow BrCH(CO_2H)_2 + Br^- + H^+$$

$$6Ce^{IV} + CH_2(CO_2H)_2 + 2H_2O \longrightarrow 6Ce^{III} + HCO_2H + 2CO_2 + 6H^+$$

$$4Ce^{IV} + BrCH(CO_2H)_2 + 2H_2O \longrightarrow Br^- + 4Ce^{III} + HCO_2H + 2CO_2 + 5H^+$$

[131] R. J. Field, E. Koros, and R. M. Noyes, *J. Amer. Chem. Soc.*, 1972, **94**, 8649.

When the bromide ion becomes too low in concentration effectively to remove the $HBrO_2$ in a rapid reaction, the latter reacts with bromate ion to yield $BrO_2^{\cdot}$ radicals, which react with cerium(III) in a one-electron transfer. The indefinite build-up of the $HBrO_2$ produced autocatalytically in this way is, however, reduced by the disproportionation of the $HBrO_2$ species. The bromide ion is regenerated, however, in the cerium(IV) oxidation of the bromomalonic acid, thus arresting the autocatalysis, terminating the formation of $HBrO_2$ by these pathways, and also initiating a repetition of the cyclic system. Manganese(II) and $[Fe(phen)_3]^{2+}$ have also been shown to act as catalysts (like Ce^{III}) in these reactions,[132] the free-radical nature of these systems being confirmed. Molecular oxygen, hydrogen peroxide, and acrylonitrile act as inhibitors for the processes, however, and chloride ions act by a different mechanism from these radical scavengers in that, in the presence of these anions, the induction period for the oscillating reaction is lengthened and the reaction is no longer periodic. The effect is probably the result of inhibition of the catalytic bromination of the malonic acid.

3 Manganese(III)

The inner-sphere oxidation of thiocyanate, thiourea, and alkyl-substituted thioureas have been investigated.[133] The reactions are rapid, the process for SCN^- being too fast to be followed by the stopped-flow method, although in this case the stoicheiometry of the reaction in excess ligand is identical to that for the thioureas,

$$2Mn^{III} + 2R_2N_2H_3CS^+ \longrightarrow 2Mn^{II} + [(R_2N_2H_2CS)_2]^{2+} + 2H^+$$

(R = H, Me, or Et), the protonated form of the ligands (LH^+) being considered to predominate under the hydrogen-ion conditions prevailing. The mechanism consistent with the experimental data may be described by

$$Mn^{3+} + H_2O \rightleftharpoons MnOH^{2+} + H^+ \qquad K_h$$

$$LH^+ \rightleftharpoons L + H^+ \qquad K_a$$

$$Mn^{3+} + LH^+ \xrightarrow{k_1} Mn^{2+} + RS^{\cdot} + 2H^+$$

$$MnOH^{2+} + LH^+ \xrightarrow{k_2} Mn^{2+} + RS^{\cdot} + H^+$$

$$Mn^{3+} + L \xrightarrow{k_3} Mn^{2+} + RS^{\cdot} + H^+$$

$$MnOH^{2+} + L \xrightarrow{k_4} Mn^{2+} + RS^{\cdot}$$

$$2RS^{\cdot} \longrightarrow RSSR$$

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[132] Z. Varadi and M. T. Beck, *J.C.S. Chem. Comm.*, 1973, 30; *Magyar Kém. Folyóirat*, 1972, **79**, 46 (*Chem. Abs.*, 1973, **78**, 89 073g).

[133] G. Davies, *Inorg. Chem.*, 1972, **11**, 2488.

where RS$^\bullet$ is the radical produced in the oxidation, and which rapidly dimerizes. The reactions are first-order with respect to each reactant, and the rate law for this mechanism may be written in the form

$$k_{\text{obs}} = \frac{k_1[\text{H}^+] + k_2K_\text{h} + k_3K_\text{a} + k_4K_\text{h}K_\text{a}[\text{H}^+]^{-1}}{([\text{H}^+] + K_\text{h})(1 + K_\text{a}[\text{H}^+]^{-1})}$$

where K_h and K_a are the hydrolysis and acid dissociation constants shown. There are two limiting cases of the rate law which may be considered:

(*a*) if $K_\text{a}(k_3 + k_4K_\text{h}[\text{H}^+]^{-1}) \ll k_1[\text{H}^+] + k_2K_\text{h}$

and $1 \gg K_\text{a}[\text{H}^+]^{-1}$

then $k_{\text{obs}}([\text{H}^+] + K_\text{h}) = k_1[\text{H}^+] + k_2K_\text{h}$

a situation which has been shown to obtain for the reaction with thiourea, and

(*b*) if $k_2K_\text{h} \gg k_1[\text{H}^+]$ in (*a*)

then $k_{\text{obs}} = k_2K_\text{h}/([\text{H}^+] + K_\text{h})$

and plots of k_{obs}^{-1} against [H$^+$] should be linear, leading to values of K_h and k_2. This limiting condition arises in the case of *NN′*-dimethyl- and *NN′*-diethylthiourea in hydrogen-ion concentrations up to ~2.5 mol l^{-1}. The rate-determining reaction is considered to involve the substitution of the inner coordination sphere of manganese(III). In the case of ethylenethiourea there is marked deviation from situation (*b*) above at lower acidities, and in the reaction of this substrate both charge and steric effects may be important in determining the substitution rate at the manganese(III) centre, the fact that the terminal nitrogen atoms in this ligand are linked through an ethylene bridge being considered to impose possible steric or solvational restrictions as compared with the other thiourea derivatives. Alkylation of the nitrogen atoms also causes a marked increase in the reaction rates with Mn^{3+}.

Kinetic studies have been made on the slow oxidation of formic acid by manganese(III)[134] in perchlorate media, both spectrophotometric and sampling techniques into iron(II) solutions and measurement of the iron(III) produced being employed. No effects of dissolved oxygen were found, the overall reaction being

$$2\text{Mn}^{\text{III}} + \text{HCO}_2\text{H} \longrightarrow 2\text{Mn}^{\text{II}} + 2\text{H}^+ + \text{CO}_2$$

At concentrations of reductant $\geqslant 0.4$ mol l^{-1} an increase in optical density in the region 260—300 nm was observed, the first-order rate constant k_0 tending toward a limiting value at high [HCO$_2$H]. Use of a Michaelis–Menten treatment confirms that two complexes are involved which are related in an acid–

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[134] C. F. Wells and D. Whatley, *J.C.S. Faraday I*, 1972, **68**, 434.

base equilibrium:

$$\mathrm{Mn^{3+} + HCO_2H \rightleftharpoons [Mn(HCO_2H)]^{3+}}$$

$$\begin{tikzcd} {\mathrm{[Mn(HCO_2H)]^{3+}}} \arrow[r, rightleftharpoons] \arrow[d, "k_1"] & {\mathrm{[Mn(HCO_2)]^{2+} + H^+}} \arrow[d, "k_2"] \\ {\mathrm{Mn^{II} + {}^{\bullet}CO_2H + H^+}} & {\mathrm{Mn^{II} + {}^{\bullet}CO_2H}} \end{tikzcd}$$

$$\mathrm{Mn^{III} + {}^{\bullet}CO_2H \xrightarrow{rapid} Mn^{II} + CO_2}$$

Evidence for radical formation was given by acrylonitrile polymerization, and hydrogen-bonding and solvent effects are considered important in the formulation of the transition-state complexes. In the reaction of olefins with aliphatic ketones in the presence of oxidizing agents (*e.g.* $\mathrm{Mn^{III}}$, $\mathrm{Ce^{IV}}$, $\mathrm{Cu^{II}}$) cyclic ketonic products are formed,[135] radical intermediates being involved. With radicals of the type $\mathrm{R\dot{C}HCH_2CH_2C(O)Et}$, the relative rates of the three oxidants are in the order $\mathrm{Cu^{II} > Ce^{IV} > Mn^{III}}$.

The composition of the $\mathrm{[Mn^{III}(cydta)]^-}$ complex ion in methanolic solutions has been reported, the equilibria involved being similar to those in aqueous media.[136] In the oxidation of acidic methanol using deuteriated compounds, the mechanism may be formulated as

$$\mathrm{[Mn^{III}(cydta)(OH_2)]^- \underset{+H^+}{\rightleftharpoons} HMn^{III}(cydta)(OH_2)}$$

$$\mathrm{HMn(cydta)(OH_2) + CH_3OH \xrightarrow{k} Mn^{II} + CH_3O^{\bullet}}$$

$$\mathrm{Mn^{III} + CH_3\dot{O} \xrightarrow{rapid} Mn^{II} + CH_2\dot{O} \rightarrow\rightarrow CO_2}$$

with rapid reaction of the radical intermediates formed. In the presence of sterically hindered phenols, under acidic conditions[137] the radicals produced from methanol decomposition are competed for by both the manganese(III) complex and the phenol.

The oxidations of hydrazine by $\mathrm{[Mn(edta)]^-}$ and $\mathrm{[Mn(P_2O_7)_3]^{9-}}$ and other oxidants have been described,[138] the consumption ratio (change in oxidant concentration divided by the change in reductant concentration) being observed to be dependent on the method of mixing the reagents, as well as on pH. The rapid reaction with $\mathrm{MnO_4^-}$ at high pH requires 4.0 moles of oxidant, with the formation of the manganate(VI) ion. Pathways for the oxidation of non-metallic substrates by metal complexes have been described diagrammatically (Figure 1), where it is considered that although lability of the oxidant to substitution may be important, it is rarely the sole factor in determining the mechanism or stoicheiometry of oxidation of a given substrate. The oxidizing dower, as measured by standard redox potentials, has a complementary effect. An example of this may be cited in the case of the direct formation of free radicals where an outer-sphere route is likely to be the least energetically

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[135] E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 1972, **94**, 2888.

[136] B. L. Poh and R. Stewart, *Canad. J. Chem.*, 1972, **50**, 3432.

[137] R. Stewart and B. L. Poh, *Canad. J. Chem.*, 1972, **50**, 3437.

[138] A. Brown and W. C. E. Higginson, *J.C.S. Dalton*, 1972, 166.

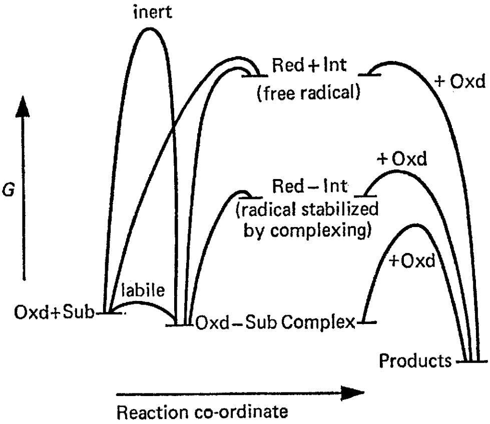

Figure 1 *Pathways in the oxidation of non-metallic substrates by metal-ion complexes. Oxd = metal complex oxidizing agent, Red = reduced form of metal complex, Sub = non-metallic reducing substrate, Int = Intermediate, a free radical if Oxd is a one-equivalent oxidant. Oxd–Sub = complex between oxidizing agent and reductant. Reaction by this route does not involve the formation of free radicals or other relatively high-energy intermediates*
(Reproduced from *J.C.S. Dalton*, 1972, 166)

favoured first step for weaker oxidizing agents but may be the preferred pathway for stronger, substitution-inert oxidants. The influence that the lability of the oxidant may have on these mechanisms may be seen in free-energy terms, and the effects of an increase in redox potential may be realized in the Figure by decreasing the free energies of activation of the various oxidation steps.

4 Iron(III)

The kinetics of the redox reaction between iron(III) and iodide ion have been reinvestigated over a very wide range of reactant conditions using the method of initial rates.[139] Both stopped-flow and conventional spectrophotometry were used, the first-order dependence on the oxidant and second-order on iodide being confirmed. No evidence was found for any intermediate complex and the reaction scheme proposed may be described as

$$Fe^{3+} + I^- \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Fe^{3+},I^- \qquad K_1$$

$$Fe^{3+},I^- + I^- \underset{k_3}{\overset{k_4}{\rightleftharpoons}} Fe^{2+} + I_2^-$$

$$Fe^{3+} + I_2^- \underset{k_5}{\overset{k_6}{\rightleftharpoons}} Fe^{2+} + I_2$$

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[139] G. S. Laurence and K. J. Ellis, *J.C.S. Dalton*, 1972, 2229.

leading to the rate expression

$$\frac{d[I_2]}{dt} = \frac{k_3K_1[Fe^{3+}][I^-]^2}{1 + (k_4[Fe^{2+}]/k_5[Fe^{3+}])}$$

The iron(II)-dependent retardation has been confirmed, although at high concentrations of Fe^{II} it would appear that the rate law may be more complex than that stated, possibly involving a term in iodide. An outer-sphere associated species is preferred to the complex FeI^{2+}, and it may be that the ion pair is a precursor to a species of the type $[I^-, Fe^{3+}, I^-]$, which undergoes a relatively rapid electron-transfer reaction in competition with the formation of the inner-sphere complex:

$$Fe^{3+}, I^- \rightleftharpoons FeI^{2+}$$

A stopped-flow study of the oxidation of ascorbic acid[140] has revealed the existence of an intermediate complex exhibiting a broad absorption band with $\lambda_{max} = 560$ nm (Figure 2). Optical density changes are consistent with a reaction (H_2A = ascorbic acid)

$$Fe^{3+} + H_2A \rightleftharpoons FeHA^{2+} + H^+ \qquad K_1$$

which takes place via two steps, the first of which takes place at 0 °C at a rate which is close to the limits of detection by the apparatus owing to the small

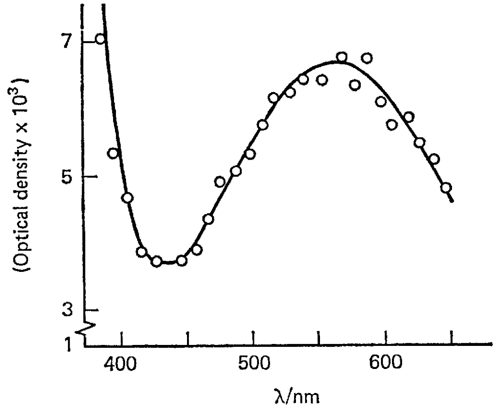

Figure 2 *Spectrum of the intermediate formed in the oxidation of ascorbate ions by iron*(III). $[Fe^{III}] = 2.5 \times 10^{-2}$ mol l^{-1}, [*ascorbic acid*] $= 2.5 \times 10^{-2}$ mol l^{-1}, $[HClO_4] = 0.2$ mol l^{-1}, $T = 25$ °C. *Observations made at maximum complex formation* (0.4 s *after mixing*)
(Reproduced from *J.C.S. Dalton*, 1972, 1667)

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[140] G. S. Laurence and K. J. Ellis, *J.C.S. Dalton*, 1972, 1667.

optical density changes. Initial rate data, however, are indicative of a rate law for this initial process which is first-order with respect to both metal ion and ligand. The second process, which does not show any appreciable change in spectrum, is considered to involve some rearrangement of the initial complex. A possibility exists that what is observed is the formation of a monochelated species with the secondary process of ring closure. Following this rearrangement, an intramolecular electron transfer from ascorbate to the iron takes place, with the reduced metal complex dissociating to produce Fe^{II} and a radical which undergoes further oxidation,

$$\mathrm{FeHA^{2+}} \rightleftharpoons [\mathrm{Fe^{2+}} \ldots \mathrm{HA^{\bullet}}] \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{H^{+}} + \mathrm{A^{\bullet -}}$$

$$\mathrm{Fe^{3+}} + \mathrm{A^{\bullet -}} \longrightarrow \mathrm{Fe^{2+}} + \mathrm{A}$$

to yield the product dehydroascorbic acid. A reaction of this type is also observed in the metal-ion [iron(III) and copper(II)] catalysis of the depolymerization of hyaluronic acid by autoxidants.[141] L-Ascorbic acid is known to depolymerize this high-molecular-weight species, the effect being due to reactions of the type

$$\mathrm{H_2A} + 2\mathrm{Fe^{III}} \longrightarrow \mathrm{A} + 2\mathrm{Fe^{II}} + 2\mathrm{H^{+}}$$

$$4\mathrm{H^{+}} + 2\mathrm{Fe^{II}} + \mathrm{O_2} \longrightarrow 4\mathrm{Fe^{III}} + 2\mathrm{H_2O}$$

$$\text{hyaluronic acid} + \mathrm{Fe^{II}} + \mathrm{O_2} \longrightarrow \mathrm{Fe^{III}} + \text{depolymerized acid}$$

It is of interest to note that when solutions of ascorbic acid and the polymer which have been treated with a sequestering resin are allowed to react, the rate is much lower, indicating the importance of the role of the metal ions. A probable inference from this is that most if not all studies of oxidation effects of L-ascorbic acid have involved metal-ion catalysis (presumably by iron or copper ions). The function of the ascorbic acid in such systems would then be to regenerate the Fe^{II} or Cu^{I} ions which are the actual catalysts. In the reaction of iron(III) with penicillamine,[142] redox reactions involving molecular oxygen are observed in basic media with the formation of red complexes. In acid conditions, however, a less stable blue species is observed.

The electron-transfer reaction between $[\mathrm{Fe(phen)_3}]^{3+}$ and sulphur(IV) occurs rapidly according to the rate law[143]

$$-\mathrm{d}[\mathrm{Fe(phen)_3^{3+}}]/\mathrm{d}t = \{k_1 + k_2[\mathrm{H^+}]^{-1} + k_3[\mathrm{HSO_3^-}]\}[\mathrm{Fe(phen)_3^{3+}}][\mathrm{HSO_3^-}]$$

the overall process involving formation of sulphate,

$$2[\mathrm{Fe(phen)_3}]^{3+} + \mathrm{HSO_3^-} + \mathrm{H_2O} \longrightarrow 2[\mathrm{Fe(phen)_3}]^{2+} + \mathrm{SO_4^{2-}} + 3\mathrm{H^+}$$

Studies were carried out in conditions of excess reductant, since in solutions where $[\mathrm{Fe(phen)_3}]^{3+}$ was present in excess competition from the aquation of the complex was observed. The mechanism involves reaction of $\mathrm{SO_3^{2-}}$ and $\mathrm{HSO_3^-}$

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[141] M. J. Harris, A. Herp, and W. Pigman, *J. Amer. Chem. Soc.*, 1972, **94**, 7570.

[142] L. G. Stadtherr and R. B. Martin, *Inorg. Chem.*, 1972, **11**, 92.

[143] D. W. Carlyle, *J. Amer. Chem. Soc.*, 1972, **94**, 4525.

and of the dinuclear species $S_2O_5^{2-}$,

$$[Fe(phen)_3]^{3+} + HSO_3^- \xrightarrow{k_1} [Fe(phen)_3]^{2+} + S^V$$

$$[Fe(phen)_3]^{3+} + SO_3^{2-} \xrightarrow{k_2} [Fe(phen)_3]^{2+} + S^V$$

$$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O \qquad K_d < 1$$

$$[Fe(phen)_3]^{3+} + S_2O_5^{2-} \xrightarrow{k_3} [Fe(phen)_3]^{2+} + S^V$$

$$[Fe(phen)_3]^{3+} + S^V \xrightarrow{\text{fast}} [Fe(phen)_3]^{2+} + S^{VI}$$

An alternative route with rapid formation of an outer-sphere complex $[Fe(phen)_3^{3+}S^{IV}]$ followed by reaction with a second mole of sulphur(IV) is also consistent with the rate law. No evidence was found for copper(II) catalysis in the reactions. The oxidation of hydroxide ion by $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ $\{[Fe(LL)_3]^{3+}\}$ according to the reaction

$$4[Fe(LL)_3]^{3+} + 4OH^- \rightleftharpoons 4[Fe(LL)_3]^{2+} + O_2 + H_2O$$

has been investigated in alkaline sodium chloride solutions,[144] a second-order rate law being observed. The rapid reaction involves the formation of the radical (HO_2^-) as an intermediate, the slow re-oxidation of the products by molecular oxygen being confirmed using an oxygen electrode. In the photoreduction of $[Fe(phen)_3]^{3+}$ in acidic media, the electron donor is the water molecule,

$$[Fe(phen)_3]^{3+} + H_2O \xrightarrow{h\nu} [Fe(phen)_3]^{2+} + H^+ + {}^{\bullet}OH$$

with secondary thermal reactions between the iron(III) complex and the hydroxyl radicals produced.[145]

Several studies have been made using the complex hexacyanoferrate(III) anion. The oxidation kinetics of triethanolamine in alkaline conditions[146]

$$N(CH_2CH_2OH)_3 + 6OH^- + 6[Fe(CN)_6]^{3-} \longrightarrow 6HCHO + NH_3 + 3H_2O + 6[Fe(CN)_6]^{4-}$$

exhibit a rate law that is first-order in amine, oxidant, and hydroxide ion, the mechanism being considered to involve intermediate anion formation of the amine (B)

$$BH + OH^- \rightleftharpoons B^- + H_2O$$

$$B^- + [Fe(CN)_6]^{3-} \xrightarrow{k_2} \text{Complex}$$

$$\text{Complex} + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} 2[Fe(CN)_6]^{4-} + \text{(product intermediates)}$$

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[144] G. Nord and O. Wernberg, *J.C.S. Dalton*, 1972, 866.

[145] E. L. Wehry and R. A. Ward, *Inorg. Chem.*, 1971, **10**, 2660.

[146] K. S. Shukla, P. C. Mathur, and O. P. Bansal, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1301.

with further rapid reaction of the intermediate products with the oxidant. The nature of the complex is not specified and medium effects have been identified, the rate decreasing linearly with decreasing dielectric constant of the solution. The importance of metal-ion-catalytic effects in the oxidations of hexacyanoferrate(III) has recently been discussed.[147] Much of the variation in kinetic data for the oxidation of thiols by this complex ion appears to arise from copper(II) ions which are present as impurities in the solutions. Using atomic absorption detection of (~ micromolar) concentrations of this ion in solutions of the hexacyanoferrate reagent,[147] it has been possible to show that in the absence of Cu^{II} there is only a slow reaction between $[Fe(CN)_6]^{3-}$ and cysteine and related thiols. A linear dependence on $[Cu^{II}]$ is observed, with no corresponding effects of Fe^{III} or Fe^{II}. The thiols also show a greater than first-order dependence in the initial rate of reaction, the equation

$$\frac{-\mathrm{d}[\mathrm{Fe(CN)}_6^{3-}]/\mathrm{d}t}{[\mathrm{thiol}]} = k_1 + k_2[\mathrm{thiol}]$$

being applicable in all cases. A mechanism consistent with a rate law which also shows both a zero-order and a first-order term in $[Fe(CN)_6]^{3-}$ in the absence of $[Fe(CN)_6]^{4-}$ may be written as shown (RSH = thiol),

$$[\mathrm{Cu^{II}(SR)}]^+ + \mathrm{RSH} \leftrightharpoons [\mathrm{Cu(SR)_2}] + \mathrm{H^+} \qquad K_2$$

$$[\mathrm{Cu^{II}(SR)_2}] + [\mathrm{Fe(CN)_6}]^{3-} \overset{k_{-1}}{\underset{k_1}{\leftrightharpoons}} [\mathrm{Cu^{III}(SR)_2}]^+ + [\mathrm{Fe(CN)_6}]^{4-}$$

$$[\mathrm{Cu^{III}(SR)_2}]^+ \xrightarrow{k_2} \mathrm{Cu^I} + \mathrm{RSSR}$$

$$[\mathrm{Cu^{II}(SR)_2}] + \mathrm{RSH} \xrightarrow{k_3} [\mathrm{Cu^ISR}] + \mathrm{RSSRH^{\bullet}}$$

$$[\mathrm{Fe(CN)_6}]^{3-} + \mathrm{RSSRH^{\bullet}} \xrightarrow{k_4} \mathrm{RSSR} + \mathrm{H^+} + [\mathrm{Fe(CN)_6}]^{4-}$$

$$[\mathrm{Fe(CN)_6}]^{4-} + \mathrm{RSSRH^{\bullet}} \xrightarrow{k_5} \mathrm{RS^-} + \mathrm{RSH} + [\mathrm{Fe(CN)_6}]^{3-}$$

$$\mathrm{Cu^ISR} + [\mathrm{Fe(CN)_6}]^{3-} \xrightarrow{\text{rapid}} [\mathrm{Cu^{II}SR}]^+ + [\mathrm{Fe(CN)_6}]^{4-}$$

$$\mathrm{Cu^I} + [\mathrm{Fe(CN)_6}]^{3-} \xrightarrow{\text{rapid}} \mathrm{Cu^{II}} + [\mathrm{Fe(CN)_6}]^{4-}$$

with the steady-state formation of both a copper(III) complex and the $RSSRH^{\bullet}$ radical. In view of the overall stoicheiometry of $[Fe(CN)_6]^{4-}$: RSH = 1 : 1 the authors make the valid point that this reaction 'provides a very clear example of a reaction which is stoicheiometrically simple but which involves several competing paths'. In a complementary paper,[148] the use of edta as a

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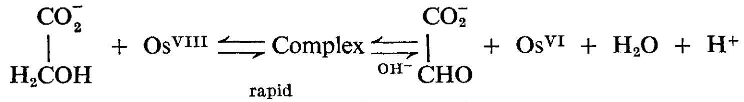
[147] G. J. Bridgart, M. W. Fuller, and I. R. Wilson, *J.C.S. Dalton*, 1973, 1274.
[148] G. J. Bridgart and I. R. Wilson, *J.C.S. Dalton*, 1973, 1281.

sequestering agent for the copper provides supporting evidence for the role of the metal ion. The copper(II)-catalysed path which predominates in the absence of the aminopolycarbonate ligand is still present but to a much less marked extent, the changes in rate being consistent with a change in the redox potential of the copper(I)/(II) couple together with differing labilities of the complexed ions in their various oxidation states compared with the aquo species. A mechanism similar to that proposed above but incorporating complex formation has been formulated. Two other studies of thiol oxidations by the $[Fe(CN)_6]^{3-}$ ion have been reported,[149, 150] but in view of the discussion above and the absence of any detailed effects of metal ions the data may have to be treated with some reserve. The reaction with 2-dimethylaminoethanethiol hydrochloride[149] exhibits simple stoicheiometry, the rate being inversely dependent on hydrogen ion, and participation of free radicals being demonstrated by the initiation of polymerization of vinyl cyanide. No effect of iron(II) on the rate is observed and the mechanism is considered to differ from that for reaction with 2-mercaptoethylamine hydrochloride. In the oxidation of thiomalic and thiolactic acids,[150] however, the rate increases with increasing $[H^+]$.

The mechanism of the osmium-tetroxide-catalysed oxidation of glycollic and lactic acids has been reported,[151] the rate being independent of oxidant concentration. Evidence is presented for complex formation, and glyoxalate and pyruvate ions are postulated as intermediates.



$$\overset{\displaystyle CO_2^-}{\underset{\displaystyle H_2COH}{|}} + Os^{VIII} \rightleftharpoons \text{Complex} \rightleftharpoons \overset{\displaystyle CO_2^-}{\underset{\displaystyle {}^{OH^-}CHO}{|}} + Os^{VI} + H_2O + H^+$$

$$Os^{VI} + 2[Fe(CN)_6]^{3-} \xrightarrow{\text{rapid}} Os^{VIII} + 2[Fe(CN)_6]^{4-}$$

which undergo rapid further oxidation. An attempted characterization of intermediates in the horseradish peroxidase system by reaction with $[Fe(CN)_6]^{3-}$ has been described.[152]

Kinetic and equilibrium studies of the reactions of iron(III) and iron(IV) dithiolate complexes with organic bases have been investigated[153] in acetonitrile solutions. Bis-(*cis*-1,2-dicyano-1,2-dithioethylene)iron(III), $[Fe(mnt)_2]^-$, reacts rapidly with pyridine and triphenylphosphine (B)

$$[Fe(mnt)_2]^- + B \rightleftharpoons [BFe(mnt)_2]^-$$

whereas the corresponding tris-iron(IV) complex, $[Fe(mnt)_3]^{2-}$, equilibrates with a formal reduction of the metal centre and the formation of a disulphide,

$$2[Fe(mnt)_3]^{2-} + 2B \rightleftharpoons 2[BFe(mnt)_2]^- + (mnt)_2^{2-}$$

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[149] R. K. Chohan, B. P. Sinha, and R. C. Kapoor, *J. Phys. Chem.*, 1972, **76**, 3641.
[150] B. P. Sinha, R. C. Kapoor, and O. P. Kachwaha, *Indian J. Chem.*, 1972, **10**, 499.
[151] V. Lal, V. N. Singh, H. S. Singh, and M. P. Singh, *Indian J. Chem.*, 1972, **10**, 392.
[152] M. L. Cotton and H. B. Dunford, *Canad. J. Chem.*, 1973, **51**, 582.
[153] J. K. Yandell and N. Sutin, *Inorg. Chem.*, 1972, **11**, 488.

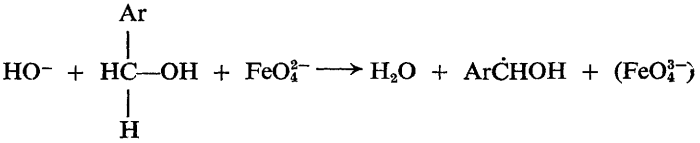
The rate with triphenylarsine oxide is first-order with respect to both the iron(IV) complex and the base. The reaction mechanism is considered to involve the attack of the nucleophile on $[Fe(mnt)_3]^{2-}$ (or on a half-bonded intermediate)

$$[Fe(mnt)_3]^{2-} + Ph_3AsO \longrightarrow [(Ph_3AsO)Fe(mnt)_2]^- + mnt^-$$

$$mnt^- + mnt^- \xrightarrow{\text{fast}} (mnt)_2^{2-}$$

$$mnt^- + [Fe(mnt)_3]^{2-} \xrightarrow{\text{fast}} [Fe(mnt)_2]^- + (mnt)_2^{2-}$$

followed by either disulphide formation or the reduction of a second iron(IV) complex by the radical formed. The oxidation of substituted benzyl alcohols with ferrate(VI) ion has been reported,[154] the presence of electron-withdrawing substituents increasing the rate. The reactions are fast at high pH (~12—13) and a mechanism is proposed where a proton is removed by hydroxide ion with the electron transfer to the ferrate(VI) ion,



$$HO^- + \text{HC(Ar)(H)—OH} + FeO_4^{2-} \longrightarrow H_2O + Ar\dot{C}HOH + (FeO_4^{3-})$$

$$Ar\dot{C}HOH + FeO_4^{2-} \xrightarrow{\text{rapid}} ArCHO + HFeO_4^{2-}$$

The presence of electron-withdrawing groups assists the rate-determining removal of the proton by base, a factor supported by high isotope effects.

5 Cobalt(III)

The existence of solely monomeric species in dilute cobalt(III) solutions in aqueous perchloric acid has been confirmed by the use of silver(II) as a potential mediator in potentiometric measurements of the cobalt(II)/cobalt(III) couple,[155]

$$Co^{III} + Ag^{I} \rightleftharpoons Co^{II} + Ag^{II}$$

$$Ag^{II} + e^- \rightleftharpoons Ag^{I}$$

where Co^{III} represents the ions $[Co(H_2O)_6]^{3+}$ and the conjugate base $Co(OH)^{2+}$. In the concentration range $[Co^{III}] = 5 \times 10^{-4}$—$5 \times 10^{-3}$ mol l^{-1}, with $[Co^{II}] \sim 0.02$—0.05 mol l^{-1}, the only species present are the ions indicated above. This evidence supports recent kinetic and isotope-distribution studies where no dimeric ions have been encountered.

Stopped-flow studies have been made on the cobalt(III) oxidation of salicylate ions in perchloric acid.[156] In excess ligand the formation of both mono-

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[154] R. J. Audette, J. W. Quail, and P. J. Smith, *J.C.S. Chem. Comm.*, 1972, 38.

[155] G. Davies and B. Warnqvist, *J.C.S. Dalton*, 1973, 900.

[156] R. G. Sandberg, J. J. Auborn, E. M. Eyring, and K. O. Watkins, *Inorg. Chem.*, 1972, **11**, 1952.

and di-co-ordinated complexes has been observed, the optical density changes at 400 nm showing two distinct features, an initial increase associated with the formation of the mono-co-ordinated species and a slower subsequent decrease attributed to the formation of the di-salicylate complex. The rate of intramolecular electron transfer in these ions is much lower than has been observed for other intermediates, the formation of pink cobalt(II) solutions being observed only after ~1 h. Rate data have been derived for the separate reactions from the first 70% of the initial increase and the decreasing portion of the optical density *vs.* time curve, the following reaction scheme being consistent with the data (HA = salicylic acid):

$$Co^{3+} + H_2O \rightleftharpoons [Co(OH)]^{2+} + H^+ \qquad K_h$$

$$Co^{3+} + HA \xrightarrow{k_1} [Co(HA)]^{3+}$$

$$[Co(OH)]^{2+} + HA \xrightarrow{k_2} [Co(OH)(HA)]^{2+}$$

$$[Co(HA)^{3+} + H_2O \rightleftharpoons [Co(OH)(HA)]^{2+} + H^+ \qquad K_2$$

$$[Co(HA)]^{3+} + HA \xrightarrow{k_4} [Co(HA)_2]^{3+}$$

$$[Co(OH)(HA)]^{2+} + HA \xrightarrow{k_5} [Co(OH)(HA)_2]^{2+}$$

An interesting feature of these reactions is the lack of any contribution from the reverse reactions (k_{-1}, k_{-4}), although a small intercept in plots of the observed rate constant against ligand concentration observed by the authors may arise from this source. Rate constants for the various reactions have been derived from hydrogen-ion dependences of the observed rates. The stabilization of the hydroxy-acid complex with respect to intramolecular electron transfer is thought to result from the complex ions being in a low-spin state, the transfer of electrons from ligand to metal being made more difficult owing to the filled t_{2g} orbitals. Also if the two oxygens of the salicylate ligand have empty π-orbitals capable of overlapping with the filled cobalt t_{2g} orbitals then some stability is conferred on these orbitals from the gain of ligand orbital character. The π-interaction of this type is considered to cause an increase in the D_q value for the complex, thus making it more stable.

The cobalt(III) oxidation of bromide and chloride ions has been reported in moderately concentrated (~5 mol l^{-1}) perchloric acid,[157] the previous evidence for the existence of a chloro-complex being confirmed. The reaction order with respect to bromide ion is, however, no longer unity. Conventional techniques have been used to investigate the reaction with hydroxylamine,[158] under the same conditions. The reaction stoicheiometry was found to be dependent on the concentrations of the initial reagents. With a six-fold excess

[157] B. Sramkova, J. Sramek, and J. Zýka, *Coll. Czech. Chem. Comm.*, 1972, **37**, 518.
[158] B. Sramkova, J. Sramek, and J. Zýka, *Analyt. Chim. Acta*, 1972, **62**, 113.

of oxidant present, the six-electron oxidation to nitrate,

$$6Co^{III} + NH_2OH + 2H_2O \longrightarrow 6Co^{II} + NO_3^- + 7H^+$$

takes place, the order with respect to the hydroxylamine being dependent on the concentration of the substrate (0.46—0.82). In conditions of excess hydroxylamine, however, $[NH_2OH]/[Co^{III}] \geqslant 8/1$, the reaction stoicheiometry was 1 : 1,

$$Co^{III} + NH_2OH \longrightarrow Co^{II} + \tfrac{1}{2}N_2 + H_2O + H^+$$

the reaction order with respect to both reagents being unity and, the rate being inversely proportional to hydrogen-ion concentration. The mechanism is considered to involve the formation of the $NH_2O^{\cdot}$ radical:

$$[Co(OH)]^{2+} + NH_3OH^+ \xrightarrow{k_1} Co^{II} + NH_2O^{\cdot} + H_2O + H^+$$

$$Co^{3+} + NH_3OH^+ \xrightarrow{k_2} Co^{II} + NH_2O^{\cdot} + H^+$$

$$2NH_2O^{\cdot} \xrightarrow{\text{rapid}} N_2 + 2H_2O$$

In the presence of excess oxidant, however, the further reactions proposed are

$$Co^{II} + Co^{III} \rightleftharpoons [Co^{3+}(H_2O)Co^{2+}]$$

$$[Co^{3+}(H_2O)Co^{2+}] + NH_2O^{\cdot} \longrightarrow 2Co^{II} + HNO + H^+$$

$$4Co^{III} + HNO + 2H_2O \xrightarrow{\text{rapid}} NO_3^- + 4Co^{II} + 5H^+$$

the latter process probably involving a series of single-electron-transfer steps. The formation of the mixed oxidation complex is postulated to explain the cobalt(II)-ion catalysis of the formation of nitrate ion. Conventional and stopped-flow techniques have been used to investigate the oxidation of isopropyl alcohol by cobalt(III).[159] The rate is first-order with respect to both oxidant and reductant, and there is no evidence for any intermediate complexes even under conditions of very high (~ 3.5 mol l^{-1}) isopropyl alcohol concentration. Hydrogen-ion-dependence studies indicate the reaction of both Co^{3+} and $CoOH^{2+}$ with the unprotonated alcohol, with the formation of a radical which then reacts rapidly with a second mole of oxidant to yield the product. As in the oxidations of secondary alcohols by Mn^{III} and Ce^{IV}, the rate constants follow the order t-butyl alcohol $\ll$ isopropyl alcohol $<$ cyclohexanol, and in accord with redox potentials the rates of oxidation of isopropyl alcohol are in the sequence $Co^{III} > Ce^{IV} > Mn^{III}$.

The spontaneous reduction of the complex ion $[Co(NH_3)_3(OH_2)_3]^{3+}$ (probably in the form of the 1,2,3-isomer) has been investigated at high temperatures.[160] The reaction product is the cobalt(II) ion, the rate law having the form

$$-d[Co(NH_3)_3(H_2O)_3^{3+}]/dt = \{k_1 + k_2'/[H^+]\}[Co(NH_3)_3(H_2O)_3^{3+}]$$

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[159] R. Varadarajan and C. F. Wells, *J.C.S. Faraday I*, 1973, **69**, 521.

[160] S. Lum, W. D. Stanley, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1293.

the acid-independent term being shown to contribute only slightly as a reaction pathway. The mechanism postulated involves the formation of a conjugate-base complex which undergoes internal electron transfer:

$$\begin{tikzcd}
{[Co(NH_3)_3(OH_2)_3]^{3+}} \arrow[rr, rightleftharpoons] \arrow[dr, "k_1"'] & & {[Co(NH_3)_3(OH_2)(OH)]^{2+} + H^+} \arrow[dl, "k_2"] \\
& Co^{II} + \text{oxidized products of } NH_3 \text{ and/or } H_2O &
\end{tikzcd}$$

A similar study of the corresponding reaction of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ has been reported,[161] the rate law being identical to that shown above. At 80 °C, the rates are in the order en < dien < NH_3 for the co-ordinating ammine.

Hydridopentacyanocobaltate(III) reacts with carbon monoxide in aqueous media,[162]

$$[Co(CN)_5H]^{3-} + 2CO + OH^- \longrightarrow [Co(CN)_3(CO)_2]^{2-} + 2CN^- + H_2O$$

according to the rate law

$$-d[Co(CN)_5H^{3-}]/dt = k_0[Co(CN)_5H^{3-}][OH^-]$$

The mechanism is similar in form to that for other reactions of the hydridopentacyano-complex, including the reaction with $[Fe(CN)_6]^{3-}$, involving the formation of the cobalt(I) complex $[Co(CN)_5]^{4-}$,

$$[Co(CN)_5H]^{3-} + OH^- \rightleftharpoons [Co(CN)_5]^{4-} + H_2O$$

$$[Co(CN)_5]^{4-} \longrightarrow [Co(CN)_4]^{3-} + CN^-$$

$$[Co(CN)_4]^{3-} + CO \xrightarrow{\text{rapid}} [Co(CN)_4(CO)]^{3-} \xrightarrow[\text{rapid}]{+\text{CO}} [Co(CN)_3(CO)_2]^{2-} + CN^-$$

The dissociation of $[Co(CN)_5]^{4-}$ is considered reasonable in view of the known behaviour of isoelectronic five-co-ordinate d^8 complexes, *e.g.* $[Ni(CN)_5]^{3-}$, to undergo processes of this type and since the complex has an eighteen-electron valence shell the substitution of CN^- by CO would not be expected to take place *via* an associative process. Reductive degradation of nitrogen-containing ligands in the presence of cobalt(III) ions has been reported.[163] The complexes $[Co(dmgH)_2(H_2O)Cl]$ (dmgH = dimethylglyoximato) and $[Co(bipy)_3]^{3+}$ react with BH_4^- in aqueous buffer with decomposition of the complex and degradation of the ligand to ammonia.

6 Vanadium(V)

The oxidation of iodide by vanadium(V) has been studied in the absence of oxygen, kinetic data being derived using the method of initial rates.[164] In the

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[161] S. Lum, L. Ereshefsky, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1591.
[162] G. Guastalla, J. Halpern, and M. Pribanic, *J. Amer. Chem. Soc.*, 1972, **94**, 1575.
[163] J. Chatt, C. M. Elson, and G. J. Leigh, *J. Amer. Chem. Soc.*, 1973, **95**, 2408.
[164] F. Secco, S. Celsi, and C. Grati, *J.C.S. Dalton*, 1972, 1675.

range of hydrogen-ion concentrations used (0.05—0.4 mol l^{-1}) the oxidant is considered to be present as the tetrahydroxovanadium(IV) ion, the reaction

$$2H_4VO_4^+ + 2I^- + 4H^+ \longrightarrow 2VO^{2+} + I_2 + 6H_2O$$

conforming to the rate law

$$\frac{-d[V^V]}{dt} = k_1[V^V][H^+][I^-] + k_2[V^V][I^-][H^+]^2 + k_3[V^V][H^+]^2[I^-]^2$$

The postulated mechanism involves complex formation prior to the rate-determining redox step, *e.g.* for the pathway k_1 the reactions formulated are

$$H_4VO_4^+ + H^+ \underset{\text{rapid}}{\rightleftharpoons} [V(OH)_3]^{2+} + H_2O$$
$$[V(OH)_3]^{2+} + I^- \rightleftharpoons [V(OH)_3I]^+$$
$$[V(OH)_3I]^+ \longrightarrow [V(OH)]^{2+} + OH^- + HIO$$

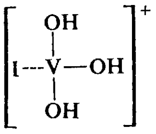
the role of the proton being to weaken the strong V—O bond. In conditions of high iodide concentration, the k_3 pathway involves the reaction

$$[V(OH)_2I]^{2+} + I^- \longrightarrow [V(OH)_2]^+ + I_2$$

The products V^{III} and HIO react rapidly with the reactants to yield the observed products:

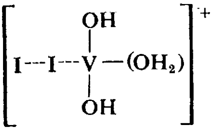
$$V^{III} + V^V \longrightarrow 2V^{IV}$$
$$HIO + I^- + H^+ \longrightarrow I_2 + H_2O$$

The configurations of the transition states for these two processes have been formulated as (2) and (3), respectively, although in the latter case if a one-electron transfer from iodide to vanadium(V) took place the radical ion I_2^-



$$\left[I\text{---}V(OH)_2\text{—}OH \right]^+$$

(2)



$$\left[I\text{---}I\text{---}V(OH)_2\text{—}(OH_2) \right]^+$$

(3)

might be formed. The corresponding reaction with hydroxylamine has been described,[165] in which the two-term rate law involves a second-order reaction between the reactants (VO_2^+ and NH_3OH^+) and a term which is second-order in oxidant concentration:

$$-d[V^V]/dt = k_1[NH_3OH^+][V^V] + k_2[NH_3OH^+][V^V]^2$$

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[165] G. Bangtsson, *Acta Chem. Scand.*, 1972, **26**, 2492.

A mechanism accounting for the data may be written as

$$V^{V} + NH_3OH^+ \underset{\text{rapid}}{\rightleftharpoons} [V^{V}(NH_3OH)]^+ \quad K$$

$$[V^{V}(NH_3OH)]^+ \xrightarrow{k_1} V^{IV} + NH_2O^{\bullet} + H^+$$

$$V^{V} + [V^{V}(NH_3OH)]^+ \xrightarrow{k_2} 2V^{IV} + HNO^{\bullet}$$

with fast subsequent reaction of the radical intermediates. The reaction of vanadium(v) with a vanadium(v) complex is also a feature of the reaction with hydrazine[166] in acid media,

$$4VO_2^+ + N_2H_6^{2+} + 2H^+ \longrightarrow 4VO^{2+} + N_2 + 4H_2O$$

In this case, the mechanism proposed is (protonation of the hydrazine omitted)

$$V^{V} + N_2H_4 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [V^{V}(N_2H_4)]$$

$$V^{V} + [V^{V}(N_2H_4)] \xrightarrow{k_2} 2V^{III} + N_2$$

$$V^{III} + V^{V} \xrightarrow{\text{fast}} 2V^{IV}$$

although the involvement of an electron transfer to yield V^{IV} and the radical N_2H_2 would conform to the same kinetic law. A hydrogen-ion dependence on the rate is observed which is attributed to differently protonated forms of the hydrazine.

No intermediate is observed in the hydrogen-ion-dependent oxidation of arsenic(III),[167] where the mechanism

$$H_3AsO_3 + V^{V} + H_2O \xrightarrow{\text{slow}} H_2AsO_3^+ + H_3O^+ + V^{III}$$

$$H_2AsO_3^+ + H_3O^+ \xrightarrow{\text{fast}} H_3AsO_4 + 2H^+$$

$$V^{V} + V^{III} \xrightarrow{\text{fast}} 2V^{IV}$$

is preferred to one involving the formation of the free radical $H_2AsO_3^{\bullet}$ since no evidence was found for polymerization on the addition of acrylonitrile. A variation in rate behaviour in sulphuric and perchloric acids has been established in that whereas the rate is retarded by sulphate ion [probably owing to vanadium(v)–sulphate complex formation], in the presence of perchlorate a marked acceleration is observed.

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[166] G. Bangtsson, *Acta Chem. Scand.*, 1971, **25**, 2989.

[167] B. B. Pal, D. C. Mukherjee, and K. K. Sengupta, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3433.

7 Halogens and Halogen Ions

The reaction of chlorine with uranium(IV),

$$U^{4+} + Cl_2 \xrightarrow{2H_2O} UO_2^{2+} + 2Cl^- + 4H^+$$

has been studied in perchlorate media,[168] the rate law at $[H^+] \geqslant 0.8$ mol l^{-1} being of the form

$$-d[U^{IV}]/dt = k_0[U^{IV}][Cl_2][H^+]^{-2}$$

The mechanism postulated involves two principal reaction paths,

$$[U(OH)_2]^{2+} + Cl_2 \xrightarrow{k_1} UO_2^{2+} + 2Cl^- + 2H^+$$

and

$$[U(OH)]^{3+} + HOCl \xrightarrow{k_1} UO_2^{2+} + Cl^- + 2H^+$$

the first pathway predominating. A decrease in rate with increasing chloride-ion concentration is observed which is due almost entirely to the formation of chloro-complexes, particularly UCl^{3+}, which react at negligible rates compared with the uncomplexed species. In the reaction of chlorine with phenol,[169] at $pH \leqslant 2$, the rapid formation of an intermediate $[Cl_2 \cdot PhOH]$ has been observed, the rate of which is first-order with respect to both reagents, and independent of chloride-ion concentration. A second reaction corresponding to the decomposition of the intermediate, the rate of which is dependent both on hydrogen and chloride ions, takes place *via* several pathways,

$$-d[Cl_2 \cdot PhOH]/dt = \{k_1[H^+][Cl^-] + k_2[H^+] + k_3\}[Cl_2 \cdot PhOH]$$

The reaction products are chlorophenols and no effect of these species is observed in the kinetic data, the rates falling in the order phenol > *m*-chlorophenol > *o*-chlorophenol > *p*-chlorophenol ≫ 2,4-dichlorophenol.

The oxidation of propan-2-ol by chlorine has also been reported, with chloride-ion catalysis of the reaction.[170] The data have been treated to include the two forms of the oxidant,

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl$$

and are consistent with Cl_2 being a much more significant oxidant than HOCl, an effect which was also observed in the phenol reaction. An amperometric study of the corresponding reaction with bromine,[171] however, reveals a more complex rate law, the observed reduction in the rate with increasing bromide-ion concentration being attributed to the formation of kinetically inactive Br_3^-.

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[168] A. Adegite and M. H. Ford-Smith, *J.C.S. Dalton*, 1973, 138.
[169] E. Grimley and G. Gordon, *J. Phys. Chem.*, 1973, **77**, 973.
[170] N. Ventakasubramanian and N. S. Srinivasan, *Indian J. Chem.*, 1972, **10**, 1085.
[171] J. G. Mason and L. G. Baird, *J. Amer. Chem. Soc.*, 1972, **94**, 6117.

The rate is also dependent on hydrogen ions,

$$\frac{-\mathrm{d}[\mathrm{Br_2}]}{\mathrm{d}t} = \frac{k_2[\mathrm{Br_2}]_\mathrm{t}\,[\mathrm{PrOH}]_\mathrm{t}}{(1 + K[\mathrm{Br^-}])(1 + K_\mathrm{a}[\mathrm{H^+}])}$$

where $[\mathrm{Br_2}]_\mathrm{t}$ and $[\mathrm{PrOH}]_\mathrm{t}$ represent the total concentrations of the reagents, K the formation constant for the tribromide ion, and K_a the acidity constant for the protonation of the alcohol. The protonated form of the alcohol is considered to be kinetically unreactive and the variation in rate with acid at constant ionic strength is thought to arise from activity-coefficient effects. In the oxidations of formate and oxalate by aqueous bromine,[172] although the reactions are apparently similar, differing rate laws are observed, *viz*

$$\frac{-\mathrm{d}[\mathrm{Br_2}]_\mathrm{t}}{\mathrm{d}t} = \frac{k[\mathrm{ox^{2-}}][\mathrm{Br_2}]_\mathrm{t}}{[\mathrm{Br^-}](1 + K[\mathrm{Br^-}])}$$

and

$$\frac{-\mathrm{d}[\mathrm{Br_2}]_\mathrm{t}}{\mathrm{d}t} = \frac{k_1K_\mathrm{a}[\mathrm{HCOO^-}][\mathrm{Br_2}]_\mathrm{t}}{[\mathrm{H^+}](1 + K_\mathrm{a}[\mathrm{Br^-}])}$$

where $\mathrm{ox^{2-}}$ = oxalate and K_a is the ionization constant for formic acid. In the former case, the rate-determining step is considered to be the attack of HOBr on the hydrogen oxalate ion, whereas in the latter bromine is the oxidizing agent.

The reactions of bromine and iodine with uranium(IV),

$$\mathrm{U^{IV}} + \mathrm{Hal_2} + 2\mathrm{H_2O} \longrightarrow \mathrm{UO_2^{2+}} + 2\mathrm{Hal^-} + 4\mathrm{H^+}$$

have been investigated spectrophotometrically.[173] In the iodine reaction, where decrease of the rate with increasing $[\mathrm{I^-}]$ is observed, the rate law

$$-\mathrm{d}[\mathrm{I_2}]_\mathrm{t}/\mathrm{d}t = k_2'[\mathrm{U^{IV}}][\mathrm{I_2}]_\mathrm{t}[\mathrm{H^+}]^{-2}$$

obtains although some deviation is observed at lower hydrogen-ion concentrations. The mechanism is considered to involve the complementary two-electron transfer

$$\mathrm{U^{IV}} + \mathrm{I_2} \longrightarrow \mathrm{U^{VI}} + 2\mathrm{I^-}$$

although the sequence of one-electron steps

$$\mathrm{U^{IV}} + \mathrm{I_2} \rightleftharpoons \mathrm{U^{V}} + \mathrm{I_2^-}$$
$$\mathrm{U^{V}} + \mathrm{I_2^-} \longrightarrow \mathrm{U^{VI}} + 2\mathrm{I^-}$$

would be kinetically indistinguishable. The effect of added anions has been investigated, in the case of sulphate, the complexes $\mathrm{USO_4^{2+}}$ and $\mathrm{U(SO_4)_2}$ being kinetically significant. The reaction with bromine has been shown to take place with a rate law similar to that described above, although in this case, unlike the iodide system, there is no reaction of the tribromide ion.

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[172] R. H. Smith, *Austral. J. Chem.*, 1972, **25**, 2503.
[173] A. Adegite and M. H. Ford-Smith, *J.C.S. Dalton*, 1973, 134.

A comparison has been made[173] between the oxidations of uranium(IV) by halogens and the corresponding reactions of iron(II). Although the former reactions are thermodynamically more favoured and whereas those involving uranium(IV) are complementary those of iron(II) are not, the iron(II) reactions are faster, and the variation in rate constants from chlorine to iodine ($\sim 10^6$) is greater for iron(II) than for uranium(IV) ($\sim 10^2$). The increase in rate constants from I_2 to Cl_2 in both cases probably results from increasingly favourable entropy factors. The reduced rates for U^{IV} may be a consequence of the need to remove the less accessible 5*f*-orbital electrons in this reductant compared with 3*d* in the case of iron(II).

The non-complementary oxidation of vanadium(III) by bromine has been studied,[174]

$$2V^{3+} + Br_2 + 2H_2O \longrightarrow 2VO^{2+} + 2Br^- + 4H^+$$

the rate being inversely dependent on hydrogen-ion concentration. The mechanism postulated,

$$V^{3+} + H_2O \rightleftharpoons VOH^{2+} + H^+$$

$$VOH^{2+} + Br_2 \xrightarrow{k_1} VOH^{3+} + Br_2^-$$

$$VOH^{2+} + Br_2^- \xrightarrow{k_2} VOH^{3+} + 2Br^-$$

$$VOH^{3+} \xrightarrow{\text{fast}} VO^{2+} + H^+$$

involving the rate-determining reaction of VOH^{2+} and Br_2. The contribution of a pathway with V^{3+} as reactant is considered negligible. The reaction is catalysed by chloride ions, however, probably as a result of an addition process where the VCl^{2+} complex ion acts as an oxidant. When allowance is made for the hydrolysis of the vanadium(III) ion, the rate constant $k_1 \sim 1.8 \times 10^3$ l mol^{-1} s^{-1} is considered to be of the order where inner-sphere oxidation in a substitution-controlled process may be operative.

A study has been made of the oxidation of vanadium(IV) by both chlorine and hypochlorous acid.[175] Both reactions are first-order with respect to each reactant, the stoicheiometry of the HOCl system conforming to the equation

$$2VO^{2+} + HOCl \longrightarrow 2VO_2^+ + Cl^- + 3H^+$$

The rate law derived is of the form

$$\frac{-0.5\,d[V^{IV}]}{dt} = \left\{\frac{k_a}{1 + (k_b/k_c)[H^+]}\right\}[V^{IV}][HOCl$$

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[174] A. Adegite and M. H. Ford-Smith, *J.C.S. Dalton*, 1972, 2113.
[175] K. Dreyer and G. Gordon, *Inorg. Chem.*, 1972, **11**, 1174.

consistent with the proposed mechanism,

$$\mathrm{VO^{2+} + HOCl \underset{k_a}{\overset{k_b}{\rightleftharpoons}} VOOCl^+ + H^+}$$

$$\mathrm{VOOCl^+ \xrightarrow{k_c} VO_2^+ + Cl^\bullet}$$

$$\mathrm{VO^{2+} + Cl^\bullet \xrightarrow[H_2O]{fast} VO_2^+ + 2H^+ + Cl^-}$$

The corresponding reaction with chlorine, however, obeys a rate law of the form

$$-0.5\,\mathrm{d}[\mathrm{V^{IV}}]/\mathrm{d}t = k_{\mathrm{Cl}}[\mathrm{V^{IV}}][\mathrm{Cl_2}]/[\mathrm{H^+}]^2$$

and in this oxidation it is proposed that the increase in the squared term in hydrogen ion is accounted for by hydrolysis of a $\mathrm{V^{IV}}$–$\mathrm{Cl_2}$ complex. In this regard it is not unlike the situation proposed for $\mathrm{U^{IV}}$ reactions of this type where two protons are considered to dissociate from the metal ion prior to the rate-determining step.

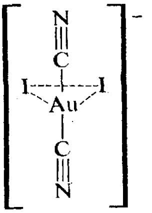
The oxidative addition of iodine to the dicyanoaurate(I) anion[176]

$$\mathrm{[Au(CN)_2]^- + I_2 \rightleftharpoons [Au(CN)_2I_2]^-}$$

obeys the rate expression

$$\mathrm{d}[\mathrm{Au(CN)_2I_2^-}]/\mathrm{d}t = k_\alpha[\mathrm{Au(CN)_2^-}][\mathrm{I_2}] + k_\beta[\mathrm{Au(CN)_2^-}][\mathrm{I_3^-}]$$

The corresponding reactions of $\mathrm{[Au(CN)_2]^-}$ with $\mathrm{Cl_2}$ and $\mathrm{Br_2}$ are too rapid to be measured. The reaction is thought to proceed in a single step to give the *trans*-$\mathrm{[Au(CN)_2I_2]^-}$ isomer, suggesting that the reaction is inner-sphere and that the transition state has a configuration (4), in which the I—I axis is normal to the C—Au—C axis. An outer-sphere mechanism would on the other hand give either $\mathrm{[Au(CN)_2(H_2O)_2]^+}$ or $\mathrm{[Au(CN)_2(OH)_2]^-}$ as products. An interesting feature of the reaction is that whereas normally the ratio of rates of reaction $k(\mathrm{I_2})/k(\mathrm{I_3^-})$ is >1, in this system the ratio is 6.4×10^{-3}.



(4)

Ionic strength effects have been investigated in the oxidation of iron(II) by

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[176] M. H. Ford-Smith, J. J. Habeeb, and J. H. Rawsthorne, *J.C.S. Dalton*, 1972, 2116.

chlorate in strongly acid media,[177]

$$6\mathrm{Fe}^{\mathrm{II}} + \mathrm{ClO}_3^- + 6\mathrm{H}^+ \longrightarrow 6\mathrm{Fe}^{\mathrm{III}} + \mathrm{Cl}^- + 3\mathrm{H}_2\mathrm{O}.$$

A third-order rate-determining step involving iron(II), ClO_3^-, and a proton is suggested, and slight differences in rate have been noted using Li^+ and Na^+ as counter-ions in the perchlorate electrolyte. Chloride ion has been shown to inhibit the vanadium(IV)–chlorate redox reaction.[178] When the VO^{2+} ion is present in excess, in the presence of initially added chloride ion, the stoicheiometry is four, whereas in the absence of initial Cl^-, 5 moles of reductant are required. The rate law under both conditions is of the form

$$\mathrm{Rate} = \left\{\frac{k_1 + k_2[\mathrm{H}^+]}{1 + K[\mathrm{Cl}^-]}\right\}[\mathrm{V}^{\mathrm{IV}}][\mathrm{ClO}_3^-]$$

The change in stoicheiometry as a function of Cl^- is considered to arise from differences in the rate of reaction between HOCl and Cl^- to form Cl_2 or HOCl and vanadium(IV) to form V^V. Complex formation between V^{IV} and added Cl^- results in the decrease in the rate. The corresponding reduction of bromate by neptunium(V) in perchlorate solutions,[179] where four moles of reductant are consumed per mole of bromine(V), has been shown to have an induction period in at least one pathway. The rate law is complex, having the form

$$k = \{\alpha[\mathrm{H}^+]^2/(1 + \beta[\mathrm{H}^+])\}[\mathrm{Br}^{\mathrm{V}}]^2$$

The reaction scheme may be similar to that proposed for other redox reactions of the Br^V species,

$$\mathrm{BrO}_3^- + \mathrm{HBrO}_2 + \mathrm{H}^+ \rightleftharpoons 2\mathrm{BrO}_2 + \mathrm{H}_2\mathrm{O}$$
$$\mathrm{BrO}_2 + \mathrm{Np}^{\mathrm{V}} + \mathrm{H}^+ \rightleftharpoons \mathrm{HBrO}_2 + \mathrm{Np}^{\mathrm{VI}}$$
$$2\mathrm{HBrO}_2 \longrightarrow \mathrm{BrO}_3^- + \mathrm{HOBr} + \mathrm{H}^+$$

where the direct reaction of Np^V and BrO_3^- is considered to be slow and bromine dioxide is the oxidizing species. The kinetics of the reaction between BrO_3^- and I^- have been investigated in unbuffered media at constant pH.[180] The reaction is first-order with respect to both oxidant and reductant and second-order in hydrogen ion, the reactive species being $HBrO_3$ and the intermediate HOI. Comparisons have been made between the oxidations, in acid media, of ethylene, propylene, and butylene glycols and of primary and secondary alcohols by bromate ion and chromium(VI).[181] In the case of the glycols, unlike the metal complex, the rate decreases with increasing methylation. The rate-determining process in the reactions of the alcohols is a C—H bond rupture.

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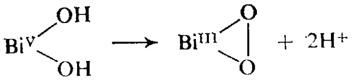
[177] K. P. Ang, G. A. Creak, and W. L. Kwik, *J.C.S. Dalton*, 1972, 2560.
[178] W. S. Melvin and G. Gordon, *Inorg. Chem.*, 1972, **11**, 1912.
[179] G. C. Knight and R. C. Thompson, *Inorg. Chem.*, 1973, **12**, 63.
[180] A. I. Morozov, M. S. Sytilin, and I. A. Makolkin, *Zhur. fiz. Khim.*, 1972, **46**, 2279.
[181] A. C. Chatterjee, *Indian J. Chem.*, 1972, **10**, 831.

The interaction of halide ions and other reductants with Bi^V has been investigated,[182] all the oxidations obeying the rate law

$$-d[Bi^V]/dt = k_0[Bi^V]$$

The rates are independent of hydrogen ion in the concentration range 0.5—2.0 mol l^{-1}, the rate-determining process involving formation of a Bi^{III} peroxo-complex



$$Bi^{III}(O_2) + X^- \xrightarrow{\text{rapid}} Bi^{III} + X_2 \text{ products}$$

(in preference to a mechanism in which free $^{\cdot}OH$ radicals are produced), where $X^- = I^-, Br^-, Cl^-$, or SCN^-. Tl^+ and $[IrCl_6]^{3-}$ are also oxidized. No detectable reactions were noted with CN^-, OCN^-, or N_3^- although it may be that a redox reaction does occur and that neither reactant nor product species absorbs in the visible–u.v. region. The energy of activation for the reactions is very low (~2 kcal mol^{-1}) and there is no evidence for a mechanism involving $Bi^{III}-X$ complex formation.

The reaction between iron(II) and chlorine(III) has been shown to occur *via* a one-electron-transfer mechanism,[183] the rates being unaffected by the presence of chloride ion (and phenol), which were added to eliminate complicating side-reactions from the primary reaction product chlorine(I):

$$HClO_2 + 2Fe^{2+} + 2H^+ \longrightarrow 2Fe^{3+} + HOCl + H_2O$$

Under the moderately acidic conditions used, a small amount (~3%) of iron(III) dimer was produced. The rate law derived may be expressed as

$$-d[Fe^{II}]/dt = k_1[Fe^{II}][Cl^{III}] + k_2[Fe^{II}][Cl^{III}]/[H^+]$$

the hydrogen-ion dependence indicating the existence of two parallel pathways, the $[H^+]$-independent route being considered to involve the formation of the activated complex $[FeClO_2H]^{2+}$,

$$HClO_2 \rightleftharpoons H^+ + ClO$$

$$Fe^{II} + HClO_2 \xrightarrow{k_1} Fe^{3+} + Cl^{II}$$

$$Fe^{II} + ClO_2^- \xrightarrow{k_2'} Fe^{3+} + Cl^{II}$$

$$Fe^{II} + Cl^{II} \xrightarrow{\text{rapid}} Fe^{3+} + HOCl$$

Comparison of the results of the present investigation with those for other inner- and outer-sphere oxidants suggests that two-electron transfers must be

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[182] M. H. Ford-Smith and J. J. Habeeb, *J.C.S. Dalton*, 1973, 461.

[183] M. G. Ondrus and G. Gordon, *Inorg. Chem.*, 1972, **11**, 985.

preceded by substitution of the oxidant into the inner co-ordination sphere of the metal ion, whereas if only one electron is exchanged either pathway would be available. In the reaction of uranium(IV) with chlorine(III), with phenol present, the stoicheiometry is consistent with the process[184]

$$U^{IV} + Cl^{III} + \text{phenol} \longrightarrow U^{VI} + H^+ + \text{chlorophenols}$$

The rate law is first-order in both oxidant and reductant with an inverse term in hydrogen-ion concentration. The results of an ^{18}O tracer study indicate that the principal reaction pathway involves a two-electron oxygen-atom transfer from the oxidant to the reductant.

The hydrolysis of cyanogen chloride is the rate-determining step in the destruction of cyanide in industrial wastes by chlorination.[185] This reaction has been studied in borax-buffered media, the rate being dependent on pH. The reaction of cyanogen chloride with sulphite ion has also been investigated kinetically, and in this case a stable adduct (2 : 2 stoicheiometry) is formed at pH$\leqslant$9 which is considered to have a six-membered S—N—C ring configuration, the sulphur being oxidized to a formal oxidation state of +6. At higher pH's the ring breaks down, however, probably owing to attack of hydroxide ion at the C or S atoms. A complex reaction with industrial associations is the autocatalytic oxidation of hydrobromic acid by nitric acid in the presence of HNO_2, which yields bromine as a product. Kinetic studies[186] reveal a reaction order of 1.5 in $[HNO_2]$ and of between 1 and 2 with respect to bromide ion. The mechanism of the oxidation of formaldehyde by chloride in aqueous media has been described,[187] the overall reaction order being two. The rate-determining step is considered to involve the reaction of hydrated formaldehyde

$$HCH(OH)_2 + ClO_2^- \longrightarrow HCO_2H + ClO^- + H_2O$$

with the formation of chlorine(I). The rate is increased in the presence of Ag^+, Ce^{III}, and F^- ions.

A detailed study of the chlorination of anisole has been undertaken,[188] the rate data obeying a three-term rate law of which two pathways include a term that is second-order in [HOCl]. The mechanism of reaction in these instances is considered to involve the rate-determining formation of chlorine monoxide,

$$2HOCl \rightleftharpoons Cl_2O + H_2O$$
$$Cl_2O + AH \longrightarrow \text{products}$$

where AH = anisole and the products include chloroanisoles. No term in the rate law is consistent with the rate-determining formation of Cl^+ and the authors comment 'it is now extremely improbable that Cl^+ is significantly involved in any thermal reaction ever studied in solution'. Detailed kinetic

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[184] R. Buchacek and G. Gordon, *Inorg. Chem.*, 1972, **11**, 2154.

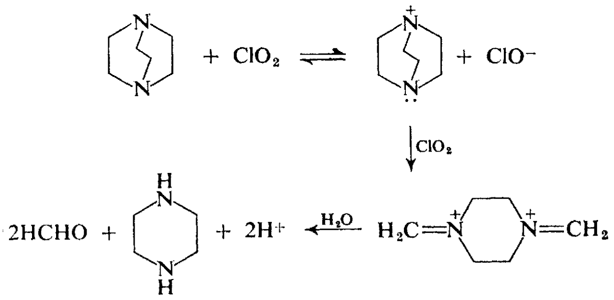
[185] P. L. Bailey and E. Bishop, *J.C.S. Dalton*, 1973, 912, 917.

[186] H. Feilchenfeld, S. Manor, and J. A. Epstein, *J.C.S. Dalton*, 1972, 2675.

[187] V. P. Kudesia, *Bull. Soc. chim. belges*, 1972, **81**, 623 (*Chem. Abs.*, 1973, **78**, 48 512f).

[188] C. G. Swain and De L. R. Crist, *J. Amer. Chem. Soc.*, 1972, **94**, 3195.

studies have also been made of the oxidation of amines by chlorine dioxide.[189] Stopped-flow techniques have been used to monitor both the disappearance of the oxidant and the formation and decomposition of a radical intermediate in the reaction with triethylenediamine, consistent with the mechanism



8 Copper(II) and Copper(III) Complexes

The kinetics and mechanism of the oxidation of thiosulphate by copper(II) ammine complexes have been reported,[190] the initial reaction being the formation of the tetrathionate ion. In the experimental conditions used, the predominant oxidant species are $[\mathrm{Cu(NH_3)_4(H_2O)_2}]^{2+}$ (~97%) and $[\mathrm{Cu(NH_3)_3(H_2O)_3}]^{2+}$ (~3%). The reactions were carried out in the absence of oxygen since an oxidation route of this type may also contribute. Stoicheiometric studies indicated a disproportionation reaction of the tetrathionate product if the reaction mixture was allowed to stand for some time prior to analysis. The reaction order with respect to both reagents was unity, although at concentrations >0.1 mol l^{-1} of $\mathrm{S_2O_3^{2-}}$ some tendency for involvement of higher complex formation was observed. The rate law was of the form ($\mathrm{Cu^{II}}$ = ammoniated complex)

$$-\mathrm{d}[\mathrm{Cu^{II}}]/\mathrm{d}t = k_0[\mathrm{Cu^{II}}][\mathrm{S_2O_3^{2-}}]/[\mathrm{NH_3}]$$

and the mechanism may be explained on the basis of the scheme

$$[\mathrm{Cu(NH_3)_4}]^{2+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Cu(NH_3)_3(H_2O)}]^{2+} + \mathrm{NH_3}$$

$$[\mathrm{Cu(NH_3)_3(H_2O)}]^{2+} + \mathrm{S_2O_3^{2-}} \xrightarrow{k_1} [\mathrm{Cu(NH_3)_3S_2O_3}] + \mathrm{H_2O}$$

$$[\mathrm{Cu(NH_3)_3(S_2O_3)}] \longrightarrow [\mathrm{Cu(NH_3)_3}]^{+} + \mathrm{S_2O_3^{-}}$$

$$2\mathrm{S_2O_3^{-}} \xrightarrow{\text{fast}} \mathrm{S_4O_6^{2-}}$$

where a rapid intramolecular redox reaction generates the $\mathrm{S_2O_3^{-}}$ radical, which rapidly dimerizes. Evidence for the associated complex is given by the observation that on addition of the $\mathrm{S_2O_3^{2-}}$ ions to the copper(II)–ammine

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[189] G. T. Davis, M. M. Demek, and D. H. Rosenblatt, *J. Amer. Chem. Soc.*, 1972, **94**, 3321.
[190] J. J. Byerley, S. A. Fouda, and G. L. Rempel, *J.C.S. Dalton*, 1973, 889.

solution there was an initial increase in optical density at 612 nm. Copper(II)–pyridine complexes have also been used[191] in the catalytic oxidation of thiols to disulphide, in DMF solutions.

The oxidation of alkyl radicals by copper(II) involves the transient formation of alkyl-copper complexes,[192] and a general scheme has been proposed for the electron-transfer processes (R = radical, X = ligand) in which the formation of the complex is followed by either oxidative elimination, (e), oxidative displacement, (d), or oxidative solvolysis, (s):

$$\mathrm{R^{\bullet} + CuX_2 \rightleftharpoons [RCuX_2]}$$

$$\mathrm{[RCuX_2] \xrightarrow{(e)} R(-H) + HX + Cu^{I}X}$$

$$\mathrm{RCuX_2 \overset{(d)}{\rightleftharpoons} R^{+}Cu^{I}X_2^{-} \longrightarrow RX + Cu^{I}X}$$

$$\begin{tikzcd}
\mathrm{[RCuX_2]} \arrow[r, "(s)", harpoon, shift left] & \mathrm{RCuX^{+}X^{-}} \arrow[l, harpoon, shift left] \arrow[r, "\mathrm{LiClO_4}", harpoon, shift left] \arrow[dr, harpoon, shift left] & \mathrm{RCuX^{+}ClO_4^{-} + LiX} \arrow[l, harpoon, shift left] \arrow[d, harpoon, shift left] & \\
 & & \mathrm{R^{+}CuX} \arrow[ul, harpoon, shift left] \arrow[u, harpoon, shift left] \arrow[r, "+\ \mathrm{SH}"] & \mathrm{RS + Cu^{I}X}
\end{tikzcd}$$

The detailed mechanisms have been found to be strongly dependent on the ligand. In the presence of acetate, oxidative elimination is promoted, whereas if the copper is complexed with trifluoromethanesulphonate the oxidative solvolysis pathway is observed with even the simplest alkyl radicals. If either of these two routes is hindered or unavailable, the oxidative displacement, involving an intramolecular transfer of a ligand from the metal ion to the alkyl group, is encountered, this latter mechanism being a feature of the oxidation of the methyl radical. The rapid oxidation of the 4-(cyclohex-1-enyl)butyl radical in benzene has been investigated at high temperatures.[193]

The oxidation of alcohols by diperiodatocuprate(III) in aqueous base has been reported,[194] the rate law for primary and secondary alcohols having the form

$$\frac{-\mathrm{d}[\mathrm{Cu^{III}}]}{\mathrm{d}t} = \frac{k[\mathrm{Cu^{III}}][\mathrm{ROH}]}{[\mathrm{H_3IO_6^{2-}}](1 + a/[\mathrm{OH^-}])}$$

The addition of periodate anion (a reaction product) reduced the rate dramatically, suggesting an auto-inhibitory mechanism. The mechanism proposed is

[191] H. Akashi, *Yuki Gosei Kagaku Kyokai Shi*, 1972, **30**, 967 (*Chem. Abs.*, 1973, **78**, 88 973p).
[192] C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 843.
[193] A. L. J. Beckwith, G. E. Gream, and D. L. Struble, *Austral. J. Chem.*, 1972, **25**, 1081.
[194] W. G. Movius, *Inorg. Chem.*, 1973, **12**, 31.

described by the scheme (L = periodate)

$$\mathrm{Cu(HL)_2} \rightleftharpoons \mathrm{CuL(HL)} + \mathrm{H^+} \qquad K_1$$
$$\mathrm{CuL(HL)} \rightleftharpoons \mathrm{CuL} + \mathrm{HL} \qquad K_2$$
$$\mathrm{ROH} + \mathrm{CuL} \xrightarrow{k_0} \text{products}$$

in which there is loss of a periodate ligand from the copper(III) complex prior to the rate-determining step. If K_2 is small, the observed rate law is adhered to, where $k = k_0K_2$ and $a = K_W/K_1$. It is of interest that methanol and ethanol are oxidized at the same rate within experimental error and secondary alcohols (*e.g.* propan-2-ol) react at just less than half the rate, possibly as a result of steric factors. In the case of benzyl and allyl alcohols, however, where the rate is a factor of 10 greater than for the primary compounds, the stabilizing effect of any radicals formed is considered to be important.

9 Peroxodisulphate

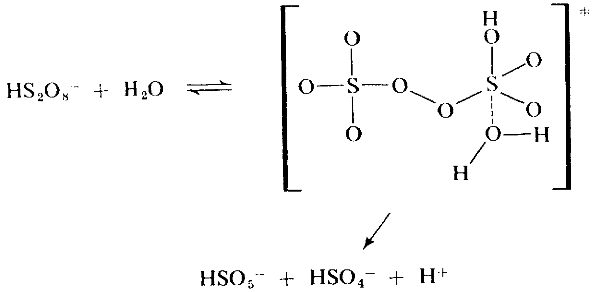
A detailed study has been made[195] of the oxidation of vanadium(IV) by peroxodisulphate in weakly acidic media:

$$\mathrm{S_2O_8^{2-}} + 2\mathrm{VO^{2+}} + 2\mathrm{H_2O} \longrightarrow 2\mathrm{VO_2^{+}} + 2\mathrm{HSO_4^-} + 2\mathrm{H^+}$$

In the hydrogen-ion concentration range 0.1—0.5 mol l^{-1}, with the oxidant in large excess, the rate becomes independent of vanadium(IV) concentration at levels greater than $\sim 10^{-3}$ mol l^{-1}. The rate of formation of vanadium(V) was also shown to be twice the rate of disappearance of oxidant, the order with respect to hydrogen ion being unity. At sufficiently high concentrations of reductant, the rate law conforms to the expression

$$-\mathrm{d[V^V]}/\mathrm{d}t = k_2[\mathrm{H^+}][\mathrm{S_2O_8^{2-}}] + k_1[\mathrm{S_2O_8^{2-}}]$$

the overall rate being lower than for the corresponding reaction with peroxodiphosphate, where the mechanism is considered to be inner-sphere. In the present system the proposed mechanism involves an activated complex which is both solvated and protonated,



$$\mathrm{HSO_5^-} + 2\mathrm{VO^{2+}} + \mathrm{H_2O} \longrightarrow 2\mathrm{VO_2^{+}} + \mathrm{HSO_4^-} + 2\mathrm{H^+}$$

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[195] S. A. Frennesson and S. Fronaeus, *Acta Chem. Scand.*, 1972, **26**, 3917.

which decomposes to yield the peroxomonosulphate ion. This reagent then acts as the oxidant in a rapid reaction sequence with two moles of vanadium(IV). Evidence for a reaction of this type was yielded by addition of oxovanadium(IV) to a solution in which the redox reaction was complete. Peroxomonosulphate ion was then added and immediately an amount of V^{IV} equivalent to that of the peroxomonosulphate was oxidized to V^{V}.

The copper(II)-catalysed oxidation of hypophosphite by $S_2O_8^{2-}$ in perchloric acid media has been described,[196] the rate law having the form

$$\frac{-d[S_2O_8^{2-}]}{dt} = \frac{k_0K[Cu^{II}][S_2O_8^{2-}][H_3PO_2]}{[H^+] + K_d + K[H_3PO_2]}$$

where K_d is the dissociation constant for hypophosphorous acid and K is the equilibrium constant for formation of the Cu^{II}–$H_2PO_2^-$ complex. A mechanism consistent with the rate law is presented in the reaction scheme

$$Cu_2^+ + H_3PO_2 \rightleftharpoons CuH_2PO_2^+ + H^+$$

$$CuH_2PO_2^+ + S_2O_8^{2-} \xrightarrow{k_1} Cu^{II} + H_2PO_2^{\cdot} + SO_4^{-} + SO_4^{2-}$$

$$H_2PO_2^{\cdot} + S_2O_8^{2-} \longrightarrow H_2PO_2^+ + SO_4^{-} + SO_4^{2-}$$

$$H_2PO_2^+ + H_2O \longrightarrow H_3PO_3 + H^+$$

$$CuH_2PO_2^+ + SO_4^{-} \longrightarrow Cu^{II} + SO_4^{2-} + H_2PO_2$$

$$H_2PO_2^{\cdot} + SO_4^{-} \longrightarrow H_2PO_2^+ + SO_4^{2-}$$

in which the radical ion SO_4^{-} and the species $H_2PO_2^{\cdot}$ are produced as intermediates. A possible identification of metal-ion catalysis in the k_1 reaction step involves the oxidation of the hypophosphite to yield Cu^{I}, which is subsequently rapidly re-oxidized to Cu^{II} by the peroxodisulphate. The reaction rate is decreased by the presence of both Mn^{II} and HSO_4^-. Two studies have been reported in which silver(I) ions catalyse reactions of $S_2O_8^{2-}$. The oxidation of maleic acid exhibits a rate law that is first-order in Ag^{I} and $S_2O_8^{2-}$ concentrations only,[197] the rate-limiting step corresponding to the formation of silver(III),

$$Ag^{I} + S_2O_8^{2-} \longrightarrow Ag^{III} + 2SO_4^{2-}$$

which then oxidizes the organic substrate. A similar rate law is observed in the corresponding reaction of α-alanine,[198] in which case a radical chain mechanism involving Ag^{II} is considered. Small negative salt effects are exhibited by NH_4NO_3, $NaNO_3$, and K_2SO_4. Free-radical mechanisms have also been proposed for the oxidations of malonic acid and glucose,[199] where a complex between the oxidant and the sugar is formed, the overall reaction involving both C—C bond cleavage and oxidation of the terminal group.

[196] R. Swaroop and Y. K. Gupta, *J.C.S. Dalton*, 1972, 851.

[197] B. P. Yadava, and S. N. Shukla, *Current Sci.*, 1972, **41**, 811.

[198] G. Chandra and S. N. Srivastava, *J. Inorg. Nuclear Chem.*, 1972, **34**, 197.

[199] W. C. Vasudeva and S. Wasif, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3153; W. C. Vasudeva, M. I. Taha, and S. Wasif, *ibid.*, p. 3159.

The mechanisms of decomposition of peroxomono-sulphates and -phosphates in alkaline media have been investigated,[200] the rates being first-order with respect to hydroxide ion and the peroxo-species. The reaction is considered to proceed *via* a one-electron transfer from the OH^- to the peroxo-anion,

$$O_3SOO^{2-} + OH^- \longrightarrow SO_4^{2-} + [2O^-] + H^+$$
$$2O^- + H_2O \longrightarrow \tfrac{1}{2}O_2 + 2OH^-$$

10 Miscellaneous Redox Reactions

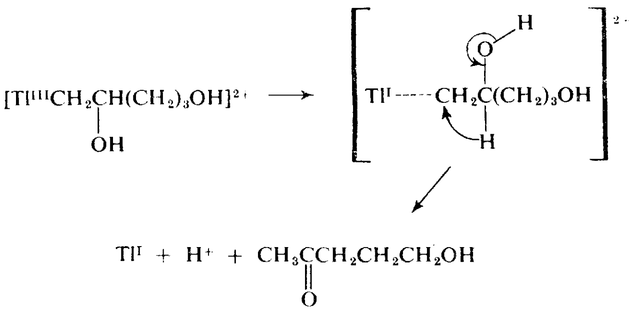
The reduction of iridium(IV) by ascorbic acid has been studied in 80% acetone–water mixtures,[201] the rate being first-order with respect to each reactant and inversely proportional to $[H^+]^2$. The reaction involves the formation of an ascorbate free radical, $AH^\bullet$:

$$H_2IrCl_6 \rightleftharpoons HIrCl_6^- + H^+$$
$$H_2A \rightleftharpoons HA^- + H^+$$
$$HIrCl_6^- + HA^- \xrightarrow{\text{slow}} HIrCl_6^{2-} + AH^\bullet$$
$$HIrCl_6^- + HA^\bullet \xrightarrow{\text{fast}} HIrCl_6^{2-} + A + H^+$$

Evidence has been presented for adduct formation in the oxidation of certain olefinic compounds by thallium(III).[202] Alkenols react with the oxidant in a stoicheiometric ratio of 1 : 1 and two types of behaviour have been described depending on the reducing substrate. In the case of prop-1-en-3-ol, pent-1-en-5-ol, and hex-1-en-6-ol, spectroscopic changes monitored using a stopped-flow apparatus are consistent with two separate reactions: (*a*) an oxythallation,

$$Tl^{III} + CH_2{=}CHR + H_2O \longrightarrow [Tl^{III}CH_2{-}CH(R)OH]^{2+} + H^+$$

followed by (*b*) a de-metallation and formation of the oxidation products; *e.g.* for pent-1-en-5-ol, reaction (*b*) may be represented as



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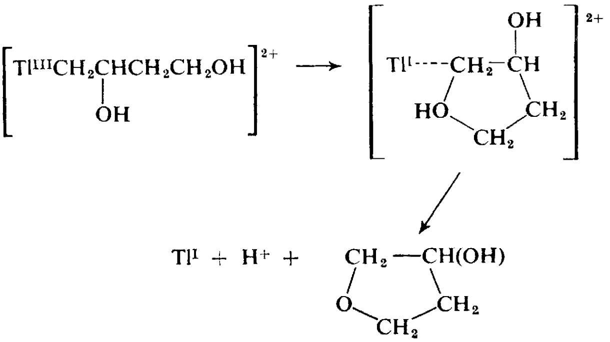
[200] V. A. Lunenok-Burmakina and G. P. Aleeva, *Zhur. fiz. Khim.*, 1972, **46**, 2788.
[201] S. P. Mushran, M. C. Agrawal, and K. C. Gupta, *Indian J. Chem.*, 1972, **10**, 642.
[202] J. E. Byrd and J. Halpern, *J. Amer. Chem. Soc.*, 1973, **95**, 2586.
[203] P. Ablev J. E. Bvrd and J. Halpern *J. Amer. Chem. Soc.*. 1973. **95**. 2591.

For reactions of but-1-en-4-ol and pent-1-en-4-ol, however, no step (*b*) was observed, the rates being second-order overall. In these reactions it would appear that enhancement of reaction (*b*) is the result of neighbouring-group participation to form a cyclic structure,



A similar situation exists in the hydroxymercuration and thallium(III) oxidation of cycloalkenes and cycloalkanes,[203] the rate laws showing strict second-order behaviour for both metal ions. In the thallium(III) reactions two products have been observed, a 1,2-diol and a ketone or aldehyde. Two-electron coupling with Tl^{III} trifluoroacetate has been shown to promote oxidative phenol coupling.[204] The mechanism of oxidation of olefins by palladium(II) has been investigated.[205] In the presence of $PdCl_2$ in aqueous media, the data conform to the rate expression

$$\frac{-\mathrm{d}[\text{olefin}]}{\mathrm{d}t} = \frac{k_1[\mathrm{PdCl}_4^{2-}][\text{olefin}]}{[\mathrm{H}^+][\mathrm{Cl}^-]^2}$$

Product studies on the oxidation of cyclohexene by a combination of $PdCl_2$ and $CuCl_2$ in acetic acid show that in addition to cyclohex-2-en-1-ol and cyclohex-3-en-1-ol acetates obtained in the absence of Cu^{II}, the saturated disubstituted chloroacetate or diacetate derivatives are also observed. The relative activities of tetra-, penta-, and hexa-chlororhodate(III) complexes as catalysts for the oxidation of ethylene to acetaldehyde in aqueous acid media have been described,[206] and in the presence of iron(III) and other oxidants in the same media the complex ion $[RhCl_5(H_2O)]^{2-}$ is considered to promote the reaction.

The mechanism of redox isomerization of *af*-dichloro-*bc*-bis(pyridine)-*de*-trimethyleneplatinum(IV) (5) to the platinum(II) complex of pyridinium

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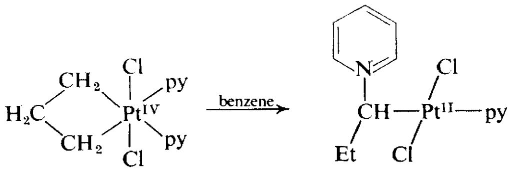
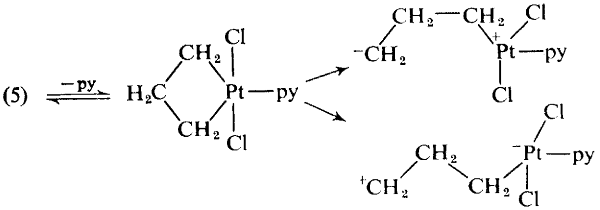
[204] M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *J. Amer. Chem. Soc.*, 1973, **95**, 612.
[205] P. M. Henry, *J. Amer. Chem. Soc.*, 1972, **94**, 4437, 7305.
[206] B. R. James and M. Kastner, *Canad. J. Chem.*, 1972, **50**, 1698, 1708.

propylide (6) has been described.[207] Analogues of (5) containing 3- or 4-picoline also give ylide species. On prolonged heating both (5) and (6) give *trans*-$[Pt^{II}(py)_2Cl_2]$. The reaction is considered to involve a rate-determining

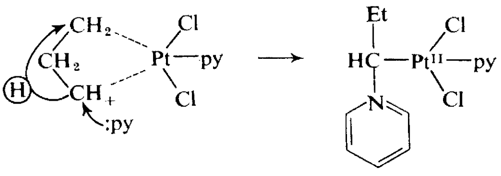


(5) (6)

dissociation of a pyridine ligand to give a five-co-ordinate intermediate which can recombine with pyridine to form (5) or rearrange by heterolytic cleavage of a Pt—C bond to produce a complex which may be formulated in two ways:



A concerted mechanism incorporating attack of a pyridine and a hydride shift would then yield the product (6):



(6)

The rate of exchange of oxygen atoms between *trans*-dioxobis(ethylenediamine)rhenium(v) ion, $[Re(en)_2O_2]^+$, and solvent water has been measured using ^{18}O-labelling techniques,[208] and is generally dependent on the nature of the cation of the supporting electrolyte. When the ion is oxidized, a general feature is the complete transfer of the *trans*-[O=Re=O] unit to the product ReO_4^- ion.

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[207] R. D. Gillard and M. F. Pilbrow, *J.C.S. Dalton*, 1973, 102.

[208] L. B. Kriege and R. K. Murmann, *J. Amer. Chem. Soc.*, 1972, **94**, 4557.

The reaction of tetracyanonickelate(II) with hydroxylamine in aqueous media,[209]

$$[Ni(CN)_4]^{2-} + NH_2OH + \tfrac{1}{2}O_2 + OH^- \longrightarrow [Ni(CN)_3(NO)]^{2-} + CN^- + 2H_2O$$

conforms to the rate expression

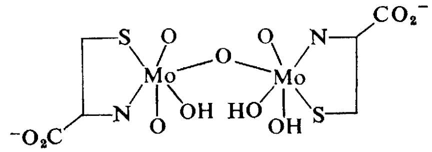
$$\text{Rate} = k[Ni(CN)_4^{2-}][NH_2OH][OH^-]^3$$

the rate being increased by metal ions and inhibited by cyanide. The data may be interpreted in terms of the mechanism

$$[Ni(CN)_4]^{2-} + NH_2OH + 3OH^- \underset{K}{\overset{\text{rapid}}{\rightleftharpoons}} [Ni(CN)_3(NO)]^{4-} + 3H_2O + CN^-$$

$$[Ni(CN)_3(NO)]^{4-} + \tfrac{1}{2}O_2 + H_2O \longrightarrow [Ni(CN)_3(NO)]^{2-} + 2OH^-$$

The importance of the redox nature of molybdenum centres in biological systems has been recognized in several studies. Model systems for nitrogenase, involving molybdate, catalytic amounts of iron(II), and cysteine, effect the reduction of aliphatic nitriles to alkanes and ammonia in the presence of sodium borohydride.[210] The reaction is accelerated by substrate concentrations of ATP, the active species being considered to be mononuclear molybdenum–thiol complexes. The dinuclear molybdenum complex (7) formed by hydrolysis from the di-oxo-bridged species has been shown to react fairly rapidly with flavin mononucleotide,[211] the molybdenum(V) being oxidized to Mo^{VI}. In the presence of excess cysteine, which suppresses a hydrolysis side-reaction, the reaction at pH ~10 essentially goes to completion, and, in contrast to previous work in acidic conditions, the kinetic data preclude the possibility of Mo^{IV} as the active intermediate and are compatible with a two-electron transfer from the complex to the flavin. The importance of the sulphur-containing ligands in the complex is reinforced by the observation that a dimeric complex similar to that above in which the cysteine residues have been replaced by OH, H_2O, or (borate) buffer shows little or no reactivity towards the flavin. The molybdenum(VI) oxidation of cyclic polyketones containing five carbonyl groups has been investigated photometrically in acidic media.[212] A one-electron reduction to Mo^V takes place and oxidation of the organic group is limited to two electrons. The epoxidation of olefins, *e.g.*



(7)

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[209] J. Veprek-Siska and S. Lumak, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3846.

[210] G. N. Schrauzer, P. A. Doemeny, R. H. Frazier, and G. W. Kiefer, *J. Amer. Chem. Soc.*, 1972, **94**, 7378.

[211] P. Kroneck and J. T. Spence, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 177.

[212] J. F. Verchere and M.-B. Fleury, *Bull. Soc. chim. France*, 1972, 2611.

cyclohexene, with alkyl hydroperoxides is catalysed by molybdenum(VI) acetylacetone complexes,[213] and in the reaction of 2,3-dimethylbut-2-ene, dimeric molybdenum species have been postulated as intermediates. The mechanism of the photochemical reduction of octacyanomolybdate(V) ion in aqueous solution has been reported,[214]

$$[\mathrm{Mo(CN)_8}]^{3-} \xrightarrow{\mathrm{OH^-}} \underset{\text{yellow}}{[\mathrm{Mo(CN)_7(OH)}]^{4-}} \xrightarrow{\text{rapid}} \underset{\text{blue}}{[\mathrm{Mo(CN)_4O(OH)}]^{3-}}$$

with the blue tetracyano-oxohydroxomolybdate(IV) complex ion as product. The existence of cyanogen and other nitrogen-containing species as products of the oxidation of $\mathrm{CN^-}$ has been confirmed but no $\mathrm{O_2}$ or $\mathrm{H_2O_2}$ was detected after photolysis.

The rapid oxidation of hydroxide ion by the cation containing three ruthenium atoms in non-integral oxidation states,[215a] $[\mathrm{(H_3N)Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5}]^{7+}$ (8), has been described, the corresponding 6+ cationic complex (9) being the product of the one-electron redox process. The corresponding oxidant in which two ethylenediamine ligands replace the four ammonias on the central ruthenium is reduced faster but the activation enthalpy is similar.

A more recent study, however, has produced evidence for an intermediate in this reaction.[215b] The previous spectrophotometric measurements were made at wavelengths of greatest absorbance difference between the reactant and product ions, the main spectroscopic change being complete within a few milliseconds. In the region of relatively low u.v. peaks, a second, slower change is observed to follow the initial reaction, this second process having no effect on the visible spectrum, suggesting that the intermediate has a spectrum in the visible region similar to (9). The measurements made in this latter region indicate that the reactive form of the intermediate (10) is that of a conjugate acid, the reaction scheme being represented as ($\mathrm{NH_3}$ ligands omitted for clarity)

$$\mathrm{HO^-} + [\mathrm{RuORuORu}]^{7+} \xrightarrow{\text{slow}} [\mathrm{RuORu(OH)ORu}]^{6+} \qquad \text{(i)}$$

$$2[\mathrm{RuORu(OH)ORu}]^{6+} \xrightarrow{\text{rapid}}$$

$$\underset{(9)}{[\mathrm{RuORuORu}]^{6+}} + \underset{(10)}{[\mathrm{Ru(OO)RuORu}]^{6+}} + \mathrm{H_2O}$$

$$\underset{(10)}{[\mathrm{Ru(OO)RuORu}]^{6+}} + \mathrm{H^+} \longrightarrow [\mathrm{RuORu(OH)ORu}]^{7+}$$

$$(\textit{in acid}) \quad 2[\mathrm{RuORu(OH)ORu}]^{7+} \longrightarrow$$

$$[\mathrm{RuORuORu}]^{6+} + [\mathrm{RuORuORu}]^{7+} + \tfrac{1}{2}\mathrm{HO}_2^{\cdot} + \tfrac{1}{2}\mathrm{H^-}$$

$$4\mathrm{HO}_2^{\cdot} \xrightarrow{\text{rapid}} 2\mathrm{H_2O} + 3\mathrm{O_2}$$

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[213] R. A. Sheldon, *Rec. Trav. chim.*, 1973, **92**, 367.

[214] C. W. Gray and J. T. Spence, *Inorg. Chem.*, 1971, **10**, 2751.

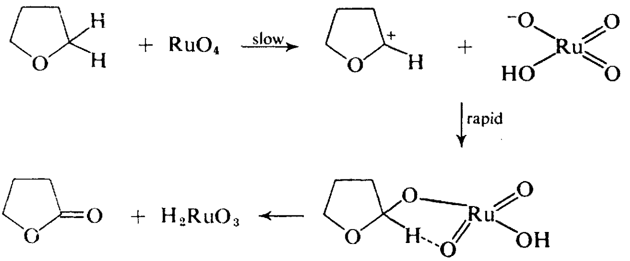
[215] (*a*) J. E. Earley and T. Fealey, *Inorg. Chem.*, 1973, **12**, 323; (*b*) J. E. Earley and H. Razavi, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 331.

The decomposition of the conjugate acid of the intermediate is dependent on the acidity of the medium product. Studies have shown that after the initial reaction has been allowed to take place, re-acidification in the presence of a trace of catalyst yields a mixture of (9) with some 25% of (8) even though the spectrum of (8) had been destroyed by the initial addition of base, whereas in basic media only the product (9) is generated:

$$2[\mathrm{RuORu(OH)ORu}]^{7+} \longrightarrow \underset{(9)}{2[\mathrm{RuORuORu}]^{6+}} + 2\mathrm{H}^+ + \mathrm{O}_2$$

In the initial reaction (i), the nucleophilic attack of the base takes place at the central ruthenium atom of (8), the facile oxidation being favoured by (*a*) non-labile, non-acidic ligands occupying all the co-ordination sites on the ruthenium atoms and so preventing an inner-sphere binding of the OH^- and (*b*) the tendency of the ruthenium to assume a co-ordination number of seven utilizing low-lying antibonding orbitals of the metal cluster to accept electrons from the nucleophile. The presence of vicinal oxygens would allow for formation of the dioxygen ligand with its attendant enhancement of the stability of the intermediate.

The rates of hydrolysis of monomeric ruthenium(II) chloride complexes which are generated electrochemically have been reported[216] and are much more rapid than those observed for the corresponding ruthenium(III) species. It is suggested that Ru^{II} chloride complexes may exist as unstable intermediates when the ruthenium(III) species are reduced. Ruthenium(II) dimethyl sulphoxide complexes have been shown to be the products of refluxing the hydrated ruthenium(III) chloride with DMSO.[217] The use of ruthenium tetroxide as an oxidant has also been described.[218] In the oxidation of tetrahydrofuran in aqueous perchloric acid, an inverse hydrogen-ion dependence is observed, the proposed mechanism involving hydride abstraction with recombination to yield an ester. A scheme consistent with isotope-labelling data may be represented as



In the corresponding reaction with propan-2-ol, however, a five-electron

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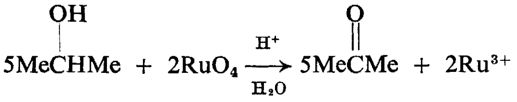
[216] P. E. Dumas and E. E. Mercer, *Inorg. Chem.*, 1972, **11**, 531.
[217] I. P. Evans, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 204.
[218] D. G. Lee and M. Van den Engh, *Canad. J. Chem.*, 1972, **50**, 2000, 3129.

change is observed,



$$5\mathrm{Me}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HMe} + 2\mathrm{RuO_4} \xrightarrow[\mathrm{H_2O}]{\mathrm{H^+}} 5\mathrm{Me}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Me} + 2\mathrm{Ru^{3+}}$$

the reduced ruthenium ion being characterized spectrophotometrically. A hydride-abstraction mechanism is considered to be operative.

The oxidation of titanium(III) chloride by chlorinated alkyl cyanides has been shown[219] to result in the formation of Ti^{IV}–chloroalkyl cyanide species, the mechanism suggested involving the transfer of a chlorine atom from the co-ordinated alkyl cyanide to the metal followed by loss of a CCl_2CN group. A comparative spectro-electrochemical, stopped-flow kinetic, and polarographic study has been made on the Ti^{III}–hydroxylamine reaction.[220] The rate has been shown to be dependent on pH, and in the presence of ~0.2M-oxalic acid (H_2ox) the proposed reaction scheme may be expressed as

$$\mathrm{Ti^{III}} + \mathrm{NH_3OH^+} \xrightarrow{k} \mathrm{Ti^{IV}} + \mathrm{H_2O} + \mathrm{NH_2^{\bullet}}$$

$$\mathrm{NH_2^{\bullet}} + \mathrm{H_2ox} \xrightarrow{\text{rapid}} \mathrm{NH_3} + \text{products}$$

the oxalic acid acting as a scavenger for the amino-radicals.

The silver(II) oxidations of hydroxylamine and *O*-methylhydroxylamine have been investigated in perchloric acid media[221] (1.03—5.83 mol l^{-1}). In the presence of excess oxidant, the reaction products from NH_3OH^+ and $NH_3OCH_3^+$ are NO_3^- and NO_3^- + CO_2, respectively. In the hydroxylamine reaction, no dependence of the rate on either Ag^I or ionic strength is observed. Both reactions show inverse dependences on the hydrogen-ion concentrations, the effect arising from differences in the reactivities of the Ag^{2+} and $AgOH^+$ ions. The overall kinetics conform to a second-order rate law, the mechanism for the oxidation of hydroxylamine being described by the scheme

$$\mathrm{Ag^{2+}} + \mathrm{NH_3OH^+} \xrightarrow{k_0} \mathrm{Ag^+} + \mathrm{NH_2O^{\bullet}} + 2\mathrm{H^+}$$

$$\mathrm{AgOH^+} + \mathrm{NH_3OH^+} \xrightarrow{k_1} \mathrm{Ag^+} + \mathrm{NH_2O^{\bullet}} + \mathrm{H_3O^+}$$

$$2\mathrm{H_2O} + 5\mathrm{Ag^{II}} + \mathrm{NH_2O^{\bullet}} \xrightarrow{\text{fast}} 5\mathrm{Ag^+} + \mathrm{NO_3^-} + 6\mathrm{H^+}$$

Evidence that the radical produced derives from the loss of the hydroxyl and not the amine hydrogen may be found from a consideration of the results for *O*-methylhydroxylamine. If the first step in both compounds involved the loss of the amine protons, the rates would be expected to be similar, whereas that

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[219] G. W. Fowles, K. C. Moss, D. A. Rice, and N. Rolfe, *J. C. S. Dalton*, 1972, 915.
[220] M. Petek, T. E. Neal, R. L. McNeely, and R. W. Murray, *Analyt. Chem.*, 1973, **45**, 32.
[221] D. S. Honig, K. Kustin, and J. F. Martin, *Inorg. Chem.*, 1972, **11**, 1895.

for NH_3OH^+ is more than an order of magnitude greater than that for the NH_3OMe^+ reaction. In the latter case, the mechanism involves processes of the type shown ($Ag^{II} = Ag^{2+}$ or $AgOH^+$):

$$Ag^{II} + NH_3OMe^+ \longrightarrow Ag^+ + {}^{\bullet}NHOMe + 2H^+$$

$$ {}^{\bullet}NHOMe + Ag^{II} \xrightarrow{\text{fast}} Ag^I + [\text{Intermediate}]$$

$$nH_2O + [\text{Intermediate}] + 10Ag^{II} \longrightarrow NO_3^- + CO_2 + 10Ag^+ + xH^+$$

In both reactions it is evident that $AgOH^+$ is a more reactive species toward the substrates than Ag^{2+}; however, both species may be reacting *via* direct electron transfer. Pathways in which Ag^{III} might be considered a reactive species are excluded since a second-order dependence on $[Ag^{II}]$ and an inverse first-order dependence on $[Ag^I]$ would be predicted in this situation. The use of silver(II) as a reagent for oxidative cleavage of hydroquinone ethers has been reported.[222] In the apparently homogeneous reaction between Ag^I and chloro-amines,[223] in the presence of base, the rate is probably promoted by a trace of silver metal and is sensitive to oxygen.

The kinetics of the reduction of gold(III) by thiomorpholine (L) have been investigated in 50/50 v/v ethanol–water mixtures in the presence of halide ions,[224] the mechanism involving reactive hydrolysed anionic forms of the oxidant,

$$AuX_4^- + H_2O \rightleftharpoons [AuX_3OH^-] + H^+ + X^-$$

$$[AuX_3OH^-] + L \xrightarrow{\text{rapid}} [AuX_3L] + OH^-$$

$$[AuX_3L] + H_2O \xrightarrow{\text{rapid}} [AuX_2(OH)L] + H^+ + X^-$$

$$[AuX_2(OH)L] + L \longrightarrow AuXL + LO + H^+ + X^-$$

All the complexes are sulphur-bonded to the metal and the mechanism proposed is not too different from that for the corresponding reaction of $[Pd^{IV}Cl_6]^{2-}$.

A kinetic investigation has been made of the oxidation of formic acid by neptunium(VII) in aqueous perchlorate solutions:[225]

$$2Np^{VII} + HCO_2H \longrightarrow 2Np^{VI} + 2H^+ + CO_2$$

The data are consistent with a rate law of the form

$$-d[Np^{VII}]/dt = \{k_1 + k_2/[H^+]\}[Np^{VII}][HCO_2H]$$

Deuterium isotope effects have been studied using D_2O, HCO_2D, and DCO_2H, and the mechanism is considered to involve either successive one-electron steps

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[222] C. D. Snyder and H. Rapoport, *J. Amer. Chem. Soc.*, 1972, **94**, 227.
[223] O. E. Edwards, D. Vocelle, and J. W. ApSimon, *Canad. J. Chem.*, 1972, **50**, 1167.
[224] D. De Filippo, F. Devillanova, and C. Preti, *Inorg. Chim. Acta*, 1971, **5**, 103.
[225] M. Thompson and J. C. Sullivan, *Inorg. Chem.*, 1972, **11**, 1707.

or the sequence

$$\mathrm{Np^{VII}} + \mathrm{HCO_2H} \longrightarrow \mathrm{Np^{V}} + \mathrm{CO_2} + 2\mathrm{H^+}$$

$$\mathrm{Np^{VII}} + \mathrm{Np^{V}} \xrightarrow{\text{rapid}} 2\mathrm{Np^{VI}}$$

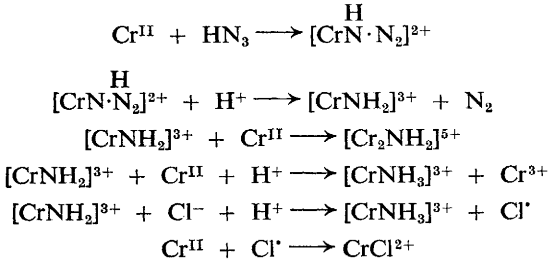
Evidence for the origin of the hydrogen-ion term deriving from the acid dissociation of the HCO_2H species is supported by the observation that whereas the k_1 term shows no isotope effects, the k_2 term shows a ratio $k_2^{H}/k_2^{D} = 4.2 \pm 0.5$, a value comparable in magnitude to the ratio (2.9) of the respective ionization constants.

11 Metal-ion Reductants

The kinetics and mechanism of the reduction of hydrazoic acid by chromium(II) and vanadium(II) have been reported,[226] both reactions yielding 1 mole each of nitrogen and $[Cr(NH_3)]^{3+}$ per two moles of reductant consumed. No hydrogen-ion dependence of the rates was observed over the range $[H^+] = 0.1$—1.0 mol l^{-1}, the overall kinetics being second-order,

$$-\mathrm{d}[\mathrm{HN_3}]/\mathrm{d}t = k_1[\mathrm{M^{II}}][\mathrm{HN_3}]$$

Since hydrazoic acid is a two-electron oxidant, the rate behaviour requires an intermediate oxidation state of one of the reactants, and in the case of Cr^{II} there is evidence for preliminary formation of a Cr—N bond; a possible mechanism involves an oxidation to a Cr^{IV} state with subsequent reaction with a second mole of reductant, *e.g.*



$$\mathrm{Cr^{II}} + \mathrm{HN_3} \longrightarrow [\mathrm{Cr\overset{H}{N}\cdot N_2}]^{2+}$$

$$[\mathrm{Cr\overset{H}{N}\cdot N_2}]^{2+} + \mathrm{H^+} \longrightarrow [\mathrm{CrNH_2}]^{3+} + \mathrm{N_2}$$

$$[\mathrm{CrNH_2}]^{3+} + \mathrm{Cr^{II}} \longrightarrow [\mathrm{Cr_2NH_2}]^{5+}$$

$$[\mathrm{CrNH_2}]^{3+} + \mathrm{Cr^{II}} + \mathrm{H^+} \longrightarrow [\mathrm{CrNH_3}]^{3+} + \mathrm{Cr^{3+}}$$

$$[\mathrm{CrNH_2}]^{3+} + \mathrm{Cl^-} + \mathrm{H^+} \longrightarrow [\mathrm{CrNH_3}]^{3+} + \mathrm{Cl^{\bullet}}$$

$$\mathrm{Cr^{II}} + \mathrm{Cl^{\bullet}} \longrightarrow \mathrm{CrCl^{2+}}$$

This scheme is consistent with the fact that one mole of $[Cr(NH_3)]^{3+}$ is produced per mole of Cr^{3+}, that small amounts of a dimeric species are formed, and with the observation that $CrCl^{2+}$ is produced in the presence of chloride ion even at fairly low concentrations. The mechanism of the vanadium(II) reaction is not as readily described, the results being compatible with either an inner-sphere or an outer-sphere pathway. The spectrum of an intermediate complex formed in the chromium(II) reduction of isonicotinic acid has been described, the initial stage of the reaction involving partial

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[226] R. G. Linck, *Inorg. Chem.*, 1972, **11**, 61.

electron transfer from the reductant to the organic acid.[227] The reduction of t-butyl peroxide by Cr^{II} results in the formation of an alcohol radical which may react with a second mole of reductant to yield the methylpenta-aquochromium(III) cation,[228]

$$Bu^tOOH + Cr^{2+} \longrightarrow Bu^tO^{\bullet} + Cr^{3+} + OH^-$$

$$Bu^tO^{\bullet} + Cr^{2+} \longrightarrow \text{acetone} + [Cr(H_2O)_5Me]^{2+}$$

$$Bu^tO^{\cdot} + Cr^{2+} + H_2O \longrightarrow Bu^tOH + Cr^{3+} + OH^-$$

in a pathway which competes with the major reaction in which the alcohol is produced. The cation formed is not stable at room temperature and decomposes to methane. The reaction of chromium(II) with cephalosporic acids has been reported,[229] the interaction of a carbonium ion with the reducing centre being considered a possible reaction pathway.

The rapid reaction of the aquopenta-ammineruthenium(II) cation with hydrazoic acid yields NH_3, N_2, and ruthenium(III) complexes,[230] the ammonia produced being co-ordinated to the oxidized metal centre with the formation of $[Ru(NH_3)_6]^{3+}$ {compare the corresponding reaction with $[Cr(H_2O)_6]^{2+}$, ref. 225}. One mole of nitrogen is produced per mole of azide ion and the mechanism is considered to involve the co-ordination of the hydrazoic acid into the labile co-ordination sphere of the $[Ru(NH_3)_5(H_2O)]^{2+}$ ion:

$$[(H_3N)_5Ru(OH_2)]^{2+} + HN_3 \longrightarrow [(H_3N)_5Ru(N_3H)]^{2+} + H_2O$$

$$[(H_3N)_5Ru(N_3H)]^{2+} \longrightarrow [(H_3N)_5Ru^{IV}\underset{\cdot\cdot}{\ddot{N}}H]^{2+} + N_2$$

$$[(H_3N)_5Ru^{IV}NH]^{2+} + H^+ \longrightarrow [(H_3N)_5Ru^{IV}(NH_2)]^{3+}$$

$$[(H_3N)_5Ru^{IV}(NH_2)]^{3+} + [Ru(NH_3)_5]^{2+} \xrightarrow[+H^+]{\text{rapid}}$$

$$[Ru(NH_3)_6]^{3+} + [Ru^{III}(NH_3)_5(H_2O)]^{3+}$$

The ruthenium complex $[Ru(NH_3)_5NH]^{2+}$ is not considered to be a nitrene complex but rather a species where an imido-group is co-ordinated. The mechanism accounts for the fact that no free ammonia was observed, so that N—N bond cleavage must have occurred after the Ru—N bond was formed.

The reduction of alkyl halides by iron(II) porphyrins and heme proteins has been investigated,[231] with three general transformations taking place, either (*a*) coupling, (*b*) hydrogenolysis, or (*c*) elimination of vicinal halides

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[227] D. Katakis and E. Vrachnou-Astra, *Chim. Chron.*, 1972, **38**, 210 (*Chem. Abs.*, 1973, **78**, 48 450j).

[228] M. Ardon, K. Woolmington, and A. Pernick, *Inorg. Chem.*, 1971, **10**, 2812.

[229] M. Ochiai, O. Aki, A. Morimoto, T. Okada, and H. Shimadzu, *J.C.S. Chem. Comm.*, 1972, 800.

[230] P. S. Sheridan and F. Basolo, *Inorg. Chem.*, 1972, **11**, 2721.

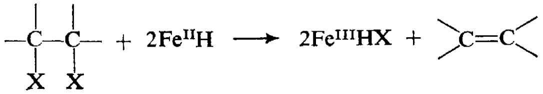
[231] R. S. Wade and G. E. Castro, *J. Amer. Chem. Soc.*, 1973, **95**, 226, 231.

($Fe^{II}H$ = heme):

$$(a)\qquad 2RX + 2Fe^{II}H \longrightarrow 2Fe^{III}HX + R_2$$

$$(b)\qquad RX + 2Fe^{II}H + H^+ \longrightarrow Fe^{III}HX + Fe^{III}H + RH$$

(*c*)



$$-\underset{X}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- + 2Fe^{II}H \longrightarrow 2Fe^{III}HX + >C=C<$$

The kinetic data are consistent with a mechanism in which a cleavage to radicals ($\rightarrow Fe^{III}HX$ + R) is the rate-determining process, the reaction in this regard being somewhat similar to the reduction of organic halides by Cr^{II}, with some inner-sphere character. The rapid oxidation of haemoglobin and myoglobin by bromomalononitrile, whereas cytochrome *c* is inert, is consistent with this proposal since the globins are characterized by a protein conformation which allows easy access to one of the axial positions on the iron whereas in the cytochrome the heme is enveloped in such a manner as to block off the axial ligands. In the reactions of bis(dioximinato)cobalt(II) complexes with organic halides,[232]

$$2[Co^{II}(dmgH)_2B] + RX \longrightarrow [RCo(dmgH)_2B] + [XCo(dmgH)_2B]$$

where $dmgH_2$ = dimethylglyoxime and RX = benzyl halide, the rates are markedly dependent on the phosphine group, B. For the sterically hindered ligand $P(cyclo\text{-}C_6H_{11})_3$ the rate is $\sim 3 \times 10^3$ times slower than for the reaction where B = PMe_3. A free-radical mechanism similar to that described above is proposed, and marked increases in activity in the sequence $RCl < RBr < RI$ have been observed. The fact that the presence of electron-withdrawing substituents on the group B enhances the rate is considered to confirm the suggestion that the reactivity of cobalt(II) complexes of this type is strongly influenced by the axial ligands. The reaction of iron(II)–salen complexes with organic nitro-compounds and halides leads to deoxygenation and dehalogenation:[233]

$$Fe^{II}\,salen + PhNO_2 \longrightarrow Fe(salen)_2O + PhN(O){=}NPh$$

The redox reactions of cobalt cyanide complexes with borohydide ion have been reported,[234] the reactive species in the reduction of $[Co(CN)_5]^{3-}$ being the hydrolysed ion BH_3OH^-. The overall reaction is rapid ($k \sim 10^6\ l\ mol^{-1}\ s^{-1}$) and is controlled by the formation of the hydrolysed species.

In the reaction of sulphur dicyanide with thiocyanate ion[235] the species $(SCN)_2$ is produced as an intermediate,

$$S(CN)_2 + SCN^- + H_3O^+ \longrightarrow (SCN)_2 + HCN + H_2O$$

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[232] J. Halpern and P. F. Phelan, *J. Amer. Chem. Soc.*, 1972, **94**, 1881.
[233] C. Floriani and G. Fachinetti, *J.C.S. Chem. Comm.*, 1973, 17.
[234] J. Hanzlik and A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1972, **37**, 693.
[235] D. F. Kerr and I. R. Wilson, *J.C.S. Dalton*, 1973, 459.

the rate being first-order with respect to $S(CN)_2$ and conforming to the rate law

$$k_{obs} = k_1 + k_2[SCN^-]$$

in the presence of excess thiocyanate at constant $[H^+]$ and [HCN]. The products of decomposition of the $(SCN)_2$ are SCN^-, HCN, H^+, SO_4^{2-}, and HOCN, and are consistent with the several reaction pathways. The disproportionation of dithionate ion,

$$H^+ + {}^-O_3S{-}SO_3^- \longrightarrow SO_2 + HSO_4^-$$

has been shown[236] to be catalysed by hydrogen ions at high temperatures. The rate constant is a function of acidity but temperature-dependence studies show the Arrhenius plots to be curved.

12 Pulse Radiolysis and Flash Photolysis Studies

Quantitative data for this section are collected in Table 2.

Table 2 *Rate constants derived from pulse radiolysis and flash photolysis studies*

Reaction	$k_{25\,°C}$/ l mol^{-1} s^{-1}	I/mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
$Fe^{2+} + OH^{\cdot}$	2.3×10^8	0.1	$\leqslant 1$	—	238[a]
$Fe^{2+} + OD^{\cdot}$	9.4×10^7	0.1	$\leqslant 1$	—	238[a]
$[Fe(CN)_6]^{4-} + OD^{\cdot}$	9.8×10^9	0.1	—	—	238
$Fe^{2+} + Br_2^-$	3.6×10^6	0.2	25.5	−42	241
$Fe^{2+} + Cl_2^-$	4.0×10^6	0.2	31.5	−21	241[b]
$Fe^{2+} + Cl_2^-$	1.0×10^7	0.2	22.7	−42	241[c]
$OH^{\cdot} + N_2H_4$	1.4×10^{10}	—	—	—	245
$OH^{\cdot} + N_2H_5^+$	1×10^9	—	—	—	245
$N_2H_3^{\cdot} + N_2H_3^{\cdot}$	1.2×10^9	—	—	—	245
$e^- +$ PNBPA	8×10^{10}	—	—	—	246[d]
$CO_2^{\cdot} +$ PNBPA	1.9×10^{10}	—	—	—	246[d]
$e^- + HgCl_2$	4×10^{10}	—	—	—	250
$H^{\cdot} + HgCl_2$	1×10^{10}	—	—	—	250
$HgCl + HgCl$	4×10^9	—	—	—	250
$Cr^{2+} + \dot{C}H_2CO_2H$	2.5×10^8	0.1—1.0	—	—	254
$Cr^{2+} + \dot{C}H_2OH$	1.6×10^8	0.1—1.0	—	—	254
$Cr^{2+} + Me\dot{C}HOH$	7.9×10^7	0.1—1.0	—	—	254
$Cr^{2+} + Me\dot{C}_2OH$	5.1×10^7	0.1—1.0	—	—	254
$Cr^{2+} + Me_2\dot{C}HOEt$	3.4×10^7	0.1—1.0	—	—	254

[a] No temperature dependence noted in the range 17—67 °C. [b] Inner-sphere reaction. [c] Outer-sphere reaction. [d] Complex = *p*-nitrobenzoatopenta-amminecobalt(III).

A review of reactions of the solvated electron has recently been published.[237] The oxidation of iron(II) by hydrolysed radicals has been investigated by pulse

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[236] W. Y. W. Lew and R. E. Powell, *Inorg. Chem.*, 1973, **12**, 957.

[237] F. S. Dainton, 'Chemical Kinetics', Physical Chemistry, Vol. 9, M.T.P. International Review of Science, Butterworths, London, 1972.

radiolysis,[238] the rate of reaction of $^{\bullet}OH$ being ~2.5 times greater than that involving $^{\bullet}OD$ radical. The reaction is seen to be a simple electron transfer, the isotope effect being due to differences in the energies of hydration. In the case of the corresponding reaction with $[Fe(CN)_6]^{4-}$, the rate data in D_2O and H_2O are identical, and in this case, since there is no hydrogen-atom abstraction and no water molecules are present in the inner co-ordination sphere of the iron(II), hydration effects are considered to be less important. The nature of the hydroperoxyl radical in aqueous media has been discussed[239] together with methods for its preparation. Complexation with various metal ions (Ce^{III}, Ti^{IV}, V^{V}) has been confirmed from e.s.r. measurements. The reactions of this radical with iron(II) have been investigated,[240] the initial product being an outer-sphere hydroperoxo-complex which subsequently reacts with a second iron(II) ion in a fast reversible process to yield a dinuclear bridged species, slower secondary dissociations of both complexes being observed. It is of interest that although the activation energy for the initial reaction is 10 ± 1 kcal mol^{-1}, no variation of rate with temperature was observed for the reaction of Fe^{2+} with $^{\bullet}OH$ radicals. The oxidation of iron(II) by the halogen radical ions Br_2^- and Cl_2^-, generated by flash photolysis, has been studied,[241] the reaction product in the case of Br_2^- being the complex $FeBr^{2+}$. When de-aerated solutions of Fe^{II}, H^+, and Br^- were photolysed, an initial increase in absorbance was observed (corresponding to the formation of Br_2^- ion), followed by a slower decrease in which two reactions are considered to take place, the second of which is attributed to the dissociation of the $FeBr^{2+}$ complex. In the reaction with chloride ion, however, the absorbance changes are markedly different, and after formation of the intermediate two reactions are important:

$$Fe^{2+} + HO_2^{\bullet} \longrightarrow Fe^{3+}\cdot HO_2^-$$

$$\begin{tikzcd}
Fe^{3+}\cdot HO_2^- + Fe^{2+} \arrow[r, shift left] \arrow[d, "k_\alpha"] & {[Fe^{3+}\cdot HO_2^-\cdot Fe^{2+}]} \arrow[l, shift left] \arrow[d, "k_\beta"] \\
Fe^{3+} + HO_2^- & Fe^{3+} + Fe^{2+}\cdot HO_2^-
\end{tikzcd}$$

$$Fe^{2+} + Cl_2^- \longrightarrow FeCl^{2+} + Cl^-$$

$$Fe^{2+} + Cl_2^- \longrightarrow Fe^{3+}_{aq} + 2Cl^-$$

The mechanism in the bromine anion reaction is considered to involve an inner-sphere substitution-controlled process whereas in the chlorine system

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[238] G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J.C.S. Faraday I*, 1972, **68**, 2053.
[239] G. Czapski, *Israel J. Chem.*, 1972, **10**, 987.
[240] G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J.C.S. Faraday I*, 1973, **69**, 236.
[241] A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 804.

the two paths represented above correspond to inner- and outer-sphere reactions. The kinetic parameters for the inner- and outer-sphere reactions are not very different but the activation enthalpy for the latter reaction is lower, reflecting the lower reorganizational energy requirements involved in this pathway.

The oxidation of bromide ions by $^{\cdot}OH$ has been investigated.[242, 243] The formation of the Br_2^- radical anion as an intermediate is postulated, a mechanism consistent with the data being represented by the following scheme:[243]

$$\begin{aligned}
&Br^- + {}^{\cdot}OH \rightleftharpoons BrOH^-\\
&BrOH^- \longrightarrow Br^{\cdot} + OH^-\\
&BrOH^- + H^+ \longrightarrow H_2O + Br^{\cdot}\\
&BrOH^- + Br^- \longrightarrow OH^- + Br_2^-\\
&Br^- + Br^{\cdot} \longrightarrow Br_2^-\\
&Br_2^- + Br^{\cdot} \longrightarrow Br_3^-
\end{aligned}$$

Rate constants for the reactions of Cl_2^- with charged and neutral surfactants have also been derived.[244]

In the one-electron oxidation of hydrazine[245] with hydroxyl radicals, the reaction rates are dependent on the state of protonation of the molecule,

$$^{\cdot}OH + N_2H_4 \xrightarrow{k_1} {}^{\cdot}N_2H_3 + H_2O$$

the rate for the reaction of the protonated ion $N_2H_5^+$ being a factor of ~14 slower than for the reaction shown. The u.v. spectrum of the hydrazyl radical formed has been derived, the mode of its decay being a second-order process to yield tetrazane, N_4H_6. Evidence has also been presented for the formation of N_3H_3, which is one of the products of the unimolecular decomposition of tetrazane.

A transient species has been detected in the reaction of the solvated electron with cobalt(III) penta-ammine complexes.[246] In the reaction of e_{aq}^- (or CO_2^-) with $[(p\text{-}O_2NC_6H_4CO_2)Co^{III}(NH_3)_5]^{2+}$ (PNBPA) an intermediate is observed (PNBPA$^-$) in which the electron transferred is localized on the co-ordinated *p*-nitrobenzoato-ligand. This species then decays in a ligand–metal intramolecular electron transfer with the formation of cobalt(II):

$$(O_2NC_6H_4CO_2)Co^{III}(NH_3)_5 \longrightarrow Co^{II} + O_2NC_6H_4CO_2^- + 5NH_3$$

In the reductions of $[Co^{III}(bipy)_3]^{3+}$ and $[Co^{III}(terpy)_3]^{3+}$ with e_{aq}^-, transients are also observed,[247] which are also considered as radical anions of the

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[242] D. Behar, *J. Phys. Chem.*, 1972, **76**, 1815.

[243] D. Zehavi and J. Rabani, *J. Phys. Chem.*, 1972, **76**, 312.

[244] J. H. Fendler, E. J. Fendler, G. Bogan, L. K. Patterson, and K. M. Bansal, *J.C.S. Chem. Comm.*, 1972, 14.

[245] E. Hayon and M. Simic, *J. Amer. Chem. Soc.*, 1972, **94**, 42.

[246] M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 1972, **94**, 1757.

[247] J. H. Baxendale and M. Fiti, *J.C.S. Dalton*, 1972, 1995.

pyridyl ligands rather than excited spin states of the metal ion. The products are the corresponding cobalt(II) species. The intermediate formed has also been shown to react with oxygen and $[Cr(CN)_6]^{3-}$ but not with Zn^{2+}. Aspects of the reactions of the pentacyanocobaltate(I) ion $[Co(CN)_5]^{4-}$, generated from $[Co(CN)_5]^{3-}$ and the solvated electron, have recently been reviewed.[248] The reductions of cobalt(III) and ruthenium(III) hexa-ammine complexes by aliphatic radicals have been investigated.[249] Radicals on the carbon atom α to an HO or H_2N group are considered stronger reductants than those on a carbon α relative to a carboxylic acid or amide group. Outer-sphere mechanisms of reaction are proposed, the order of reactivity of the radicals in the case of the $[Ru(NH_3)_6]^{3+}$ system being $^{\bullet}CH_2OH > Me\dot{C}HOH > Me_2\dot{C}OH > Me\dot{C}(OH)COO^- > MeC(O)\dot{C}(O^-)Me$, although the reverse order holds for reactions with $[Co(NH_3)_6]^{3+}$ and Cu^{2+}_{aq}. The reduction of mercuric chloride by hydrated electrons and reducing radicals has been reported,[250] the first step being a dissociative electron capture to yield Cl^- and HgCl. The reaction of HgCl with oxygen has been studied kinetically, as has its rate of dimerization to Hg_2Cl_2.

Pulse radiolysis techniques have been used to confirm that in the oxidized form of the $[Ni(dimethylglyoxime)_2]^+$ complex produced on reaction with $NH_2^{\bullet}$ radicals the metal ion is in the +3 and not the +4 oxidation state.[251] The corresponding ammoniacal nickel(III) complexes have been generated in a similar manner[252] and the absorption spectra of these unstable species measured. In the case of the ethylenediamine species, the rate of decay of the complex is governed by a second-order rate law, the products being mainly NH_3 and NH_2CH_2CHO. No evidence for nickel(IV) was obtained in these studies. Tervalent nickel was also confirmed as an unstable reaction product in the reaction of Ni^+ with N_2O.[253] The reactions with Co^+ and Cd^+ have also been investigated. The reactions are considered to take place with oxygen-atom transfer:

$$M^+ + N_2O \longrightarrow N_2 + MO^+$$

the order of reactivity being $Co^+ > Zn^+ \geqslant Ni^+ > Cd^+$. The precise nature of the hyperoxidized metal-ion complexes is not known but chain-kinetic experiments tend to indicate two forms MO^+ and MO(OH), the second of which may result from hydrolysis of the former.

The formation of chromium–carbon σ-bonds in aqueous media has been investigated,[254] the specific rates of reaction of chromium(II) with aliphatic radicals being measured. Pulse radiolysis of solutions of Cr^{II} and organic molecules generates $^{\bullet}OH$ and $H^{\bullet}$ radicals which react with the organic species

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[248] J. Halpern, G. Guastalla, and J. Bercaw, *Coordination Chem. Rev.*, 1972, **8**, 167.

[249] H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, 1972, **94**, 6944.

[250] N. B. Nazhat and K.-D. Asmus, *J. Phys. Chem.*, 1973, **77**, 614.

[251] J. Lati and D. Meyerstein, *Israel J. Chem.*, 1972, **10**, 735.

[252] J. Lati and D. Meyerstein, *Inorg. Chem.*, 1972, **11**, 2393, 2397.

[253] G. V. Buxton, F. S. Dainton, and D. R. McCracken, *J.C.S. Faraday I*, 1973, **69**, 243.

[254] H. Cohen and D. Meyerstein, *J.C.S. Chem. Comm.*, 1972, 320.

to yield radicals. A correlation of reaction rates of these transients with Cr^{II} has been made in that the order of reactivity $\cdot CH_2CO_2H > \cdot CH_2OH > Me\dot{C}HOH > (Me)_2\dot{C}OH > Me\dot{C}HOEt$ is in agreement with the order of spin densities of the unpaired electron on the α carbon atom, calculated from hyperfine splitting constants obtained from e.s.r. measurements. The second-order rate constants vary by about an order of magnitude, and one of the major factors influencing the rate is the probability of localizing the unpaired electron on a given carbon atom and the nature of its orbital, the differences in rate being too large to be explained solely in terms of steric hindrance.

The effects of solvent on the reactivity of the solvated electron have been discussed.[255] The rates of reaction of e^-_{sol} with various compounds have been measured in liquid 2-methyltetrahydrofuran, and a comparison with data in other solvents suggests that neither a Hammett-type correlation of rate constants with substituent constants, σ, nor the correlation with electron absorption coefficients in the gas phase can be used to describe the reactivity of these solutes towards the electron in solution.

The reaction of hydrogen atoms with glutathione disulphide (RSSR) has been investigated[256] and the spectrum of the $RS^\cdot$ radical obtained. Rates of reaction of RSSR with electrons are a factor of four slower than for the $H^\cdot$ atom, leading to the formation of the $RSSR^{\cdot-}$ radical anion. The rates of reaction of hydrated electrons with other thiol-containing compounds in solution show the rate constants to be strongly dependent on the acid–base properties of the thiol species, the rates decreasing on deprotonation of both the amino- and mercapto-groups.[257]

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[255] J. Teply and I. Janovsky, *Chem. Phys. Letters*, 1972, **17**, 373.
[256] A. Shafferman, *Israel J. Chem.*, 1972, **10**, 725.
[257] M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, 1973, **77**, 990.

3

Reactions involving Oxygen and Hydrogen Peroxide

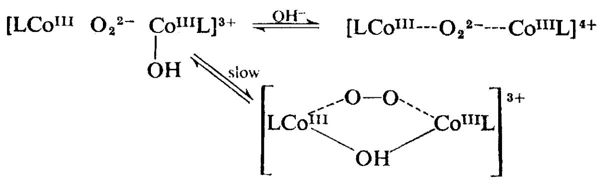
BY A. McAULEY

1 Cobalt(II) Complexes

The mechanism of formation of oxygenated adducts of cobalt(II) and of the oxidized products continues to receive considerable attention. The oxygen complexes of triethylenetetraminecobalt(II) have been described.[258] Potentiometric measurements and oxygen-absorption studies indicate that in the pH range 4—8 the product formed is a dinuclear species, and that an acid–base equilibrium is established at a rate lower than for oxygen uptake. The oxygenated species at pH 9 is destroyed on addition of acid, molecular oxygen being released in the reversible system. It is considered that the species formed under the conditions employed are labile cobalt(III) complexes with the dinegative O_2^{2-} ion co-ordinated. Evidence in support of the increase in oxidation state of the metal centres is given from the observation that addition of base to the oxygenated species leads to hydrolysis of one of the co-ordinated water molecules, behaviour which would not be expected in the pH range studied for the corresponding cobalt(II) complexes. The reaction mechanism may be illustrated by Scheme 1, in which L = triethylenetetramine.

$$Co^{2+} + LH_n^{n+} \rightleftharpoons CoL^{2+} + nH^+$$

$$2CoL^{2+} + O_2 \rightleftharpoons [LCo^{II}\text{---}O_2\text{---}Co^{II}L]^{4+}$$



$$[LCo^{III}\ O_2^{2-}\ Co^{III}(OH)L]^{3+} \underset{}{\overset{OH^-}{\rightleftharpoons}} [LCo^{III}\text{---}O_2^{2-}\text{---}Co^{III}L]^{4+}$$

Scheme 1

The slower formation of the μ-hydroxo-μ-peroxo complex ion is the predominant step at high pH's and leads to irreversibility in the exchange of the

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[258] R. Nakon and A. E. Martell, *J. Amer. Chem. Soc.*, 1972, **94**, 3026.

oxygen. A similar reaction scheme is considered to describe the reaction of cobalt(II) with *NNN'''N'''*-diglycylethylenediaminetetra-acetate,[259] where the bonding in the oxygenated species is again thought to involve Co^{III}. Two protons are observed to be released per mole of ligand on reaction, indicating ionization of the amide nitrogens with formation of a complex of composition $[Co_2O_2(H_{-2}L)_2]^{8-}$. The species is remarkably stable with respect to irreversibility of oxygenation and may be a model system for further study of cobalt(II) peptide reactions of this type. In the corresponding reactions of cobalt(II)–polyamines where there is insufficient ligand present or where the chelating agent has too few donor sites, μ-hydroxo-bridged species are formed.[260] The species are again viewed as cobalt(III) peroxo-bridged complexes. A rapid auto-oxidation reaction has been observed in solutions where cobalt(II), tetraethylenepentamine, and ascorbic acid are mixed. The rate of reaction is attributed to the formation of a mixed-ligand complex where after oxygenation it is possible for the electron transfer to take place directly from the ascorbic acid to the cobalt(III) centres. Oxygen uptake in aqueous solutions of cobalt(II) and ethylenediamine is at a maximum when the relative concentration ratios are 1 : 3.[261] The reaction products, however, which have been isolated by addition of alcohol to the reaction media, show varying stoicheiometries. Calorimetric studies of the oxygenation of ethylenediamine and histidine complexes show that the reactions are characterized by large negative heat and entropy changes.[262] Dinuclear complexes of polyamine ligands where O_2 is a bridging group have been prepared[263] and are found to liberate oxygen spontaneously in acidic solutions. The aerial oxidation of 1,2,4-trimethylbenzene in the presence of cobalt(II) picolinate has been described,[264] a mixture of substituted benzoic and terephthalic acids being produced. The kinetics of the oxidation reaction of mesitylene by cobalt(II) complexes are not simple, a rapid initial uptake of oxygen being observed.

The thermodynamics of reaction of molecular oxygen with five- and six-co-ordinate amine complexes of $\alpha,\beta,\gamma,\delta$-tetra-(*p*-methoxyphenyl)porphinatocobalt(II) in toluene have been investigated.[265] In the absence of oxygen, the differences in thermodynamic stability of the five-co-ordinate complexes with amines may derive in part from extra stabilization of the cobalt–nitrogen bond arising from involvement of the π^* orbitals of the aromatic amines in some degree of π back-bonding. In the reactions of these five-co-ordinate complexes with O_2, the negative heat and entropy effects identified for the simple amine complexes are again observed, but no apparent relationship between the dissociation constant of the conjugate acid of the amine and ΔG or ΔS has been

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[259] R. Nakon and A. E. Martell, *Inorg. Chem.*, 1972, **11**, 1002.

[260] R. Nakon and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1365.

[261] P. Bijl and G. De Vries, *J.C.S. Dalton*, 1972, 303.

[262] H. K. J. Powell and G. H. Nancollas, *J. Amer. Chem. Soc.*, 1972, **94**, 2664.

[263] M. Zehnder and S. Fallab, *Helv. Chim. Acta*, 1972, **55**, 1691.

[264] A. D. Stefanova, D. I. Dimitrov, and L. K. Jankov, *Monatsh.*, 1972, **103**, 1011; A. D. Stefanova, L. K. Jankov, and D. I. Dimitrov, *ibid.*, p. 786.

[265] F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 1150, 1154.

found. Similar studies have been made at low temperatures on the corresponding reaction of the protoporphyrin(IX) dimethyl ester complexes, using pyridine and imidazole ligands as bases.[266] Kinetic studies have been made on these reactions,[267] where the formation of the peroxo-bridged species conforms to a rate law which is first-order with respect to cobalt and oxygen. The order in amine (A) varies with increasing concentration, the rate-determining step involving a slow rearrangement of the 1 : 1 oxygenated complex (CoP = porphyrin complex):

$$\mathrm{CoP} + \mathrm{A} \rightleftharpoons \mathrm{ACoP}$$

$$\mathrm{ACoP} + \mathrm{O_2} \rightleftharpoons \mathrm{ACoP(O_2)}$$

$$\mathrm{ACoP(O_2)} \xrightarrow{\text{slow}} \mathrm{ACoP(O_2)^*}$$

$$\mathrm{ACoP(O_2)} + \mathrm{ACoP} \xrightarrow{\text{fast}} \mathrm{ACoP(O_2)PCoA}$$

When imidazole ligands are present in the fifth co-ordinating position, the rates are markedly increased compared with those for the other amines and this may reflect some hydrogen-bonding between the co-ordinated oxygen and the acidic proton on the imidazole ring.

Several papers have been published on the reactions of cobalt(II)–Schiff base complexes. A correlation between electronic structure and the chemical parameters of oxygenation has been described,[268] the predominant single factor which is controlled by the fifth (axial) ligand being the energy change in the process $\mathrm{Co^{II}} \rightarrow \mathrm{Co^{III}}$. The latter oxidation state is favoured if the d_{z^2} level of cobalt(II) is raised, making this electronic configuration less stable. Several optically active complexes of this type have been prepared[269] and their reactivities with oxygen compared. Five-co-ordination is considered an essential feature for oxygenation but it is not always necessary to have a large concentration of the thermodynamically stable five-co-ordinate species in order that oxygen is taken up at a reasonable rate. High reactivity in dimethylformamide solutions is observed although not explained. Steric effects may be important and related to two factors, the repulsive interaction of axial substituents of the diamine ring with the oxygen molecules approaching the metal centre and also the repulsive interaction with the axial base donor which is then maintained at a distance from the cobalt atom greater than would be observed in other complexes of this type. The structure of the oxygen complex $[\mathrm{Co(bzacn)(py)O_2}]$, where bzacn is *NN'*-bis(ethylene)bis(benzoylacetoinimide), which provides configurational models for bonding in haemoglobin, has been

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[266] H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, 1972, **94**, 1559.

[267] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, 1973, **95**, 1142.

[268] E. I. Ochiai, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1727.

[269] C. Busetto, F. Cariati, A. Fusi, M. Gulotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J.C.S. Dalton*, 1973, 754.

reported.[270] An e.s.r. study of the cobalt(II)–salen complex[271] has shown that the reversible room-temperature oxygenation

$$2[\mathrm{Co(salen)}] + \mathrm{O_2} \rightleftharpoons [\mathrm{(salen)CoO_2Co(salen)}]$$

occurs in solvents in which the electronic configuration is $(d_{xy})^2(d_{xz})^2(d_{az})^2$ $(d_{z^2})^1(d_{x^2-y^2})^0$ whereas no such reaction occurs at room temperature in solvents such as dimethylformamide, where there are two electrons in the d_{z^2} orbital and only one in the d_{xy}.

2 Iron(II) Complexes

The effect of the structure of amino-acid ligands on the oxidation of iron(II) complexes in aqueous sulphate media has been investigated.[272] At 40 °C, the rate of reaction of oxygen with 0.25M-iron(II) is accelerated more by β-amino-acids than by α-amino-acids, the electron-transfer process being considered to take place more readily in a six-membered than in a five-membered ring. A high catalytic activity of histidine was observed, where the relative positions of the amino- and carboxy-groups is seen to be an important factor. The order of reactivity follows the sequence glycine < alanine < isoleucine < norleucine. Studies on the oxidation of iron(II) cyanates have been reported.[273] Complete oxidation to the iron(III) state takes place in methanol if the iron(II) : cyanate concentration ratio is maintained at 1 : 3, the reaction product being bridged dinuclear species. Chloride ion, however, retards the reaction. A review of the factors involved in aerial oxidation of iron(II) in aqueous media has also been published.[274]

Tris(biacetylbismethylimine)iron(II) has been observed to undergo a free-radical chain auto-oxidation in aqueous acidic (sulphate) media in the presence of molecular oxygen.[275] The rate of oxidation of the aliphatic di-imine ligands is accelerated by iron(III) but retarded by iron(II); the rate-determining process is the attack by oxygen on the co-ordinated ligands, about four moles of O_2 being absorbed. The presence of free radicals has been confirmed by the polymerization of acrylonitrile added to the reaction mixture. A dependence of rate on hydrogen-ion concentration has been described, decreasing acidity causing a decrease in rate. Comparison of the data with those of the corresponding cyclohexane-1,2-dionebismethylimine complex, which reacts faster, whereas the tris(glyoxalbismethylimine) complex does not react under these conditions, suggests that oxidation occurs at the methyl (or methylene) groups attached to the carbon atoms of the di-imine skeleton, without cleavage of the metal–ligand bond or oxidation of the iron(II).

[270] G. A. Rodley and W. T. Robinson, *Nature*, 1972, **235**, 438.

[271] E. I. Ochiai, *J.C.S. Chem. Comm.*, 1972, 489.

[272] A. N. Astanina, A. P. Rudenko, and N. A. Kuznetsova, *Zhur. fiz. Khim.*, 1972, **46**, 369.

[273] M. Quastlerova-Hvastijova, J. Kohout, and J. Gazo, *Coll. Czech. Chem. Comm.*, 1972, **37**, 2891.

[274] H. Tamura, K. Goto, and M. Nagayama, *Shikizai Kyokaishi*, 1972, **45**, 629 (*Chem. Abs.*, 1973, **78**, 62 710a).

[275] H. L. Chum, A. M. G. Da Costa, and P. Krumholz, *J.C.S. Chem. Comm.*, 1972, 772.

3 Other Metal Complexes

The oxidation of copper(I) by oxygen in the presence of chloride ions has been studied potentiometrically,[276] the rate being a function of hydrogen-, copper(I)-, and chloride-ion concentrations. In HCl–LiCl media the data are consistent with the reaction scheme

$$[\mathrm{CuCl}_n]^{x-} + \mathrm{O}_2 \rightleftharpoons [\mathrm{CuCl}_n\cdot\mathrm{O}_2]^{x-} + \mathrm{H_2O}$$

$$[\mathrm{CuCl}_n\cdot\mathrm{O}_2]^{x-} + \mathrm{H}^+ \xrightarrow{\text{slow}} [\mathrm{Cu^{II}Cl}_n]^{(x-1)-} + \mathrm{HO}_2^{\bullet}$$

$$3[\mathrm{CuCl}_n]^{x-} + \mathrm{HO}_2^{\bullet} \xrightarrow{+3\mathrm{H}^+} 3[\mathrm{Cu^{II}Cl}_n]^{(x-1)-} + 2\mathrm{H_2O}$$

The rate-determining step is thought to involve the attack of a proton on the oxygenated copper(I) species to yield the $\mathrm{HO}_2^{\bullet}$ radical. The reaction has also been studied in 0.2—0.8M-HCl solutions,[277] the rate being first-order with respect to both $\mathrm{Cu^I}$ and oxygen concentrations. Copper(II) ions retard the rate, however, possibly owing to a chloro-bridged dinuclear complex between the copper-(I) and -(II) oxidation states. The effect of copper(II) ions on the enzymic activity of polyphenol oxidase has been suggested as a possible analytical method for trace (10^{-6} g l^{-1}) quantities of this ion in aqueous solution.[278] Chemical bonding of the polyphenol oxidase to polyacrylamide renders the enzyme insoluble and copper ions may then be removed. The resulting apoenzyme may be reactivated by incubation with 10—200 ng of copper ions and the extent of reaction with catechol in the presence of oxygen is a direct measure of the copper(II) concentration in the enzyme.

The oxidation of $[\mathrm{Ru(NH_3)_6}]^{2+}$ by molecular oxygen,[279]

$$2[\mathrm{Ru(NH_3)_6}]^{2+} + \mathrm{O}_2 + 2\mathrm{H}^+ \longrightarrow 2[\mathrm{Ru(NH_3)_6}]^{3+} + \mathrm{H_2O_2}$$

takes place quantitatively, the data being consistent with a rate law

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = k[\mathrm{Ru(NH_3)_6^{2+}}][\mathrm{O}_2]$$

no hydrogen-ion dependence on the rate being observed over the range 1.0M-H$^+$—pH 6.05. The first step in the corresponding reaction with $[\mathrm{Ru(en)_3}]^{2+}$ takes place sufficiently rapidly that no side reactions arising from oxidation of the ligand occur. These reactions are of interest in that whereas most studies of this type involving transition-metal ions have dealt with inner-sphere processes, it is clear that oxidation by molecular oxygen can take place whilst the primary co-ordination sphere remains intact. The rate data do not

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[276] D. V. Sokol'skii, Y. A. Dorfman, and L. S. Ernestova, *Zhur. fiz. Khim.*, 1972, **46**, 1855.

[277] T. Yano, T. Suetaka, and T. Umehara, *Nippon Kagaku Kaishi*, 1972, **11**, 2194 (*Chem. Abs.*, 1973, **78**, 34 391d).

[278] J. V. Stone and A. Townshend, *J.C.S. Dalton*, 1973, 495.

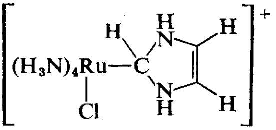
[279] J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, 1973, **12**, 639.

allow for distinction between two possible mechanisms (*a*) and (*b*):

$$\begin{gathered}[\mathrm{Ru(NH_3)_6}]^{2+} + \mathrm{O_2} \rightleftharpoons [\mathrm{Ru(NH_3)_6}]^{3+} + \mathrm{O_2^-}\\ \mathrm{O_2^-} + [\mathrm{Ru(NH_3)_6}]^{2+} \underset{\text{rapid}}{\overset{+2\mathrm{H^+}}{\rightleftharpoons}} \mathrm{H_2O_2} + [\mathrm{Ru(NH_3)_6}]^{3+} \qquad (a)\end{gathered}$$

$$\begin{gathered}[\mathrm{Ru(NH_3)_6}]^{2+} + \mathrm{O_2} \rightleftharpoons [\mathrm{Ru^{IV}(NH_3)_6O_2}]^{2+}\\ [\mathrm{Ru(NH_3)_6O_2}]^{2+} + [\mathrm{Ru(NH_3)_6}]^{2+} \xrightarrow{\text{rapid}} 2[\mathrm{Ru(NH_3)_6}]^{3+} + \mathrm{H_2O_2} \qquad (b)\end{gathered}$$

In (*a*) the equilibrium constant for the first reaction is $\sim 10^{-8}$ and in (*b*) the formation of a ruthenium(IV) complex of co-ordination number seven is postulated. The activation parameters for the reactions of both $[\mathrm{Ru(NH_3)_6}]^{2+}$ and $[\mathrm{Ru(en)_3}]^{2+}$ have been measured and are very similar, being characterized by moderate $-\Delta S^{\neq}$ values. The secondary oxidation of $[\mathrm{Ru(NH_3)_6}]^{2+}$ by $\mathrm{H_2O_2}$ is a very slow reaction (see below), and in the conditions employed the authors consider that the reaction observed was in fact a pathway involving catalysis by iron salts. The oxidation of the trinuclear ruthenium complex $[\mathrm{RuORuORu}]^{6+}$ by both $\mathrm{O_2}$ and $\mathrm{H_2O_2}$ has been shown[214b] to be slow. The acid-catalysed aquation of $[\mathrm{(H_3N)_5Ru(imid)}]^{2+}$ (imid = imidazole) is about 500 times faster than that of the corresponding penta-ammine–pyridine complex,[280] and although the major product is $[\mathrm{(H_3N)_5Ru(OH_2)}]^{2+}$, about 10% of the product ruthenium after aerial oxidation has been isolated as a solid of composition $[\mathrm{(H_3N)_4Ru^{III}(imid)Cl_3}]$. The cation (1) in this complex is considered to involve bonding of the ruthenium centre to the C-2 of the imidazole ring. The 4,5-dimethyl analogue may be prepared directly from the reaction of $[\mathrm{(H_3N)_5RuOH_2}]^{2+}$ with a dimethylimidazole buffer at pH 5.5 in air.



(1)

The influence of complexing on the rate of oxidation of titanium(III) by molecular oxygen has been investigated in hydrochloric acid media.[281] Using concentrations of reductant 0.05—0.4M in 1—8M-HCl, the reaction order was unity with respect to $[\mathrm{Ti^{III}}]$, the rate passing through a maximum at 5M-$\mathrm{H^+}$. In solutions of 1—3M-HCl, the reactant species are believed to be $\mathrm{Ti^{3+}}$ and $\mathrm{Ti(OH)^{2+}}$ whereas under conditions of $[\mathrm{Cl^-}] \geq 5\ \mathrm{mol\ l^{-1}}$, chloro-complexes are the reactive ions. In the reaction of the corresponding tris-acetylacetonate complexes,[282] an intermediate has been detected using e.s.r.

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[280] R. J. Sundberg, R. E. Shepherd, and H. Taube, *J. Amer. Chem. Soc.*, 1972, **94**, 6558.

[281] D. P. Fel'dman and B. P. Matseevskii, *Latv. P.S.R. Zinat. Akad. Vestis. khim. Ser.*, 1972, **5**, 558 (*Chem. Abs.*, 1973, **78**, 34 436x).

[282] G. Y.-S. Lo and C. H. Brubaker, jun., *J. Inorg. Nuclear Chem.*, 1972, **34**, 2375.

techniques, the titanium(IV) species possibly having a structure of the type $[(acac)_2Ti—O—Ti(acac)_2]$.

N.m.r. relaxation rates of $^{205}Tl^I$ in aqueous media show a marked dependence on the presence of molecular oxygen,[283] where a complex is considered to be formed. The interaction may be due to the oxygen molecule penetrating the loose solvation sphere of the thallium(I) to form a weak complex *via* the 6*s* lone-pair electrons. E.s.r. studies[284] on the rhodium(I)–molecular oxygen adduct formed in dimethylformamide containing chloride ions show the presence of a paramagnetic species which may be described as a rhodium(II)–superoxide complex. This observation is consistent with the proposed formation of Rh^{II} complexes in catalytic oxidations. Mixed-oxidation-state complexes of amminedinitrogenosmium ions have been prepared[285] by the action of heat on $[(NH_3)_5OsN_2]^{2+}$ with *cis*-$[(NH_3)_4Os(N_2)_2]^{2+}$ followed by acidification and oxidation by air. The designation of an intermediate oxidation state on the osmium is consistent with the observation that these complexes containing the $[OsNNOs]^{5+}$ unit are stable in acid for days whereas the $[(H_3N)_5OsN_2]^{3+}$ ion loses N_2 much more rapidly. Enthalpies of oxidation of Cr^{II} and V^{II} in sulphate media have been reported,[286] the calorimetric data indicating that the heat of reaction for the former (-18 kcal mol^{-1}) is almost 10 kcal mol^{-1} more exothermic than that for the latter.

The kinetics and mechanism of the metal-chelate-catalysed oxidation of pyrocatechols to quinones have been investigated.[287] Comparisons have been made of the base- and Mn^{II} ion-catalysed auto-oxidations of 3,5-di-t-butylpyrocatechol (3,5-DTBP) to the corresponding *o*-quinone (3,5-DTBQ) with the rates when manganese(II)–4-nitrocatechol, manganese(II)–tetrabromocatechol and cobalt(II)–4-nitrocatechol (Co^{II}–4NC) were present as catalysts. The rates are dependent on hydrogen-ion concentration, and the stoicheiometry and products depend on the nature of the catalytic reagent, *viz.*

$$\text{3,5-DTBP} + O_2 + Mn^{II} \longrightarrow \text{3,5-DTBQ} + H_2O_2$$

whereas in the presence of the cobalt chelate,

$$\text{3,5-DTBP} + \tfrac{1}{2}O_2 + [Co^{II}\text{–4NC}] \longrightarrow \text{3,5-DTBQ} + H_2O$$

the decomposition of the product H_2O_2 having been catalysed by the cobalt(II) complex. The rate data are consistent with a 1 : 1 chelate (ML) as the catalytic reagent in mild alkaline conditions which reacts with an anionic (deprotonated) form of the catechol (C^-) to yield a ternary complex prior to the electron-transfer step, *e.g.*

$$ML + C^- \rightleftharpoons [MLC]^-$$
$$MLC^- + O_2 \rightleftharpoons [ML(C)(O_2)]^-$$

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[283] M. Bacon and L. W. Reeves, *J. Amer. Chem. Soc.*, 1973, **95**, 272.
[284] B. R. James, F. T. T. Ng, and E. I.Ochiai, *Canad. J. Chem.*, 1972, **50**, 590.
[285] R. H. Magnusson and H. Taube, *J. Amer. Chem. Soc.*, 1972, **94**, 7213.
[286] Y. G. Stenin and E. I. Khanaev, *Zhur. fiz. Khim.*, 1972, **46**, 2961.
[287] C. A. Tyson and A. E. Martell, *J. Amer. Chem. Soc.*, 1972, **94**, 939.

The co-ordination of the two ligands in the plane of the metal ion would then permit a π-bonded interaction of the oxygen molecule with the metal centre.

Stereoselective auto-oxidations have also been described in the reactions of dimeric vanadium(IV)–tartrate complexes.[288] The rate of uptake of O_2 in the presence of these complexes is dependent on the isomeric form (D, L, or *meso*) of the ligand, the influence of pH being observed to be important. The overall stoicheiometry conforms to the equation

$$O_2 + 4V^{IV} + 4H^+ \rightleftharpoons 4V^V + 2H_2O$$

with the possibility of some reduction by the tartrate ion at higher pH's of the vanadium(V) produced. A reaction scheme may be expressed as

$$V^{IV}{}_2 \xrightarrow{O_2} \text{intermediate (A)} \xrightarrow{O_2} \text{orange } V^V \text{ species (B)}$$

where the complex ion (B) is considered by comparison of Raman spectra to be the decavanadate(V) ion. Solutions of the intermediate (A), which is thought to be a mixed-valence V^{IV}–V^V species, are sensitive to pH changes. A possibility exists that (A) may contain a peroxo-bridge, but no evidence for this was derived on testing with luminol. The spectra of D-(A), L-(A) and *meso*-(A) differ, however, and rate of uptake of oxygen in the pH range 3—7 is in the order *meso* > D > L. The stability constants for the dimeric vanadium(IV)–tartrate bridged complex ions are in the order $K_{LL} > K_{DD} \gg K_{meso-meso}$, which is the converse for that found for auto-oxidation, suggesting that reaction with molecular oxygen takes place *via* monomeric vanadium(IV) ions to yield a vanadium(V)–tartrate complex which then combines with a V^{IV} species still present to give the mixed-oxidation-state dimer (A).

The mechanism of oxidation of cerium(III) and silver(I) ions by ozone has been reported.[289] The reaction is second-order overall in aqueous nitric acid and proceeds *via* a free-radical mechanism,

$$O_3 + M^{n+} \underset{\text{slow}}{\rightleftharpoons} MO_3^{n+} \xrightarrow{k_1} MO^{n+} + O_2$$

$$MO^{n+} + H_2O \longrightarrow M^{(n+1)+} + OH^- + HO^\bullet$$

$$M^{n+} + HO^\bullet \xrightarrow{\text{rapid}} M^{(n+1)+} + OH^-$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

where the hydroxyl radicals formed are rapidly reduced by a further reaction with the metal ion. The decomposition of the MO_3^{n+} complex is thought to involve the transfer of an electron from a lone pair on the oxidant to the free *d*-orbitals of the metal ion. No effect of cerium(IV) was detected at low concentrations.

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[288] R. D. Gillard and R. A. Wiggins, *J.C.S. Dalton*, 1973, 125.

[289] Y. E. Ivanov, G. P. Nikitina, M. F. Pushlenkov, and V. G. Shumkov, *Zhur. fiz. Khim.*, 1972, **46**, 2149.

4 Reactions of Hydrogen Peroxide

Continuous-flow e.s.r. studies have been made on the oxidation of vanadium(IV) by hydrogen peroxide.[290] Both the VO^{2+} ion and the intermediate complex formed, $[OVOO]^{2+}$, have been monitored over a wide range of initial V^{IV}, H_2O_2, and H^+ concentrations. In the presence of excess H_2O_2, a mechanism accounting for the deviation from pseudo-first-order kinetics may be represented as

$$VO^{2+} + H_2O_2 \underset{k_1}{\overset{k_2}{\rightleftarrows}} [OVOOH]^+ + H^+$$

$$[OVOOH]^+ \xrightarrow{k_3} VO_2^+ + HO^\bullet$$

$$VO^{2+} + H_2O_2 \xrightarrow{k_4} VO_3^+ + H_2O$$

$$VO^{2+} + HO^\bullet \longrightarrow VO_2^+ + H^+$$

$$VO_3^+ + HO^\bullet \longrightarrow \text{intermediate} + \text{products}$$

The reaction to produce the peroxovanadium(V) complex, $[VO_3]^+$, is faster than the first two steps, and the redox reactions involving the radicals are also assumed to be rapid. A possible formulation of the intermediate as $[OVOO]^{2+}$ is also proposed, the e.s.r. spectrum being consistent with a vanadium(V) complex containing a paramagnetic oxygen ligand. The products are, however, pH dependent in that below pH 2 the $[VO_3]^+$ ion is formed, whereas at pH 4 the diperoxovanadium(V) ion $[VO_5]^-$ predominates. The inner-sphere nature of the redox reaction has been confirmed in that whereas iminodiacetic acid does not affect the rate of V^{IV} decay, edta lowers the rate by a factor of more than 100, supporting a mechanism of this type for the initial equilibrium. Confirmation of the formation of the $[VO(O_2)]^+$ and $[VO(O_2)_2]^-$ ions has been obtained in a stopped-flow investigation over a reduced pH range.[291] Second-order behaviour was observed, the rate-determining step involving the reaction

$$V^{IV} + H_2O_2 \longrightarrow V^V + HO^- + HO^\bullet$$

the hydroxyl radicals formed reacting with excess oxidant. Increase in pH results in an increase in reaction rate.

The kinetics and mechanism of formation of the complex between plutonium(IV) and H_2O_2,[292]

$$2Pu^{IV} + H_2O_2 \rightleftarrows [Pu(OO)(OH)Pu]^{5+} + 3H^+$$

have been investigated,[291] the rate law conforming to the expression

$$d[\text{Complex}]/dt = \{k_a[H^+]^{-1} + k_b[H^+]^{-2}\}[H_2O_2][Pu^{IV}]^2$$

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[290] H. B. Brooks and F. Silicio, *Inorg. Chem.*, 1971, **10**, 2530.

[291] A. Samuni, D. Meisel, and G. Czapski, *J.C.S. Dalton*, 1972, 1273.

[292] A. Ekstrom and A. McLaren, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1009.

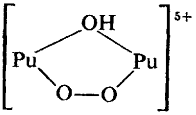
Several forms of the reductant are present under the experimental conditions used, the hydrogen-ion dependences being ascribed to the reaction of hydroxo-complexes:

$$\mathrm{Pu^{IV} + H_2O \rightleftharpoons [PuOH]^{3+} + H^+}$$

$$\mathrm{Pu^{4+} + [PuOH]^{3+} \rightleftharpoons [Pu_2(OH)]^{7+}}$$

$$\mathrm{2[PuOH]^{3+} \rightleftharpoons [Pu_2(OH)_2]^{6+}}$$

$$\mathrm{[Pu_2(OH)]^{7+} + H_2O_2 \longrightarrow}$$



The oxidation of tin(II) by hydrogen peroxide does not follow a simple rate law.[293] Second-order plots from absorbance *versus* time curves show deviations from linearity, particularly during the initial rapid portion of the reaction, and there is spectroscopic evidence for the formation of an intermediate absorbing in the ultraviolet. The overall stoicheiometry of the reaction, where 1 g atom of $\mathrm{Sn^{II}}$ reacts with 1 mol of $\mathrm{H_2O_2}$, is adhered to in ratios of $\mathrm{Sn^{II} : H_2O_2}$ varying from 20 : 1 to 1 : 20. The reaction rate is inhibited by copper(II) ions where the kinetic behaviour becomes second-order. The mechanism suggested involves both one- and two-equivalent oxidations and it is of interest that the extent of reaction as monitored by chemical quenching [using cerium(IV)] and spectrophotometry shows marked differences. The kinetics of the oxidations of chromium(II), titanium(III), and vanadium(IV) have been investigated[291] using stopped-flow techniques. Under experimental conditions where $\mathrm{[Cr^{II}] \gg [H_2O_2]}$ the rate law

$$-\mathrm{d[Cr^{II}]}/\mathrm{d}t = 2k_2\mathrm{[Cr^{II}][H_2O_2]}$$

holds, the reduction of the peroxide taking place *via* two consecutive steps:

$$\mathrm{Cr^{II} + H_2O_2} \xrightarrow{k_2} \mathrm{Cr^{III} + HO^{\bullet} + HO^-}$$

$$\mathrm{Cr^{II} + HO^{\bullet}} \xrightarrow{k_3} \mathrm{Cr^{III} + HO^-}$$

No difference in k_2 values was observed in perchlorate or sulphate media (0.1M). In conditions of excess oxidant, however, the decay of $\mathrm{Cr^{II}}$ fitted neither first- nor second-order rate laws, possibly as a result of side reactions of the type

$$\mathrm{HO^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O}$$

$$\mathrm{HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2}$$

$$\mathrm{Cr^{II} + HO_2^{\bullet} \longrightarrow Cr^{III} + HO_2^-}$$

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[293] N. A. Daugherty and J. H. Niewahner, *Inorg. Chem.*, 1972, **11**, 535.

The corresponding reaction with titanium(III) in excess exhibited second-order behaviour, the production of OH radicals as intermediates being confirmed by the addition of propan-2-ol, which reacts rapidly with $HO^{\bullet}$ and thereby decreased (by a factor of 2) the rate of decay of reductant. Confirmation that any secondary rate constants (k_3) are much greater than that for the rate-determining initial step have been derived from a study of the reductants with hydroxyl radicals. The k_3 values for the reactions of Cr^{II} and Ti^{III} are 1.2×10^{10} and 3×10^{9} l mol^{-1} s^{-1} respectively. An independent investigation of the Ti^{III}–H_2O_2 reaction[294] in the presence of metal ions has been carried out. The mechanisms of redox systems in the presence of Ce^{IV} and Fe^{II} ions are considered in terms of induced electron transfer. The reaction with iron(III), however, has been shown[295] to be inhibited by tetranitromethane. The oxidation of ferrocene (Fc) by H_2O_2 in ~40% methanol containing 0.2M-sulphuric acid is slow and autocatalytic.[296] Two reactions are observed; the preliminary formation of a blue, semi-oxidized, dimeric cation (Fc_2^+) is followed by a second-order reaction

$$Fc_2^+ + H_2O_2 \longrightarrow Fc^+ + \text{reduced species}$$

in which the ferrocinium ion is formed.

The oxidation of $[Ru(NH_3)_6]^{2+}$ by H_2O_2 is very slow and is probably catalysed by iron impurities in the complex.[279] The reaction shows a zero-order dependence on ruthenium(II) and extrapolation of data from experiments with added iron(III) indicates that much of the observed rate for the process is the result of the iron(III) pathway, with little or no contribution from the intrinsic reaction. The corresponding reaction with O_2 is at least 10^4 times faster. The mechanism of the catalytic decomposition of H_2O_2 by chromium(VI) in neutral media has been reported.[297] In dilute hydrogen peroxide solutions ($\lesssim 1.5$M), the formation of an intermediate complex $[Cr_2O_9]^{2-}$ has been proposed:

$$[Cr_2O_7]^{2-} + H_2O_2 \rightleftharpoons [Cr_2O_9]^{2-} + 2H_2O$$
$$[Cr_2O_9]^{2-} \longrightarrow [Cr_2O_7]^{2-} + O_2$$

The activation parameters and reaction order vary with increasing concentration of the peroxide, the differences being described in terms of a second peroxo-complex $[HCrO_6]^-$, which increases in concentrations of H_2O_2 up to ~10M.

The oxidation of indigo carmine by H_2O_2 is catalysed by the metal ions[298]

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[294] L. J. Csanyi, F. Cseh, and F. Szil, *Acta Chim. Acad. Sci. Hung.*, 1972, **75**, 1 (*Chem. Abs.*, 1973, **78**, 48 497e).

[295] B. V. Erofeev and V. A. Plakhotnik, *Doklady Akad. Nauk S.S.S.R.*, 1972, **206**, 110 (*Chem. Abs.*, 1973, **78**, 34 386f).

[296] C. Le Feuvre and R. Gaboriand, *Compt. rend.*, 1973, **276**, *C*, 9 (*Chem. Abs.*, 1973, **78**, 102 474k).

[297] N. I. Korneeva, V. I. Shekhobalova, and N. I. Kobozev, *Zhur. fiz. Khim.*, 1972, **46**, 362; N. I. Kobozev, V. I. Shekhobalova, and N. I. Korneeva, *ibid.*, p. 1461.

[298] A. Krause and E. Nowakowski, *Sci. Pharm.*, 1972, **40**, 178 (*Chem. Abs.*, 1973, **78**, 8285c).

Cu^{II}, Fe^{III}, Cr^{III}, Cr^{VI}, and $[Fe(CN)_6]^{4-}$, whereas La^{3+}, Bi^{3+}, Mn^{2+}, and WO_4^{2-} inhibit the reaction. In contrast, however, WO_4^{2-} promotes the decomposition of H_2O_2 alone. The oxidation of pyrocatechol violet in the presence of amino-acid complexes of copper(II) has been suggested as a means of determining ultramicroquantities of amino-acids;[299] *e.g.* in the presence of glycine the 1 : 1 complex acts as a catalyst, the pH-dependent reaction in borate buffer obeying the rate law (PV = pyrocatechol violet)

$$\text{Rate} = k_0[\text{Cu(gly)}][H_2O_2][\text{PV}][\text{borate}]^{-1}$$

Hydrazine has been considered to react with hydrogen peroxide to yield water and N_2. The results, however, were not reproducible,[300] the reaction rates being apparently first-order with respect to peroxide and zero-order in hydrazine. The presence of edta completely suppresses the reaction, the results being compatible with complex formation between trace metal ions in the water and the hydrazine, the resultant species then catalysing the decomposition reaction.

The catalysis of the reaction of chlorine with hydrogen peroxide by Mn^{II}–Mn^{III} ion pairs has been described,[301] where it is postulated that a free-radical chain mechanism is initiated,

$$Mn^{III} + H_2O_2 \rightleftharpoons [MnO_2H]^{2+} + H^+$$
$$[MnO_2H]^{2+} + Cl_2 \longrightarrow Mn^{II} + H^+ + Cl^- + O_2 + Cl^{\bullet}$$
$$Mn^{II} + Cl^{\bullet} \longrightarrow Mn^{III} + Cl^-$$

in which the manganese(III) is regenerated. In conditions where increase in the Mn^{II} concentration no longer affects the reaction rate, the reaction is first-order with respect to Cl_2 and H_2O_2:

$$\text{Rate} = \{k_0 + k_1[Mn^{III}]\}[Cl_2][H_2O_2]$$

From hydrogen-ion-dependence studies, the possibility of the formation of $[MnOOH]^+$ as an intermediate which could undergo electron exchange with Mn^{III} has also been considered. This catalytic reaction has also been recently re-appraised,[302] and a mechanism has also been proposed for the uncatalysed step, the results being consistent with the formation of the intermediate HOOCl, which is assumed to be in steady-state concentrations:

$$H_2O_2 + Cl_2 \rightleftharpoons HOOCl + H^+ + Cl^-$$
$$HOOCl \longrightarrow H^+ + O_2 + Cl^-$$

The mechanism proposed for the manganese(II)–(III) promotion of the rate has been questioned (see above), especially on the basis of lack of hydrogen-ion-

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[299] T. J. Janjic and C. A. Milovanovic, *Analyt. Chem.*, 1973, **45**, 390.

[300] L. P. Kuhn and C. Wellman, U.S. Nat. Tech. Inform. Serv., A.D. Rep. 1972, No. 746 956 (*Chem. Abs.*, 1973, **78**, 34 419u).

[301] J. I. Morrow and L. Silver, *Inorg. Chem.*, 1972, **11**, 231.

[302] G. Davies and K. Kustin, *Inorg. Chem.*, 1973, **12**, 961.

dependence data, and a sequence of possible steps has been suggested. The possible formation of Mn^{III}–chloro-complexes has been considered, and support for the existence of a manganese(II)–peroxo-species in aqueous acid media is thought to be necessary. The mechanism of decomposition of hydrogen peroxide by iodine in acid media has been investigated,[303] use being made of the formation of solid Tl^{I} iodide to control the iodide concentration. The rates of oxygen evolution and proton formation are consistent with the mechanism

$$HIO_2 + H_2O_2 \longrightarrow HIO + H_2O + O_2$$
$$H_2OI^+ + H_2O_2 \longrightarrow HIO_2 + H^+ + H_2O$$
$$H_2OI^+ \rightleftharpoons HIO + H^+$$
$$HIO + H_2O_2 \longrightarrow H^+ + I^- + H_2O + O_2$$
$$I^- + H^+ + H_2O_2 \longrightarrow HIO + H_2O$$
$$HIO_2 + H^+ + I^- \longrightarrow 2HIO$$

in which a steady-state concentration of HIO_2 is assumed to be present. The present data are considered related to a system in which the oscillating decomposition of peroxide occurs and in which iodate may play an important role. Little reaction between phosphine and H_2O_2 is observed in the absence of Br^-. When the bromide anion is present, however, potentiometric data are consistent[304] with a quantitative reduction of the peroxide, the mechanism involving the intermediate formation of bromine,

$$2Br^- + H_2O_2 \xrightarrow{+2H^+} Br_2 + 2H_2O$$
$$PH_3 + 4Br_2 + H_2O \longrightarrow H_2PO_4^- + 8Br^- + IH^+$$

with tentative evidence presented for a $[PH_3 \cdot Br]$ intermediate.

Use has been made of *in situ* radiolysis in the characterization of metal complexed hydroxo-species which are intermediates generated in the reaction of metal ions with hydrogen peroxide.[305] Formation of such species is considered to involve two processes, either direct interaction of the metal ion with HO_2^- or by a one-electron oxidation of the peroxo-complexes by $HO^{\bullet}$ or H_2O_2. Several studies have been made of oxidations involving Fenton's reagent. Carbonyl compounds such as acetone are readily attacked by hydroxyl radicals produced in the reaction of iron(II) with H_2O_2.[306] The resulting carbonyl conjugated radicals are however reduced by addition of iron(II). The competitive kinetics were investigated by dropwise addition of H_2O_2 to the iron(II)–substrate solutions and show the course of the reaction and the stoicheiometry $\Delta[Fe^{II}]/\Delta[H_2O_2]$ to be dependent on the fate of the organic radicals formed. In the case of a solution containing methanol and acetone,

[303] I. Matsuzaki, R. Simic, and H. A. Liebhafsky, *Bull. Chem. Soc. Japan*, 1972, **45**, 3367.
[304] D. V. Sokol'skii, Y. A. Dorfman, and T. L. Rakitskaya, *Zhur. fiz. Khim.*, 1971, **45**, 2771.
[305] A. Samuni, *J. Phys. Chem.*, 1972, **76**, 2207.
[306] C. Walling and G. M. El-Taliawi, *J. Amer. Chem. Soc.*, 1973, **95**, 844.

the following reaction scheme is proposed:

$$\mathrm{Fe^{2+} + H_2O_2 \xrightarrow{k_1} Fe^{3+} + HO^- + HO^{\bullet}}$$

$$\mathrm{HO^{\bullet} + Fe^{2+} \xrightarrow{k_2} Fe^{3+} + HO^-}$$

$$\mathrm{HO^{\bullet} + MeOH \xrightarrow{k_{31}} H_2O + MeO^{\bullet}}$$

$$\mathrm{HO^{\bullet} + Me_2CO \xrightarrow{k_{32}} H_2O + {}^{\bullet}CH_2COMe}$$

$$\mathrm{MeO^{\bullet} + Fe^{3+} \xrightarrow{k_4} Fe^{2+} + product}$$

$$\mathrm{{}^{\bullet}CH_2COMe + Fe^{2+} \xrightarrow{k_5} Fe^{3+} + {}^{-}CH_2COMe \xrightarrow{+H^+} MeCOMe}$$

Application of steady-state treatments of the kinetics yields the stoicheiometric equation

$$\frac{\Delta[\mathrm{Fe^{II}}]}{2\Delta[\mathrm{H_2O_2}] - \Delta[\mathrm{Fe^{2+}}]} = \frac{k_2[\mathrm{Fe^{2+}}]}{k_{31}[\mathrm{MeOH}]} + \frac{k_{32}[\mathrm{Me_2CO}]}{k_{31}[\mathrm{MeOH}]}$$

from which ratios of the relative rate constants may be derived. The acetone thus acts as a hydroxyl trap and retards the oxidation of the methanol. Significant oxidation pathways in reactions of this type have also been assessed using redox titration techniques[307] where the procedure assists in defining the overall reaction and represents a means whereby both an estimate of relative rates of oxidation and the extent of reaction of the peroxide with the organic substrate may be measured. The extent of reactivity of the substrates towards dissolved oxygen has also been considered, the peroxide utilized in the reaction decreasing as the concentration of oxygen in solution increases. In the oxidation of carbohydrates and other polyhydroxy-compounds, a cyclic process is described in which ene-diols are formed which reduce iron(III).

The catalysis by chelated diketonates of vanadium(IV) and by $[\mathrm{MoO_2(acac)_2}]$ of the reactions of t-butyl hydroperoxide with cyclohexene or cyclo-octene have been investigated,[308] the products being only t-butyl alcohol and the corresponding epoxycycloalkanes. The reactions are highly selective and in the case of the vanadium-catalysed systems the rate law is of the form

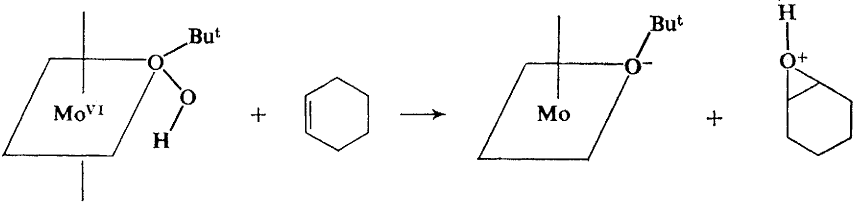
$$\text{Rate} = \frac{k[\text{olefin}][\mathrm{V_0}]}{(1/[\mathrm{P}]K_p) + 1}$$

where $[\mathrm{V_0}]$ is the total concentration of added vanadium, [P] is that of the hydroperoxide, and K_p is the association constant for the formation of the vanadium hydroperoxide complex which is considered to be a reactive intermediate. Competitive inhibition by $\mathrm{Bu^tOH}$ is observed, reflecting the formation of complexes between the alcohol and the catalytic complex. In the

[307] D. L. Ingles, *Austral. J. Chem.*, 1972, **25**, 87, 97, 105.

[308] C.-C. Su, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, 1973, **12**, 337.

reactions with $[MoO_2(acac)_2]$, however, where the rates are $\sim 10^2$ faster than for the vanadium species, a more complex rate equation is derived resulting from the formation of molybdenum–hydroperoxide, molybdenum–olefin, and molybdenum–hydroperoxide–olefin complexes. A possible scheme may involve a reaction of the type shown in Scheme 2, although the possibility of the interaction of a ternary complex in the rate-determining process may also have to be taken into account.



Scheme 2

A reaction scheme has been proposed[309] for the catalysis of the disproportionation of H_2O_2 by the cobalt(III)–haematoporphyrin complex of haematoporphyrin(IX), $[Co^{III}HP]$, which represents a model for catalase-like activity. Unlike other cobalt(III) complexes, the axial co-ordinating positions are labile in this complex. In the pH range 5.5—6.5, initial rate data exhibit an inverse dependence on hydrogen-ion concentration, the rate data being consistent with the reactions

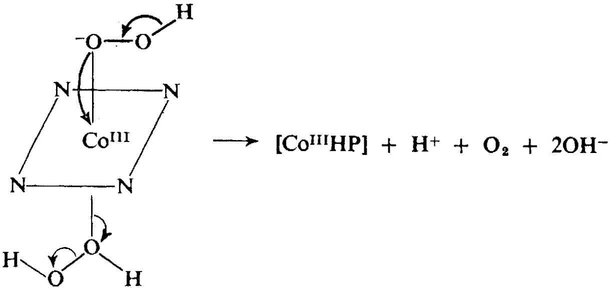
$$H_2O_2 \rightleftharpoons HOO^- + H^+$$

$$[Co^{III}HP] + HOO^- \rightleftharpoons [(HP)Co^{III}(OOH^-)]$$

$$[(HP)Co^{III}(OOH^-)] + H_2O_2 \rightleftharpoons [(HP)Co^{III}(H_2O_2)(OOH^-)]$$

$$[(HP)Co^{III}(H_2O_2)(OOH^-)] \longrightarrow [Co^{III}HP] + H_2O + OH^- + O_2$$

A *trans* configuration of the ligands is suggested for the reactive complex



Scheme 3

[309] P. Waldmeier and H. Sigel, *Inorg. Chem.*, 1973, **11**, 2174.

[310] P. Waldmeier and H. Sigel, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1741.

containing the (OOH^-) and the H_2O_2 groups and the involvement of the metal centre in the electron-transfer process is considered essential (Scheme 3; N_4 = HP). Activity of this type is inhibited by amino-acids, adenine, and related ligands, where formation of a complex adduct similar to that illustrated is restricted as a result of competition by the nitrogen-donor bases for the axial (fifth and sixth) positions of the primary co-ordination sphere of the cobalt centre. Some peroxidase-like activity of the complex in the presence of these bases is observed with oxidation of the ligands. Catalytic activity *via* intermediate complex formation has also been described[311] in the reactions of $[CoN_4Cl_2]^+$ ions [N_4 = py_4, $(phen)_2$, or $(bipy)_2$]. The stability constants for the species $[Co(HO_2)N_4]^{2+}$ fall in the sequence py > bipy > phen, which also is the order of activity towards the peroxide. The mechanism of reaction of manganese(II)–histidine[312] and –1,10-phenanthroline[313] complexes has also been investigated. In these reactions, however, no peroxo-complex formation is observed, and it is suggested that the catalase and peroxidase activity for the histidine complexes derives from the outer-sphere electron transfer between $[Mn(his)_2]$ and the HO_2^- ion or a neutral hydrogen peroxide molecule. A radical chain mechanism is considered operative and the presence of borate buffer accelerates the rate owing to ternary complex formation between the borate anion and the $[Mn(his)_2]$ complex.

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[311] G. A. Shagisultanova and N. P. Glukhova, *Zhur. fiz. Khim.*, 1972, **46**, 508.

[312] A. Y. Sychev and V. G. Isak, *Zhur. fiz. Khim.*, 1972, **46**, 1864, 2164.

[313] Y. D. Tiginyanu, A. Y. Sychev, and V. M. Berdnokov, *Zhur. fiz. Khim.*, 1971, **45**, 1723, 2533.

Part II

SUBSTITUTION AND RELATED REACTIONS

By

J. BURGESS
D. N. HAGUE

1

Non-metallic Elements

BY J. BURGESS

As in Volumes 1 and 2 of this Report, substitution, addition, dissociation, and intramolecular rearrangement reactions of the non-metallic elements will be discussed in this chapter. A few reactions of compounds of the metallic elements of Groups III and IV will also be discussed, in cases where a mention in this chapter seems more appropriate than in Chapter 3.

1 Group III

Boron.—*Tetrahedral Anions.* The stepwise hydrolysis of the $[BH_4]^-$ anion has been investigated in some detail in 88% methanol solution, 0.1—1.1M acid. The first step, which results in the production of $[BH_3(OH_2)]$, is rapid, even at -78 °C. The rate law for the subsequent hydrolysis of this species to $[BH_2(OH_2)_2]^+$ is

$$-d[BH_3(OH_2)]/dt = \{k_1 + k_2[H^+]\}[BH_3(OH_2)]$$

with $k_1 = 0.0015\ s^{-1}$ and $k_2 = 0.0016\ l\ mol^{-1}\ s^{-1}$ at -78 °C. The two remaining steps were studied at -36 °C; both exhibited simple first-order kinetics. Alkaline hydrolyses of the related anions $[BH_3(OH)]^-$, $[BH_2(OH)_2]^-$, and $[BH(OH)_3]^-$ also follow first-order kinetics in strongly alkaline solution, with rate constants of $1.8 \times 10^{-4}\ s^{-1}$ at 20 °C, $2.2 \times 10^{-5}\ s^{-1}$ at 0 °C, and $1.1 \times 10^{-3}\ s^{-1}$, again at 0 °C, respectively.[1] The lifetimes of $[BF_2(OH)_2]^-$ and $[BF(OH)_3]^-$ are much less than those of $[BF_4]^-$ or $[BF_3(OH)]^-$. That of one fluorine in $[BF_2(OH)_2]^-$ appears, from ^{19}F n.m.r. spectroscopy, to be about 0.6×10^{-3} s at 27 °C.[2] A qualitative impression of the effect of nickel(II) on the kinetics of hydrolysis of $[BF_4]^-$ has been afforded by a study of $Ni(BF_4)_2$ solutions.[3] The mechanism of halogen-exchange reactions[4] of $[BX_4]^-$ anions has been studied by n.m.r. spectroscopy. The most likely first step is dissociation:

$$BX_4^- \rightleftharpoons BX_3 + X^- \qquad (1)$$

The BX_3 may then react with the replacing halide Y^- to give $[BX_3Y]^-$, and

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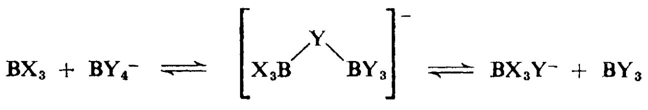
[1] F. T. Wang and W. L. Jolly, *Inorg. Chem.*, 1972, **11**, 1933.

[2] R. E. Mesmer and A. C. Rutenberg, *Inorg. Chem.*, 1973, **12**, 699.

[3] V. N. Plakhotnik and V. V. Varekh, *Russ. J. Phys. Chem.*, 1972, **46**, 1783.

[4] J. C. Lockhart, 'Redistribution Reactions', Academic Press, New York, 1970.

thence by three similar steps for complete exchange to give $[BY_4]^-$. Alternatively the BX_3 generated according to equation (1) may react with $[BY_4]^-$, giving a transition state or transient intermediate containing two boron atoms:



(1)

The intermediate species (1) is reminiscent of the known $[B_2F_7]^-$ anion.[5]

Hydrolyses of pyrrolyl-1-borate anions $[BPh_n(C_4H_4N)_{4-n}]^-$ are second-order reactions, and are catalysed by acids. The activation enthalpy for hydrolysis of the $[B(C_4H_4N)_4]^-$ anion, which is 14.8 ± 0.9 kcal mol^{-1}, is intermediate between those for the hydrolyses of the $[BH_4]^-$ and $[BPh_4]^-$ anions.[6]

Boron–Hydrogen Compounds. Reactions of tetraborane with Lewis acids can result in symmetrical or unsymmetrical cleavage of the former molecule. The alternative courses of reaction are slightly different for 2,4-dimethylenetetraborane. This undergoes symmetrical cleavage with trimethylphosphine, but the boron hydride framework is extensively broken down by reaction with ammonia or with trimethylamine.[7] Experiments on the hydrolysis of diborane at −78 °C, in acid aqueous methanol, have yielded further evidence for asymmetric cleavage of this compound.[8] The application of topological methods to establishing mechanisms of nucleophilic and electrophilic substitution in boron hydrides has been discussed in detail.[9]

Several reports deal with intramolecular processes of neutral and anionic boron–hydrogen species. There are two modes of intramolecular hydrogen exchange within B_4H_{10}. The faster process exchanges hydrogen atoms between the bridge and four of the terminal positions. This process has a rate constant of 1.7×10^{-3} s^{-1} at 22.5 °C and an activation energy of *ca.* 18.5 kcal mol^{-1}. The slower process exchanges hydrogen atoms between the bridge and the remaining two terminal positions. The rate constant is 5×10^{-5} s^{-1} at 22.5 °C and the activation energy *ca.* 21.5 kcal moi^{-1}. Several mechanisms are discussed, but the evidence available at present is insufficient for an unequivocal choice to be made.[10] Both $[B_{11}H_{11}]^{2-}$ and $[B_{11}H_7Br_4]^{2-}$ isomerize readily in solution; the half-lives are within the n.m.r. time-scale range at low temperatures. These observations contrast with the general impression that isomerizations of $[B_nH_n]^{2-}$ are generally difficult, slow processes.[11] Rearrangements in eleven-particle polyhedra have been probed by ^{11}B n.m.r. spectroscopy, and

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[5] J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 1972, **11**, 940.

[6] J. Emri, B. Györi, and P. Szarvas, *Z. anorg. Chem.*, 1973, **400**, 321.

[7] R. E. Bowen and C. R. Phillips, *J. Inorg. Nuclear Chem.*, 1972, **34**, 382.

[8] P. Finn and W. L. Jolly, *Inorg. Chem.*, 1972, **11**, 1941.

[9] I. R. Epstein, *Inorg. Chem.*, 1973, **12**, 709.

[10] R. Schaeffer and L. G. Sneddon, *Inorg. Chem.*, 1972, **11**, 3098.

[11] E. I. Tolpin and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1973, **95**, 2384.

possible mechanisms discussed.[12] ^1H and ^{11}B n.m.r. spectroscopy have been used to demonstrate tautomerism of bridging protons in $[2\text{-}MeB_5H_7]^-$ and isomerization of $[1\text{-}MeB_5H_7]^-$ to $[2\text{-}MeB_5H_7]^-$.[13]

Boron–Nitrogen Compounds. The formation of adducts Me_3N,BXY_2 has been studied, by n.m.r. and isotopic labelling techniques, in relation to mechanisms of halogen exchange in boron trihalide adducts. Me_3N,BF_3 reacts with BCl_3 in methylene chloride solution without boron–nitrogen bond breaking. The mechanism of halogen exchange can therefore either involve halide dissociation from the boron or halogen-bridge formation {as mentioned above (*cf.* ref. 5) for halide exchange with $[BX_4]^-$ anions}. The pattern of reactivities and products for the above and analogous reactions favours the halogen-bridging mechanism, except possibly when iodide is leaving from the boron. These mechanisms for these reactions in solution contrast with the boron–nitrogen bond-fission mechanism established for the same halogen-exchange reactions in the gas phase.[14] Various reorientation processes within the adduct Me_3B,NMe_3 can be detected by ^1H n.m.r. spectroscopic techniques. For reorientation of the boron methyl groups about their C_3 axes, the variation of spectra between -194 and -143 °C indicates an activation energy of 1.9 ± 0.1 kcal mol^{-1}.[15] Donor–acceptor bond-breaking reactions are rapid for the closely related boron–sulphur adducts Me_2S,BX_3, in methylene chloride solution.[16]

Rate constants are reported for the hydrolysis of 16 borazines $R^1R^2R^3B_3N_3R^4{}_3$, where R^1, R^2, R^3 = *e.g.* H, Me, Ph, Cl, or Br, and R^4 = *e.g.* Me, Ph, or *o*-tolyl, in 90% tetrahydrofuran–10% water. The kinetics are first-order; there is some slight evidence for steric factors affecting reactivities.[17] The adduct *o*-toluidine–phenyldichloroborane reacts according to Scheme 1; the orthoboronation sequence was elucidated by deuterium labelling and intermediate characterization. Orthoboronation occurs most easily for boron tri-iodide adducts; there is some indirect evidence for the possible intermediacy of diamineboronium cations.[18] The much greater reactivity of R_2BCl, compared with R_3B, towards organic azides has been ascribed to the greater Lewis acidity of the former. This greater Lewis acidity favours the formation of the intermediate azide–boron adduct.[19]

Aluminium.—Plots of pH against time have been determined for basic solutions of aluminium perchlorate. It seems possible to follow five stages of polymerization in such solutions.[20] A spectrophotometric study of the reaction of hexa-

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[12] R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.*, 1973, **12**, 785.

[13] V. T. Brice and S. G. Shore, *Inorg. Chem.*, 1973, **12**, 309.

[14] B. Benton-Jones and J. M. Miller, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 485.

[15] T. T. Ang and B. A. Dunell, *J.C.S. Faraday II*, 1972, **68**, 1331.

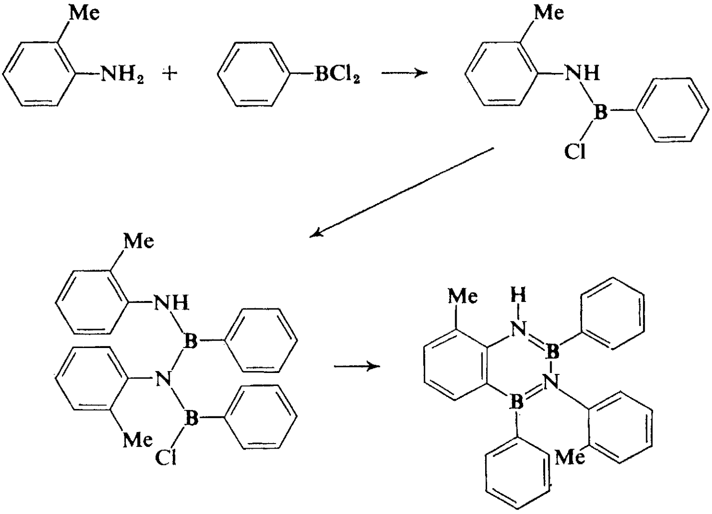
[16] M. J. Bula and J. S. Hartman, *J.C.S. Dalton*, 1973, 1047.

[17] I. B. Atkinson, D. C. Blundell, and D. B. Clapp, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3037.

[18] J. R. Blackborow and J. C. Lockhart, *J.C.S. Dalton*, 1973, 1303.

[19] H. C. Brown, N. M. Midland, and A. B. Levy, *J. Amer. Chem. Soc.*, 1972, **94**, 2114.

[20] Yu. A. Volokhov, N. I. Eremin, and V. E. Mironov, *Issled. Obl. Neorg. Tekhnol.*, 1972, 255; N. I. Smirnov, Yu. A. Volokhov, N. I. Eremin, and V. E. Mironov, *ibid.*, p. 251 (*Chem. Abs.*, 1972, **77**, 144 267e, 144 292j).



Scheme 1

aquoaluminium(III) with methylthymol blue (mtb) indicates that the apparent activation energy for the formation of $[Al(mtb)]^{3+}$ is 17.4 kcal mol^{-1}. The activation entropy is +2.2 cal deg^{-1} mol^{-1}.[21] Aquation of $[Al(mtb)]^{3+}$ and of $[Al(mtb)_2]^{3+}$ is acid-catalysed. Activation parameters for hydrolysis at pH = 0.55 are E_a = 18.3 kcal mol^{-1} and $\Delta S^{\ddagger} = -12.5$ cal deg^{-1} mol^{-1} for the mono-mtb complex, and E_a = 20.1 kcal mol^{-1} and $\Delta S^{\ddagger} = -7.3$ cal deg^{-1} mol^{-1} for the bis-mtb complex.[22]

Kinetic results for methyl exchange have been determined from n.m.r. studies of Al_2Me_6–$GaMe_3$, $AlMe_3$(base)–$GaMe_3$, and Al_2Me_6–$AlMe_3$(base) mixtures in cyclopentane or decalin solution. The kinetic pattern corresponds neither to simple first-order nor to simple second-order processes. The remarkably fast exchange in solutions containing Al_2Me_6 and $AlMe_3$(base), where the base is co-ordinated *via* a Group VI element, is ascribed to an associative mechanism in which the second lone pair of the Group VI element of the co-ordinated base interacts with the Al_2Me_6.[23] Methyl exchange between Al_2Me_6 and $GaMe_3$ or $ZnMe_2$ is stated to occur by an initial rate-determining dissociation of the Al_2Me_6 dimer. From rates of methyl exchange in these systems and an estimated rate of dimerization of $AlMe_3$ it has proved possible to suggest a mechanism for bridge $\rightleftharpoons$ terminal methyl-group exchange in Al_2Me_6.[24] Rates of methyl exchange between $GaMe_3$ and $CdMe_2$ in cyclo-

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[21] T. V. Mal'kova and V. D. Ovchinnikova, *Russ. J. Inorg. Chem.*, 1972, **17**, 813.

[22] T. V. Mal'kova, V. D. Ovchinnikova, and G. V. Ryzhalova, *Russ. J. Inorg. Chem.*, 1972, **17**, 194.

[23] T. L. Brown and L. L. Murrell, *J. Amer. Chem. Soc.*, 1972, **94**, 378.

[24] E. A. Jeffery and T. Mole, *Austral. J. Chem.*, 1973, **26**, 739.

pentane or toluene, between $InMe_3$ and $ZnMe_2$ in diethyl ether or triethylamine, and in diethyl ether solutions of $CdMe_2$ depend greatly both on the natures of the metal centres and on the co-ordinating ability of the solvent.[25]

Intramolecular rearrangement of tristropolonatoaluminium(III) complexes is discussed, along with similar processes for analogous cobalt(III) and rhodium(III) complexes, in Section 9 of Chapter 3.[26]

Gallium.—Kinetics of chloride exchange with $[GaCl_4]^-$ have been monitored, in concentrated hydrochloric acid, by ^{35}Cl nuclear relaxation. The activation parameters are $\Delta H^{\neq} = 30.1\ kJ\ mol^{-1}$ and $\Delta S^{\neq} = -24\ J\ K^{-1}\ mol^{-1}$.[27] The rate-determining step in the formation of gallium(III)–methylthymol blue complexes is loss of water from the hexa-aquocation $[Ga(OH_2)_6]^{3+}$. This conclusion was based on the observed lack of dependence of the reaction rate on the concentration of methylthymol blue.[28] Some methyl-exchange reactions involving trimethylgallium have already been mentioned in the section on aluminium (p. 120).

2 Group IV

Carbon.—Two further papers on the kinetics of hydration of carbon dioxide have been published.[29] A kinetic study of the reaction of carbon disulphide with the disulphide anion indicates that the initial step is the bimolecular reaction

$$CS_2 + S_2^{2-} \longrightarrow CS_4^{2-}$$

From the published rate constants at 0, 10, and 20 °C one can calculate an activation energy of 20.5 ± 0.4 kcal mol^{-1} for this reaction.[30] Rate constants for decomposition of the trithiocarbonate anion, CS_3^{2-}, and its protonated derivatives, in aqueous solution have been estimated.[31]

The kinetics of the acid hydrolysis of cyanide ion were studied several decades ago. The kinetics of base hydrolysis of cyanide ion have only recently been investigated, though the reaction products were established as formate ion and ammonia many years ago. Rates of alkaline hydrolysis are first-order in cyanide ion, zero-order in hydroxide. The rate-determining step cannot therefore be attack of hydroxide at cyanide ion. However, both water attack at cyanide or hydroxide attack at hydrocyanic acid are consistent with the reported rate law. The overall kinetic pattern for the reaction, including the

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[25] J. Soulati, K. L. Henold, and J. P. Oliver, *J. Amer. Chem. Soc.*, 1971, **93**, 5694.

[26] S. S. Eaton, J. R. Hutchinson, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 6411.

[27] S. F. Lincoln, A. Sandercock, and D. R. Stranks, *J.C.S. Chem. Comm.*, 1972, 1069.

[28] T. V. Mal'kova and V. D. Ovchinnikova, *Trudy Ivanovsk. khim.-tekhnol. Inst.*, 1970, 59 (*Chem. Abs.*, 1972, **77**, 52 788x).

[29] L. C. Garg and T. H. Maren, *Biochim. Biophys. Acta*, 1972, **261**, 70; R. G. Khalifah, *J. Biol. Chem.*, 1971, **246**, 2561.

[30] H. Dautzenberg, J. Schumann, and B. Philipp, *Faserforsch. Textiltech.*, 1971, **22**, 546 (*Chem. Abs.*, 1972, **76**, 104 313q).

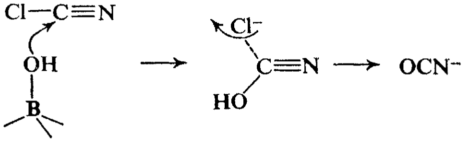
[31] V. A. Kremer and L. A. Zatuchnaya, *Kontrol Tekhnol. Protsessov Obogashch. Polez. Iskop.*, 1971, 132 (*Chem. Abs.*, 1973, **78**, 48 522j).

effects of added salts and of solvent variation (ethanol–water mixtures), suggests that the latter alternative [equations (2) and (3)] is the more likely.[32]

$$\mathrm{CN^- + H_2O \underset{fast}{\rightleftharpoons} HCN + OH^-} \qquad (2)$$

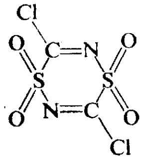
$$\mathrm{HCN + OH^- \xrightarrow{slow} products} \qquad (3)$$

General base catalysis of the hydrolysis of cyanogen chloride is reported,[33] as, for example, by borax (Scheme 2). At pH = 10.1, the activation energy is



Scheme 2

59.1 kJ $\mathrm{mol^{-1}}$, which result may be compared with a value of 51.9 kJ $\mathrm{mol^{-1}}$ reported earlier[34] for hydrolysis at pH = 11. The effects of ammonia, hydrogen peroxide, cyanide ion, and carbonate ion on hydrolysis rates were determined. The catalytic effect of chlorine is ascribed to base catalysis by the species $\mathrm{Cl_2OH^-}$, an entity previously proposed as an intermediate in the hydrolysis of chlorine.[33] The kinetics and mechanism of the formation and dissociation of the adduct between cyanogen chloride and sulphide ion (2)



(2)

have been described. Formation takes place by attack of sulphite ion at the carbon atom of the cyanogen chloride, and has an activation energy of 54 kJ $\mathrm{mol^{-1}}$. Decomposition in basic solution is a second-order process overall – first-order in hydroxide ion – and has an activation energy of 58.3 kJ $\mathrm{mol^{-1}}$.[35] This value is noticeably similar to that for hydrolysis of cyanogen chloride itself.

Silicon.—What is claimed to be the first unequivocal evidence for the operation of an $S_{\mathrm{H}}2$ mechanism* at silicon in solution has been presented for the

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* There has been some controversy (see ref. 36) over the precise definition and usage of the term $S_{\mathrm{H}}2$.

[32] G. H. Wiegand and M. Tremelling, *J. Org. Chem.*, 1972, **37**, 914.

[33] P. L. Bailey and E. Bishop, *J.C.S. Dalton*, 1973, 912.

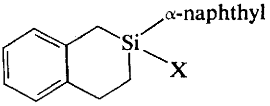
[34] G. E. Eden and A. B. Wheatland, *J. Soc. Chem. Ind.*, 1950, **69**, 166.

[35] P. L. Bailey and E. Bishop, *J.C.S. Dalton*, 1973, 917.

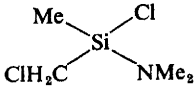
[36] W. A. Pryor, *Nature*, 1971, **231**, 181; R. A. Jackson, *ibid.*, p. 181.

photochemically initiated reaction between organodisilanes and 1,2-dibromoethane.[37] Kinetic evidence for the slow formation of a five-co-ordinate intermediate for nucleophilic substitution has been detailed. The reactions concerned are competitive reactions of an excess of a Grignard reagent or an allyllithium compound with a pair of silicon substrates which differ only in their leaving groups, for example (3) with X = F or Me.[38] Topological aspects of possible intramolecular isomerization in five-co-ordinate intermediates in associative nucleophilic substitution at Group IVB atoms have been considered.[39]

Chloride exchange at silicon in the chlorosilane (4) has been studied by n.m.r. spectroscopy. This proved a doubly useful technique in this situation, for as the CH_2Cl protons are diastereotopic both stereochemical and kinetic information can be derived from the n.m.r. spectra. The reaction of (4) with chloride ion from tetraethylammonium chloride in methylene chloride solution is first-order in each component, has an activation energy of about 4 kcal mol^{-1}, and proceeds with inversion.[40] This last observation parallels that of inversion accompanying chloride exchange at chlorosilanes R_3SiCl in acetone–dioxan mixtures.[41] The application of kinetic methods to problems in analysis is illustrated by analysis for fluorosilicate anions. Here $[SiF_6]^{2-}$ can be distinguished from $[SiF_5(OH_2)]^-$ and other aquofluorosilicon(IV) species through the difference in mechanisms of hydrolysis. $[SiF_6]^{2-}$ differs from the mixed aquofluoro-complexes in that it alone cannot hydrolyse by an S_N1cb mechanism.[42]



(3)



(4)

The reactions of *trans*-(+)-[PtCl(SiMePh{1-naphthyl})$(PPhMe_2)_2$] and of its PPh_3 analogue with lithium aluminium hydride, triethylsilane, or thiophenol involve silicon–platinum bond cleavage. There is predominant retention of configuration at the silicon centre. A mechanism involving successive oxidative addition and reductive elimination steps, with platinum(IV) intermediates, is thought to operate for these reactions.[43]

A qualitative study of the reactions

$$(Me_3Si)_2NM + SiMe_3X \longrightarrow N(SiMe_3)_3 + MX$$

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[37] A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, 1972, **94**, 1384.

[38] R. J. P. Corriu and B. J. L. Henner, *J.C.S. Chem. Comm.*, 1973, 116.

[39] M. Gielen, C. Dehouck, and B. DePoorter, *Chem. Weekblad*, 1972, **68**, 15 (*Chem. Abs.*, 1973, **78**, 48 478z).

[40] S. DiStefano and H. Goldwhite, *J.C.S. Chem. Comm.*, 1972, 1195.

[41] M. W. Grant and R. H. Prince, *J. Chem. Soc.* (*A*), 1969, 1138.

[42] I. G. Ryss and V. N. Plakhotnik, *Russ. J. Phys. Chem.*, 1971, **45**, 818.

[43] C. Eaborn, D. J. Tune, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1972, 1223.

showed that reactivity trends were M = Na > Li, X = CN > I ≫ Cl. There was evidence for a transient intermediate in the reactions which involved Me_3SiCN.[44] In the liquid phase trisilazane, $N(SiH_3)_3$, or methyldisilazane, $MeN(SiH_3)_2$, undergo condensation reactions to give silane and silazane oligomers. Boron compounds, such as diborane or 1-BrB_5H_8, which are weakly acidic but not strong enough to form a stable adduct, catalyse these condensations. The isolation and characterization of $[(SiH_3)_2N]_2SiH_2$ and of $(SiH_3{\cdot}N{\cdot}Me)_2SiH_2$ permits some speculation on the mechanism.[45] When Me_2SiCl_2 and $Me(O)P(OMe)_2$ are mixed, they start condensing at once, by formation of MeCl and an —Si—O—P— bridge. The final oligomeric product contains an alternating —Si—O—P—O—Si—O—P—O— backbone. The complementary reaction between $Me_2Si(OMe)_2$ and $Me(O)PCl_2$ goes much more slowly. Its first stage is exchange between P—Cl and Si—OMe.[46]

Germanium.—The effect of the nature of univalent cations M^+ (M = Li, Na, K, Cs, or Me_4N) on the rate of alkaline hydrolysis of $[GeF_6]^{2-}$ has been examined.[47] The reaction of hexamethyldigermane with 1,2-dibromoethane, under photochemical conditions, is thought to have an S_H2 mechanism.[37]

Tin.—The application of a full n.m.r. lineshape-fitting exercise[48] to halogen exchange with Me_2SnX_2 in toluene solution gives some kinetic evidence relevant to the assignment of mechanism. Reaction through a five-co-ordinate intermediate is suggested.[49] A similar treatment of the kinetics of halogen exchange with Me_3SnX has been described.[50]

The solvolysis of *trans*-$[SnCl_4(py)_2]$ in triethyl phosphate has been monitored conductimetrically. Observed first-order rate constants are a function of complex concentration, so the mechanism must be more complicated than straightforward nucleophilic substitution. The composite activation parameters for this solvolysis are reported, to an incredibly high level of precision, as $\Delta H^{\ddagger} = 34.98\ \text{kcal mol}^{-1}$ and $\Delta S^{\ddagger} = 40.49\ \text{cal deg}^{-1}\,\text{mol}^{-1}$. The reaction of *trans*-$[SnCl_4(py)_2]$ with acetyl chloride in triethyl phosphate results in replacement of py by Cl^-. This reaction occurs much more rapidly than solvolysis; rates and activation parameters are reported for the two stages which can be distinguished kinetically.[51]

Lead.—An analysis of kinetic parameters and standard free energies of transfer of the reactants for the reaction of tetra-alkyl-lead compounds with iodine suggests that the charge separation in the transition state for this S_E2

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[44] M. Murray, G. Schirawski, and U. Wannagat, *J.C.S. Dalton*, 1972, 911.

[45] W. A. Scantlin and A. D. Norman, *Inorg. Chem.*, 1972, **11**, 3082.

[46] J. R. van Wazer and S. H. Cook, *Inorg. Chem.*, 1973, **12**, 909.

[47] N. F. Kulish, T. G. Shukstelinskaya, and T. N. Delyukina, *Vopr. Khim. khim. Tekhnol., Respub. Mezhvedom. Temat. Nauch.-Tekh. Sbornik*, 1972, 95 (*Chem. Abs.*, 1973, **78**, 102 458h).

[48] S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, 1973, **95**, 670.

[49] S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, 1973, **95**, 673.

[50] S. O. Chan and L. W. Reeves, *Inorg. Chem.*, 1973, **12**, 1704.

[51] R. C. Paul, V. P. Kapila, and J. C. Bhatia, *J. Inorg. Nuclear Chem.*, 1973, **35**, 833.

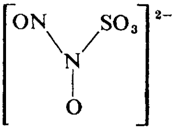
reaction is probably greater than in the Menschutkin reaction of *NN*-dimethylaniline with methyl iodide.[52] Earlier workers suggested that the effects of solvent variation on reactivity in these reactions could be ascribed to initial state–solvent interactions.[53] It now seems more likely that initial state–solvent and transition state–solvent interactions are both important in determining reactivity. However, the conclusions are not entirely unequivocal, as the interpretation depends on an assessment of the relative importance of charge separation and polarizability and may in certain cases be complicated by a change of mechanism from S_E2(open) to S_E2(cyclic).[52]

3 Group V

Nitrogen.—*Oxoanions.* Peroxonitrite ion reacts with the nucleophiles cyanide, iodide, or thiocyanate in alkaline solution. These reactions involve an associative mechanism for oxygen atom transfer to the nucleophile, to leave nitrite ion.[54] In aqueous solution the *N*-hydroxohydroxylamine-*N*-sulphonate anion (5) decomposes to nitrous oxide and sulphate. In the pH range 6—10 the rate law is

$$-\mathrm{d}[\mathrm{ON(SO_3)NO^{2-}}]/\mathrm{d}t = k[\mathrm{ON(SO_3)NO^{2-}}][\mathrm{H^+}]$$

Thus it is the conjugate acid of the anion which actually undergoes decomposition. *cis*-Hyponitrite ion is a suggested intermediate. The activation parameters



(5)

are $\Delta H^{\ddagger} = 11.4 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2 \pm 3$ cal deg^{-1} mol^{-1}. The decomposition of the *N*-hydroxohydroxylamine-*N*-sulphonate anion is specifically catalysed by boric acid. The mechanism for this catalysis may involve the co-ordination of the boric acid to a sulphonate oxygen atom. This would generate an intermediate similar to the species $B(HSO_4)_4^-$, known to exist in concentrated sulphuric acid. The activation enthalpy for this catalysed decomposition, 5 ± 1 kcal mol^{-1}, is much less than that for the uncatalysed reaction.[55] Effects of added salts on rates of labelled oxygen exchange between nitrate and water have been discussed in terms of ion association[56] and of the effect of the added cations on the structural properties of the water.[57]

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[52] M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

[53] G. Pilloni and G. Tagliavini, *J. Organometallic Chem.*, 1968, **11**, 557.

[54] M. N. Hughes, H. G. Nicklin, and W. A. C. Sackrule, *J.C.S. Dalton*, 1971, 3722.

[55] E. G. Switkes, G. A. Dasch, and M. N. Ackermann, *Inorg. Chem.*, 1973, **12**, 1120.

[56] M. O. Tereshkevich, S. A. Volkova, A. V. Kuprik, R. E. Duglach, and T. S. Kuratova, *Teorya Rastvorov*, 1971, 178 (*Chem. Abs.*, 1972, **77**, 156 902w).

[57] M. I. Valenchuk and M. O. Tereshkevich, *Russ. J. Phys. Chem.*, 1972, **46**, 1650.

Simple Compounds. The kinetics of chlorination of ammonia by Me_3CCOCl, producing successively NH_2Cl, $NHCl_2$, and NCl_3, have been investigated in cyclohexane solution containing 0.2M-t-butyl alcohol. Possible mechanisms are discussed.[58] Flash photolysis and pulse radiolysis of aqueous solutions of hydroxylamine involve

$$NH_2OH \longrightarrow NH_2 + OH$$

as the primary photoprocess, with NHOH also involved as an intermediate. The photolysis of the NH_3OH^+ cation was similarly investigated.[59] The stoicheiometry of photolysis of aqueous solutions of hydrazoic acid is

$$HN_3 + H_2O \longrightarrow N_2 + NH_2OH$$

The quantum yield is unity. The suggested mechanism, involving singlet NH as an intermediate, is supported by the results of ancillary experiments on photolyses conducted in the presence of chloride ion or of allyl alcohol.[60]

The rate law for the reaction of chlorine monoxide and nitrosyl chloride, in solution in Frigen 113,

$$Cl_2O + NOCl \longrightarrow Cl_2 + NO_2Cl$$

is

$$-d[NOCl]/dt = k_2[Cl_2O][NOCl]$$

The activation enthalpy is 7.5 kcal mol^{-1} and the frequency factor $10^{4\cdot 2}$. The rate law and kinetic parameters are best interpreted in terms of the following reaction sequence:[61]

$$Cl_2O + NOCl \underset{\text{fast}}{\rightleftharpoons} Cl_2O,NOCl$$

$$Cl_2O,NOCl \xrightarrow{\text{r.d.s.}} Cl_2 + NO_2Cl$$

Oxygen exchange between nitric oxide and water only takes place at an appreciable rate in the presence of nitrites.[62] Oxygen-18 tracer studies suggest that the rate law is probably

$$\text{Rate} = k[NO][HNO_2][H^+]$$

It is thence proposed that oxygen exchange takes place by attack of nitric oxide at $H_2NO_2^+$, possibly with the generation of $N_2O_2^+$ as an intermediate.[63] Such attack by nitric oxide would parallel that by acetate in the acetate-catalysed exchange of oxygen between water and nitrite.[64] The rate law for

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[58] P. Bekiaroglou, A. Drusas, and G.-M. Schwab, *Z. phys. Chem. (Frankfurt)*, 1972, **77**, 43.
[59] D. Behar, D. Shapira, and A. Treinin, *J. Phys. Chem.*, 1972, **76**, 180.
[60] D. Shapira and A. Treinin, *J. Phys. Chem.*, 1973, **77**, 1195.
[61] H. Martin, J. Robisch, H.-D. Knauth, and K.-G. Prusseit, *Z. phys. Chem. (Frankfurt)*, 1972, **77**, 227.
[62] F. T. Bonner, *Inorg. Chem.*, 1970, **9**, 190.
[63] F. T. Bonner and S. Jordan, *Inorg. Chem.*, 1973, **12**, 1363.
[64] C. A. Bunton and M. Masui, *J. Chem. Soc.*, 1960, 304.

nitrogen exchange between nitric oxide and nitrite,

$$\text{Rate} = k[\text{NO}][\text{HNO}_2]$$

suggests that HN_2O_3 is involved as an intermediate or at least as the transition state.[63] The kinetic pattern for oxygen exchange and for nitrogen exchange between nitric oxide and nitric acid is complicated by an induction period, which corresponds to the build-up of catalytically effective amounts of nitrite.[65] The kinetics of the forward and backward reactions of the equilibrium

$$\text{NEt}_3 + \text{SO}_2 \rightleftharpoons \text{Et}_3\text{N,SO}_2$$

were studied voltamperometrically in dimethyl sulphoxide solution. An unexpectedly slow forward reaction was discussed with reference to a postulated transition state $Et_3N\cdots SO_2\cdots OSMe_2$.[66] There is a reference to the hydrolysis of sulphur trioxide adducts of nitrogen bases in the sulphur section of this chapter (p. 137).

Miscellaneous. Several studies of the kinetics and mechanisms of reactions of nitrogen compounds have already been alluded to in previous sections (boron, silicon) of this chapter. They include the hydrolysis of borazines,[17] the formation of adducts Me_3N,BX^1X^2,[14] the condensations of trisilazane and of methyldisilazane,[45] and the reaction[44]

$$(\text{Me}_3\text{Si})_2\text{NM} + \text{SiMe}_3\text{X} \longrightarrow \text{MX} + \text{N(SiMe}_3)_3$$

Reactions of phosphonitrilic halides are dealt with in the next section on phosphorus; intramolecular rearrangements of all the Group V elements are discussed together at the end of this Group V section.

Phosphorus.—*Oxoanions.* Oxygen-18 tracer experiments suggest that the reaction of peroxomonophosphate, PO_5^{3-}, with hydroxide ion takes place by an associative mechanism. Both oxygen–oxygen bond fission and electron transfer take place in the $[PO_5^{3-}\cdots OH^-]$ transition state postulated.[67] This mechanism is similar to that established, in a more detailed kinetic and tracer investigation, for the reaction of peroxomonosulphate with hydroxide (p. 135). The kinetics of the hydrolyses of several condensed phosphates have been studied in aqueous solution, at $6 < \text{pH} < 9$. The phosphates involved were the $P_3O_{18}^{3-}$, $P_6O_{33}^{3-}$, $P_7O_{38}^{3-}$, $P_8O_{43}^{3-}$, $P_9O_{48}^{3-}$, and $P_{10}O_{53}^{3-}$ anions.[68] Converse reactions in which larger condensed phosphates are built up from smaller units such as diphosphate, diphosphite, and triphosphate have S_N2 mechanisms.[69] The formation of oligomers containing the alternating backbone

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[65] S. Jordan and F. T. Bonner, *Inorg. Chem.*, 1973, **12**, 1369.

[66] R. Bonnaterre and G. Cauquis, *Bull. Soc. chim. France*, 1972, 3297.

[67] V. A. Lunenok-Burmakina and G. P. Aleeva, *Russ. J. Phys. Chem.*, 1972, **46**, 1591.

[68] L. M. Ukrainskaya and L. I. Kuznetsov-Fetisov, *Trudy Kazansk. khim.-tekhnol. Inst.*, 1971, 14 (*Chem. Abs.*, 1972, **77**, 156 930d).

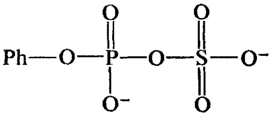
[69] N. Yoza, M. Tokuda, T. Inoue, and S. Ohashi, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 385.

—O—Si—O—P—O—Si—O— has been mentioned in the section on silicon (p. 124).[46]

Previous experiments have established that the likely mechanism for hydrolysis of the monofluorophosphate anion, PO_3F^{2-}, is[70]

$$H_2PO_3F + H^+ \rightleftharpoons H_3PO_3F^+$$
$$H_3PO_3F^+ + H_2O \longrightarrow H_3PO_4 + HF + H^+$$

A deuterium kinetic isotope effect of 2.1 is consistent with this mechanism. Activation energies for solvolysis by H_2O and by D_2O are the same, 16.9 ± 0.8 and 16.7 ± 0.3 kcal mol^{-1}, respectively.[71] In aqueous solution, magnesium(II) ions have only a small catalytic effect on the hydrolysis of phenyl phosphosulphate (6). In acetonitrile–water mixtures the catalytic effect of magnesium(II) is much greater, varying markedly with solvent composition. The catalytic effect of the magnesium(II) is ascribed to the greater hydrolysis rate for the 1 : 1 complex, with the magnesium(II) co-ordinated to a phosphate oxygen atom.[72]



$$Ph{-}O{-}P(=O)(O^-){-}O{-}S(=O)_2{-}O^-$$

(6)

Phosphazenes. In Volume 2 of this Report the mechanism of the reaction of $[PNCl_2]_3$ with dimethylamine in tetrahydrofuran solution was described.[73] Further work on the reaction of chlorocyclotriphosphazanes, this time with methylamine, again shows the important role of the tetrahydrofuran solvent in making the reaction go. Activation parameters have been determined. Comparison of the kinetic parameters for the reactions with methylamine and with dimethylamine shows that both basicity and steric requirements are important in determining reactivity in these reactions.[74] A comparison of the kinetics of reaction of $P_3N_3Cl_5(NHMe)$ plus $NHMe_2$ with those for the converse reaction $P_3N_3Cl_5(NMe_2)$ plus NH_2Me shows that rates are much more dependent on the nature of the incoming group than on the nature of substituents already present in the phosphazene.[75] The intermediacy of donor–acceptor complexes in the reaction of $[PNCl_2]_3$ with pyridine has been suggested.[76] The reaction of $[PNCl_2]_3$ with Ph_3SnLi or $Bu^n{}_3SnLi$ does not follow the expected route of nucleophilic replacement of chloride on phosphorus by the SnR_3 group.

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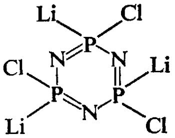
[70] L. N. Devonshire and H. H. Rowley, *Inorg. Chem.*, 1962, **1**, 680.
[71] K. W. Min, D. G. Rands, and R. L. Bain, *Inorg. Chem.*, 1972, **11**, 184.
[72] W. Tagaki, Y. Asai, and T. Eiki, *J. Amer. Chem. Soc.*, 1973, **95**, 3037.
[73] J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc.* (*A*), 1971, 2429.
[74] J. M. E. Goldschmidt and E. Licht, *J.C.S. Dalton*, 1972, 728.
[75] J. M. E. Goldschmidt and E. Licht, *J.C.S. Dalton*, 1972, 732.
[76] T. P. Zeleneva, O. B. Khachaturyan, and B. I. Stepanov, *Trudy Mosk. khim.-tekhnol. Inst.*, 1970, 147 (*Chem. Abs.*, 1972, **76**, 18 398q).

Rather there occurs rupture of the phosphazene ring with concomitant formation of the appropriate Sn_2R_6 compound. The species (7) is suggested as an intermediate in the reaction sequence.[77]



(7)

Both product characterization and kinetic studies have been described for alkaline hydrolysis of fluoroalkoxycyclophosphazenes. The reactions exhibit second-order kinetics. A comparison of the rates of reaction of the trimers $[NP(OCH_2CF_3)_2]_3$, $[NP(OCH_2C_2F_5)_2]_3$, and $[NP(OCH_2C_3F_7)_2]_3$ shows that the ease of leaving is in the order $OCH_2C_2F_5 > OCH_2CF_3 > OCH_2C_3F_7$. Tetrameric cyclophosphazenes usually react somewhat faster than trimeric cyclophosphazenes, as in chloride exchange or aminolysis. This is also the case in the present system, for alkaline hydrolysis of $[NP(OCH_2CF_3)_2]_4$ and of $[NP(OCH_2C_3F_7)_2]_4$ is slightly faster than that of the trimers cited earlier. All the fluoroalkoxy-derivatives hydrolyse more quickly than other cyclophosphazenes; this is ascribed to electron withdrawal by the fluorine atoms facilitating nucleophilic attack at the phosphorus. Oxygen-18 tracer studies confirmed that these reactions do indeed involve cleavage of phosphorus–oxygen, rather than carbon–oxygen, bonds.[78] Faster reactions of tetrameric cyclophosphazenes than of their trimeric analogues are also observed in the reactions of NMe_2-substituted derivatives with antimony trifluoride. This reaction provides a convenient alternative route to fluorophosphazene derivatives. A step-wise non-germinal mechanism is thought to operate, as in the generation of fluorophosphazenes from chlorophosphazenes.[79] A general and comprehensive review of cyclophosphazene chemistry includes a short section on mechanisms of substitution in this type of compound.[80]

Other Compounds. The products of hydrolysis of PF_2Cl have been established, and thence a mechanism through intermediates OPF_2H and F_2POPF_2 has been suggested. Rates of redistribution reactions in PCl_3–PBr_3 mixtures are very sensitive to traces of water. Under strictly anhydrous conditions redistribution reactions were shown, using ^{31}P n.m.r. spectroscopy, to occur very much more slowly than had been reported earlier.[81] Phosphoryl and thiophosphoryl compounds, $R_2P(O)X$ and $R_2P(S)X$ respectively, react with hexamethyldisiloxane, $(Me_3Si)_2O$, or with hexamethyldisilthiane, $(Me_3Si)_2S$, to give

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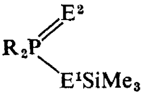
[77] H. Prakash and H. H. Sisler, *Inorg. Chem.*, 1972, **11**, 2258.
[78] H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, 1972, **94**, 119.
[79] P. Clare, D. Millington, and D. B. Sowerby, *J.C.S. Chem. Comm.*, 1972, 324.
[80] H. R. Allcock, *Chem. Rev.*, 1972, **72**, 315.
[81] A. D. Jordan and R. G. Cavell, *Inorg. Chem.*, 1972, **11**, 564.

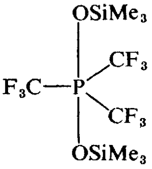
esters (8) (E^1 = O or S and E^2 = O or S):

e.g. $R_2P(O)X + (Me_3Si)_2O \longrightarrow R_2P(O)OSiMe_3 + Me_3SiX$

Five-co-ordinate phosphoranes are intermediates in these reactions; for the reaction where R = X = CF_3 the intermediate (9) was isolated and characterized.[82] There is preparative evidence for an S_N2 mechanism for the following reactions:[83]



(8)



(9)

$$(CF_3)_2PF + (Me_3Si)_2O \longrightarrow (CF_3)_2POSiMe_3 + Me_3SiF$$
$$(CF_3)_2PCl + (Me_3Si)_2S \longrightarrow (CF_3)_2PSSiMe_3 + Me_3SiCl$$

Mechanisms of reactions of organophosphorus compounds are comprehensively reviewed elsewhere.[84]

Antimony.—The exchange reaction between Me_3SbCl_2 and $Me_3SbCl(NO_3)$ can be monitored by ^1H n.m.r. spectroscopy. In nitrobenzene, activation parameters of $\Delta H^{\ddagger} = 10.6 \pm 2.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16 \pm 6$ cal deg^{-1} mol^{-1} (at 32 °C) have been estimated from rate constants determined over the temperature range 20—60 °C. The negative activation entropy may be the consequence of a four-centre transition state or of solvent-ordering in a transition state $Me_3SbCl^+Y^-$, with Y = Cl or NO_3. The rate constant for the reaction in methylene chloride is about seven times smaller than that in nitrobenzene, at 64 °C.[85] The observations from a Mössbauer study of hydrolysis of antimony trichloride are consistent with a stepwise hydrolysis mechanism; no kinetic results are available.[86] Some kinetic information on fluoride-exchange reactions can be gleaned from a ^{19}F n.m.r. study of fluorocarbenium ions in HF–SbF_5–SO_2ClF media.[87] The newly demonstrated polyantimonate $[SbO_3]_n{}^{n-}$ transforms into the normal $[Sb(OH)_6]^-$ form very slowly at 25 °C, quickly at 100 °C, in the presence of tetramethylammonium hydroxide.[88] Rates of transformation of the water-soluble α-form of anti-

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[82] R. G. Cavell, R. D. Leary, and A. J. Tomlinson, *Inorg. Chem.*, 1972, **11**, 2578.

[83] R. G. Cavell, R. D. Leary, A. R. Sanger, and A. J. Tomlinson, *Inorg. Chem.*, 1973, **12**, 1374.

[84] 'Organophosphorus Chemistry', ed. S. Trippett (Specialist Periodical Reports), The Chemical Society, London, Vol. 4, 1973; Vol. 5, 1974; P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem. Internat. Edn.*, 1973, **12**, 91.

[85] C. G. Moreland and R. J. Beam, *Inorg. Chem.*, 1972, **11**, 3112.

[86] A. Vertes and M. Ranogajec-Komor, *Magyar Kém. Folyóirat*, 1972, **78**, 380 (*Chem. Abs.*, 1972, **77**, 79 953j).

[87] G. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, 1972, **37**, 1169.

[88] J. Lefebvre and J. Lemerle, *Compt. rend.*, 1971, **273**, *C*, 1201.

monic acid into the water-soluble γ-form and into the water-insoluble β-form have been measured under various conditions of concentration and ionic strength.[89]

Intramolecular Processes.—*Inversion.* The first report of kinetics of racemization of a pyramidal monoarsine reveals that the barrier for AsMeEtPh is, as would be expected from the known configurational stability of arsines, high. In fact $\Delta G^{\ddagger} = 42.4$ kcal mol^{-1} at 217.6 °C in decalin solution.[90] Silyl substituents are known to reduce the barrier to inversion in pyramidal phosphorus compounds. They have the same effect for arsenic compounds, for the barrier to inversion is about 18 kcal mol^{-1} lower in AsPr^{i}Ph(SiMe$_3$) than in AsMeEtPh.[91] A more organic example is provided by inversion in the arsindole (10). Here, again as in analogous phosphorus cases, the barrier is considerably lower than in related acyclic compounds.[92]

Simple electronegativity considerations suggest that the barrier to pyramidal inversion should increase when a trimethylsilyl group attached to phosphorus is replaced by a trimethoxysilyl group. In fact the reverse is the case, as has been discovered by estimating the barrier to inversion for PPr^{i}Ph{Si(OMe)$_3$}, in deuteriotoluene. It proved necessary to invoke negative hyperconjugation to explain this unexpected result.[93]

Linear free-energy relationships connect inversion barriers at several pairs of atoms taken from the group N, P, As, C, O, Si, and S.[94] The adequacy of molecular orbital calculations in estimating barriers to inversion and to rotation about single bonds has been assessed for several nitrogen compounds, including ammonia.[95] The effect of the presence of fluorine bonded to nitrogen both on inversion at nitrogen in *N*-fluoro-amines and on rotation about carbon–nitrogen bonds in *N*-fluoro-amides has been examined.[96] The barriers to rotation about nitrogen–silicon bonds are much lower than those for rotation about nitrogen–phosphorus or nitrogen–sulphur bonds. The potentially diastereotopic methyl groups are equivalent at all accessible temperatures for six compounds of general formula (11).[97] A barrier of 9.2 kcal mol^{-1} (at −108 °C) has been found for inversion of the *N*-germyl imine (12). This barrier is much less than those known for *N*-alkyl- or *N*-arylimines.[98]

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[89] J. Lemerle, *Rev. Chim. minérale*, 1972, **9**, 863 (*Chem. Abs.*, 1973, **78**, 164 725b).

[90] G. H. Senkler and K. Mislow, *J. Amer. Chem. Soc.*, 1972, **94**, 291.

[91] R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, and K. Mislow, *J. Amer. Chem. Soc.*, 1972, **94**, 2859.

[92] R. H. Bowman and K. Mislow, *J. Amer. Chem. Soc.*, 1972, **94**, 2861.

[93] R. D. Baechler and K. Mislow, *J.C.S. Chem. Comm.*, 1972, 185.

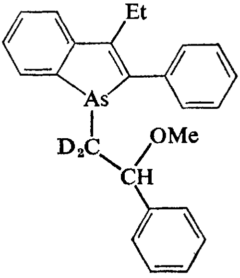
[94] R. D. Baechler, J. D. Andose, J. Stackhouse, and K. Mislow, *J. Amer. Chem. Soc.*, 1972, **94**, 8060, and refs. therein.

[95] L. C. Allen and J. Arents, *J. Chem. Phys.*, 1972, **57**, 1818.

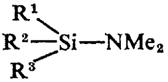
[96] J. Cantacuzene, J. Leroy, R. Jantzen, and F. Dudragne, *J. Amer. Chem. Soc.*, 1972, **94**, 7924.

[97] S. Chan, S. DiStefano, F. Fong, H. Goldwhite, P. Gysegem, and E. Mazzola, *Inorg. Chem.*, 1973, **12**, 51.

[98] R. J. Cook and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6703.

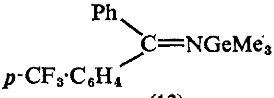


(10)



$R^1R^2R^3Si{-}NMe_2$

(11)



$Ph(p\text{-}CF_3{\cdot}C_6H_4)C{=}NGeMe_3$

(12)

Pseudorotation. Intramolecular rearrangement of PF_4H and of PF_3H_2 is briefly mentioned in a paper on the vibrational spectra of these compounds.[99] The barrier to intramolecular rearrangement in PF_4H can be estimated from earlier reports that all four fluorines are equivalent in n.m.r. spectra from +32 °C down to −114 °C and a recent statement that PF_4H has a trigonal-bipyramidal structure, with the hydrogen atom equatorial, in $CHClF_2$ solution below −120 °C. Both ^1H and ^{19}F n.m.r. spectra were obtained under these conditions.[100] Second-order intermolecular fluoride exchange has recently been claimed for Me_3PF_2 and Me_2PF_3. This is contrary to earlier descriptions of intramolecular pseudorotation by the Berry mechanism for these compounds, and contrasts with recent evidence for intramolecular rearrangement in Ph_2PF_3. The barrier to rearrangement in this last compound is *ca.* 20 kcal mol^{-1}.[101]

A general graphical topological approach to representing intramolecular processes of trigonal-bipyramidal molecules has been presented,[102] and these processes have been used to illustrate a general topological treatment of polytopal isomerizations.[103]

All previous n.m.r. studies of compounds ML_5 with five identical groups attached to the central atom in trigonal-bipyramidal geometry ('octahedral' IF_5 and polymeric SbF_5 are thus excluded) have indicated very low barriers to intramolecular rearrangement. One has to turn to transition-metal derivatives to find higher barriers. For although such compounds as $[Fe(CO)_5]$ and $[Os(PF_3)_5]$ also appear to have very low barriers to intramolecular rearrangement, the barrier for the $[Rh\{P(OMe)_3\}_5]^+$ cation is 7.4 kcal mol^{-1} at −107 °C, in CD_2Cl_2–$CHClF_2$ solution. That this pseudorotation is intramolecular is shown by the persistence of the coupling to ^{103}Rh, which has a nuclear spin of $\frac{1}{2}$.[104] Recent work[105] has failed to substantiate an earlier claim[106] for stereo-

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[99] R. R. Holmes and C. J. Hora, *Inorg. Chem.*, 1972, **11**, 2506.

[100] A. H. Cowley and R. W. Braun, *Inorg. Chem.*, 1973, **12**, 491.

[101] C. G. Moreland, G. O. Doak, and L. B. Littlefield, *J. Amer. Chem. Soc.*, 1973, **95**, 255.

[102] A. T. Balaban, *Rev. Roumaine Chim.*, 1973, **18**, 841.

[103] W. G. Klemperer, *J. Amer. Chem. Soc.*, 1972, **94**, 8360.

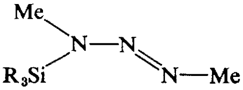
[104] J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, 1973, **95**, 1344.

[105] E. L. Muetterties, *J.C.S. Chem. Comm.*, 1973, 221.

[106] R. B. King and M. S. Saran, *Inorg. Chem.*, 1972, **11**, 2112.

chemical rigidity of the t-butyl isocyanide complex $[Co(CNCMe_3)_5]^+$ at temperatures below −30 °C.

Miscellaneous. It is possible to monitor several reactions of silyltriazenes (13) by ^1H n.m.r. spectroscopy. $1 \rightleftharpoons 3$ migration of the silyl groups occurs by an associative intramolecular mechanism with a transition state (14). The order of migration rates for various SiR_3 groups is R = Et < Me < OMe < Cl.[107] At lower temperatures it is possible to isolate *cis*- and *trans*-isomers. Isomerization of these compounds occurs by inversion at nitrogen. Activation parameters for the isomerization of (15) are strongly solvent dependent. Thus, for example, the activation energy and activation entropy for *cis*→*trans* isomerization are 7.7 kcal mol^{-1} and −47 cal deg^{-1} mol^{-1} in pentane, but 19.1 kcal mol^{-1} and −9 cal deg^{-1} mol^{-1} in ether.[108] It is also possible to monitor rotation about the nitrogen–nitrogen single bond by variable-temperature ^1H n.m.r. spectroscopy of appropriate silyltriazenes.[109] The dimethylamino-proton region of the n.m.r. spectrum of the aminophosphinite (16), in CF_2Cl_2–$CFCl_3$ solution, varies greatly with temperature, but the ^{19}F n.m.r. and $OSiMe_3$ proton n.m.r. are very nearly independent of temperature. These observations are explained by a freezing-out of the movement of one of the NMe_2 groups at low temperatures. It is not possible to decide whether this is due to restriction of rotation about the phosphorus–NMe_2 or phosphorus–$OSiMe_3$ bonds.[83] N.m.r. and i.r. spectroscopy both suggest that the equilibrium (17)$\rightleftharpoons$(18) is established in solution, for example in tetrachloroethane. Thermodynamic, but not kinetic, parameters were obtained.[110]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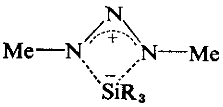
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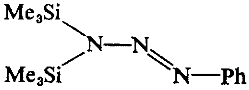
(15)

Several cyclopentadienyl derivatives of Group IV elements have long been known to behave as fluxional molecules. Now ^{19}F n.m.r. spectroscopy of $P(h^1\text{-}C_5H_5)F_2$ shows that this Group V derivative is also a fluxional molecule. No quantitative kinetic data were quoted, but a qualitative impression can be

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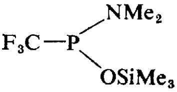
[107] N. Wiberg and H. J. Pracht, *Chem. Ber.*, 1972, **105**, 1388.

[108] N. Wiberg and H. J. Pracht, *Chem. Ber.*, 1972, **105**, 1392.

[109] N. Wiberg and H. J. Pracht, *Chem. Ber.*, 1972, **105**, 1399.

[110] R. A. Zingaro, K. J. Irgolic, D. H. O'Brien, and L. J. Edmondson, *J. Amer. Chem. Soc.*, 1971, **93**, 5677.



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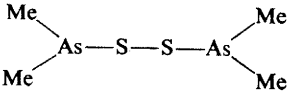
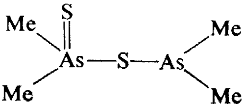


(17)



(18)

extracted from the published description of the variation of the spectrum with temperature.[111]

4 Group VI

Oxygen.—The rates of hydrolysis of oxygen difluoride in basic aqueous solution show a one-third-order dependence on hydroxide-ion concentration. At pH = 10, the activation energy for this hydrolysis is 8.5 kcal mol^{-1}.[112] The rate law for photolysis of hydrogen peroxide, in the presence of hydroxylamine or of methylamine, is

$$-\mathrm{d}[H_2O_2]/\mathrm{d}t = k_0I_0[H_2O_2]$$

Quantum yields, which were pH dependent, were lower in the presence of the named additives. A chain mechanism for these photolyses is presented and discussed.[113]

Sulphur.—The hydrolysis of elemental sulphur,

$$4S + 4H_2O \rightleftharpoons 3H_2S + HSO_4^- + H^+$$

has been examined over the temperature range 200—320 °C in sealed tubes. Exchange of ^{18}O between water and bisulphate ion proved too fast for the quenching techniques used, but the half-life for ^{34}S exchange between hydrogen sulphide and bisulphate ion is of the order of a day.[114]

Activation parameters for the alkaline hydrolysis of pyrosulphate ($S_2O_7^{2-}$) have been recorded as $E_a = 11.0 \pm 0.12$ kcal mol^{-1} and $\Delta S^{\ddagger} = 39.05 \pm 0.41$ cal deg^{-1} mol^{-1}.[115] Initial rates of reaction of thiosulphate with hydrochloric acid, in aqueous solution, indicate the rate law

$$-\mathrm{d}[S_2O_3^{2-}]/\mathrm{d}t = k[S_2O_3^{2-}]^2[H^+]$$

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[111] J. E. Bentham, E. A. V. Ebsworth, H. Moretto, and D. W. H. Rankin, *Angew. Chem. Internat. Edn.*, 1972, **11**, 640.

[112] S. N. Misra and G. H. Cady, *Inorg. Chem.*, 1972, **11**, 1132.

[113] B. Sethuram and T. N. Rao, *Z. phys. Chem. (Frankfurt)*, 1973, **85**, 137.

[114] B. W. Robinson, *Earth Planet. Sci. Letters*, 1973, **18**, 443 (*Chem. Abs.*, 1973, **78**, 164 702s).

[115] I. G. Ryss and A. Kh. Drabkina, *Kinetika i Kataliz*, 1973, **14**, 242 (*Chem. Abs.*, 1973, **79**, 10 307a).

The rate-determining step is therefore thought to be reaction between $S_2O_3^{2-}$ and its conjugate acid $HS_2O_3^-$; the eventual product is colloidal sulphur. At an ionic strength of 0.035 mol l^{-1}, the activation energy is $15.9_3 \pm 0.1_6$ kcal mol^{-1} and the frequency factor $1.64(\pm 0.13) \times 10^{11}$.[116] The rate of subsequent formation of elemental sulphur is a function of the surface area of that sulphur which has already precipitated.[117] In acid solution dithionates decompose thus:

$$S_2O_6^{2-} + H^+ \longrightarrow SO_2 + HSO_4^-$$

The dependence of the rate of this reaction on the acidity function h_- in sulphuric acid of concentration 7—10 mol l^{-1} suggests that the transition state is derived from monoprotonated dithionate. The Arrhenius plot for this reaction is curved: a surprisingly high activation enthalpy of 52 kcal mol^{-1} (25 °C) is reported.[118] The rate law for the reaction of peroxomonosulphate with hydroxide is

$$-d[SO_5^{2-}]/dt = k_2[SO_5^{2-}][OH^-]$$

The activation parameters are $E_a = 17.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18$ cal deg^{-1} mol^{-1}. The negative activation entropy and the rate law are both consistent with associative attack of the hydroxide at the sulphur atom. ^{18}O Tracer experiments, in which the isotopic distribution of evolved oxygen was determined, suggest a redox radical mechanism involving a one-electron transfer from the hydroxide to the peroxomonosulphate and cleavage of the oxygen–oxygen bond of the latter.[119]

The kinetics of the reaction between peroxomonosulphate and thiocyanate were earlier interpreted in terms of the intermediacy of species such as HS(O)CN, $(SCN)_2$, and HO(SO)CN. No definite proof of this is available, but the detection of similar intermediates, RSO_2CN and R(SO)CN, in reactions between alkyl thiocyanates and peroxomonosulphate lends support to the intermediacy of HS(O)CN and HO(SO)CN in the peroxomonosulphate–thiocyanate reaction.[120] The kinetics of decomposition of the *N*-nitrosohydroxylamine-*N*-sulphonate anion to sulphate and nitrous oxide have already been described under nitrogen.[55] The mechanism of substitution at sulphur(IV) in sulphinyl compounds, RS(O)Y, is still a topic of unresolved discussion, despite much effort in this area. The question awaiting answer is whether the mechanism is simple S_N2 or whether there is a four-co-ordinate intermediate of significant lifetime.[121,122] Though the determination of Brønsted coefficients did not provide definite mechanistic evidence relating to substitution at

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[116] F. Johnston and L. McAmish, *J. Colloid Interface Sci.*, 1973, **42**, 112 (*Chem. Abs.*, 1973, **78**, 76 377j).

[117] S. Tuzun, *Turk fiz. Dernegi Bul.*, 1972, No. 116 (*Chem. Abs.*, 1973, **78**, 102 476n).

[118] W. Y. W. Lew and R. E. Powell, *Inorg. Chem.*, 1973, **12**, 957.

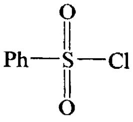
[119] V. A. Lunenok-Burmakina and G. P. Aleeva, *Russ. J. Phys. Chem.*, 1972, **46**, 1591.

[120] G. J. Bridgart and I. R. Wilson, *Austral. J. Chem.*, 1971, **24**, 2481.

[121] J. L. Kice and C. A. Walters, *J. Amer. Chem. Soc.*, 1972, **94**, 590.

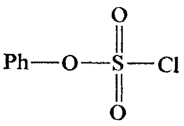
[122] L. Senatore, E. Ciuffarin, A. Fava, and G. Levita, *J. Amer. Chem. Soc.*, 1973, **95**, 2918.

sulphur(IV),[122] the determination of these coefficients for the reactions of four-co-ordinate sulphur(VI), in the form of benzenesulphonyl chloride (19), proved more fruitful. A large effect of solvent composition on Brønsted coefficients was observed for the reaction of benzenesulphonyl chloride with pyridines or with primary amines in aqueous dioxan and aqueous acetonitrile. This was interpreted in terms of varying degrees of bond making in transition-state formation for different nucleophiles and different solvent mixtures.[123] Both rate constants and activation enthalpies are markedly different for the reaction of benzenesulphonyl fluoride with aniline, n-butylamine, or hydroxide from the values for reaction of the other benzenesulphonyl halides with these same reagents. This difference in kinetic characteristics is interpreted in terms of significant sulphur to nucleophile bonding in the transition states for the reaction of benzenesulphonyl chloride, bromide, and iodide, in contrast to rate-determining sulphur–fluorine bond breaking in the corresponding reactions of benzenesulphonyl fluoride.[124] Steric effects on the reactivity of 4-substituted benzenesulphonyl chlorides with 2-methyl- and 2,6-dimethylaniline suggest that there is less bond making involved in the generation of the transition state when there are electron-releasing substituents present in the (substituted) benzenesulphonyl chloride.[125] Phenyl chlorosulphate (20) reacts with methoxide by parallel sulphur–oxygen and sulphur–chlorine bond-breaking pathways. The activation parameters for these two routes differ considerably: $\Delta H^{\ddagger} = 90.0\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^{\ddagger} = +29\ \mathrm{J\ K^{-1}\ mol^{-1}}$ for the sulphur–oxygen bond-breaking route, but $\Delta H^{\ddagger} = 63.2\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^{\ddagger} = 58\ \mathrm{J\ K^{-1}\ mol^{-1}}$ for the alternative sulphur–chlorine bond-breaking route.[126]



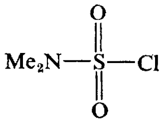
$\mathrm{Ph{-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}{-}Cl}$

(19)



$\mathrm{Ph{-}O{-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}{-}Cl}$

(20)



$\mathrm{Me_2N{-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}{-}Cl}$

(21)

The value of $\Delta C_p^{\ddagger}$ of $-76\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ for hydrolysis of dimethylsulphamoyl chloride (21) in aqueous solution indicates a degree of solvent reorganization during transition-state formation that is similar to that involved in the S_N1 hydrolysis of tertiary halides.[127] For organic solvolyses, $\Delta C_p^{\ddagger} = ca.\ -50\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ for S_N2 reactions and $\Delta C_p^{\ddagger} = ca.\ -80\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ for S_N1 reactions. However, the situation with respect to substitution in sulphur is complicated by the reported value of $\Delta C_p^{\ddagger} = -72\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$ for hydrolysis of 4-methylbenzenesulphonyl chloride, which should (see

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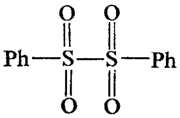
[123] L. J. Stangeland, L. Senatore, and E. Ciuffarin, *J.C.S. Perkin II*, 1972, 852.
[124] E. Ciuffarin, L. Senatore, and M. Isola, *J.C.S. Perkin II*, 1972, 468.
[125] O. Rogne, *J.C.S. Perkin II*, 1972, 472.
[126] E. Buncel, L. I. Choong, and A. Raoult, *J.C.S. Perkin II*, 1972, 691.
[127] E. C. F. Ko and R. E. Robertson, *J. Amer. Chem. Soc.*, 1972, **94**, 573.

previous paragraph) be S_N2 in character.[128] There has been some discussion on the determination and meaningfulness both of $\Delta C_p^{\ddagger}$ from $\partial \Delta H^{\ddagger}/\partial T$ and of $\partial \Delta C_p^{\ddagger}/\partial T$.[129]

The reactivity of sulphur(VI) in (22) towards nucleophilic attack has been

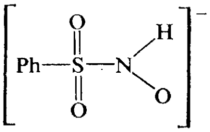


$PhSO_2-SO_2Ph$

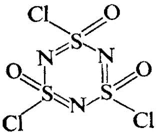
(22)

investigated for some twenty nucleophiles. The reactivity trend is very similar to that exhibited by carbon(IV), except that fluoride ion is a markedly better nucleophile towards sulphur(VI) than would be predicted from its nucleophilicity towards carbon(IV). However, it has been shown earlier that fluoride ion is also more reactive towards phosphorus(V) than would be expected from its behaviour towards organic substrates.[130]

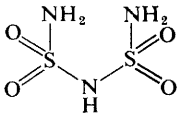
Rate constants and activation parameters have been determined for the decomposition of the benzenesulphydroxamate anion (23). This decomposition is not hydrolytic in nature, but involves dissociation of the anion into $PhSO_2$ and HNO, which latter eventually gives nitrous oxide.[131] The silver salt of trisulphimide, $Ag_3(NSO_2)_3,5H_2O$, has been identified as the product of hydrolysis of α-sulphanuric chloride (24) under mild conditions in aqueous silver nitrate solution. This suggests that all three sulphur–chloride bonds in (24) undergo hydrolysis before ring cleavage; the final hydrolysis products are imidosulphamide (25) and sulphuric acid.[132]



(23)



(24)



(25)

Activation parameters for the hydrolysis of the sulphur trioxide adduct of tetramethylhexamethylenediamine are $E_a = 24.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9.6 \pm 0.4$ cal deg^{-1} mol^{-1}. Investigation of the kinetics of hydrolysis of the sulphur trioxide adduct of tetramethylethylenediamine was precluded by the low solubility of this adduct.[133]

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[128] R. E. Robertson and B. Rossall, *Canad. J. Chem.*, 1971, **49**, 1441.

[129] J. M. W. Scott and R. E. Robertson, *Canad. J. Chem.*, 1972, **50**, 167; S. Wold, *J. Phys. Chem.*, 1972, **76**, 369.

[130] J. L. Kice and E. Legan, *J. Amer. Chem. Soc.*, 1973, **95**, 3912.

[131] F. Seel and C. Bliefert, *Z. anorg. Chem.*, 1972, **394**, 187.

[132] A. C. Hazell, *Acta Chem. Scand.*, 1972, **26**, 2542.

[133] L. P. Bogdanova and T. N. Kotlyar, *Kinetika i Kataliz*, 1973, **14**, 245 (*Chem. Abs.*, 1973, **79**, 10 303w).

The possibility of a hydrolytic pathway for fluoride exchange should always be borne in mind. Previous reports of n.m.r. spectra, both ^1H and ^{19}F, of Me_2N,SF_3 and of Et_2N,SF_3 spoke of poor resolution, attributed to line-broadening from fluoride exchange. Under rigorously anhydrous conditions the n.m.r. spectra of these two compounds are well resolved. Moreover, when $(Me_3Si)_2NH$ was added to SF_4 to take out the last traces of water and of hydrogen fluoride, the temperature at which line-broadening began to be significant in the ^{19}F n.m.r. spectrum was 30 °C higher than heretofore reported.[134]

Variable-temperature n.m.r. spectroscopy indicates barriers ($\Delta G^{\ddagger}$) of 10.3 and 11.4 kcal mol^{-1} for intramolecular rearrangement of $S(NEt_2)_2$ and $S(NPr^i_2)_2$ at -61 °C, in CCl_2F_2 solution. This rearrangement is rotation about a sulphur–nitrogen bond rather than inversion at nitrogen. Similar barriers to internal rearrangement are observed for $S_2(NR_2)_2$, where R = Me, Et, or Pr^i. Here again the observed barrier is attributed to rotation about a sulphur–nitrogen bond rather than to rotation about the sulphur–sulphur bond or inversion at nitrogen.[135] Inversions at sulphur bonded to platinum(II) or palladium(II)[136] and at sulphur bonded to gold(III)[137] in appropriate square-planar complexes are discussed in Chapter 2.

Selenium.—^{18}O tracer studies of oxygen exchange between selenate and water indicate a rate law

$$\text{Rate} = k[H^+][HSeO_4^-] \qquad (4)$$

At high acidities (above about $1.5M$-H_2SeO_4) a second term in $[H^+]^2[HSeO_4^-]^2$ begins to become significant. The reported activation parameters are listed in the Table. The mechanism corresponding to equation (4) is thought to be associative attack by water at the selenium in H_2SeO_4. The term in $[H^+]^2[HSeO_4^-]^2$ at high acid concentrations is attributed to an associative reaction involving two H_2SeO_4 molecules.[138] The effects of added ions on ^{18}O exchange rates between selenate and water have been studied.[56]

Table *Activation parameters for oxygen exchange between selenate or selenite anions and water*

Anion	*Conditions*	E_a/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
Selenate	pH = 1.12, 60—95 °C	23.1	−5	138
	$1.64M$-H_2SeO_4, 30—50 °C	21.8	−10	138
Selenite	pH = 9.1	14.0		139
	pH = 10.1	19.6		139

[134] A. F. Janzen, J. A. Gibson, and D. G. Ibbott, *Inorg. Chem.*, 1972, **11**, 2853.
[135] V. W. Hu, J. W. Gilje, and T. T. Bopp, *Inorg. Chem.*, 1973, **12**, 955.
[136] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.
[137] F. Coletta, R. Ettorre, and A. Gambaro, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 667.
[138] A. Okumura and N. Okazaki, *Bull. Chem. Soc. Japan*, 1973, **46**, 1080.

Oxygen exchange between selenite and water obeys a more complicated rate law. At 0 °C, $8.7 < \text{pH} < 12.5$, this is

$$\text{Rate} = k_1[\text{SeO}_3^{2-}] + k_2[\text{HSeO}_3^-] + k_3[\text{HSeO}_3^-]^2 + k_4[\text{HSeO}_3^-][\text{SeO}_3^{2-}] \quad (5)$$

Composite activation energies are listed in the Table. At high selenite concentrations, when the k_3 and k_4 terms of equation (5) become important, mechanisms involving reaction between two selenite units make a significant contribution to the exchange process. It is possible that the Se–O–Se linked species involved are intermediates rather than simply transition states, in the light of the known $[\text{Se}_2\text{O}_5]^{2-}$ anion.[139]

5 Group VII

Fluorine and Chlorine.—The kinetics of hydrolysis of oxygen difluoride have been mentioned in the section on oxygen (p. 134). Some qualitative kinetic observations derive from a ^{19}F n.m.r. study of the ClF_n^+ cations, with $n = 2$, 4, or 6. Thus solutions containing the ClF_4^+ cation, which is presumably isostructural with SF_4, in HF–AsF_5 show two lines below −70 °C, only one broad line above. It is not possible to tell whether the line coalescence can be assigned to intramolecular rearrangement or intermolecular fluoride exchange. Fluoride exchange is detectable between ClF_2^+ and HF, in the presence of AsF_5, but no exchange is observed between ClF_6^+ and HF. These facts can be rationalized by the plausibility of

$$\text{ClF}_2^+ + \text{HF}_2^- \rightleftharpoons \text{ClF}_3 + \text{HF}$$

and the unlikelihood of[140]

$$\text{ClF}_6^+ + \text{HF}_2^- \rightleftharpoons \text{ClF}_7 + \text{HF}$$

Radiolysis and photodecomposition of chlorite and chlorate have been studied in aqueous solution. Reaction schemes, rate constants, and quantum yields are reported.[141] The first stage in the reaction of chlorine with phenol is the second-order formation of $[\text{Cl}_2\cdot\text{PhOH}]$, with a rate constant $k_2 = 2.3 \times 10^4$ l mol^{-1} s^{-1} at 5 °C. This $[\text{Cl}_2\cdot\text{PhOH}]$ intermediate, whose properties are similar to those of known charge-transfer compounds of halogens with aromatic compounds, decomposes by three parallel pathways. Chlorine reacts more slowly with chlorophenols than with phenol itself.[142] The reaction of chlorine dioxide with phenol follows a comparable rate law:

$$-\text{d}[\text{ClO}_2]/\text{d}t = \{k_1 + k_2[\text{H}^+]^{-1}\}[\text{ClO}_2][\text{phenol}]$$

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[139] A. Okumura and N. Okazaki, *Bull. Chem. Soc. Japan*, 1973, **46**, 1084.
[140] K. O. Christe, J. F. Hon, and D. Pilipovich, *Inorg. Chem.*, 1973, **12**, 84.
[141] G. V. Buxton and M. S. Subhani, *J.C.S. Faraday I*, 1972, **68**, 947, 958, 970.
[142] E. Grimley and G. Gordon, *J. Phys. Chem.*, 1973, **77**, 973.

Activation parameters are $\Delta H_1^{\ddagger} = 11.6 \pm 0.3$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -21 \pm 0.5$ cal deg^{-1} mol^{-1} for the k_1 path, and $\Delta H_2^{\ddagger} = 13.5 \pm 0.3$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -22 \pm 1$ cal deg^{-1} mol^{-1} for the k_2 path.[143]

Exchange between chloride ion and chlorine in aqueous solution can be monitored by n.m.r. spectroscopy below about −35 °C; above this temperature linewidths are controlled by relaxation processes rather than by chemical exchange. The chemical exchange takes place *via* the equilibrium

$$\mathrm{Cl^-} + \mathrm{Cl_2} \underset{k_2}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{Cl_3^-}$$

The value of k_2 in 6M chloride solution, extrapolated to 25 °C, is 9×10^6 l mol^{-1} s^{-1}.[144]

Bromine.—Oxygen exchange between bromate and water has been much studied in acid solution. The first quantitative study in alkaline solution, reported last year, shows that the overall rate law for this oxygen exchange is

$$\text{Rate} = \{k_0 + k_1[\mathrm{OH^-}] + k_2[\mathrm{H^+}]^2\}[\mathrm{BrO_3^-}] \qquad (6)$$

In alkaline solution the activation parameters are $\Delta H^{\ddagger} = 22.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19$ cal deg^{-1} mol^{-1}, determined from k_1 values [equation (6)]. The activation parameters for exchange with D_2O are the same, within experimental uncertainty.[145] The kinetic salt effect was also studied for this bromate–water oxygen exchange. The experiments in alkaline solution were not successful, but sufficient results were obtained to yield further information germane to the k_0 and k_2 paths of equation (6).[146] The effects of added cations (Li^+, Na^+) on oxygen-exchange rates between bromate and water have been discussed in terms of ion association.[56]

Iodine.—IO_2, IO_3, and IO_4^{2-} are postulated intermediates in the flash photolysis and radiolysis of aqueous iodate solutions at pH 7. The IO_2 disappears by a second-order process.[147] The reaction of iodate with iodide in acid solution has been studied at very low iodide concentrations, $< 10^{-7}$ mol l^{-1}, in order to gain background information pertaining to oscillating reactions involving these compounds and hydrogen peroxide.[148]

The reaction of iodide with iodine

$$\mathrm{I_2} + \mathrm{I^-} \underset{k_f}{\overset{k_b}{\rightleftharpoons}} \mathrm{I_3^-}$$

is too fast to follow by conventional *T*-jump techniques, but has been monitored by a recently developed laser *T*-jump apparatus. At 25 °C and an ionic strength of 0.02 mol l^{-1}, $k_f = 6.2(\pm 0.8) \times 10^9$ l mol^{-1} s^{-1} and $k_b = 8.2(\pm 1.0) \times 10^6$ s^{-1}. This value of k_f is reasonably close to the earlier

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[143] E. Grimley and G. Gordon, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2383.

[144] H. W. Dodgen, A. D. Jordan, and R. B. Jordan, *J. Phys. Chem.*, 1973, **77**, 2149.

[145] H. Gamsjäger, A. Grütter, and P. Baertschi, *Helv. Chim. Acta*, 1972, **55**, 781.

[146] H. Gamsjäger and P. Baertschi, *Helv. Chim. Acta*, 1972, **55**, 2154.

[147] F. Barat, L. Gilles, B. Hickel, and B. Lesigne, *J. Phys. Chem.*, 1972, **76**, 302.

[148] R. Furuichi, I. Matsuzaki, R. Simic, and H. A. Liebhafsky, *Inorg. Chem.*, 1972, **11**, 952.

estimate from ^{127}I n.m.r. of $5.4 \times 10^{10}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, at 35 °C, a value considered unreasonably high at the time. The rate of the forward reaction is thus extraordinarily high, but is still within the diffusion-controlled limit, *ca.* $1.5 \times 10^{10}\ \mathrm{s^{-1}}$ at 25 °C. The mechanism proposed includes an outer-sphere complex,

$$I_2 + I^- + H_2O \rightleftharpoons I_2(OH_2)I^- \rightleftharpoons I_3^- + H_2O$$

with the left-hand equilibrium being set up at diffusion-controlled rates and the right-hand equilibrium providing the 'rate-determining step'.[149]

Previous studies of the iodide–tri-iodide exchange reaction have been discussed in terms of a dissociation–formation model:

$$I_3^- \rightleftharpoons I_2 + I^-$$

The use of this model leads to derived rate constants which exceed the diffusion-controlled limit. Further ^{127}I n.m.r. studies and a reconsideration of earlier published experimental data lead to a new proposal of an associative mechanism for iodide exchange, in which iodide attacks at one end of the tri-iodide. It is possible, from the observed kinetic pattern, that the I_4^{2-} so generated has a sufficient lifetime to be considered an intermediate rather than a transition state.[150] A transfer diffusion investigation of the same reaction also culminates in the proposal of an associative mechanism, with a linear I_4^{2-} transition state. Allowing for the non-spherical nature of the tri-iodide, it is possible to calculate a diffusion-controlled rate constant, which turns out to be the same as the experimentally determined (by this method or from ^{127}I n.m.r.) second-order rate constant.[151] Some calculations on the transition state have been made in connection with this transfer diffusion study of the iodide–tri-iodide exchange reaction.[152] Further study of the iodide–thiocyanate reaction has resulted in an estimate of the association constant for the initial rapid association of the reactants to give the intermediate charge-transfer complex I_2,SCN^-.[153]

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[149] D. H. Turner, G. W. Flynn, N. Sutin, and J. V. Beitz, *J. Amer. Chem. Soc.*, 1972, **94**, 1554.

[150] E. E. Genser and R. E. Connick, *J. Chem. Phys.*, 1973, **58**, 990.

[151] I. Ruff, V. J. Friedrich, and K. Csillag, *J. Phys. Chem.*, 1972, **76**, 162.

[152] I. Ruff, V. J. Friedrich, and K. Csillag, *Magyar Kém. Folyóirat*, 1972, **78**, 449.

[153] I. Országh, G. Bazsa, and M. T. Beck, *Inorg. Chim. Acta*, 1972, **6**, 271.

2

Inert Metal Complexes: Co-ordination Number Four

BY J. BURGESS

1 Tetrahedral Complexes

The titles of this section have, in the interests of reasonable brevity, been somewhat oversimplified. For in this section we shall deal not only with inert complexes of co-ordination number four of undisputed tetrahedral stereochemistry, but also with some complexes and oxoanions of uncertain co-ordination number or stereochemistry and some complexes of undoubted lability. Thus, for instance, several reactions of molybdates and of vanadates are included in this section as they seem less inappropriate here than elsewhere in this Report. The arrangement of sections is by order of Periodic Table groups.

Group V.—*Vanadium.* The kinetics of formation of $[VO_2(H_2edta)]^-$ from vanadate and edta have been examined in acid $(1.5 < pH < 2)$ aqueous solution, using stopped-flow techniques. The rate law is

$$\frac{-d[VO_3^-]}{dt} = \frac{k[edtaH_2^{2-}][V^V]}{1 + k^1[edtaH_2^{2-}]}$$

The most likely mechanism is that of a pre-equilibrium

$$[V(OH)_4]^+ \rightleftharpoons [VO(OH)_2]^+ + H_2O \qquad (1)$$

followed by bimolecular reaction with edta:

$$[VO(OH)_2]^+ + edtaH_2^{2-} \longrightarrow [VO_2(edtaH_2)]^- + H_2O \qquad (2)$$

Rate constants were estimated for the forward and reverse reactions of equilibrium (1) and for the bimolecular step (2).[1] The study of the reaction of vanadate with edta over a wide pH range is complicated by the existence of variously protonated and deprotonated forms of the reactants. Thus the overall kinetic scheme is complicated. The reaction of vanadate with alizarin (1,2-dihydroxyanthraquinone) is simpler, as there are only two reaction paths. These are the reactions of $[VO_2(OH)_3]^{2-}$ and of $[VO_2(OH)_2]^-$ with the alizarin monoanion.[2] Formation reactions of V^V are also important in some reactions – for example the oxidation of ascorbic acid by vanadium(v) proceeds by

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[1] J. Lagrange and P. Lagrange, *Bull. Soc. chim. France*, 1972, 19.
[2] K. Kustin and D. L. Toppen, *J. Amer. Chem. Soc.*, 1973, **95**, 3564.

rapid complex formation followed by rate-determining redox decomposition of this complex.[3]

Base hydrolysis of decavanadate follows the rate law

$$-d[V_{10}O_{28}^{6-}]/dt = \{k_1 + k_2[OH^-]\}[V_{10}O_{28}^{6-}]$$

The rate constants show some dependence on the nature of the cation present from the added MOH. This is ascribed to significant ion-association, which is not too surprising with a 6− anion, albeit a relatively large one. At a pH between 9 and 10, and at an ionic strength of 2.5 mol l^{-1} (NaCl), the activation parameters are $\Delta H^{\ddagger} = 28.3 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = +17 \pm 2$ cal deg^{-1} mol^{-1}. There is a marked similarity of the kinetic pattern here to that established for the paramolybdate ($[Mo_7O_{24}]^{6-}$) anion.[4]

Group VI.—*Chromium.* The kinetics of the reaction

$$HCrO_4^- + HS_2O_3^- \rightleftharpoons [O_3CrSSO_3]^{2-} + H_2O \qquad (3)$$

have been determined in aqueous solution at 25 °C. The rate constant for the forward reaction is 2.0×10^4 l mol^{-1} s^{-1}, for the reverse reaction 2.1 s^{-1}. The electronic spectrum of the product, and its formation constant, suggest the bonding of chromium to thiosulphate sulphur hinted at in equation (3).[5] In the reaction of $HCrO_4^-$ with thiocyanate it is not possible to tell whether there is chromium–sulphur or chromium–nitrogen bonding in the product. This does not prevent the elucidation of the rate law for the reaction.[6] The current interest in substitution at $HCrO_4^-$ is connected with investigations of the mechanisms of oxidation of a variety of substrates by chromium(VI). In these redox reactions the initial step is often postulated as formation of a chromium(VI)–substrate adduct.[5,7] Thiosulphate catalyses hydrolysis of $Cr_2O_7^{2-}$; it has now been shown that the above-mentioned $[O_3CrSSO_3]^{2-}$ anion is an intermediate in this $Cr_2O_7^{2-}$ hydrolysis. This is claimed as the first *direct* evidence for catalysis of hydrolysis of dichromate by a nucleophile.[5] The influence of added cations (Na^+, NMe_4^+) and added organic cosolvents (dioxan) on acid hydrolysis of dichromate has been studied using the *T*-jump technique. The results obtained were interpreted in terms of the effects of the additives on the structure of the solvent.[8]

Molybdenum. The protonation of the $[MoO_4]^{2-}$ anion, determined by ultrasonic techniques, is about ten times slower than that of the $[Mo_7O_{24}]^{6-}$ anion. This difference is ascribed to the necessity of changing the stereochemistry about the molybdenum from tetrahedral to octahedral on adding H^+ to the $[MoO_4]^{2-}$ anion.[9] *T*-Jump studies of molybdate solutions show two relaxations,

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[3] K. Kustin and D. L. Toppen, *Inorg. Chem.*, 1973, **12**, 1404.
[4] J. B. Goddard and A. M. Gonas, *Inorg. Chem.*, 1973, **12**, 574.
[5] K. A. Muirhead, G. P. Haight, and J. K. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 3006.
[6] C. T. Lin and J. K. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 3011.
[7] A. Haim, *Inorg. Chem.*, 1972, **11**, 3147.
[8] R. Koren and B. Perlemutter-Hayman, *J. Phys. Chem.*, 1972, **76**, 582.
[9] D. S. Honig and K. Kustin, *J. Phys. Chem.*, 1972, **76**, 1575.

which have been assigned to the following reactions:

$$7[MoO_4]^{2-} + 8H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4H_2O$$
$$[Mo_7O_{24}]^{6-} + [MoO_4]^{2-} + 4H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 2H_2O$$

The rate of 'heptamerization' of the $[MoO_4]^{2-}$ anion is remarkably high, which again suggests that monomeric molybdate in acid solution is octahedral, perhaps $[MoO(OH)_5]^-$ or $[Mo(OH)_6]$, rather than tetrahedral.[10] The kinetic pattern for the reaction of molybdate with catechol is interpreted in terms of the reaction of the incoming ligand with either of the two tetrahedral species $[MoO_4]^{2-}$ or $[MoO_3(OH)]^-$.[11]

Tungsten. Rate laws and rate constants have been determined, and reaction mechanisms proposed, for reactions of dodecatungstosilicate, $[SiW_{12}O_{40}]^{4-}$, and of dodecatungstophosphate, $[PW_{12}O_{40}]^{3-}$, with vanadium(IV), VO^{2+}. Two parallel paths are suggested for each reaction, rate-determining loss of one tungstate unit followed by rapid reaction with VO^{2+}, and equilibrium formation of an ion-pair between the reactants followed by rate-determining interchange within this ion-pair.[12] The heteropolytungstates $[SiW_{11}O_{39}]^{8-}$ and $[P_2W_{17}O_{61}]^{10-}$ react with hexachlororhenate(IV); rapid oxidation of the products has prevented a kinetic study of these reactions.[13] The left→right reaction of the heteropolytungstate equilibrium

$$2[PVW_{11}O_{40}]^{4-} \rightleftharpoons [PV_2W_{10}O_{40}]^{5-} + [PW_{12}O_{40}]^{3-}$$

is second-order in the $[PVW_{11}O_{40}]^{4-}$ anion. The reaction proceeds in this direction at $pH > 1.5$ since under these conditions the $[PW_{12}O_{40}]^{3-}$ anion rapidly gives $[PW_{11}O_{39}]^{7-}$. The mechanism proposed here resembles that proposed for disproportionation of 'heteropoly blues', for example the $[PW^{V}W^{VI}O_{40}]^{4-}$ anion.[14]

Group VIII.—*Cobalt.* Chelate ring inversion in the pseudo-tetrahedral compound $[Co(tmeda)(NO)_2]^+$ is discussed with other similar chelate ring inversions for octahedral complexes in Section 9 of Chapter 3.[15]

Nickel. Kinetics of redistribution reactions involving pairs of complexes $[Ni(LL)_2]$ and $[Ni(LL')_2]$ have been investigated, in C_2Cl_4 or $CDCl_3$ solution, by n.m.r. spectroscopy. The ligands LL and LL′ are asymmetric bidentate salicylaldiminato- or β-ketoiminato-derivatives. Reversible second-order kinetics are reported, with no evidence for persistent mixed complexes $[Ni(LL)(LL')]$. Activation energies are in the range 64—120 kJ mol^{-1}.[16] The thermodynamic determinations which form the background to these re-

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[10] D. S. Honig and K. Kustin, *Inorg. Chem.*, 1972, **11**, 65.
[11] K. Kustin and Sung-Tseun Liu, *J. Amer. Chem. Soc.*, 1973, **95**, 2487.
[12] P. Souchay and G. Salamon-Bertho, *Compt. rend.*, 1972, **274**, *C*, 1677.
[13] B. Charreton and R. Meunier, *Compt. rend.*, 1972, **275**, *C*, 945.
[14] D. P. Smith and M. T. Pope, *Inorg. Chem.*, 1973, **12**, 331.
[15] K. G. Caulton, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 533.
[16] J. C. Lockhart and W. J. Mossop, *J.C.S. Dalton*, 1973, 662.

distribution kinetic studies have been published separately.[17] There is n.m.r. evidence for bridged intermediates in reactions between $[Ni(LL)_2]$ and $[Zn(LL)_2]$, where LL = an *N*-methylsalicylaldimino-ligand.[18]

Rates of tetrahedral⇌square-planar interconversions for compounds $[NiX_2(PR_3)_2]$ are faster, for a given phosphine PR_3, when X = Cl than when X = Br.[19, 20] Activation enthalpies for the tetrahedral→square-planar reaction lie between 9.2 and 10.7 kcal mol^{-1} (indeed they are equal within the quoted experimental uncertainty of ± 1.0 kcal mol^{-1}), and activation entropies lie between -3 and $+1$ cal deg^{-1} mol^{-1}, for four compounds of this type. Whereas steric factors are unimportant in determining the thermodynamics of these tetrahedral⇌square-planar systems, they are important in determining reactivities.[20]

2 Square-planar Complexes

Platinum(II).—*General.* The normal rate law for nucleophilic substitution at platinum(II) complexes, as at other square-planar d^8 complexes, is

$$-d[\text{complex}]/dt = \{k_1 + k_2[Y]\}[\text{complex}] \qquad (4)$$

in which Y is the incoming nucleophile. The k_2 term usually corresponds to simple associative substitution (S_N2), but in certain reactions there are indications that this k_2 pathway may consist of two steps. One such reaction is that of *trans*-$[Pt(PEt_3)_2(R)Cl]$, where R = phenyl, *o*-tolyl, or mesityl, with pyridine in methanolic solution. The kinetic evidence for an intermediate, of formula $[Pt(PEt_3)_2(R)(MeOH)]^+$, was presented briefly some years ago;[21] it has now been discussed in detail, in a more accessible journal.[22] In this case the two stages of the k_2 reaction are solvolysis and subsequent replacement of solvent by the incoming ligand. An alternative two-stage sequence involves the formation and subsequent decay of a five-co-ordinate platinum(II) intermediate. Indirect support for the operation of such a mechanism,* at least in favourable circumstances, is provided by the characterization of several more stable five-co-ordinate platinum(II) complexes. A spectroscopic investigation of one of these, $[PtCl(PEt_3)_2(phen)]^+$, suggested that it had a trigonal-bipyramidal structure (1).[23]

The values of the rate constants k_1 and k_2 of equation (4) for any given reaction are solvent-dependent. One way of probing some effects of the tetragonally interacting solvent molecules would be to replace one of them by

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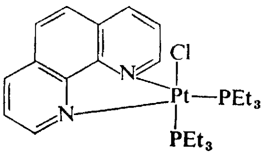
* See also, for instance, ref. 44 below.

[17] J. C. Lockhart and W. J. Mossop, *J.C.S. Dalton*, 1973, 19.
[18] M. N. S. Hill, S. Karunaratne, and J. C. Lockhart, *J.C.S. Chem. Comm.*, 1973, 50.
[19] G. N. LaMar and E. O. Sherman, *J. Amer. Chem. Soc.*, 1970, **92**, 2691.
[20] L. Que and L. H. Pignolet, *Inorg. Chem.*, 1973, **12**, 156.
[21] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Soc. Peloritana Sci. fis. mat. natur.*, 1968, **14**, 341 (*Chem. Abs.*, 1971, **74**, 35 109x).
[22] V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1972, 1857.
[23] K. R. Dixon and A. D. Rattray, *Canad. J. Chem.*, 1973, **51**, 618.



(1)

boron trifluoride. It proved impossible to put this idea into practice in the system investigated, as the selected platinum(II) substrate, which was *trans*-$[Pt(py)_2(NO_2)_2]$, reacted not with one but with two boron trifluoride molecules in all attempts to form the mono-adduct.[24]

Normally, substitution at platinum(II) in solution is nucleophilic in character. It is interesting therefore to note the first report of an S_H2 substitution at platinum(II),[25] which is reported for the reactions of *cis*-$[PtR_2L_2]$, where R = Me, Et, CH_2Ph, or CH_2SiMe_3 and L = a phosphine, with $^{\bullet}OBu^t$ or $^{\bullet}SPh$ radicals. Indeed this is the first report of radical substitution at any transition-metal centre.

Solvent Effects. Kinetic parameters for the reaction of $[Pt(dien)Br]^+$ with 3-cyanopyridine have been determined in deuterium oxide solution, in order to make a comparison of reactivities in deuterium oxide and in ordinary water. To avoid any complications from protium–deuterium exchange between solvent and co-ordinated ligand, the perdeuterio-diethylenetriamine complex was used as substrate in deuterium oxide solvent. The kinetic parameters are compared in Table 1. The results were discussed in terms of an associative mechanism and the smaller solvating effects of D_2O compared with H_2O.[26]

Table 1 *Kinetic parameters for the reaction between* $[Pt(dien)Br]^+$ *and* 3-*cyanopyridine in* H_2O *and* D_2O (*at* 30 °C)

Complex	*Solvent*	$10^3k_2/$ l mol^{-1} s^{-1}	$\Delta H_2^{\ddagger}/$ kcal mol^{-1}	$\Delta S_2^{\ddagger}/$ cal deg^{-1} mol^{-1}	*Ref.*
$[Pt(dien)Br]^+$	H_2O	3.03	17.5	−12	27
$[Pt([^2H_5]dien)Br]^+$	D_2O	2.86	15.6	−19	26

The variation of aquation rates of *cis*-$[PtL_2Cl_2]$, where L = acetoxime,[28] dimethylamine,[29] or ethylamine,[28] with solvent composition in mixed aqueous solvents has been studied. As some of the results are fairly inaccessible, a

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[24] D. Humphreys and P. J. Staples, *J.C.S. Dalton*, 1973, 897.
[25] D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 350.
[26] S. C. Chan and F. T. Wong, *Z. anorg. Chem.*, 1972, **387**, 120.
[27] S. C. Chan and F. T. Wong, *Austral. J. Chem.*, 1968, **21**, 2873.
[28] V. D. Panasyuk, N. F. Falendysh, and N. A. D'yachenko, *Russ. J. Inorg. Chem.*, 1971, **16**, 1452.
[29] V. D. Panasyuk, N. F. Falendysh, and N. A. D'yachenko, *Ukrain. khim. Zhur.*, 1972, **38**, 1218.

selection of kinetic parameters for these reactions is included in Table 2. As the proportion of the organic cosolvent increases, the rate of aquation decreases. This behaviour is reminiscent of that established for aquation of both cobalt(III)- and chromium(III)-chloride complexes, and indeed for S_N1 solvolysis of t-butyl chloride. The activation parameters vary only slightly with solvent composition. Plots of logarithms of rate constants against the function $(D - 1)/(2D + 1)$ of the dielectric constants (D) of the mixed solvents are slightly curved. It is suggested that both platinum–chloride bond stretching and at least some platinum–water bond formation are involved in the generation of the transition state.[28]

Table 2 *Selected kinetic parameters for the aquation of* cis-$[PtL_2Cl_2]$ *in water and in mixed aqueous solvents*

L	*Solvent*[a]	10^5k_{45}/ s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
$EtNH_2$	Water	—	21.9	−6	28
	20% dioxan	14.1	21.5	−8	
	30% methanol	12.2	21.8	−8	
Me_2NH	Water	—	20.9	−10	29
	30% dioxan	7.6	20.4	−14	
	40% methanol	7.4	20.2	−14	
Acetoxime	Water	13.6	20.8	−11	28
	20% dioxan	6.4	21.8	−9	
	40% methanol	4.7	20.7	−13	

[a] Solvent composition quoted in % by weight.

Aquation and Anation. Kinetic parameters for the aquation of some complexes *cis*-$[PtL_2Cl_2]$ have already been discussed (see Table 2).[28, 29] The rate constant for the loss of the first bromide from *trans*-$[Pt(NH_3)_2Br_2]$ is 1.07×10^{-3} s^{-1}. This is not very different from the rate of hydrolysis of *trans*-$[Pt(NH_3)_2Cl_2]$. Bromide ion is not greatly different from chloride ion as a leaving group from platinum(II), though the former is a considerably better nucleophilic entering group. The activation parameters for the loss of the first bromide from *trans*-$[Pt(NH_3)_2Br_2]$ are $\Delta H^{\ddagger} = 18.0 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -12 \pm 2$ cal deg^{-1} mol^{-1}. From these kinetic results for bromide loss and from the relevant equilibrium data, it is possible to estimate kinetic parameters for the reverse replacement of water by bromide as $k_2 = 35$ l mol^{-1} s^{-1} at 25 °C, $\Delta H^{\ddagger} = 9.5 \pm 0.9$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -20 \pm 2$ cal deg^{-1} mol^{-1}.[30] The reported isolation of the perchlorate salt of the $[Pt(dien)(OH_2)]^{2+}$ cation is of marginal interest with respect to substitution reactions of $[Pt(dien)X]^{n+}$ cations in aqueous media.[31]

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[30] W. H. Jolley, E. D. Smith, D. S. Martin, J. C. Clardy, and J. D. Woods, *Inorg. Chem.*, 1972, **11**, 2866.

[31] R. M. Alcock, F. R. Hartley, and D. E. Rogers, *J.C.S. Dalton*, 1973, 1070.

Ligand Exchange. Bromide exchange with *trans*-$[Pt(NH_3)_2Br_2]$ follows the usual two-term rate law of equation (4) above. The k_1 term can be identified with rate-determining solvolysis (*cf.* previous paragraph) followed by more rapid bromide anation. For the direct associative path for bromide exchange, $k_2 = 0.176$ l mol^{-1} s^{-1} at 25 °C, $\Delta H^{\ddagger} = 10.9$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -25$ cal deg^{-1} mol^{-1}.[30] Direct bromide exchange, in other words without intermediate generation of free bromide ion, has been demonstrated between $[PtBr_4]^{2-}$ anions. A four-centred transition state seems likely.[30] This type of direct exchange has been suggested before,[32] but that previous suggestion was based on much more meagre evidence.

Exchange of free chloride ion with the chloride *trans* to the diethyl sulphoxide in the $[Pt(Et_2SO)Cl_3]^-$ anion is very rapid. Exchange of free chloride with the *cis*-chlorides of $[Pt(Et_2SO)Cl_3]^-$ is a first-order process whose rate constant is 1.54×10^{-4} s^{-1}. This rate of exchange is about one third of that for chloride exchange with $[Pt(DMSO)Cl_3]^-$. This small difference in exchange rates for the analogous dimethyl sulphoxide and diethyl sulphoxide complexes is attributed to steric effects.[33]

The breadth of the hydride resonances observed in ^1H n.m.r. spectra of compounds *trans*-$[Pt(H)(X)L_2]$, where X = NCS or NCO and L = PEt_3 or $AsEt_3$, was attributed to quadrupole effects.[34] Current opinion is that this line-broadening is more likely to arise from ligand-exchange processes.[35]

Leaving Groups. There is some disagreement in the literature both over the rate laws for the displacement of chloride from *trans*-$[Pt(NH_3)_2Cl_2]$ and from $[PtCl_4]^{2-}$, and indeed over the number of chloride ions which can be displaced from these complexes. The latest research in this area indicates that all the chlorides may be displaced from either complex in the reaction with allyl alcohol. The kinetic pattern, in the presence of an excess of allyl alcohol, is not that of a single first-order reaction, as neither reaction sequence appears to have a uniquely slow rate-determining step. No evidence was found for the spontaneous release of chloride from *trans*-$[Pt(NH_3)_2Cl_2]$ in aqueous media.[36] The similarity in kinetic characteristics of chloride and of bromide as leaving groups from platinum(II) has been noted above.[30]

The mechanism for the displacement of oxalate from $[Pt(ox)_2]^{2-}$ by thiocyanate is complicated. An intermediate anion $[Pt(ox)_2(SCN)_2]^{4-}$, presumably containing unidentate oxalate ligands, has been isolated and characterized as the trihydrate of its potassium salt. Other transient intermediates containing unidentate oxalate (LL), (2)—(4), are proposed, and many rate constants relating to various steps in the postulated reaction sequence have been estimated.[37]

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[32] A. A. Grinberg and G. A. Shagisultanova, *Radiokhimiya*, 1960, **2**, 592.

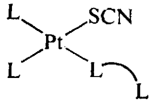
[33] Yu. N. Kukushkin, M. A. Kuz'mina, and V. N. Spevak, *Radiokhimiya*, 1971, **13**, 696 (*Chem. Abs.*, 1972, **76**, 28 216t).

[34] J. Powell and B. L. Shaw, *J. Chem. Soc.*, 1965, 3879.

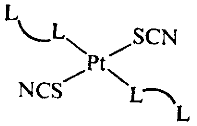
[35] M. W. Adlard and G. Socrates, *J.C.S. Chem. Comm.*, 1972, 17.

[36] A.-L. Aboul-Seoud and H. Kelm, *Ann. Chim. (Italy)*, 1972, **62**, 108.

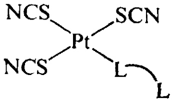
[37] A. Giacomelli and A. Indelli, *Inorg. Chem.*, 1972, **11**, 1033.



(2)



(3)



(4)

The reactions of (−)-[Pt(H)(SiR$_3$)(PPh$_3$)$_2$] or of (+)-[Pt(Cl)(SiR$_3$)(PPhMe$_2$)$_2$] with lithium aluminium hydride, thiophenol, or triethylsilane, result in platinum–silicon bond cleavage and thus provide examples of SiR$_3$ as leaving groups from platinum. However, as the reaction sequence appears to consist of consecutive oxidative addition and reductive elimination reactions, the SiR$_3$ unit really leaves from platinum(IV) rather than from platinum(II).[38]

Entering Groups. In this section we report on reactions in which the main interest lies in the entering group – the leaving group is always a halide, usually chloride.

The irreversible replacement of the first chloride in [PtCl$_4$]$^{2-}$ by dimethyl sulphoxide follows a second-order rate law, with $k_2 = 2.8 \times 10^{-3}$ l mol^{-1} s^{-1} at 25 °C, $E_a = 15.8 \pm 0.7$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -23$ cal deg^{-1} mol^{-1}. Reaction rates with dimethyl sulphoxide are faster than those with aliphatic amines; the n_{Pt} value for dimethyl sulphoxide is 1.86.[39]

The rate of reaction of *cis*-[Pt(NH$_3$)$_2$Cl$_2$] with oxalate varies only slightly with pH. This suggests that ox^{2-} and Hox$^-$ have similar reactivities, but in fact as the reaction is first-order and oxalate is a very weak nucleophile as far as platinum(II) is concerned, rate-determining aquation is the likely reaction route. Both the rate constants and the activation enthalpies for the reaction with oxalate and for aquation are remarkably similar.[40] Nitrogen bases tend to be better nucleophiles than oxalate, and the reaction of [PtCl$_4$]$^{2-}$ with 2,2′-bipyridyl in aqueous solution follows, appropriately, a second-order rate law. As in other substitution reactions of [PtCl$_4$]$^{2-}$, the k_1 term of the normal two-term rate law of equation (4) above is negligible. The variation of rate with pH shows that [PtCl$_4$]$^{2-}$ reacts more readily with bipyH$^+$ than with bipy itself. This situation contrasts with the similar reactivity of [PtCl$_4$]$^{2-}$ towards phen and phenH$^+$.[41] It may be that in the phen system the electrostatic favouring of reaction with the protonated ligand is balanced by the difficulty of

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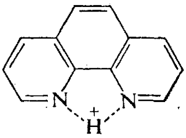
[38] C. Eaborn, D. J. Tune, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1972, 1223.

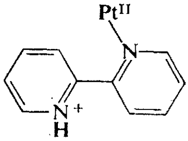
[39] Yu. N. Kukushkin and V. V. Kirillov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1351.

[40] J. E. Teggins, K. W. Lee, J. M. Baker, and E. D. Smith, *J. Coordination Chem.*, 1972, **1**, 215.

[41] D. E. Schwab and J. V. Rund, *Inorg. Chem.*, 1972, **11**, 499.



(5)



(6)

platinum–nitrogen bond formation with (5); in the bipy reaction ligand flexibility may permit easier reaction *via* transient species of the type (6).

A comparison of rate constants and activation parameters for unidentate and bidentate entering groups was made a few years ago for the reactions of [Pt(bipy)Cl_2] with a series of amines. A general pattern emerged, of lower activation enthalpies and more negative activation entropies for the bidentate entering groups (Table 3).[42] The investigation has now been extended to other bidentate (SS, NS, and OS) entering groups. A similar, though less pronounced, kinetic pattern emerges (Table 3), and can again be ascribed to the formation of a more compact transition state with the bidentate entering groups. This compactness is thought to arise from interaction between the other end of the bidentate entering ligand and a chloride of the substrate. There is one exception to the general pattern, and that is when ethanolamine is the entering group. The odd behaviour here can readily be explained by the reluctance of the oxygen atom of this bidentate ligand to become bound to the platinum.[43]

Table 3 *Activation parameters for the reaction of* [Pt(bipy)Cl_2] *with uni- and bidentate entering groups* (L) *in methanol*

L [*donor atom*(*s*)]	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
py (N)	16.3	−15	42
Bu^nNH_2 (N)	15.7	−14	
en (NN)	11.2	−28	
Et_2S (S)	10.9	−27	43
$HSCH_2CH_2SH$ (SS)	11.5	−31	
$HSCH_2CH_2NH_2$ (NS)	9.7	−37	

Kinetic parameters for the reaction of [Pt(bipy)Cl_2] with diethyl sulphide were obtained in the work described in the previous paragraph, as necessary information for the comparisons with bidentate N- and S-bonding ligands.[43] Rate constants and activation parameters for the reactions of [Pt(dien)X]$^+$, where X = Cl, Br, or I, with dialkyl sulphides have also been determined. These results may be compared with known kinetic parameters for reactions of uncharged platinum(II) complexes with thioethers. The reactions of

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[42] L. Baracco, L. Cattalini, J. S. Coe, and E. Rotondo, *J. Chem. Soc.* (*A*), 1971, 1800.
[43] E. Rotondo, V. Marsala, L. Cattalini, and J. S. Coe, *J.C.S. Dalton*, 1972, 2546.

$[Pt(dien)X]^{2+}$ are stated to occur by a two-step mechanism. It is argued, from reactivity trends for various compounds rather than from any direct evidence for an intermediate of significant lifetime, that it is the second step, the breakdown of a five-co-ordinate species $[Pt(dien)X(SR_2)]^{2+}$, that is rate-determining.[44] Kinetic parameters are also reported for the reaction of $[Pt(dien)Br]^+$ with methylamine and with ethylamine.[35]

Ring Closure. Intramolecular ring closure represents a variation on the theme of the previous section, in that the entering group is already attached at the other end of the molecule to the platinum(II). In the case of postulated intermediates containing, for example, unidentate oxalate or bipyridyl ligands, ring closure is generally fast. However, if the potentially chelating ligand bonds through one nitrogen and one oxygen, the much greater enthusiasm of platinum(II) to bond to the former often permits the isolation of unidentate ligand complexes which undergo slow ring closure by platinum–oxygen bond formation. The most commonly encountered ligand of this type is glycine. The rates of ring closure, with concomitant expulsion of chloride, of the *cis*- and *trans*-isomers of the $[Pt(NH_3)(gly)Cl_2]^-$ anion differ by a factor of 16 at 20 °C. This reactivity difference can readily be explained in terms of the relative *trans* effects of ammonia and of chloride on the ease of departure of the leaving chloride ion.[46] Rates of ring closure of *trans*-$[Pt(NH_3)(gly)X_2]^-$ anions in mixed aqueous solvents decrease as the proportion of the organic cosolvent increases. This is the usual pattern for loss of halide from platinum(II), as indeed from cobalt(III). The rates of ring closure do not correlate satisfactorily with the dielectric constants of the solvent mixtures. However, the authors claim that their results fit the expression

$$k_{obs} = k_1 + k_2[OH_2]^2$$

If this is not a fortuitous fit, then a mechanism of two parallel reactions, one involving two water molecules in the transition state and the other none, may be indicated. Though the rates of ring closure vary markedly with solvent composition, activation parameters are the same within experimental uncertainty in all the solvent mixtures (aqueous alcohols, aqueous acetone) studied.[47]

Of the two ring closures in the reaction

$$trans\text{-}[Pt(glyH)_2Br_2] \longrightarrow trans\text{-}[Pt(gly)_2] + 2H^+ + 2Br^-$$

it is the second which is thought to be rate-determining. This second ring closure consists of two parallel reactions, of (7) and its ligand-protonated derivative (8). Activation enthalpies are 18.1 ± 0.5 and 16.4 ± 0.2 kcal mol^{-1}

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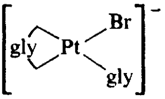
[44] S. C. Chan and S. B. Tong, *Inorg. Chim. Acta*, 1971, **5**, 634.

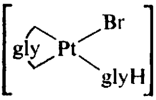
[45] S. C. Chan and F. T. Wong, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3278.

[46] L. M. Volshtein and L. F. Krylova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1648.

[47] L. M. Volshtein, L. F. Krylova, A. V. Belyaev, and I. G. Luk'yanova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1025.



(7)



(8)

respectively, and activation entropies are -16.9 and -25.6 cal deg^{-1} mol^{-1} respectively.[48]

Ring closure is also observed in the reactions of *cis*- or *trans*-$[Pt(NH_2CH_2CH_2OH)(L)Cl_2]$, where L $=$ NH_3, $NH_2CH_2CH_2OH$, or py, with bases. The kinetics of these reactions have been studied, and a mechanism has been proposed. The *cis* influence on ring closure was found to decrease in the order py $>$ $NH_2CH_2CH_2OH > NH_3$; the *trans* influences of these three ligands were very similar.[49]

Effects of Non-reacting Ligands. The longest established effect of non-reacting ligands on rates of reactions of platinum(II) complexes is the *trans* effect. Published results up to 1970 have been collected and compared, albeit in a journal not readily accessible to non-Russian readers.[50] Certain complications arise when one tries to apply the idea of hard and soft acids and bases to complexes containing a soft ligand and a soft metal, a situation common in platinum(II) chemistry. Consideration of kinetic and structural effects, the *trans* effect (*i.e.* kinetics), and the *trans* influence (ground state) have led Pearson to the following general rule: 'Two soft ligands in mutual *trans* positions will have a destabilizing effect on each other when attached to class *b* metal atoms.'[51] *cis*-Effects in platinum(II) substitutions have been investigated by way of chloride replacement by ammonia in *trans*-$[Pt(PEt_3)_2Cl_2]$, *trans*-$[Pt(PEt_3)(NH_3)Cl_2]$, and *trans*-$[Pt(NH_3)_2Cl_2]$, in methanol solution. As chloride leaves from opposite chloride in each case, one can monitor the relative *cis* effects of ammonia and triethylphosphine. Despite certain difficulties, such as parallel solvation and ammonolysis for the bis-ammonia complex, it proved possible to establish that there is only a very small difference between the *cis* effect of ammonia and that of triethylphosphine. Indeed the difference corresponds to a factor of only two for the rate constants.[52]

Dithio-oxamide (dtoa) has a high affinity for platinum(II), so the following reaction,

$$[Pt(phen)Cl_2] + dtoa \longrightarrow [Pt(phen)(dtoa)]^{2+} + 2Cl^-$$

goes to completion for the phen complex and for analogous complexes con-

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[48] G. D. Mal'chikov, T. R. Lastushkina, and L. M. Volshtein, *Russ. J. Inorg. Chem.*, 1972, **17**, 1414.

[49] Yu. N. Kukushkin, V. B. Ukraintsev, and A. I. Mokhov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1172.

[50] B. I. Peshchevitskii, G. D. Mal'chikov, and R. L. Shchekochikhina, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1972, 67 (*Chem. Abs.*, 1972, **77**, 79 970n).

[51] R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.

[52] R. G. Gunther and D. S. Martin, *Inorg. Chim. Acta*, 1972, **6**, 81.

taining substituted phen ligands. The rate-determining step is displacement of the first chloride; the usual two-term rate law [equation (4) above] holds. For a range of complexes of nine substituted phenanthrolines, and of 2,2′-bipyridyl, there is a linear free-energy relationship correlating second-order rate constants and basicities of the substituted phenanthrolines. This suggests that the effects of the substituents on reactivities operate predominantly through the σ-bonding between the nitrogen and the platinum. It is possible to rationalize small deviations from the linear plot in terms of small additional π-bonding effects.[53]

An empirical equation has been established to correlate reactivities observed in reactions of $[PtX_4]^{2-}$, where X = Cl or Br, and of $[PtLCl_3]^-$, where L = ammonia, methylamine, or pyridine, with a range of nitrogen bases.[54]

Isomerization and Inversion. The kinetics of the uncatalysed isomerization *cis*-→*trans*-$[Pt(PEt_3)_2(o\text{-tolyl})Cl]$ have been studied over the temperature range 25—45 °C in methanol and in ethanol. Isomerization rates vary with chloride concentration; the dependence is of the form $k/(1 + k'[Cl^-])$.[55] Photoisomerization of *cis*-$[Pt(gly)_2]$ is mentioned in the next section.

An earlier investigation of phosphine-catalysed isomerization of platinum(II) complexes resulted in the proposal of a mechanism in which pseudorotation in a five-co-ordinate intermediate played a central role.[56] The authors of a recent study of phosphine-catalysed isomerization of *cis*-$[PtL_2X_2]$ prefer a consecutive displacement reaction, with an ionic intermediate $[PtL_2L^1X]^+X^-$. Their conclusion is based on n.m.r. determinations both of isomerization and of ligand-exchange rates, on solvent effects on rates, and on the stabilities of species $[PtLL^1X_2]$ relative to $[PtL_2X_2]$ and $[PtL^1_2X_2]$.[57] Although these results are convincingly consistent with a consecutive-displacement mechanism, they do not seem to rule out the alternative pseudorotation scheme.

It has been proposed that the *trans*-isomer of $[Pt(C_2H_4)(\text{isoquinoline})Cl_2]$ itself consists of two isomers, one with the isoquinoline ligand in the $PtCl_2$ plane and the other with the isoquinoline perpendicular to this plane. An n.m.r. study of this system was interpreted in terms of a relatively high barrier to rotation about the platinum–nitrogen bond. This barrier was thought to originate in hydrogen-bonding interactions involving the —CH— group adjacent to the ligating nitrogen of the isoquinoline.[58] However, a subsequent reinvestigation of this system has shown that the kinetic processes responsible for the observed ^1H n.m.r. spectra are *cis*$\rightleftharpoons$*trans* isomerization and ligand exchange.[59]

[53] R. C. Conrad and J. V. Rund, *Inorg. Chem.*, 1972, **11**, 129.

[54] Yu. N. Kukushkin and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, 1972, **17**, 1407.

[55] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Accad. Peloritana Pericolanti, Cl. Sci. fis. mat. natur.*, 1970, **50**, 35 (*Chem. Abs.*, 1972, **77**, 10 140z).

[56] P. Haake and R. M. Pfeiffer, *Chem. Comm.*, 1969, 1330; *J. Amer. Chem. Soc.*, 1970, **92**, 4996.

[57] D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 1102.

[58] L. Spaulding and M. Orchin, *J.C.S. Chem. Comm.*, 1972, 1249.

[59] J. Powell and D. G. Cooper, *J.C.S. Chem. Comm.*, 1973, 486.

Inversion at the sulphur in platinum(II) and palladium(II) complexes containing thioether ligands can be monitored by n.m.r. spectroscopy.[60] Inversion is faster at sulphur bonded to palladium(II) than at sulphur bonded to platinum(II). N.m.r. studies of the platinum(II) compounds are more satisfactory, as it is possible to tell from the persistence of $^{195}Pt—S—C—^{1}H$ coupling that the observed process is intramolecular in character. To avoid complications from *cis*⇌*trans* isomerization, complexes $[Pt(RSCH_2CH_2SR)X_2]$ containing a chelating dithioether were studied. The very small effect of solvent variation (dimethyl sulphoxide, nitrobenzene, deuteriochloroform, and $CDCl_3$–CF_2Cl_2) on inversion rates is as one would expect for an intramolecular process. The rate of inversion increases as the *trans* influence of the ligand X increases.[61]

Photochemistry. The *cis*-isomer of $[PtCl_2(py)_2]$ undergoes two primary photoprocesses, isomerization and dissociation, with quantum yields of *ca.* 0.04 and 0.025 respectively (313 nm irradiation). *trans*-$[PtCl_2(py)_2]$ also undergoes parallel photoisomerization and dissociation, but with very much lower quantum yields of *ca.* 10^{-3}.[62] The effect of acidity on the photochemistry of *cis*-$[Pt(gly)_2]$ has been examined – the balance between photoisomerization and photodissociation is pH-dependent.[63] Photochemical *cis*⇌*trans* isomerization of $[Pt(gly)_2]$ is sensitized by pyrazine or by xanthone, but not by thioxanthone, quinoline, naphthalene, or biacetyl. Ni^{2+} quenches the photoisomerization, but Mn^{2+} does not. The sensitization process was shown to involve triplet–triplet intermolecular energy transfer.[64]

The predominant photoreaction of the $[Pt(C_2H_4)Cl_3]^-$ anion is loss of ethylene, which is accompanied by a little loss of *cis*-chloride. This behaviour contrasts with the corresponding thermal reaction, where the predominant reaction is loss of the chloride *trans* to the ethylene. This contrast between thermal and photochemical behaviour is novel: most photochemical reactions of platinum(II) complexes follow the same course as the corresponding thermal reactions, but occur more quickly. The photoaquation of the ethylene ligand is subject to sensitization by acetone or by acetophenone, and therefore probably occurs *via* the first excited singlet state.[65] A general model for photosubstitution reactions has been described, which is relevant to octahedral as well as to square-planar complexes.[66]

Bridged Complexes. The compounds $[Pt_2(OH)_2L_4]^{2+}$, in which L = PEt_3, PPh_3, or py, are kinetically interesting in that the μ-hydroxo-bridges remain

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[60] R. J. Cross, G. J. Smith, and R. Wardle, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 191.
[61] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.
[62] L. Moggi, G. Varani, N. Sabbatini, and V. Balzani, *Mol. Photochem.*, 1971, **3**, 141.
[63] F. Bolletta, M. Gleria, and V. Balzani, *Mol. Photochem.*, 1972, **4**, 205.
[64] F. Bolletta, M. Gleria, and V. Balzani, *J. Phys. Chem.*, 1972, **76**, 3934.
[65] P. Natarajan and A. W. Adamson, *J. Amer. Chem. Soc.*, 1971, **93**, 5599.
[66] M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, 1973, **5**, 165.

intact under conditions, for instance treatment with tertiary phosphines, in which analogous μ-chloro-complexes are rapidly cleaved.[67]

Palladium(II).—*Aquation and Anation.* In aqueous perchloric acid the aquation of $[Pd(NH_3)_4]^{2+}$ takes place in four consecutive and kinetically distinct steps, to give ultimately $[Pd(OH_2)_4]^{2+}$. Rate constants decrease steadily as the number of ammonia ligands is reduced. Activation enthalpies for the four steps all lie between 21 and 24 kcal mol^{-1}; activation entropies are between +4 and −4 cal deg^{-1} mol^{-1}.[68] Kinetic parameters for the aquation of $[PdCl_4]^{2-}$ and of $[PdBr_4]^{2-}$ appear from two sources;[69, 70] they are compared in Table 4. Faster aquation rates for $[PdBr_4]^{2-}$ compared with $[PdCl_4]^{2-}$ appear to arise solely from activation enthalpy differences.[69] Kinetic parameters for the reverse anation

Table 4 *Kinetic parameters for aquation of* $[PdX_4]^{2-}$ *anions*

X	k_{25}/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
Cl	5.6	15.2±2	−12±5	69
	8.9	12±2	−13±6	70
Br	25	12.9±2	−11±5	69
	19	11±1	−15±3	70

$$[PdX_3(OH_2)]^{4-} + X^- \longrightarrow [PdX_4]^{2-} + H_2O$$

have also been determined.[69, 70] Reactivities of these palladium complexes are compared with their platinum analogues.[70] Activation parameters for the aquation of *trans*-$[Pd(NH_3)_2(OH_2)(NO_2)]^+$ are $\Delta H^{\ddagger} = 15.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16$ cal deg^{-1} mol^{-1}, in aqueous solution.[71]

One type of reaction where a palladium(II)–platinum(II) reactivity comparison is not possible is that of substitution at $[Pd(OH_2)_4]^{2+}$. Indeed substitution reactions of this cation provide a uniquely interesting case of complex formation from a square-planar aquo-cation. The rate law for the reaction of $[Pd(OH_2)_4]^{2+}$ with chloride or bromide ion is

$$-d[Pd(OH_2)_4^{2+}]/dt = k_2[Pd(OH_2)_4^{2+}][X^-] \qquad (5)$$

A simple associative mechanism seems likely. The activation enthalpies for the reactions with chloride and with bromide are both 10 kcal mol^{-1}; the activation entropies are −6 and −3 cal deg^{-1} mol^{-1} respectively. Whereas anation of $[Pd(OH_2)_4]^{2+}$ has the simple rate law of equation (5), anation of

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[67] G. W. Bushnell, K. R. Dixon, R. G. Hunter, and J. J. McFarland, *Canad. J. Chem.*, 1972, **50**, 3694.

[68] W. J. DeBerry and R. A. Reinhardt, *Inorg. Chem.*, 1972, **11**, 2401.

[69] M. N. Vargaftik, V. A. Igoshin, and Ya. K. Syrkin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1972, 1426 (*Chem. Abs.*, 1972, **77**, 93 296d).

[70] L. I. Elding, *Inorg. Chim. Acta*, 1972, **6**, 683.

[71] V. D. Panasyuk and T. I. Denisova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1342.

$[Pd(OH_2)Cl_3]^-$ follows the two-term rate law [equation (4)] more usually encountered for square-planar complexes.[70] An associative mechanism is also proposed for the reaction of $[Pd(OH_2)_4]^{2+}$ with aromatic amines.[72]

Solvent Effects. Rate constants and activation parameters for the reactions

$$[Pd(Et_4dien)X]^+ + Y^- \longrightarrow [Pd(Et_4dien)Y]^+ + X^-$$

where X = Cl, Br, or I and Y = Cl, Br, or I, have been determined in a range of solvents in order to gain more detailed knowledge on the reaction mechanism for these pseudo-octahedral systems. Ancillary n.m.r. experiments showed that the ability of the solvents used to interact with the palladium(II) centre is in the order $H_2O > MeOH > EtOH \sim DMSO > CH_2Cl_2$. The low position of DMSO in this series is due to the steric hindrance by the bulky ligand to favourable palladium(II)–sulphur interaction. A selection of the kinetic results obtained is given in Table 5. The results in Section A of this Table show that for a given complex in a given solvent the kinetic parameters are, as one would expect for a pseudo-octahedral substrate, independent of the nature of the incoming ligand. In protic solvents, the reactivity of $[Pd(dien)X]^+$ decreases in the order X = Cl > Br > I; this reactivity decrease stems from the variation in activation enthalpies rather than that in activation entropies (Section B of Table 5). These observations suggest an associative type of mechanism with a transition state $[Pd(Et_4dien)X(solvent)]^+$. In such a mechanism the activation enthalpy would be expected to vary according to the respective strengths of the Pd—X bonds being stretched, but as the halide ion

Table 5 *Selected kinetic parameters for substitution reactions*
$[Pd(Et_4dien)X]^+ + Y^- \rightarrow [Pd(Et_4dien)Y]^+ + X^-$ (*from ref.* 73)

X	Y	*Solvent*	$10^5k/s^{-1}$ (*temperature*/°C)	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal deg^{-1} mol^{-1}
Section A					
Cl	Br	EtOH	8.1 (45.4)	18.6 ± 1.0	-19 ± 3
Cl	I	EtOH	8.0 (45.4)	18.0 ± 0.5	-21 ± 2
I	Cl	H_2O	140 (40.0)	18.6 ± 0.5	-13 ± 2
I	Br	H_2O	140 (40.0)	18.4 ± 0.5	-13 ± 2
Section B					
Cl		H_2O		16.5	−16
Br		H_2O	550 (40.2)	17.6	−13
I		H_2O	140 (40.0)	18.5	−13
Section C					
Br	Cl	DMSO	43 (41.6)	20.4 ± 1.0	-7 ± 2
I	Cl	DMSO	96 (41.6)	19.6 ± 0.5	-10 ± 2

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[72] M. N. Vargaftik, E. D. German, R. R. Dogonadze, and Ya. K. Syrkin, *Doklady Akad. Nauk S.S.S.R.*, 1972, **206**, 370 (*Chem. Abs.*, 1973, **78**, 8494v).

X^- is still a long way from leaving there may not be much difference in solvation requirements, and hence in activation entropies, in transition-state formation for the three halogeno-complexes. Reactivity trends in the aprotic solvents dimethyl sulphoxide and dimethylformamide (*cf.* Section C of Table 5), where the fastest substitution into $[Pd(dien)X]^+$ occurs for X = I, are better interpreted in terms of a dissociative mechanism, in which the solvation of the leaving halide is a significant factor but solvation at the palladium(II) is not.[73]

Rates of solvolytic replacement of the first and second chlorides of *trans*-$[Pd(py)_2Cl_2]$[74] and of the second chloride of *cis*-$[Pd(en)Cl_2]$[71] have been determined conductimetrically in a variety of mixed aqueous solvents. In general the aquation rates decrease as the proportion of organic cosolvent increases, which is the same trend as observed for aquation of platinum(II)–chloride and cobalt(III)–chloride complexes. Linear plots of logarithms of rate constants against reciprocals of dielectric constants were said to be consistent with a bimolecular mechanism for aquation. Activation parameters have been determined for several systems, and here there are some odd features. Thus the activation parameters for aquation of $[Pd(en)(OH_2)Cl]^+$ are very similar in 30% methanol, 30% dioxan, and water, but the activation energy for aquation in 30% acetone is claimed to be 11.8 kcal mol^{-1} larger than in water.[71] Again the activation energy for aquation of *trans*-$[Pd(py)_2Cl_2]$ in water is stated as 38.1 kcal mol^{-1}, drops to below 17 kcal mol^{-1} on addition of 10% of organic cosolvent (methanol, acetone, dimethylformamide, dioxan), and then stays approximately constant as the proportion of organic cosolvent is further increased.[74]

Leaving Groups. A unique example of determination of mechanism by the nature of the leaving group from palladium(II) has been described. The reaction of the $[Pd(Et_4dien)(L)]^+$ cations with bromide ion follow the 'pseudo-octahedral' rate law of equation (6),

$$-d[\text{complex}]/dt = k_1[\text{complex}] \qquad (6)$$

for L = SCN, NCS, or NCSe. However, when L = SeCN, the rate law is of the 'normal' two-term type associated with complexes containing ligands less bulky than Et_4dien:

$$-d[\text{complex}]/dt = \{k_1 + k_2[Br^-]\}[\text{complex}] \qquad (7)$$

The activation entropy corresponding to the k_2 term of equation (7) is +2 cal deg^{-1} mol^{-1}; this modestly positive value is consistent with an associative mechanism for reaction with bromide. A two-term rate law analogous to equation (7) also operates for the reactions of this $[Pd(Et_4dien)(SeCN)]^+$ cation with iodide, azide, or cyanide. It is noteworthy that the order of k_2 values is $N_3^- > Br^- > I^-$, with the reactivity trend apparently controlled by size

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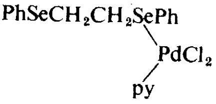
[73] R. Roulet and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 2101.

[74] V. D. Panasyuk, T. I. Denisova, and S. K. Rybak, *Russ. J. Inorg. Chem.*, 1972, **17**, 874.

rather than by nucleophilicity towards palladium(II). Such a dependence on size of incoming group is just what one would expect for associative reactions with a complex containing the bulky and obstructional ligand Et_4dien.[75]

Kinetic parameters for the displacement of the chelating diselenium ligand from $Pd(PhSeCH_2CH_2SePh)Cl_2$ by (substituted) pyridines have been evaluated in order to compare this ligand with its disulphur analogue as a leaving group. The rate-determining step is the generation of (9); subsequent reaction of (9) with another molecule of py is rapid. Activation enthalpies for the displacement of the diselenium ligand are slightly less than those for displacement of the disulphur ligand; activation entropies for the displacement of the diselenium ligand are rather more negative (Table 6). These differences may arise from different sizes and different π-bonding contributions. It is suggested that the bonding is relatively stronger in the transition states for displacement of the diselenium ligand, and that these transition states are more compact than those for displacement of the analogous disulphur ligand.[76]



(9)

Table 6 *Activation parameters for the reaction of* $Pd(PhSeCH_2CH_2SePh)Cl_2$ *and of* $Pd(PhSCH_2CH_2SPh)Cl_2$ *with pyridines (from ref.* 76)

	$\Delta H^{\neq}$/kcal mol^{-1}		$\Delta S^{\neq}$/cal deg^{-1} mol^{-1}	
Incoming ligand	Se—Se	S—S	Se—Se	S—S
py	7.6	8.9	−30	−25
3-Mepy	7.0	9.3	−32	−23
2,4-diMepy	10.4	14.0	−27	−16

The reaction of $Pd(biguanide)_2$ in aqueous hydrochloric acid–sodium chloride solutions takes place in two stages:

$$[Pd(big)_2] \longrightarrow [Pd(big)Cl_2]^- \longrightarrow [PdCl_4]^{2-}$$

The rate law for the first stage is

$$-d[Pd(big)_2]/dt = \{k_1[H^+][Cl^-] + k_2[H^+]^2[Cl^-]^2\}[Pd(big)_2]$$

The rate law for the second stage is exactly analogous. Rate constants and activation parameters for each pathway are reported.[77]

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[75] K. A. Johnson, J. C. Lim, and J. L. Burmeister, *Inorg. Chem.*, 1973, **12**, 124.

[76] L. Cattalini, J. S. Coe, F. Faraone, V. Marsala, and E. Rotondo, *Inorg. Chim. Acta*, 1972, **6**, 303.

[77] D. Banerjea and P. Banerjee, *Z. anorg. Chem.*, 1972, **393**, 295.

Rate laws for the reactions of square-planar dithiolatopalladium(II) complexes with uni- or bi-dentate nucleophiles are usually second-order in form, with a first-order dependence on each reactant. Rates of reaction of these palladium(II) complexes are much less than had been anticipated by extrapolation from reaction rates of similar nickel(II) complexes. This lower-than-expected reactivity may be ascribed to the lower stability of five-co-ordinate palladium(II) complexes, which will be intermediates or transition states in these reactions.[78]

Entering Groups. The kinetics of the reactions of $[PdCl_4]^{2-}$ with 2,2′-bipyridyl (*cf.* $[PtCl_4]^{2-}$ + bipy, above)[41] and with ethylenediamine[79] have been investigated. Whereas the reaction of $[PdCl_4]^{2-}$ with 2,2′-bipyridyl follows a simple second-order rate law, reactions of $[Pd(tu)_4]^{2+}$ with a range of amino-acids follow the usual two-term rate law [equation (4)] for substitution in square-planar complexes. There appears to be some correlation between reaction rates and pK values of the amino-acids.[80] The reactions of *cis*-$[Pd(p\text{-}YC_6H_4NC)(L)X_2]$ with *p*-substituted anilines[81] are discussed in the chapter on reactions of co-ordinated ligands.

Effects of Non-reacting Ligands. The most noticeable effect of non-leaving ligands on reactivities of square-planar compounds is that of the change in rate law from the usual two-term to the 'pseudo-octahedral' one-term form when a bulky ligand such as Et_4dien is co-ordinated to the metal centre. A series of reactions of the 'pseudo-octahedral' type has been discussed in the section on solvent effects, and an exception to 'pseudo-octahedral' behaviour noted in the leaving-group section.[75]

The relative kinetic *cis* effects of halide ligands on substitution at palladium(II) have been established by monitoring the reactions of *trans*-$[Pd(4\text{-}Cl\text{-}py)_2X_2]$ and of *trans*-$[Pd(py)_2X_2]$, where X = Cl, Br, or I, with amines or with thioethers in 1,2-dimethoxyethane solution at 25 °C. The usual two-term rate law [equation (4)] applies to these reactions, but as the k_1 terms were all small, the *cis*-effect trends have been reported only for the k_2 terms. The *cis* effects on substrate discrimination are in the order $I > Br > Cl$ for reaction with amines, and $Cl > Br > I$ for reaction with thioethers. This pattern is the same as that established for platinum(II) complexes.[82]

Isomerization and Inversion. The *cis*⇌*trans* isomerization of $[Pd\{PMe_2(o\text{-}tolyl)\}_2Cl_2]$ in chloroform solution in the presence of tertiary phosphines is thought to take place by a consecutive-displacement reaction (Scheme 1). The same mechanism also probably operates in methanol solution.[83] Thus studies of catalysed isomerization, both here and at platinum(II), seem to favour the

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[78] R. G. Pearson and M. J. Hynes, *J. Coordination Chem.*, 1972, **1**, 245.

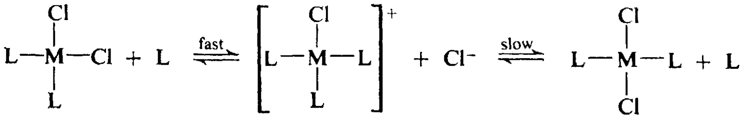
[79] R. Roulet and R. Ernst, *Helv. Chim. Acta*, 1971, **54**, 2357.

[80] O. Farooq and A. U. Malik, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3410.

[81] B. Crociani, T. Boschi, M. Nicolini, and U. Belluco, *Inorg. Chem.*, 1972, **11**, 1292.

[82] L. Cattalini, G. Marangoni, and M. Martelli, Proceedings of the 3rd Symposium on Co-ordination Chemistry, Debrecen, Hungary, 1970, vol. 1, p. 347.

[83] D. G. Cooper and J. Powell, *Canad. J. Chem.*, 1973, **51**, 1634.



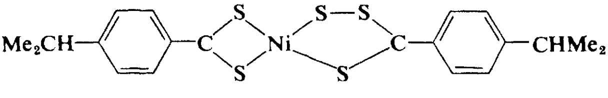
Scheme 1

consecutive-displacement mechanism rather than the alternative route involving the formation of, and pseudorotation in, a five-co-ordinate intermediate.

Linkage isomerization of thiocyanate in $[Pd(Et_4dien)(SCN)]^+$ takes place more rapidly than that of selenocyanate in $[Pd(Et_4dien)(SeCN)]^+$. This observation is consistent with a dissociative mechanism, with relief of steric strain in transition-state formation, for isomerization. The activation enthalpy for the isomerization of $[Pd(Et_4dien)(SCN)]^+$ to the N-bonded thiocyanato-isomer is 19.8 kcal mol^{-1} and for $[Pd(Et_4dien)(SeCN)]^+$ to the N-bonded isomer it is 21.0 kcal mol^{-1}; the respective activation entropies are -10 and -5 cal deg^{-1} mol^{-1}.[75]

Inversion at sulphur bonded to palladium(II) has already been mentioned with inversion at sulphur bonded to platinum(II) (p. 154).[60, 61]

Nickel(II).—The reaction of the (per)thiocumato-complex (10), $Ni(dtcu)_2S$, with triphenylphosphine is second-order, with activation parameters



(10)

$\Delta H^{\ddagger} = 6.6 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -37 \pm 2$ cal deg^{-1} mol^{-1}. The products of this reaction are $SPPh_3$ and $Ni(dtcu)_2$. The reaction of the diperthio-complex $Ni(dtcu)_2S_2$ with triphenylphosphine proceeds by a two-stage mechanism, but the rates proved too fast for monitoring by the conventional techniques available to the authors.[84]

Other kinetic studies concerned with square-planar nickel(II) complexes include those of $[Ni(trigly)]^-$ with cyanide,[85] redistribution reactions involving pairs of bis-bidentate nickel(II) complexes,[86] and square-planar$\rightleftharpoons$tetrahedral interconversions of $[Ni(tertiary\ phosphine)_2X_2]$ compounds.[87]

Gold(III).—Earlier work on the reaction of $[AuCl_4]^-$ with ethylenediamine was interpreted in terms of rate-determining reaction of $[Au(OH)Cl_3]^-$ with the conjugate acid of ethylenediamine.[88] Subsequently the kinetic pattern of the

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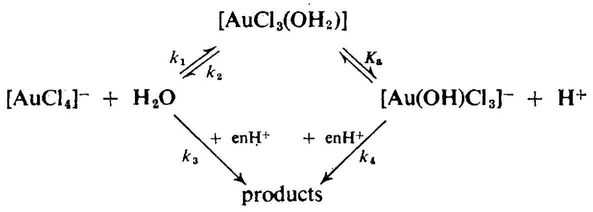
[84] J. P. Fackler, J. A. Fetchin, and D. C. Fries, *J. Amer. Chem. Soc.*, 1972, **94**, 7323.
[85] G. K. Pagenkopf, *J. Amer. Chem. Soc.*, 1972, **94**, 4359.
[86] J. C. Lockhart and W. J. Mossop, *J.C.S. Dalton*, 1973, 662.
[87] L. Que and L. H. Pignolet, *Inorg. Chem.*, 1973, **12**, 156.
[88] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 1969, **3**, 29.

reaction between $[AuCl_4]^-$ and diethylenetriamine suggested that the interpretation of the $[AuCl_4]^-$–ethylenediamine reaction may have been oversimplified.[89] This reaction has therefore been reinvestigated in detail. The reaction sequence is now established to be that shown in Scheme 2; this closely resembles the $[AuCl_4]^-$–diethylenetriamine system.[90] Rate constants and activation parameters have been determined for the reaction of $[AuCl_4]^-$ with bromide ion and with azide ion in dimethylformamide;[91] these results are compared with kinetic parameters for the same reactions in methanol solution[92] in Table 7.



Scheme 2

Table 7 *Kinetic parameters for the reactions of* $[AuCl_4]^-$ *with bromide and with azide*

Nucleophile	*Solvent*	k_2/l mol^{-1} s^{-1} (*temperature*/°C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
Br^-	DMF[a]	0.61±0.04 (24.8)	14.6±0.5	−11±1	91
	MeOH	0.14 (25.0)	12.3	−22	92
N_3^-	DMF[a]	1.90±0.06 (24.9)	10.4±0.5	−23±1.5	91
	MeOH	0.35 (25.0)	6.5	−39	92

[a] I = 0.1 mol l^{-1} ($LiClO_4$).

The hydrolysis of $[AuCl_4]^-$ had previously been studied in acetate buffers; it has now also been studied in strongly acid solution, up to 2M-$HClO_4$. From these kinetic results a value of 0.63 for the pK of $[Au(OH_2)Cl_3]$ has been estimated, which compares well with the most recent non-kinetic estimate of

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[89] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 1969, **3**, 303.

[90] P. van Z. Bekker, W. J. Louw, and W. Robb, *Inorg. Chim. Acta*, 1972, **6**, 564.

[91] G. I. Shamovskaya and B. I. Peshchevitskii, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1972, 53 (*Chem. Abs.*, 1973, **78**, 76 322n).

[92] L. Cattalini, A. Orio, and M. L. Tobe, *J. Amer. Chem. Soc.*, 1967, **89**, 3130.

0.75 ± 0.26.[93] A paper on thermodynamic properties in the $[AuCl_4]^-$–water system provides useful background information to kinetic studies of aquation of the $[AuCl_4]^-$ anion.[94]

The reactions of [Au(dien – H)Cl]$^{+}$* with thiocyanate, bromide, or nitrate in methanol solution obey the usual two-term rate law. The values for the second-order rate constants are around ten times smaller in methanol than in water. The reaction of [Au(dien – H)Cl]$^+$ with hydroxide ion is a two-stage process, in which presumably the second stage involves chelate ring opening.[95] Reactions of [Au(Me_2dien – H)Cl]$^+$ and of [Au(Me_4dien – H)Cl]$^+$ with bromide follow the usual two-term rate law [equation (4)]; the methyl substituents do not lead to pseudo-octahedral behaviour. The reaction of [Au(Et_2dien – H)Cl]$^+$ with bromide is thought to involve chelate ring opening prior to bromide attack at the gold(III) centre.[96]

The appearance of several references on inversion at sulphur bonded to platinum(II) or palladium(II) (see for instance the appropriate sections earlier in this chapter) has been followed by a report of an n.m.r. study of inversion at sulphur bonded to gold(III), in $[\{(PhCH_2)_2S\}AuCl_3]$, and to gold(I), in $[\{(PhCH_2)_2S\}AuCl]$. The inversion at sulphur bonded to gold(III) is intramolecular, with $\Delta H^{\ddagger} = 20.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9.5$ cal deg^{-1} mol^{-1} in deuteriochloroform solution. Although the inversion mechanism where the gold is transferred effectively from one lone-pair to the other on the sulphur, in other words the mechanism proposed for inversion of sulphur bonded to platinum(II) or palladium(II), is probably operative here, one cannot entirely rule out a reversible redox process.[97]

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*dien – H represents dien minus an imino-proton.

[93] P. van Z. Bekker and W. Robb, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 849.

[94] B. I. Peshchevitskii, V. I. Belevantsev, and N. V. Kurbatova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1007.

[95] B. I. Peshchevitskii and G. I. Shamovskaya, *Russ. J. Inorg. Chem.*, 1972, **17**, 1386.

[96] D. L. Fant and C. F. Weick, *Inorg. Chem.*, 1973, **12**, 1864.

[97] F. Coletta, R. Ettore, and A. Gambaro, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 667.

3

Inert Metal Complexes: Co-ordination Numbers Six and Higher

BY J. BURGESS

1 Introduction

As in previous volumes, this chapter on substitution reactions of transition-metal complexes of co-ordination number six and higher is subdivided by reaction type – aquation, base hydrolysis, formation, exchange and replacement, and isomerization – with further subdivision according to the central cation. Thus most references to substitution at cobalt(III) and chromium(III) are to be found in Sections 2 and 3 respectively, but further references to substitution at these centres will be found in subsequent sections of this chapter. Substitution at ligands rather than at central metal atoms is discussed in Chapter 5. Inert metal complexes whose central metal ions have co-ordination numbers higher than six are sufficiently rare for the appropriate references to be collected together in the final section of this chapter. In this present introductory section we mention references of general application to several aspects of substitution mechanisms, particularly those which compare substitution mechanisms at different metal centres. General reviews of the kinetics and mechanisms of substitution in complexes include one which also deals with the generation of thermodynamically unstable intermediates[1] and one which is concerned with applications in analytical chemistry.[2]

The complexes of cobalt(III) and of chromium(III) remain the most popular subjects for studies of octahedral substitution at inert centres. It now seems firmly established that substitution at halogeno–amine complexes of cobalt(III) is always dissociative in character, but there is an increasing amount of evidence which favours a degree of associative character to at least some substitutions at chromium(III).[3] Two experimental approaches which have recently given useful evidence for defining mechanisms of substitution at these two centres, and at rhodium(III), are the evaluation of volumes of activation and of so-called transition enthalpies. The results of these general studies will be described in the following paragraphs.

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[1] A. M. Sargeson, *Pure Appl. Chem.*, 1973, **33**, 527.

[2] I. P. Alimarin, *Pure Appl. Chem.*, 1973, **34**, 1.

[3] See, *e.g.* pp. 157—9 of Volume 2 of this Specialist Periodical Report.

Volumes of activation[4] for water exchange at the complexes $[M(NH_3)_5(OH_2)]^{3+}$, where M = Co, Cr, or Rh, are +1.2, −5.8, and −4.1 $cm^3 mol^{-1}$ respectively. The positive $\Delta V^{\ddagger}$ value for the cobalt(III) complex is consistent with a dissociative mechanism, whereas the negative $\Delta V^{\ddagger}$ values reported for the chromium(III) and rhodium(III) analogues suggest the operation of a different mechanism of greater associative character at these centres.[5] Volumes of activation for aquation of $[Cr(NH_3)_5X]^{2+}$ cations are −10.8, −10.2, and −9.4 $cm^3 mol^{-1}$ for the complexes with X = Cl, Br, and I, respectively. Thus these aquations, like water exchange at $[Cr(NH_3)_5(OH_2)]^{3+}$ and $[Cr(OH_2)_6]^{3+}$, appear on this evidence to be markedly associative in character and have been assigned an I_a mechanism. A plot of volumes of activation for aquation of $[Cr(NH_3)_5X]^{2+}$ cations against those for their cobalt(III) analogues has a slope of 0.43. This too suggests that these chromium(III) aquations proceed by a mechanism which differs greatly from the dissociative mechanism established for the aquation of the cobalt(III) complexes. Furthermore plots of activation volumes *versus* volumes of reaction for these $[ML_5X]^{2+}$ series of complexes have slopes of 0.6 for ML_5 = $Cr(OH_2)_5$, but of 1.0 for ML_5 = $Co(NH_3)_5$, which again indicates that the aquation mechanism for the chromium(III) complexes is much less dissociative in nature than that for the cobalt(III) series.[6]

The results of determinations of transition enthalpies indicate similar conclusions to those of activation-volume experiments. The transition enthalpy (ΔH_T) is the difference in enthalpy between the transition state and the products of a reaction. For series of compounds $[M(NH_3)_5X]^{2+}$ or $[M(OH_2)_5X]^{2+}$ reacting by a dissociative mechanism, one expects ΔH_T values to be similar for each complex in the series. For an associative mechanism one expects ΔH_T values to depend on the nature of X, for M—X bond breaking is an important aspect of the transition state to products process. The first application of this approach, to the mechanism of base hydrolysis of cobalt(III)-ammine-halide complexes, was noticeably successful.[7] More recent applications have been to aquation of the $[Co(NH_3)_5X]^{2+}$,[8] $[Rh(NH_3)_5X]^{2+}$,[9] and $[Cr(OH_2)_5X]^{2+}$ (ref. 10) series of cations. Plots of transition enthalpies against enthalpies of hydration of the respective leaving groups X^- are approximately linear. For the acid and base hydrolyses of the cobalt(III) complexes the slopes of such plots are both zero, consistent with a predominantly dissociative reaction. The plot for aquation of the $[Rh(NH_3)_5X]^{2+}$ series of complexes has a small negative slope, that for aquation of the $[Cr(OH_2)_5X]^{2+}$ series of complexes a larger negative slope.

[4] See C. A. Eckert, *Ann. Rev. Phys. Chem.*, 1972, **23**, 239 for a review of the determination of activation volumes.

[5] T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8357.

[6] G. Guastalla and T. W. Swaddle, *Canad. J. Chem.*, 1973, **51**, 821.

[7] D. A. House and H. K. J. Powell, *Chem. Comm.*, 1969, 382; *Inorg. Chem.*, 1971, **10**, 1583.

[8] H. K. J. Powell, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 157.

[9] H. K. J. Powell, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 891.

[10] H. K. J. Powell, *Austral. J. Chem.*, 1972, **25**, 1569.

These latter observations are consistent with significant associative character for the aquations of these rhodium(III) and chromium(III) complexes, with greater associative character for the latter series.

Both the activation-volume and transition-enthalpy approaches have indicated considerable associative character to the mechanisms of substitution at the chromium(III)* and rhodium(III) complexes studied. In contrast, other workers have published evidence for *D* [S_N1(lim)] substitution at other chromium(III) and rhodium(III) complexes.† One example is provided by chloride anation of the $[Rh(OH_2)_5Cl]^{2+}$ cation.[11] In this particular case the variation of rate with pH has permitted a distinction between a *D* and I_d mechanism, a distinction which is usually very difficult to make from kinetic studies of cationic complexes. Another rhodium(III) complex which is reported to undergo substitution by a *D* mechanism is the $[Rh(ox)_3]^{3-}$ anion.[12] Examples of chromium(III) complexes which react by a *D* mechanism include $[Cr(OH_2)_5Me]^{2+}$,[3] $[Cr(OH_2)_5I]^{2+}$, [3,13] $[Cr(OH_2)_5(CN)]^{2+}$,[14] and a porphyrin complex.[15] Thus the mechanism of substitution at rhodium(III) and at chromium(III) may depend greatly on the nature of the ligands bonded to the central cation. Not only does the *D* mechanism appear to operate for several rhodium(III) and chromium(III) complexes, it has also recently been postulated for substitution at several low-spin iron(II) complexes (see Sections 4 and 7 of this chapter) and at ruthenium(II) (see Section 6). Substitutions by a *D* mechanism at cobalt(III) have been reviewed.[16] The stereochemical aspects of Berry pseudorotation in the five-co-ordinate intermediates of this mechanism have been examined.[17] There have also been several recent demonstrations that the *D* mechanism operates at centres other than the octahedral complexes so far mentioned, for it has been postulated for, *e.g.*, ligand replacement at the

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* An attempt to rationalize conflicting evidence for an associative mechanism of DMSO exchange at $[Cr(DMSO)_6]^{3+}$ from the determined activation volume but for a dissociative mechanism for this exchange from the variation of exchange rate with solvent composition in DMSO–$MeNO_2$ mixtures is discussed in Section 7 of this chapter (see ref. 348).

† The contrast between the operation of *D* and *A* (or I_a) mechanisms at apparently rather similar centres is not quite as stark as it appears at first sight. Thus, for instance, the change from a cobalt(III) to an analogous rhodium(III) complex is accompanied by an increase in size of the central atom, and by an increase in crystal-field effects. The former may well encourage an I_d towards I_a or *A* tendency, the latter an I_d to *D* tendency. Again, the replacement of 'innocent' ligands such as ammonia by cyanide might be expected to improve the chances of bimolecular nucleophilic attack (I_a, *A*) at a metal with numerous t_{2g} electrons, by the withdrawal of some of this electron density from the line of approach of the potential nucleophile. Yet on the other hand the high crystal-field effect of the cyanide ligand may mean that five such ligands are sufficient to stabilize the five-co-ordinate transient intermediate of a *D* mechanism long enough for it to exercise the powers of discrimination by which it is kinetically recognized.

[11] M. J. Pavelich and G. M. Harris, *Inorg. Chem.*, 1973, **12**, 423.
[12] L. Damrauer and R. M. Milburn, *J. Amer. Chem. Soc.*, 1971, **93**, 6481.
[13] D. B. Vanderheiden and E. L. King, *J. Amer. Chem. Soc.*, 1973, **95**, 3860.
[14] A. A. Schilt and W. B. Schaap, *Inorg. Chem.*, 1973, **12**, 1424.
[15] E. B. Fleischer and M. Krishnamurthy, *J. Coordination Chem.*, 1972, **2**, 89.
[16] J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta, Rev.*, 1971, **5**, 7.
[17] C. S. Springer, *J. Amer. Chem. Soc.*, 1973, **95**, 1459.

five-co-ordinate complex [Ni(dtp)$_2$(PBu$_3$)],[18] and reactions of [Co$_2$(CO)$_8$] with alkynes (see Part IV).[19]

Whereas the assignment of mechanism to spontaneous thermal aquations may at times be uncertain, the mechanism of metal-ion-catalysed aquation of halide complexes of cobalt(III), chromium(III), and similar cations is unlikely to be other than dissociative as far as the metal(III) centre is concerned. In Volume 2 of this Report it was mentioned that the catalytic effect of metal ions on solvolysis rates of t-butyl halides could be correlated with the stability constants of the respective metal–halide complex formed.[20] Such a correlation is now reported for metal-ion catalysis of aquation of halide complexes of cobalt(III), chromium(III), and rhodium(III). Indeed this correlation is sufficiently general as to embrace such catalysts as H^+ and $HgCl^+$ as well as metal ions such as Hg^{2+} and Tl^{3+}.[21] A linear free-energy ($\Delta G^{\ddagger}$ *vs.* ΔG°) correlation has been reported for mercury(II)-catalysed aquation of a series of chromium(III) complexes.[22]

Whereas for thermal substitution the mechanistic picture is clearer for cobalt(III) complexes than for chromium(III) complexes, for photochemical reactions the reverse is the case. Currently there is much interest, and some success, in bringing the level of understanding of the photochemistry of cobalt(III) and other octahedral complexes up to that of chromium(III) complexes.[23,24] A recent review of photochemical reactions of transition-metal complexes concentrates on chromium(III) complexes, but also contains some information on cobalt(III) and platinum(II) complexes.[25]

Theoretical aspects of substitution in octahedral complexes have been discussed from a quantum mechanical viewpoint,[26] and according to the role of symmetry.[27]

2 Aquation: Cobalt(III) Complexes

Unidentate Leaving Groups.—There has been considerable interest in the aquation of the [Co(NH$_3$)$_5$X]$^{2+}$ cations. Transition enthalpies[28] (ΔH_T, the difference between the enthalpy of the transition state and the enthalpy of the products) have been estimated for aquation of the [Co(NH$_3$)$_5$X]$^{2+}$ cations with X = Cl, Br, I, or NO$_3$. For the chloro-, bromo-, and nitrato-complexes,

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[18] D. A. Sweigart and P. Heidtmann, *J.C.S. Chem. Comm.*, 1973, 556.

[19] P. C. Ellgen, *Inorg. Chem.*, 1972, **11**, 691; F. Ungvary and L. Marko, *Chem. Ber.*, 1972, **105**, 2457.

[20] E. S. Rudakov and I. V. Kozhevnikov, *Tetrahedron Letters*, 1971, 1333.

[21] I. V. Kozhevnikov and E. S. Rudakov, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 571.

[22] J. P. Birk and C. M. Ingerman, *Inorg. Chem.*, 1972, **11**, 2019.

[23] J. I. Zink, *Mol. Photochem.*, 1973, **5**, 151.

[24] M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, 1973, **5**, 165.

[25] W. L. Waltz and R. G. Sutherland, *Chem. Soc. Rev.*, 1972, **1**, 241.

[26] E. D. German and R. R. Dogonadze, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3916; *J. Research Inst. Catalysis, Hokkaido Univ.*, 1972, **20**, 34 (*Chem. Abs.*, 1973, **78**, 48 469x).

[27] K. B. Yatsimirskii, *Teor. i eksp. Khim.*, 1972, **8**, 617 (*Chem. Abs.*, 1973, **78**, 34 381a).

[28] See pp. 179—180 of Volume 1 and p. 171 of Volume 2 of this Specialist Periodical Report.

values of ΔH_T are equal within experimental uncertainty limits. The ΔH_T value for the iodo-complex is unexpectedly low, but this can be attributed to the use of a value for the activation enthalpy for aquation which is unreasonably low. The results, at least for the chloro-, bromo-, and nitrato-complexes, are consistent with a dissociative mechanism.[8]

Further evidence confirming the essentially dissociative nature of aquation of complexes $[Co(NH_3)_5X]^{n+}$ is provided by determination of the activation volumes for the compounds with X = Cl, Br, NO_3, SO_4, or NCS. As reported briefly earlier,[29] these activation volumes correlate with molar volumes of reaction. The present report quotes values for activation volumes extrapolated to zero pressure, amplifies the earlier discussion, and concludes that the aquation mechanism is one of dissociative interchange (I_d).[30]

Whereas considerations of transition enthalpies and of activation volumes have led to evidence useful in confirming the mechanism of aquation in cobalt(III)–ammine–ligand complexes, an attempt to derive similarly useful information from a comparison of kinetic and solubility parameters proved unsuccessful. No correlation was found between enthalpies of activation for aquation of complexes $[Co(NH_3)_5X]^{2+}$, with X = F, Cl, Br, I, NCS, N_3, or NO_2, and the respective enthalpies of solution of their perchlorate salts.[31] In fact it seems impossible to correlate these activation enthalpies with any other apparently reasonable parameter, though it does seem that there is a correlation between activation entropies and the entropies of solvation of the leaving anions.[32]

Fundamental to the above studies are the experimentally determined values of the activation enthalpies for aquation of the complexes $[Co(NH_3)_5X]^{2+}$. These have recently been redetermined with considerable care to give more precise values than those available in the earlier literature. For the complex with X = Cl, spectrophotometric determinations of rate constants for aquation in $0.015M\text{-}HClO_4$ over the temperature range 50—80 °C gave values for the activation energy of 23.445 kcal mol^{-1} and for the activation entropy of -8.3 cal deg^{-1} mol^{-1}. Similarly, for the complex with X = Br, this time from experiments over the temperature range 40—70 °C, an activation energy of 23.370 kcal mol^{-1} and an activation entropy of -6.0 cal deg^{-1} mol^{-1} are reported. The precision of the activation energy for aquation of the chloro-complex is indicated by the quoted standard deviation of 0.124 kcal mol^{-1}.[32]

In the final references to aquation of complexes $[Co(NH_3)_5X]^{2+}$ the interest is in the reactivity of ion pairs. Rates of aquation of the complexes with X = Cl, Br, or I increase by a factor of two to three when these cations are ion-paired with dinegative ions such as sulphate, malonate, maleate, or phthalate.[33] The role of ion pairs with uninegative anions in the aquation of

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[29] W. E. Jones and T. W. Swaddle, *Chem. Comm.*, 1969, 998.
[30] W. E. Jones, L. R. Carey, and T. W. Swaddle, *Canad. J. Chem.*, 1972, **50**, 2739.
[31] H. C. A. King, *Rev. latinoamer. Quim.*, 1972, **2**, 155.
[32] G. C. Lalor and H. Miller, *Rev. latinoamer. Quím.*, 1972, **3**, 72.
[33] M. B. M. Campbell, M. R. Wendt, and C. B. Monk, *J.C.S. Dalton*, 1972, 1714.

$[Co(NH_3)_5Cl]^{2+}$ has been the subject of controversy for some years. The effects of added chloride on aquation rates of this complex were first studied up to a concentration of 0.1M sodium chloride,[34] later up to 0.6M sodium chloride.[35] The results of the latter study, in which sodium perchlorate was used to maintain constant ionic strength, were subsequently reinterpreted in terms of three parallel I_d reaction pathways, involving chloride and perchlorate ion pairs.[36] Now the effect of added chloride on the aquation rate of the $[Co(NH_3)_5Cl]^{2+}$ cation has been investigated at chloride-ion concentrations up to 0.9M. The conclusion reached from this latest and most extensive study is that neither $[Co(NH_3)_5Cl]^{2+}\,Cl^-$ nor $[Co(NH_3)_5Cl]^{2+}\,ClO_4^-$ ion pairs play a kinetically significant role in the aquation of the $[Co(NH_3)_5Cl]^{2+}$ cation under experimental conditions so far used. Moreover the aquation rate constant for this complex is unaffected by the nature of the added anion, be it perchlorate, tetrafluoroborate, or trifluoromethylsulphonate, when the respective sodium salts are used to maintain the ionic strength of the reaction medium (I = 1.0M).[37]

The relative reactivity of pairs of chloride and bromide complexes is often reported and discussed. Recent studies in this category which refer to such pairs of cobalt(III)–amine–halide complexes include those of aquation of *cis*-$[Co(en)_2(cyclohexylamine)X]^{2+}$,[38] of *trans*-$[Co(cyclam)(NO_2)X]^+$,[39] and of *cis*-$[Co(phen)_2(NO_2)X]^+$,[40] in all cases with X = Cl or Br. Similar reactivity comparisons have been made for cobalt(III)–oxime–halide complexes, including the series *trans*-$[Co(dmgH)_2LX]$, with L = semicarbazide or thiosemicarbazide,[41] and *trans*-$[Co(dmgH)_2(tu)X]$ (in 20% ethanol).[42] In these latter cases X = Cl, Br, or I. Several of these systems will be mentioned again later, in the section on effects of non-leaving ligands.

The kinetic characteristics of both urea and thiourea as leaving groups have been investigated in cobalt(III)–oxime derivatives. Rate constants and activation parameters were determined for the loss of urea from *trans*-$[Co(dmgH)_2(urea)X]$, with X = Cl, Br, or NO_2 (or I, in 25% ethanol). The small variation in rate constant observed for aquation of this series of complexes was rationalized in terms of the known *trans* effects of these ligands in octahedral cobalt(III) complexes. The activation energies, which are in the range 52.9—64.8 kJ mol^{-1} (12.6—15.6 kcal mol^{-1}) are remarkably low for aquation of cobalt(III) complexes, while the large, negative activation entropies, -108 to -143 J K^{-1} mol^{-1} (-26 to -34 cal deg^{-1} mol^{-1}) are said to indicate an associative mechanism for these aquations.[43] The activation energy, un-

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[34] S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, 1965, 724.
[35] C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, 1967, **89**, 3141.
[36] M. G. Burnett, *J. Chem. Soc. (A)*, 1970, 2486.
[37] E. C. Barber and W. L. Reynolds, *Inorg. Chem.*, 1973, **12**, 951.
[38] N. Mullick, R. K. Nanda, and R. N. Nanda, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3731.
[39] C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216.
[40] D. M. Palade and T. N. Volokh, *Russ. J. Inorg. Chem.*, 1972, **17**, 1016.
[41] N. N. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1145.
[42] N. N. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1972, **17**, 864.
[43] N. N. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1971, **16**, 1030.

fortunately determined over only a 10 °C range of temperatures, for aquation of the similar thiourea complex *trans*-$[Co(dmgH)_2(tu)_2]^+$ is again relatively low, at 15.4 kcal mol^{-1}; the activation entropy for this aquation is -22.4 cal deg^{-1} mol^{-1}.[44] Other uncharged leaving groups whose departure from cobalt(III) has been studied include *o*- and *m*-anisidine and dimethyl sulphoxide. The kinetic study of the two substituted anilines as leaving groups was complicated by parallel loss of chloride from the complexes *cis*-$[Co(en)_2(anisidine)Cl]^{2+}$.[45] One would intuitively expect dimethyl sulphoxide to be a good leaving group from cobalt(III); this expectation is fulfilled by the qualitative observation that aquation of $[Co(NH_3)_5(DMSO)]^{3+}$ is complete within about three hours at 45 °C.[46] The subject of uncharged leaving groups will be mentioned again in the context of solvent effects on reactivity.

Rate laws and kinetic parameters have been established for sulphamate and for acetate being displaced by water from cobalt(III) centres in acid media, the former from $[Co(NH_3)_5(sulphamato)]^{2+}$ (ref. 47) and the latter from *cis*- and from *trans*-$[Co(en)_2(OAc)_2]^+$.[48] Unfortunately these systems are complicated by pre-equilibria and by isomerization, so that most of the kinetic parameters are composite quantities. Rate constants for aquation of the complexes *cis*-$[Co(en)_2(RCO_2)_2]^{2+}$, where R = CH_3, CH_2Cl, $CHCl_2$, CCl_3, or CF_3, all lie between 8.0 and $9.3 \times 10^{-6}\,s^{-1}$, at 25 °C and pH = 7. Aquation of the analogous *trans*-complexes under similar conditions shows a similar small dependence of rate on the nature of the leaving (halogeno)acetate ligand.[49] One should, however, when considering these results bear in mind that the rate constants for aquation of carboxylate complexes are generally pH-dependent (*cf.* the section on catalysed aquation below). Aquation of the $[Co(NH_3)_5(SO_4)]^+$ cation is also acid-catalysed:

$$-d[Co(NH_3)_5(SO_4)^+]/dt = \{k_0 + k_1[H^+]\}[Co(NH_3)_5(SO_4)^+]$$

The activation parameters for the non-catalysed (k_0) path are $\Delta H^{\ddagger} = 22.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.0$ cal deg^{-1} mol^{-1}.[50]

Kinetic studies of the loss of ammonia or of chelating amines from cobalt(III) complexes by aquation are rare. Parallel loss of ammonia and halide from chromium(III)–ammine–halide complexes is not uncommon, but ammonia is very much more reluctant than halides to depart from cobalt(III). In fact the potential field of kinetic studies of the loss of ammonia from cobalt(III) is small, and further restricted by the propensity of cobalt(III) to oxidize co-ordinated water. The $[Co(NH_3)(OH_2)_5]^{3+}$ cation, on warming in 1M-$HClO_4$ for twelve hours, gives $[Co(NH_3)_2(OH_2)_4]^{3+}$ and cobalt(II).[51] The

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[44] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1971, **16**, 1294.
[45] S. C. Chan and O. W. Lau, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3275.
[46] C. R. P. Mac-Coll and L. Beyer, *Inorg. Chem.*, 1973, **12**, 7.
[47] E. Sushynski, A. van Roodselaar, and R. B. Jordan, *Inorg. Chem.*, 1972, **11**, 1887.
[48] T. P. Dasgupta and M. L. Tobe, *Inorg. Chem.*, 1972, **11**, 1011.
[49] M. Yokoi and K. Kuroda, *Bull. Chem. Soc. Japan*, 1971, **44**, 3293.
[50] F. Monacelli, *Inorg. Chim. Acta*, 1973, **7**, 65.
[51] J. D. White, J. C. Sullivan, and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 4733.

$[Co(NH_3)_3(OH_2)_3]^{3+}$ cation undergoes spontaneous reduction under similar conditions; the kinetics of this reaction have been described.[52] The spontaneous reduction of $[Co(NH_3)_5(OH_2)]^{3+}$ and of $[Co(NH_3)_4(OH_2)_2]^{3+}$ is slower than their aquation, so the kinetics of aquation of these two aquo–ammine–cobalt(III) complexes can be monitored.[53] References to the spontaneous reduction of analogous cobalt(III) complexes of chelating amines are cited below, in the section on multidentate leaving groups. Further details of these studies are given in Chapter 2 of Part I (refs. 160 and 161 of that chapter).

Multidentate Leaving Groups.—The decomposition of dicarboxylate complexes of cobalt(III), particularly of $[Co(ox)_3]^{3-}$, has long been established to involve an internal redox step. Several papers published during the past couple of decades have concluded that the initial step is the charge-transfer or redox process

$$[Co(ox)_3]^{3-} \longrightarrow Co^{2+} + ox^{-} + 2ox^{2-}$$

subsequent steps involving the oxalate radical anion thus generated. In Volume 2 of this Report mention was made of an alternative mechanism in which a three-centre redox step involving a ring-opened cobalt(III)–oxalate species was invoked for the decomposition of the $[Co(ox)_3]^{3-}$ and $[Co(ox)_2(OH_2)_2]^{-}$ anions.[54] The tenability of this hypothesis has now been tested over a wide range of experimental conditions, with the conclusion that it seems a less acceptable mechanism than the simple oxalate radical mechanism outlined above.[55] A concurrent study of this $[Co(ox)_3]^{3-}$ decomposition has concentrated on the establishment of the rate law [equation (1)] and thence the determination of the kinetic parameters. The activation enthalpies for the k_1 and k_2 terms are 29.7 and 30.0 kcal mol^{-1}, the activation entropies +17.4 and +20.9 cal deg^{-1} mol^{-1} respectively. The kinetics were unaffected by added oxygen, acrylonitrile, or peroxodisulphate, but interestingly the decomposition of peroxodisulphate was claimed to be induced by the $[Co(ox)_3]^{3-}$ redox aquation. Evidence for the intermediacy of the CO_2^{-} radical in this decomposition was presented.[56]

$$-d[Co(ox)_3^{3-}]/dt = \{k_1 + k_2[H^+]\}[Co(ox)_3^{3-}] \qquad (1)$$

The kinetics of the closely related redox decomposition of $[Co(mal)_3]^{3-}$ in aqueous solution, at pH 5.6, have been re-examined by ^{14}C radiochemical tracer techniques. An activation enthalpy of 86.5 kJ mol^{-1} (20.7 kcal mol^{-1}) was deduced from series of experiments utilizing liquid scintillation monitoring and a value of 67.5 kJ mol^{-1} (16.4 kcal mol^{-1}) by proportional counting.[57] The former value is closer to previous estimates using spectrophotometry.

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[52] S. Lum, W. D. Stanley, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1293.

[53] W. D. Stanley, S. Lum, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3587.

[54] L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1970, 2836.

[55] N. S. Rowan, R. M. Milburn, and M. Z. Hoffman, *Inorg. Chem.*, 1972, **11**, 2272.

[56] M. Kimura and T. Sato, *Bull. Chem. Soc. Japan*, 1973, **46**, 471.

[57] R. van Eldik and R. Alberts, *J. S. African Chem. Inst.*, 1972, **25**, 17 (*Chem. Abs.*, 1972, **76**, 131 976q).

Mechanisms available for the aquation of carboxylato-cobalt(III) complexes have been considered, with the discussion covering such topics as cobalt–oxygen *versus* oxygen–carbon bond breaking, dechelation of multidentate carboxylate ligands,[58] and stereochemistry.[59]

The kinetic pattern and mechanism for the aquation of $[Co(bipy)_3]^{2+}$ have been elucidated as a by-product of investigating the vanadium(II) reduction of $[Co(bipy)_3]^{3+}$. The aquation mechanism for $[Co(bipy)_3]^{2+}$ bears a considerable resemblance to that for the much studied $[Fe(bipy)_3]^{2+}$ cation. In particular there is the same need to invoke intermediates containing unidentate, and unidentate monoprotonated, bipy for both complexes. The activation parameters for dissociation are $\Delta H^{\ddagger} = 12.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10$ cal deg^{-1} mol^{-1}. The activation enthalpies for aquation of this cobalt(II) complex and for its nickel(II) and iron(II) analogues are in the order, Fe^{II}(low-spin) > Ni^{II} > Co^{II}, expected from crystal-field considerations.[60]

The spontaneous reduction of cobalt(III)–ammine–water complexes has already been mentioned.[51–53] Analogous cobalt(III)–chelating amine–water complexes also undergo spontaneous redox reactions rather than ordinary aquation in acidic aqueous solution. The kinetics of several of these redox amine-loss processes have recently been described, for the complexes *cis*-$[Co(en)_2(OH_2)_2]^{3+}$,[61] $[Co(dien)(OH_2)_3]^{3+}$,[62] and $[Co(dpt)(OH_2)_3]^{3+}$.[63] There were too many complications arising from side reactions for a study of the kinetics of redox aquation of the α-$[Co(trenen)(OH_2)]^{3+}$ cation to be successful.[63]

Effects of Non-leaving Ligands.—There are three main classes of complex to be discussed in the present section. The first contains compounds of the type $[Co(en)_2LX]^{2+}$, where the leaving group X is usually chloride, and it is the effect of the ligand L on the rate of loss of X^- that is the principal feature of interest. The second contains compounds of the general formula $[CoL_4X_2]^+$, where the interest centres on the ligand or ligands L_4. Typically such studies probe the effects of varying the nature and denticity of L_4, which may range from $(NH_3)_4$ through $(en)_2$ to trien and to macrocyclic ligands such as cyclam, on the kinetic parameters for aquation and X^- loss. The third group consists of bisdioxime complexes of formula *trans*-[Co(dioxime)$_2$LX]. Here the main topic of discussion may be either the *trans* effect of L or the effect of the nature of the dioxime ligands on the loss of X^-. One general reference which lies outside this classification concerns the high *trans* effect of the sulphite ligand in cobalt(III) complex chemistry and its consequences in preparative chemistry.[64]

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[58] M. E. Farago, M. A. R. Smith, and I. M. Keefe, *Coordination Chem. Rev.*, 1972, **8**, 95.
[59] T. P. Dasgupta and M. L. Tobe, *Coordination Chem. Rev.*, 1972, **8**, 103.
[60] R. Davies, M. Green, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1171.
[61] S. Lum, L. Ereshefsky, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1591.
[62] P. Wilairat and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1833.
[63] S. Lum, L. Ereshefsky, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2401.
[64] H. Siebert and G. Wilke, *Z. anorg. Chem.*, 1973, **399**, 43, 52.

$[Co(en)_2LX]^{2+}$ *Complexes*. Kinetic parameters for aquation of complexes of the type $[Co(en)_2LX]^{2+}$ are listed in Tables 1 and 2, which are for complexes with X = Cl and with X = Br respectively. The reactivities of the chloro-complexes with L = n-, iso-, or sec-butylamine or n-propylamine are similar, though with slightly greater rates of aquation reported for the complex of the amine containing an α-methyl group.[65] Relatively rapid aquation has for the second time* been reported for the complex with L = cyclohexylamine.[67]

Table 1 *Kinetic parameters*[a] *for aquation of complexes* $[Co(en)_2LCl]^{n+}$

L	$10^6k/s^{-1}$ (*temperature*/°C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
cis-Pr^nNH_2	29 (60)	24.4	−6	65
cis-Bu^nNH_2	32 (60)	22.9	−11	65
cis-Bu^iNH_2	32 (60)	23.4	−9	65
cis-Bu^sNH_2	72 (60)	20.9	−13	65
cis-$C_6H_{11}NH_2$	51 (50.5)	—	—	66
	63.5 (50)	20.0±0.5	−18.4±0.8	67
(2; *n* = 2)	91 (60)	22.2	—	[b]
(2; *n* = 3)	25 (60)	23.6	—	[b]
(2; *n* = 4)	25 (60)	23.8	—	70
(2; *n* = 5)	31 (60)	23.6	—	70
(2; *n* = 6)	31 (60)	23.6	—	70
cis-O_2CMe	3.1 (25)	26.8±0.3	+6.7±0.8	76
cis-O_2CPh	1.2 (25)	29.3±0.7	+13.2±2.2	76
trans-CN	980 (25)	20.7	−3	81
(1; *n* = 3)	21 (65)	23.7	−10	69
(1; *n* = 6)	32 (65)	23.5	−10	69
(1; *n* = 7)	33 (65)	23.5	−10	69
(1; *n* = 8)	34 (65)	23.5	−10	69
(1; *n* = 10)	37 (65)	23.5	−10	69

[a] Error limits are quoted where these are stated in the papers cited. [b] Values for comparison, taken from S. C. Chan and F. Leh, *J. Chem. Soc.* (*A*), 1967, 1730.

Table 2 *Kinetic parameters for aquation of complexes* $[Co(en)_2LBr]^{2+}$

L	$10^4k/s^{-1}$ (*temperature*/°C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
cis-$C_6H_{11}NH_2$	1.5 (45)	22.2±0.3	−6.2±0.5	67
cis-$MeNH_2$	1.9 (65)	23.9	−5	72
cis-Bu^nNH_2	2.0 (65)	23.9	−5	72
cis-$CH_2{=}CHCH_2NH_2$	1.2 (65)	25.0	−3	72
cis-$HOCH_2CH_2NH_2$	6.3 (65)	22.5	−7	72
cis-3-Me-py		23.6	−6	75
cis-4-Me-py		23.2	−6	75

* The previous report is in ref. 66.

[65] S. C. Chan and K. M. Chan, *Z. anorg. Chem.*, 1972, **389**, 205.

[66] S. C. Chan and T. L. Cheung, *Austral. J. Chem.*, 1970, **23**, 707.

[67] N. Mullick, R. K. Nanda, and R. N. Nanda, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3731.

A dissociative mechanism with consequent relief of steric crowding in the transition state is a sufficient rationalization for these rate accelerations. An argument over the actual values for aquation rate constants of several chloro–amine complexes of this type appears to have been resolved satisfactorily.[68]

A slight variant of these kinetic studies concerns the complexes *cis*-$[Co(en)_2(LH)Cl]^{3+}$, where LH^+ is now a diamine with one nitrogen protonated rather than a simple aliphatic monoamine. The point of studying such complexes was to disentangle inductive and mesomeric effects from overall charge effects. Thence one could decide which of these was responsible for the large difference between the rates of aquation of, say, *cis*-$[Co(en)_2Cl_2]^+$ and *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$.[69] In fact as the protonated diamines used were of the formula (1) with $n \geqslant 2$, the extra positive charge on the complex may be situated a long way from the cobalt(III) centre whence the chloride is leaving. The reported similarity in rates for these complexes and their NH_3 analogue may simply be due to the cobalt atom 'seeing' very similar near surroundings and not being unduly affected by the distant positive charge in the $—NH_2(CH_2)_n\overset{+}{N}HR_2$ complexes.

$$\underset{(1)}{H_2N(CH_2)_n\overset{+}{N}H_3} \qquad\qquad \underset{(2)}{H_2N(CH_2)_nOH}$$

Another variation on the nature of L is that of using an amino-alcohol (2), which is potentially bidentate, as ligand. When L = 2-aminoethanol, then loss of X^- is accompanied by chelate ring closure rather than by aquation, but for amino-alcohols $HO(CH_2)_nNH_2$ with $n > 2$ the leaving X^- is replaced by water, leaving the amino-alcohol still as a unidentate ligand. In the former case the mechanism may be of an intramolecular S_N2 type; in the latter case normal dissociative solvolysis seems likely. Nonetheless rate constants and activation parameters for the aquation of the series of complexes *cis*-$[Co(en)_2\{H_2N(CH_2)_nOH\}Cl]^{2+}$ vary only little as n increases from 2 to 6.[70] The pH-dependence of the rate of chloride release from *cis*-$[Co(en)_2(gly)Cl]^{2+}$ suggests some associative character to this reaction, in which the unbonded carboxylate group of the glycine can approach and interact with the cobalt in the transition state. Repulsion between the negative charges on this carboxylate group and on the leaving chloride is likely to keep the degree of associative character fairly limited here.[71]

Kinetic results for aquation of *cis*-$[Co(en)_2LBr]^{2+}$ cations, where L = 2-aminoethanol, methylamine, butylamine, or allylamine, parallel those obtained earlier for aquation of the analogous chloro-complexes.[72] It has been

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[68] L. G. Reiter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 320.

[69] S. C. Chan and S. F. Chan, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1247.

[70] S. C. Chan and O. W. Lau, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2361.

[71] H. M. Comley and W. C. E. Higginson, *J.C.S. Dalton*, 1972, 2522.

[72] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Russ. J. Inorg. Chem.*, 1971, **16**, 1435.

verified that when L = 2-aminoethanol the product is *cis*-$[Co(en)_2(NH_2CH_2CH_2OH)]^{3+}$ whereas in the other cases the product is *cis*-$[Co(en)_2L(OH_2)]^{3+}$.[73]

The kinetics of ring closure of the complex *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2OH)]^{3+}$ have been studied, and are consistent with the non-observance of this species in the aquation of *cis*-$[Co(en)_2(NH_2CH_2CH_2OH)X]^{2+}$ cations. An associative mechanism for the ring closure of the aquo–ethanolamine complex is proposed.[74] The kinetics and mechanisms of analogous ring-closure reactions of similar platinum(II) complexes are discussed in the appropriate section of Chapter 2 of this Part. Kinetic parameters for aquation of the isomeric cations *cis*-$[Co(en)_2LBr]^{2+}$ with L = 3- or 4-methylpyridine show the expected similarity.[75]

Rates of aquation of the related carboxylato-complexes *trans*-$[Co(en)_2(O_2CR)Cl]^+$, where R = Me or Ph, are independent of pH, and the aquation yields predominantly the *cis*-isomers of the products. Comparison of the stereochemical courses of aquation of these complexes with those for aquation of *trans*-$[Co(en)_2(OAc)_2]^+$ and of *trans*-$[Co(en)_2Cl_2]^+$ suggest that carboxylato-ligands encourage stereochemical change in aquation of cobalt(III) complexes.[76]

The ligand trien bears a strong resemblance to $(en)_2$, so aquation of the α- and β_1-isomers of the $[Co(trien)(OH_2)Cl]^{2+}$ cation is closely related to the reactions cited in the previous paragraphs. After making allowances and corrections for subsequent racemization and isomerization, it has been deduced that aquation of these two isomers proceeds with complete retention of geometric and absolute configuration. For reaction (2) the rate constant, determined by four different methods, is between 2.15 and 2.40×10^{-5} s^{-1}, at 25 °C, pH = 2, and ionic strength 0.013—0.020 mol l^{-1}.[77] From the results given in this paper, it is possible to estimate an activation enthalpy of 24.9 kcal mol^{-1} and an activation entropy of +10 cal deg^{-1} mol^{-1} at pH = 2 but not, unfortunately, at constant ionic strength.

$$(+)\text{-}\beta_1\text{-}[Co(trien)(OH_2)Cl]^{2+} \xrightarrow{H_2O} (+)\text{-}\beta\text{-}[Co(trien)(OH_2)_2]^{3+} + Cl^- \qquad (2)$$

The separation of two geometric isomers of $[Co(tren)(NH_3)Cl]^{2+}$ has been reported. Preliminary kinetic results are that the red or β-form, with the chloride *trans* to the tertiary nitrogen of the tren, aquates with a rate constant of 2.5×10^{-6} s^{-1} (0.1M-$HClO_4$, 26 °C) and that the purple or α-form, with the

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[73] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Russ. J. Inorg. Chem.*, 1972, **17**, 1008.

[74] V. V. Udovenko, L. G. Reiter, and T. V. Batyushkina, *Russ. J. Inorg. Chem.*, 1973, **18**, 234.

[75] J. Zsakó, C. Várhelyi, and S. Bleoca, *Acta Chim. Acad. Sci. Hung.*, 1971, **70**, 175.

[76] T. P. Dasgupta, W. Fitzgerald, and M. L. Tobe, *Inorg. Chem.*, 1972, **11**, 2046.

[77] G. H. Searle and A. M. Sargeson, *Austral. J. Chem.*, 1973, **26**, 661.

chloride *cis* to the tertiary nitrogen of the tren, has an aquation rate constant of 1.2×10^{-6} s^{-1} under the same conditions.[78]

The complexes *cis*-$[Co(phen)_2(NO_2)X]^+$, with X = Cl or Br, are slightly more distant cousins of the complexes mentioned so far in this section. Kinetic parameters for aquation of these complexes,[79] and of *cis*-$[Co(phen)_2Cl_2]^+$ for comparison,[80] are reported in Table 3. The slight difference in reactivity between the chloronitro- and the dichloro-complexes masks much greater but compensating differences in the activation parameters.

Table 3 *Kinetic parameters for aquation of complexes* cis-$[Co(phen)_2LX]^+$

L	X	$10^4k/s^{-1}$ (25 °C)	$\Delta H^{\ddagger}/$ kcal mol^{-1}	$\Delta S^{\ddagger}/$ cal deg^{-1} mol^{-1}	*Ref.*
Cl	Cl	0.7	23.1	+10	80
NO_2	Cl	1.3	15.4	−23	79
NO_2	Br	1.4	18.6	−12	79

The aquation of *trans*-$[Co(NH_3)_4(CN)Cl]^+$ provides two opportunities for discussion of non-leaving ligand effects, and also provides a link with the following section. The results provide an illustration of the effect of a *trans*-cyano-ligand on the lability of co-ordinated chloride. They also form part of the series of results for aquation of analogous complexes of $(NH_3)_4$, $(en)_2$, and cyclam ligands, which are discussed in terms of the nephelauxetic effects of these ligands (*cf.* next paragraph).[81]

$[CoL_4X_2]^+$ *Complexes.* There is a smooth trend of $\Delta S^{\ddagger}$ values, though not of $\Delta H^{\ddagger}$ nor of k values, in the sequence L_4 = $(NH_3)_4$, $(en)_2$, cyclam (3), for aquation of the complexes *trans*-$[CoL_4(NCS)Cl]^+$.[82] These trends and reactivity trends for similar complexes *trans*-$[CoL_4(NO_2)X]^+$, with X = Cl or Br, and *trans*-$[CoL_4(CN)Cl]^+$, are discussed in terms of the so-called kinetic nephelauxetic effect.[39, 81, 82] The slower rate of thiocyanate release from isomers of $[Co(tetren)(NCS)]^{2+}$ [tetren = (4)] than from analogous ammonia and ethylenediamine complexes has been rationalized by invoking greater expansion of the cobalt(III) 3*d*-orbitals by the tetren.[83] Loss of chloride from $[Co(tren)Cl_2]^+$ [tren = (5)] is very much faster than from *cis*-$[Co(en)_2Cl_2]^+$.[84] This difference in reactivity arises from distortion in the former complex. Further studies of this exceptionally labile $[Co(tren)Cl_2]^+$ complex have shown that deuterium isotope effects are rather different from those for other cobalt(III)–amine–halide aquations.[85] Some preliminary preparative and kinetic observations on

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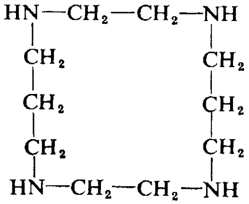
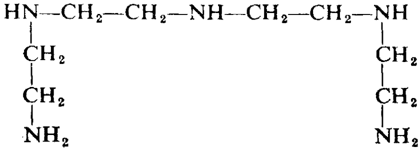
[78] C.-H. L. Yang and M. W. Grieb, *J.C.S. Chem. Comm.*, 1972, 656.
[79] D. M. Palade and T. N. Volokh, *Russ. J. Inorg. Chem.*, 1972, **17**, 1016.
[80] D. M. Palade and M. K. Boreiko, *Russ. J. Inorg. Chem.*, 1968, **13**, 1556.
[81] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1973, 1301.
[82] K. S. Mok, C. K. Poon, and H. W. Tong, *J.C.S. Dalton*, 1972, 1701.
[83] A. A. El-Awady, *J.C.S. Dalton*, 1972, 1463.
[84] S. K. Madan, W. M. Reiff, and J. C. Bailar, *Inorg. Chem.*, 1965, **4**, 1366.
[85] S. G. Zipp and S. K. Madan, *Inorg. Chim. Acta*, 1972, **6**, 401.

aquation of $[Co(LLLL)(CO_3)]^+$ cations, in which LLLL = tet-*b* (6) or tet-*d* (7), have been presented. These are to form the basis of a detailed kinetic and mechanistic study and discussion of these systems. Parallels are drawn between these complexes and nickel(II) complexes of these and related macrocyclic ligands.[86]

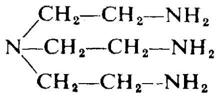


(3)

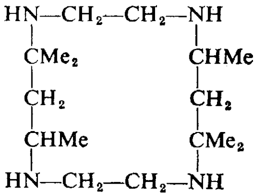


$H_2N{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_2$

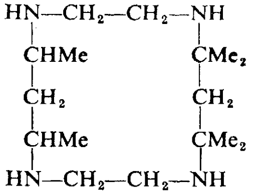
(4)



(5)



(6)



(7)

Kinetic parameters for aquation of cobalt(III) and chromium(III) complexes $[M(en)(tmd)Cl_2]^+$ and $[M(en)(tmd)(OH_2)Cl]^{2+}$ have been determined, with the primary aim of comparing reactivities, in terms of rate constants and of activation parameters, at these two metal centres. The *trans*-$[Co(en)(tmd)Cl_2]^+$ cation aquates, in 0.3F-$HClO_4$, to give predominantly *cis*-$[Co(en)(tmd)(OH_2)Cl]^{2+}$; $k = 3.96 \times 10^{-4}\ s^{-1}$ at 25 °C, $\Delta H^{\ddagger} = 23.6 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = +5$ cal deg^{-1} mol^{-1}. The *cis*-$[Co(en)(tmd)(OH_2)Cl]^{2+}$ thus generated aquates with $k = 1.03 \times 10^{-4}\ s^{-1}$ at 25 °C, $\Delta H^{\ddagger} = 18.2 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -16$ cal deg^{-1} mol^{-1}, this time in 1.0F-$HClO_4$. In the context of this section, comparisons between kinetic parameters for aquation of these (en)(tmd) complexes and their much-studied $(en)_2$ relatives can readily be made. The (en)(tmd) complexes aquate more rapidly than the $(en)_2$ complexes: the difference in structure is of course only one extra methylene group in tmd.[87] Rate constants and activation parameters have been evalu-

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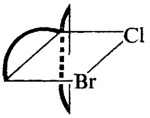
[86] N. A. P. Kane-Maguire, J. F. Endicott, and D. P. Rillema, *Inorg. Chim. Acta*, 1972, **6**, 443.

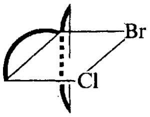
[87] M. C. Couldwell, D. A. House, and H. K. J. Powell, *Inorg. Chem.*, 1973, **12**, 627.

ated for aquation of the π-, κ-, and ω-isomers of $[Co(dien)(en)Cl]^{2+}$ and of the α- and β-isomers of $[Co(dpt)(en)Cl]^{2+}$.[88]

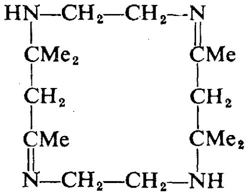
Because of their inherent strain, $[Co(tren)X_2]^+$ cations react much more rapidly than $[Co(en)_2X_2]^+$ analogues. A recent example of this is provided by the aquation of the α- and β-isomers, (8) and (9) respectively, of the $[Co(tren)BrCl]^+$ cation. Aquation of the α-isomer results in loss of chloride, with an activation enthalpy of 18.3 ± 0.8 kcal mol^{-1} and an activation entropy of -13.5 ± 2.7 cal deg^{-1} mol^{-1}. Aquation of the β-isomer results in loss of bromide, with an activation enthalpy of 16.0 ± 0.2 kcal mol^{-1} and an activation entropy of -9.0 ± 0.7 cal deg^{-1} mol^{-1}.[89]



(8)



(9)



(10)

Previous results pertaining to the kinetics of aquation of $[CoL_4(CO_3)]^+$ complexes[90, 91] have led to the belief that the low rates observed when L_4 = *e.g.* tet-*b* (6) or *trans*-[14]-diene (10) might be ascribable to steric factors. This may well be true, but the recent report of similarly slow hydrolysis for complexes with L_4 = $(bipy)_2$ or $(phen)_2$ show that at least in these cases some other factor, presumably the amount of electron release by the ligands and the consequent effect on cobalt(III)–carbonate bonding, is involved. The rate law is shown as equation (3); in fact k_0 values are very small. Values of k_1, with corresponding activation parameters, are listed in Table 4.[92]

$$-d[Co(LL)_2(CO_3)^+]/dt = \{k_0 + k_1[H^+]\}[Co(LL)_2(CO_3)^+] \qquad (3)$$

Table 4 *Kinetic parameters for aquation of* $[Co(LL)_2(CO_3)]^+$

LL	10^4k_1/ l mol^{-1} s^{-1} (25 °C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
bipy	2.2	22.3 ± 1.7	-1.5 ± 4.8	92
phen	1.5	20.4 ± 1.9	-8.6 ± 5.1	92
$(NH_3)_4$	15 000	15.3 ± 1.0	-6.3 ± 3.8	90
$(en)_2$	6 000	13.8 ± 1.0	-7.4 ± 3.0	91
trans-[14]-diene (10)	80	~24	—	91
tet-*b* (6)	1	—	—	91

[88] T. K. Huan, J. N. Mulvihill, A. R. Gainsford, and D. A. House, *Inorg. Chem.*, 1973, **12**, 1517.

[89] S.-T. Yuan, W. V. Miller, and S. K. Madan, *Inorg. Chim. Acta*, 1973, **7**, 134.

[90] K. V. Krishnamurthy, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 1970, **70**, 171 and refs. therein (see particularly pp. 190—192).

[91] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 1971, **93**, 91.

[92] D. J. Francis and R. B. Jordan, *Inorg. Chem.*, 1972, **11**, 461.

The most dramatic example of non-leaving-ligand effects in complexes of this type is provided by reactions of tetra-(*N*-methyltetrapyridyl)porphine complexes of cobalt(III). Here rates of substitution are several orders of magnitude faster than for the other cobalt(III) complexes discussed in this section.[93]

Dioximato-complexes. Kinetic parameters[41, 42, 94, 95] for aquation of a range of complexes *trans*-[Co(dmgH)$_2$LX] are collected together in Table 5. In most discussions of these results, reactivities are compared with those for aquation of the reference compounds *trans*-[Co(dmgH)$_2$(OH$_2$)X]. The *trans*-labilizing series of ligands in this class of dioximato-complexes appears to be

Table 5 *Kinetic parameters for aquation (halide replacement) of* trans-[Co(dmgH)$_2$LX]

L[a]	X	10^5k/s^{-1} (*temperature*/°C)	E_a/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Conditions*	*Ref.*
tu	Cl	8.61 (25)	22.2	−5	20% EtOH; pH = 3; I = 0.5	42
tu	Br	1.59 (25)	22.4	−8		42
tu	I	0.19 (25)	24.5	−5		42
tsca	Cl	438 (25)	17.0	−14		41
tsca	Br	47.9 (25)	18.9	−12		41
tsca	I	5.67 (25)	20.7	−11		41
sca	Cl	349 (25)	19.2	−7		41
sca	Br	41.1 (25)	21.0	−6		41
sca	I	4.85 (25)	23.4	−2		41
NH$_3$	Cl	—	29.0	+4	pH = 1 (HClO$_4$)	94
NH$_3$	Br	1.54 (65)	29.2	+4		95
NH$_3$	I	0.45 (65)	30.7	+6		95

[a] tu = thiourea, tsca = thiosemicarbazide, sca = semicarbazide.

thiosemicarbazide > semicarbazide > thiourea > water > ammonia

In fact aquation of *trans*-[Co(dmgH)$_2$(NH$_3$)X] in dilute acid results in parallel loss of ammonia and of halide, though in strong acid, for example 1M-HClO$_4$, only halide is displaced.[95] Aquation of *trans*-[Co(dmgH)$_2$(NO$_2$)$_2$]$^-$ or of *trans*-[Co(dmgH)$_2$(OH$_2$)(NO$_2$)] results in loss of nitrito-ligands. There is acid catalysis of these aquations, as it is possible to protonate nitrito-ligands. The difference in kinetic parameters for aquation of *trans*-[Co(dmgH)$_2$(NO$_2$)-(NO$_2$H)] and of *trans*-[Co(dmgH)$_2$(OH$_2$)(NO$_2$H)]$^+$ is explained in terms of differences in π-bonding between cobalt and water or a nitrito-ligand.[96]

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[93] R. F. Pasternack and M. A. Cobb, *Biochem. Biophys. Res. Comm.*, 1973, **51**, 507.

[94] J. Zsakó, Z. Finta, and C. Várhelyi, *Teor. Rastvorov, Alma-Ata*, 1971, 315 (*Chem. Abs.*, 1972, **77**, 169 276v).

[95] C. Várhelyi, J. Zsakó, and Z. Finta, *Z. anorg. Chem.*, 1973, **397**, 83.

[96] J. Zsakó, Z. Finta, and C. Várhelyi, Proceedings of the 3rd Symposium on Coordination Chemistry, Debrecen, Hungary, 1970, Vol. 1, p. 333; Vol. 2, p. 207.

Aquation of *trans*-[Co(dmgH)$_2$(urea)X] results in the loss of urea rather than of halide. The reported kinetic parameters, $12.7 < \Delta H^{\ddagger} < 15.6$ kcal mol^{-1} and $-34 < \Delta S^{\ddagger} < -25$ cal deg^{-1} mol^{-1}, are thus not strictly comparable with the results in Table 5. The effects of varying X on the reactivities of these complexes mirror the expected *trans*-effect order in this type of complex.[43] There has been one other kinetic study of substitution at dioximato-cobalt(III), and that was of the reaction of *trans*-[Co(dmgH)$_2$L(OH$_2$)]$^{n+}$, where L = OH$_2$, py, or NO_2^-, with pyridine.[97] Though these are formation reactions, their close similarity to the other systems in this and the preceding paragraph suggested that they be mentioned here.

Rates of aquation of *trans*-[Co(α-benzildioxime)$_2$(OH$_2$)X], with X = Cl, Br, or I, are much greater than those of analogous dimethylglyoxime complexes. The activation energy for aquation of the compound with X = Cl is 26.3 kcal mol^{-1}, whereas that for *trans*-[Co(dmgH)$_2$(OH$_2$)Cl] is 23.4 kcal mol^{-1}; the differences in rate constants are reflected in differences in activation energies.[98] The kinetics of aquation of *trans*-[Co(α-benzildioxime)$_2$LX], with L = thiourea, urea, or semicarbazide and X = Cl, or Br, have also been examined. From these results and those mentioned earlier in this paragraph one can extract a *trans*-effect series for various ligands L in this type of complex.[99] Reactivity differences between these α-benzildioximato-complexes and their dimethylglyoximato-analogues are attributed to the electron-donating properties of the phenyl groups in the α-benzildioxime ligands.

Kinetic parameters for aquation of *trans*-[Co(LL)(LLH)(NO$_2$)$_2$]$^-$ anions are similar for LLH = cyclopentanedionedioxime and cyclohexanedionedioxime. The activation enthalpies for aquation of these complexes are rather less than for the analogous dimethylglyoxime complex. Rates of aquation of these complexes are a function of the pH of the medium, as protonation of nitro-ligands is possible.[100]

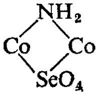
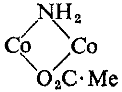
Bridged Dicobalt Complexes.—Aquation of the monohydroxo-bridged cation [(NH$_3$)$_5$Co·OH·Co(NH$_3$)$_5$]$^{5+}$ in aqueous HClO$_4$ (10^{-4}—2M), at an ionic strength of 2.0M (LiClO$_4$), follows the rate law

$$-\mathrm{d[complex]/d}t = \{k_0 + k_1[\mathrm{H^+}]\}[\mathrm{complex}] \qquad (4)$$

Kinetic parameters for the two aquation pathways are reported in Table 6. The kinetic characteristics of aquation of this complex are compared with those for other bridged dicobalt complexes containing various combinations of hydroxo- and amido-bridges. There is also some comparison with aquation of bridged complexes of other metals: thus, for instance, aquation of [(NH$_3$)$_5$Cr·OH·Cr(NH$_3$)$_5$]$^{5+}$ follows a rate law of type (4) above but with no measurable contribution from the k_1 term.[101]

[97] N. M. Samus' and T. S. Luk'yants, *Russ. J. Inorg. Chem.*, 1972, **17**, 390.
[98] N. M. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1578.
[99] N. M. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1973, **18**, 229.
[100] C. Várhelyi, J. Zsakó, and Z. Finta, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2583.
[101] R. K. Wharton and A. G. Sykes, *J.C.S. Dalton*, 1973, 439.

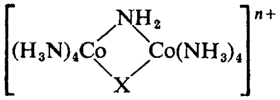
Table 6 *Kinetic parameters for the aquation of bridged dicobalt complexes [subscripts correspond with those in equation* (4) *of the text]*

Complex[a]	k_0/s^{-1} (*temperature*/°C)	$\Delta H^{\ddagger}_0$/ kcal mol^{-1}	$\Delta S^{\ddagger}_0$/ cal deg^{-1} mol^{-1}	k_1/l mol^{-1} s^{-1} (*temperature*/°C)	$\Delta H^{\ddagger}_1$/ kcal mol^{-1}	$\Delta S^{\ddagger}_1$/ cal deg^{-1} mol^{-1}	*Ref.*
Co·OH·Co	7.58×10^{-3} (25)	20.1 ± 0.7	-1 ± 2	5.37×10^{-3} (25)	12.0 ± 0.8	-29 ± 3	101
	3.85×10^{-5} (25)	16.4 ± 0.4	-30 ± 1	8.6×10^{-6} (25)	16.4 ± 1.6	-36 ± 5	104
	5.9×10^{-7} (50)			9.4×10^{-7} (50)			105

[a] In each complex the remaining ligands on the cobalt atoms are all ammonias.

There have been several somewhat inconsistent investigations and discussions concerning aquation of dihydroxo-bridged dicobalt complexes.[102] In the most recent paper on this topic the consequences of the application of the rate law of equation (4) above to both hydroxo-bridges have been considered. The approach of El-Awady and Hugus[102b] is preferred.[103] However, medium effects of the lithium and sodium cations may be significantly different, and indeed appear to have given a spurious hydrogen-ion-dependence term in at least one rate law in this area. One should also draw the attention of readers to mixing effects in stopped-flow experiments, which have been found to be particularly important when solutions of non-equivalent perchlorate concentration are mixed. The possible magnitude of such effects is strikingly illustrated by Figure 2 of this reference.[103]

The kinetic pattern for aquation of the newly characterized μ-amido-μ-selenato-dicobalt complex (11)[104] is similar to that established for its μ-amido-μ-sulphato-analogue. In both cases the product is (12), and there is strong kinetic evidence for transient intermediates of the type (13). A rate law of the form shown in equation (4) above operates; kinetic parameters for aquation of the μ-amido-μ-selenato-complex are included in Table 6. A preliminary report on the kinetics of aquation of the closely related acetato-complex (14) indicates that the rate law of equation (4) also applies here,[105] but the rate law for aquation of the μ-amido-μ-phosphato-complex (15) is more complicated.[106]

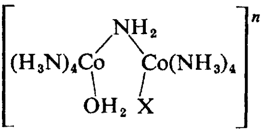


(11) X = SeO_4^{2-}

(12) X = OH^-

(14) X = $MeCO_2^-$

(15) X = $H_2PO_4^-$



(13)

Some qualitative information on the lability of several μ-peroxo-dicobalt ammine or amine compounds can be gleaned from a primarily spectroscopic paper dealing with these species.[107] Further mention of kinetic studies of bridged dicobalt complexes will be found later in this chapter, in the sections on metal-ion-catalysed aquation and on formation reactions.

μ-Superoxo-dicobalt(III) complexes, unlike their μ-peroxo-analogues, tend to be photosensitive. Recent discussions of the photochemistry of such dicobalt

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[102] (*a*) A. B. Hoffman and H. Taube, *Inorg. Chem.*, 1968, **7**, 903; (*b*) A. A. El-Awady and Z. Z. Hugus, *ibid.*, 1971, **10**, 1415; (*c*) M. M. deMaine and J. B. Hunt, *ibid.*, 1971, **10**, 2106.

[103] J. D. Ellis, K. L. Scott, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, 1972, **11**, 2565.

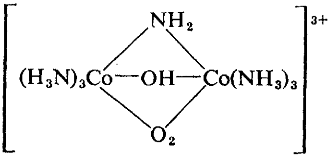
[104] S.-W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1973, 504.

[105] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 2364.

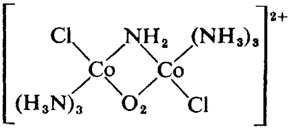
[106] J. D. Edwards, S.-W. Foong, and A. G. Sykes, *J.C.S. Dalton*, 1973, 829.

[107] Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1971, **44**, 3373.

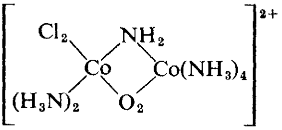
complexes are concerned with two symmetrical, (16) and (17), and one unsymmetrical, (18), species. In all cases the overall reaction is aquation and redox, with both cobalt(III) complexes and aquo-cobalt(II) among the products. The product distribution, $[Co(NH_3)_4(OH_2)Cl]^{2+}$, $[Co(NH_3)_4(OH_2)_2]^{3+}$, and Co^{2+}_{aq}, from (17) depends on the wavelength of irradiation. Photoaquation of (18) produces all the cobalt(III) in the form of penta-ammine complexes $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5(OH_2)]^{3+}$; μ-amido-bridge cleavage thus occurs at only one position.[108]



(16)



(17)



(18)

Solvent Variation.—The unexpectedly rapid aquation of $[Co(tren)Cl_2]^+$ has been probed by the use of deuterium isotope effects, both for the ligand and for the solvent. For most cobalt(III)–amine–halide complexes, both amine deuteriation and solvent deuteriation result in lower rates of reaction. In the case of this $[Co(tren)Cl_2]^+$ cation, the reactivity pattern differs somewhat from the normal in that the ratio $k(H_2O)/k(D_2O)$ is the same for both the complex containing $[^2H_6]$tren and that containing the undeuteriated tren ligand. However, this isotope effect is small, which shows that any specific interactions between ligands and solvent have a very much smaller effect on reactivity than the steric distortion of the tren ligand in this complex.[85]

Rate constants for halide loss from *trans*-$[Co(dmgH)_2(L)X]$, with L = semicarbazide or thiosemicarbazide and X = Cl, Br, or I,[41] and from *trans*-$[Co(\alpha\text{-benzildioximeH})_2(L)X]$, where X = Cl or Br,[98] both show the expected gentle decrease with increasing organic component in various alcohol– and dioxan–water mixtures. A linear plot of logarithms of rate constant against reciprocal dielectric constant for the latter compounds, taken in conjunction with the determined dependence of the rate constant on ionic strength in aqueous solution, was said to indicate a dissociative mechanism.[98]

Solvent effects on rates of aquations which involve the displacement of a neutral ligand provide useful information for comparison with the more widely studied situations where the leaving group is anionic, generally chloride.

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[108] J. S. Valentine and D. Valentine, *Inorg. Chem.*, 1973, **12**, 1697.

Kinetic studies have been started* on DMSO as a leaving ligand, from the $[Co(NH_3)_5(DMSO)]^{3+}$ cation.[46] More detailed information is available for urea and for thiourea as displaced groups, from *trans*-$[Co(dmgH)_2(urea)X]$[109] and from the *trans*-$[Co(dmgH)_2(thiourea)_2]^+$ cation[44] respectively. In both cases the same relatively small decrease in rate with increasing proportion of organic co-solvent is observed here as for halides as leaving groups. The linearity of the dependence of the logarithms of rate constants for the aquation of the thiourea complex on reciprocal dielectric constants is interpreted in terms of a dissociative mechanism, which seems plausible in the light of the known marked *trans* effect of thiourea.[44] A rather similar dependence of rate constants for aquation of *trans*-$[Co(dmgH)_2(urea)X]$ on solvent composition is interpreted very differently.[109] Here the authors concentrate on the observation that rate constants are a function of the solvent composition but are not particularly sensitive to variation in the nature of the co-solvent, and thence suggest an associative mechanism. As there is a rough correlation between the compositions and the reciprocal dielectric constants for the solvent mixtures used here, and the variations of rate constants are rather small, it seems difficult to place too much faith in these methods of assigning mechanisms. The authors of the paper on the urea complex also point to negative activation entropies as indicative of an associative mechanism, but again the magnitudes and signs of activation entropies for reactions in polar solvents are not as reliable a guide to mechanism as they are in inert solvents or in the gas phase. The effect of solvent composition on reaction rates for formation reactions which are closely complementary to the above aquations, for example the reaction of $[Co(dmgH)_2(OH_2)L]^+$ with L, where L = (substituted) thiourea, are discussed in Section 6 of this chapter.

Rate constants and activation parameters are reported for the aquation of *trans*-$[Co(dmgH)_2(tu)X]$, with X = Cl, Br, or I, in 20% ethanol.[42] Kinetic parameters are also reported for the aquation of *trans*-$[Co(dmgH)_2(py)Cl]$ in 10% ethanol; here the activation energy is 27.1 kcal mol^{-1} and the activation entropy is +10 cal deg^{-1} mol^{-1}.[110] The precision of these values may not be very high as rate constants were determined only over a 10 °C temperature range (30—40 °C).

The kinetics of solvolysis of cobalt(III) complexes in non-aqueous solvents are comparatively rarely studied. The solvolysis of the $[Co(NH_3)_5Cl]^{2+}$ cation in liquid ammonia has been monitored spectrophotometrically; the kinetic

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* A recently published communication on the kinetics of the forward and reverse reactions $[Co(NH_3)_5(DMSO)]^{3+} + H_2O \rightleftharpoons [Co(NH_3)_5(OH_2)]^{3+}$ + DMSO, studied over a range of DMSO–water solvent compositions, presents evidence which greatly favours the operation of an I_d rather than a D mechanism for these reactions (W. L. Reynolds, S. Ašperger, and M. Biruš, *J.C.S. Chem. Comm.*, 1973, 822).

[109] N. M. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1971, **16**, 1445.

[110] V. R. Vijayaraghavan and M. Santappa, *Current Sci.*, 1971, **40**, 623 (*Chem. Abs.*, 1972, **76**, 63 983n).

pattern is simple first-order. Solvolysis rates are proportional to the reciprocal of the ammonium-ion concentration (varied by the addition of ammonium perchlorate), which suggests a mechanism analogous to base hydrolysis in water.[111]

Solvents such as 97% sulphuric acid and molten ammonium hydrogen sulphate are much further removed from water than any solvent mentioned so far in this section. Kinetic studies of the decomposition of $[Co(NH_3)_6]^{3+}$ and of $[Co(NH_3)_5(SO_4)]^+$ in these solvents have indicated that the rate-determining step is a substitution process, in which ammonia is replaced by bisulphate. The activation energy for such a process is about 40 kcal mol^{-1} in these solvents. This slow substitution is followed by more rapid redox processes.[112]

Catalysed Aquation.—In 1971 Rudakov and Kozhevnikov[113] reported a correlation between the rate constants for metal-ion (M^{n+}) catalysed solvolysis of t-butyl halides and the stability constants of the respective complexes $MX^{(n-1)+}$. Now these authors have shown that a similar correlation applies, albeit rather approximately, to metal-ion catalysis of aquation of halogeno-cobalt(III), -chromium(III), and -rhodium(III) complexes. In fact the catalysts mentioned include not only metal ions such as Hg^{2+}, Tl^{3+}, and Ag^+, but also complexes such as $HgCl^+$ and $TlCl^{2+}$. This correlation can be improved by making an allowance for the different coulombic repulsions in systems of different charge products. If the rate constant for the catalysed aquation is k_1 and that for uncatalysed aquation k_0, the stability constant of the metal-ion complex produced K, the product of the charges on the reactants z_Az_B, and C is a coulombic interaction constant, then the correlation conforms to the equation

$$\log(k_1/k_0) = -0.7 + 0.84 \log K - Cz_Az_B$$

This equation and that for catalysis of t-butyl halides are very similar, so the catalytic activities of the respective cations in the solvolyses of the inorganic and of the organic halides must also be similar.[114]

Mercury(II) remains the favourite catalyst for chloro-cobalt(III) complex aquations. Kinetic results have been reported for aquation of *cis*-$[Co(en)_2LCl]^{2+}$, where L = n-, iso-, or sec-butylamine,[65] of *cis*-$[Co(en)_2(LH)Cl]^{3+}$, where L = an aliphatic diamine,[69] of the π-, κ-, and ω-isomers of $[Co(dien)(en)Cl]^{2+}$,[88] and of *trans*-$[Co(en)_2(OAc)Cl]^+$.[76] In the last case the rate law was established as

$$-d[\text{complex}]/dt = \{k_1 + k_2[Hg^{2+}]\}[\text{complex}]$$

where k_1 equalled the rate constant for uncatalysed aquation, and $HgCl^+$ was found to be comparably effective as a catalyst to Hg^{2+}. The mercury(II)-catalysed aquation of $[Co(NH_3)_5Cl]^{2+}$ is enormously accelerated by micelles of

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[111] S. Balt and G. F. Pothoff, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1015.
[112] R. A. Sutula and J. B. Hunt, *Inorg. Chem.*, 1972, **11**, 1879.
[113] E. S. Rudakov and I. V. Kozhevnikov, *Tetrahedron Letters*, 1971, 1333.
[114] I. V. Kozhevnikov and E. S. Rudakov, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 571.

sodium dodecyl, tetradecyl, or hexadecyl sulphates; accelerations of over a million times are cited.[115] Polyethylenesulphonate, polystyrenesulphonate, and polyphosphate accelerate mercury(II), thallium(III), and silver(I) catalysis of aquation of $[Co(NH_3)_5Br]^{2+}$ by factors of between ten and ten thousand. For mercury(II) and silver(I) catalysis, both the activation enthalpy and the activation entropy are decreased in the presence of the polyelectrolytes. Thus, for example, the presence of 18.5×10^{-4} equivalents per litre of sodium polyethylenesulphonate reduces $\Delta H^{\neq}$ from 14.1 to 4.5 kcal mol^{-1} and $\Delta S^{\neq}$ from -7 to -23 cal deg^{-1} mol^{-1}. For thallium(III) catalysis the presence of the polyelectrolyte has little effect on the activation enthalpy, and increases the activation entropy. Thus in 18.5×10^{-4} equivalents per litre sodium polyethylenesulphonate, $\Delta H^{\neq}$ is reduced only from 10.2 to 9.9 kcal mol^{-1}, whereas $\Delta S^{\neq}$ changes from -23 cal deg^{-1} mol^{-1} in the absence of the polyelectrolyte to -9 cal deg^{-1} mol^{-1} in its presence. The different behaviour in thallium(III) catalysis is ascribed to the stronger hydration of the Tl^{3+} cation.[116]

Rate constants and activation parameters have been determined for thallium(III)-catalysed aquation of a series of cations *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$, where R = H, Me, Et, Pr^n, or Pr^i. The second-order rate law followed by these reactions is consistent with either of two likely mechanisms. The first is one-step attack of the thallium(III) at the co-ordinated chloride – S_E2 attack at the thallium(III), S_N1 at the cobalt. The other mechanism is rapid pre-equilibrium formation of a chloride-bridged cobalt(III)–thallium(III) species whose decomposition is rate-determining:

$$Co^{III}{-}Cl^{2+} + Tl^{3+} \underset{\text{rapid}}{\rightleftharpoons} [Co{-}Cl{-}Tl]^{5+} \xrightarrow{\text{r.d.s.}} \text{products}$$

In principle it is possible to distinguish between the two possibilities by a sufficient increase in reagent concentration; in practice a sufficiently high concentration is unattainable in the present system. A technically much more difficult method of distinguishing between the above two mechanisms involves isotopic fractionation experiments, a method used to make a similar mechanistic distinction for similar mercury(II)-catalysed aquations. A comparison of the relative effectiveness of thallium(III) and of mercury(II) as catalysts for aquation of the above complexes reveals that the activation enthalpies for the two catalysts are almost the same for a given complex – the difference lies in the activation entropies. Thallium(III) is a more effective catalyst for removing bromide from cobalt(III), specifically from *cis*-$[Co(en)_2(NH_3)Br]^{2+}$, than it is for removing chloride.[117] It is interesting to contrast this result with the earlier demonstration that whereas in mercury(II)-catalysed aquation of the $[Co(NH_3)_5Cl]^{2+}$ and of the *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ cations there is evidence for a stable Co—Cl—Hg intermediate, there is no evidence for a

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[115] J.-R. Cho and H. Morawetz, *J. Amer. Chem. Soc.*, 1972, **94**, 375.

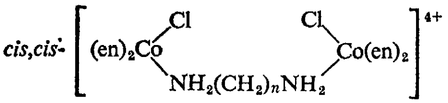
[116] N. Ise and Y. Matsuda, *J.C.S. Faraday I*, 1973, **69**, 99.

[117] S. C. Chan and S. F. Chan, *Austral. J. Chem.*, 1973, **26**, 1235.

persistent Co—Cl—Tl intermediate in the thallium(III)-catalysed aquation of these three complexes.[118]

An example of a kinetic study of the mercury(II)-catalysed aquation of a dinuclear chloro-complex of cobalt(III) is provided by that of the newly prepared and characterized dicobalt cations (19) with $2 \leqslant n \leqslant 6$. The kinetic pattern is that of a two-stage reaction, with the second step only slightly slower than the first. The reactivity of these complexes increases steadily as the polymethylene bridge lengthens; the observed first-order rate constant for removal of the first chloride is $3.3 \times 10^{-4}\ s^{-1}$ when $n = 2$ and $51 \times 10^{-4}\ s^{-1}$ when $n = 6$, at 25 °C and a mercury(II) concentration of $0.16\ mol\ l^{-1}$. The intermediacy of chloride-bridged (Co—Cl—Hg) species is assumed, though there is no direct evidence for such intermediates in these reactions.[119]

Lead(II) is rarely used as a catalyst for aquation of halogeno-complexes. However, its catalysis of aquation of *cis*-$[Co(en)_2(gly)Cl]^+$ has been studied and compared with that of $[Co(edtra)Cl]^{2-}$; interestingly the extent of pre-association between complex and Pb^{2+} seems to be similar in these two cases, despite the opposite charges on the two complexes. In the uncatalysed aquation of *cis*-$[Co(en)_2(gly)Cl]^+$ (see above) some associative character, minimized by the electrostatic repulsion between the carboxylate and the outgoing chloride, was proposed. In the lead(II)-catalysed aquation, the association of the Pb^{2+} with the carboxylate end of the glycine ligand will more than counterbalance its negative charge, permitting a high degree of associative character to the chloride loss here.[71]



(19)

In acid solution ($HClO_4$–$LiClO_4$) the rate law for the aquation of $[Co(NH_3)_5(ONO)]^{2+}$ indicates acid catalysis:

$$-d[\text{complex}]/dt = \{k_1[H^+] + k_2[H^+]^2\}[\text{complex}]$$

If halide or thiocyanate ions are also present, a third term, $k_3[H^+][X^-][\text{complex}]$, appears in the rate law. This term suggests that NOCl, NOBr, NOI, or NOSCN may be intermediates in the aquation by this pathway. If this be so, these compounds NOX may prove to be good nitrosating agents for aquo-metal complexes; they are active nitrosating agents for organic compounds.[120] Rates of aquation of the *trans*-$[Co(nioxH)_2(NO_2)_2]^-$ anion increase with increasing acid concentration owing to the greater lability of species containing protonated ligands, either —NO_2H or —$nioxH_2$. The activation enthalpy for

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[118] S.-W. Foong, B. Kipling, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 118.
[119] M. D. Alexander and H. G. Kilcrease, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1583.
[120] D. E. Klimek, B. Grossman, and A. Haim, *Inorg. Chem.*, 1972, **11**, 2382.

loss of —NO_2H is almost 6 kcal mol^{-1} less than that for loss of unprotonated —NO_2.[121] Similarly the activation enthalpy for aquation of *trans*-$[Co(dmgH)_2(NO_2)(NO_2H)]$ is 5.2 kcal mol^{-1} less than that of *trans*-$[Co(dmgH)_2(NO_2)_2]^-$.[96] The rate law for the aquation of the $[Co(NH_3)_5(SO_4)]^+$ cation indicates parallel uncatalysed and acid-catalysed pathways. The activation parameters for the latter are $\Delta H^{\ddagger} = 28.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = +9.2$ cal deg^{-1} mol^{-1}.[50]

Acid catalysis of the aquation of *cis*- and of *trans*-$[Co(en)_2(O_2CMe)_2]^+$ has already been mentioned.[48] A more extensive study of the aquation of carboxylato-cobalt(III) complexes has dealt with *cis*-$[Co(en)_2(O_2CR)_2]^+$, with R = H, Me, Et, or Pr, *cis*-$[Co(NH_3)_4(O_2CMe)_2]^+$, *cis*-$[Co(bipy)_2(O_2CMe)_2]^+$, and *trans*-$[Co(en)_2(O_2CH)_2]^+$; in each case loss of the first carboxylato-group was monitored. In all cases aquation rates depended on acid concentration, which pattern of behaviour was ascribed to a fast pre-equilibrium ligand protonation followed by rate-determining aquation of the protonated species. The observed reactivity trend for variation of the alkyl group of the carboxylato-ligand could be rationalized in terms of inductive and steric effects. An ^{18}O tracer study of the aquation of this *cis*-$[Co(en)_2(O_2CMe)_2]^+$ cation demonstrated that this proceeded solely by cobalt–oxygen bond fission.[122]

The effects of added cations on the kinetics of aquation of the *trans*-$[Co(benzylglyoximato)_2(SO_3H)Cl]^-$ anion have been investigated for a large selection of cations. The effects of added Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+; Mg^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}; and Ce^{3+} on aquation rates, and of the unicharged cations named on activation parameters, are reported. The rate of aquation decreases on adding cations, and the decrease observed is a function of the size and charge of the added ion. This trend has been ascribed to the formation of ion pairs. Both the activation energy and the activation entropy decrease slightly but regularly from added Li^+ to added Cs^+. It was argued that this evidence indicated an associative mechanism. However, one has reservations about this argument as the reported activation parameters are composite quantities and the authors appear not to have separated the enthalpies and entropies of ion-pair formation therefrom in order to obtain the real activation parameters for the actual aquation process.[123] Other aquation reactions of cobalt(III) complexes in which ion-pairing has a significant effect on the kinetics include those of $[Co(NH_3)_5X]^{2+}$ cations in the presence of sulphate or dicarboxylates[33] and of $[Co(tetren)(NCS)]^{2+}$ in perchloric and acetic acids.[83]

Bromine, but not the Br_3^- anion, accelerates the elimination of bromide and consequent ring closure, from $[Co(edta)Br]^-$. Formally this appears similar to the known catalytic effect of iodine on the aquation of $[Cr(OH_2)_5I]^{2+}$, but in fact the mechanisms of these two reactions differ markedly. Whereas the $[CrI]^{2+}$–iodine reaction is thought to proceed by the following ligand-

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[121] Z. Finta, J. Zsakó, and C. Várhelyi, *Rev. Roumaine Chim.*, 1971, **16**, 1731.
[122] T. J. Przystas, J. R. Ward, and A. Haim, *Inorg. Chem.*, 1973, **12**, 743.
[123] G. P. Syrtsova and A. N. Lokhmatova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1165.

oxidation route,[124]

$$\mathrm{CrI^{2+} + I_2 \underset{\text{fast}}{\rightleftharpoons} CrI_2^{3+} + I^-}$$

$$\mathrm{CrI_2^{3+} \xrightarrow{\text{slow}} Cr(OH_2)^{3+} + I_2}$$

the $[\mathrm{Co(edta)Br}]^-$–bromine reaction involves direct nucleophilic attack of the bromine at the co-ordinated bromide, with subsequent departure of the $\mathrm{Br_3^-}$ leaving group.[125]

A few years ago the kinetics of heterogeneous catalysis of the aquation of the $[\mathrm{Co(NH_3)_5Br}]^{2+}$ cation were investigated[126] – some of the catalysts employed [*e.g.* mercury(II) and silver(I) compounds] were closely related to the metal-ion catalysts discussed earlier in this section. A recent reinvestigation of some of these systems shows that part of the catalytic effect of these solids can be ascribed to redox processes operating in parallel to simple catalysed aquations.[127]

Photochemistry.—Irradiation of cobalt(III)–ammine–halide and related complexes at charge-transfer absorption frequencies results in redox decomposition, with a reasonable quantum yield, but irradiation of these complexes at a ligand-field ($d \rightarrow d$) frequency, which results, at least initially, in photo-aquation, generally shows a very low quantum yield. For example, the quantum yields for photoredox decomposition of $[\mathrm{Co(edtaH)X}]^-$ anions are between 0.06 and 0.45, depending on the nature of X (= Cl, Br, or $\mathrm{NO_2}$) and on which charge-transfer band is irradiated, but the quantum yields for aquation caused by ligand-field-band irradiation are between 0.004 and 0.03.[128] A recently discovered exception to this generalization is the photoaquation of the $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ cation, where the only detectable primary photoreaction resulting from irradiation at its 520 nm $d \rightarrow d$ absorption is replacement of ammonia by water with the relatively high quantum yield of approximately 0.2.[129] The irradiation of solutions containing $[\mathrm{Co(NH_3)_5(O_2CH)}]^{2+}$ at 366 nm, in the ligand-field absorption region, also results in predominant loss of ammonia. This behaviour parallels that noted previously for the acetato-analogue. Irradiation of this formato-complex at 254 nm, in the charge-transfer region, results in photoreduction with the generation of cobalt(II), ammonia, carbon dioxide, and hydrogen. There is evidence from flash photolysis experiments for some isomerization to a short-lived C-bonded formato-complex previous to charge transfer.[130]

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[124] J. H. Espenson, *Inorg. Chem.*, 1965, **4**, 1834.

[125] W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, 1973, **12**, 958.

[126] M. D. Archer and M. Spiro, *J. Chem. Soc.* (*A*), 1970, 68, 73, 78.

[127] R. J. Mureinik, A. M. Feltham, and M. Spiro, *J.C.S. Dalton*, 1972, 1981.

[128] P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, 1973, **95**, 2470.

[129] G. Ferraudi and J. F. Endicott, *J.C.S. Chem. Comm.*, 1973, 674.

[130] A. F. Vaudo, E. R. Kantrowitz, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1971, **93**, 6698; E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, 1972, **76**, 2492.

Flash photolysis studies of neutral aqueous solutions of the $[Co(NH_3)_4(CO_3)]^+$ (refs. 131, 132) and $[Co(en)_2(CO_3)]^+$ (ref. 131) cations suggest that the CO_3^- radical is a transient intermediate in the redox photoaquation of these complexes. These studies also implicated the $[Co(NH_3)_4(OH_2)(CO_3)]^+$ cation as an intermediate in photoaquation of $[Co(NH_3)_4(CO_3)]^+$; the aquo-carbonato-intermediate decays by a pH-dependent process.[131] The CO_3^- radical has again been reported as an intermediate in photoredox aquation of the $[Co(NH_3)_5(CO_3)]^+$ and $[Co(en)_2(CO_3)]^+$ cations. There is evidence from the kinetics of decay of this carbonato-radical that at pH = 7 it exists in the protonated form, HCO_3, rather than as CO_3^-.[133]

The current state of knowledge concerning photoaquation of the $[Co(NH_3)_6]^+$ cation is succinctly summarized in the introduction to a paper whose main concern is the sensitization of this reaction, in ethanol–water solution. The efficiencies of biacetyl and of quinoline as sensitizers were assessed. There exist conflicting reports on the former; the present authors aver that it does not sensitize this photoreaction efficiently.[134] The sensitization of photodecomposition of the $[Co(NH_3)_5Br]^{2+}$ cation by the $[Ru(bipy)_3]^{2+}$ cation has been studied, both in aqueous and in propan-2-ol–water solutions.[135] Sensitized photoaquations of cobalt(III) complexes are discussed in a paper whose principal subject is the sensitization of photoaquation of tris-oxalato-complexes, including $[Co(ox)_3]^{3-}$, again by the $[Ru(bipy)_3]^{2+}$ cation.[136] The first example of an efficient photoreaction of a cobalt(III)–amine complex under irradiation at a ligand-field frequency has been afforded by the reaction of $[Co(en)_3]^{3+}$ with $[Fe(CN)_6]^{4-}$. This system was investigated in 4M-NaCl solution to minimize ion-pairing and its attendant complications.[137] The photochemistry of some μ-superoxo-cobalt(III) complexes has already been discussed in the earlier section of this chapter on bridged dicobalt species.[108]

Irradiation of aqueous solutions of $[Co(edtaH)X]^-$, where X = Cl, Br, or NO_2, at a charge-transfer frequency leads to the expected redox decomposition. The oxidation of the edta ligand may involve the intermediacy of *N*-methylethylenediaminetriacetate radicals. The carboxylate charge-transfer excited state is presumed to have a lower dissociation energy than the halide or nitrite to cobalt charge-transfer state. Irradiation of these $[Co(edtaH)X]^-$ complexes at a ligand-field frequency leads to photoaquation, with loss of X^-, and in the case of the $[Co(edtaH)(NO_2)]^-$ anion to linkage isomerization as well.[128] Photoaquation of the three complexes $[Co(edtaH)X]^-$ cited here, and of $[Co(edta)]^-$, is sensitized by the $[Ru(bipy)_3]^{2+}$ cation.[135] Photoaquation of the $[Co(edta)]^-$ anion, both unsensitized and in the presence of the $[Ru(bipy)_3]^{2+}$

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[131] V. W. Cope, S. Chen, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1973, **95**, 3116.
[132] V. W. Cope and M. Z. Hoffman, *J.C.S. Chem. Comm.*, 1972, 227.
[133] S. Chen, V. W. Cope, and M. Z. Hoffman, *J. Phys. Chem.*, 1973, **77**, 1111.
[134] H. D. Gafney and A. W. Adamson, *J. Phys. Chem.*, 1972, **76**, 1105.
[135] P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, 1973, **77**, 1823.
[136] J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, 1973, **95**, 5159.
[137] N. A. P. Kane-Maguire and C. H. Langford, *J.C.S. Chem. Comm.*, 1973, 351.

cation, has been compared with that of other edta complexes of transition-metal cations, particularly of $[Fe(edtaH)(OH_2)]$.[138]

The photochemical decomposition of cobalt(III)–ammine–oxalate complexes involves primarily redox processes,[139] as does that of the *cis*-$[Co(bipy)_2Cl_2]^+$ cation.[140] The quantum yield for the photoredox aquation of $[Co(phen)_3]^{3+}$ is very low – lower even than those for cobalt(III)–amine complexes.[141] The quantum yield for photoreduction of $[Co($*trans*-$[14]$-diene$)Cl_2]^+$ is similar to that for photoreduction of $[Co(tetren)Cl]^{2+}$; both of these quantum yields are much less than that for the photoreduction of $[Co(NH_3)_5Cl]^{2+}$. Thermal back-reactions are important in determining the overall kinetic pattern for the photoreaction of the $[Co($*trans*-$[14]$-diene$)Cl_2]^+$ cation.[142]

Photoaquation studies of cyano-cobalt(III) complexes include those of the biacetyl-sensitized reaction of the $[Co(CN)_6]^{3-}$ anion,[143] and of the photoredox behaviour of the $[Co(CN)_5(N_3)]^{3-}$ anion.[144] The balance between photoaquation and photoredox processes differs for the $[Co(CN)_5X]^{n-}$ and $[Co(NH_3)_5X]^{m+}$ series of complexes.[144] Irradiation of the complexes $[Co(CN)_4(SO_3)X]^{n-}$, where X = OH_2, OH, or SO_3, at a ligand-field frequency (*e.g.* 366 nm) results mainly in the photodissociation of the sulphito-ligand; irradiation at a charge-transfer frequency (*e.g.* 254 nm) results in parallel substitution and redox reactions. Interestingly there is no loss of cyanide, in contrast with photoreactions of $[Co(CN)_5X]^{3-}$, where X = Cl, Br, or I, or indeed of $[Co(CN)_6]^{3-}$.[145] The anions $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(CN)_5(OH)]^{3-}$ readily photoaquate at room temperature, though they do not undergo thermal aquation at this temperature. The hydroxo-complex is more labile with respect to cyanide loss than its aquo-analogue.[146]

It is several years since sufficient pattern had emerged in photoreactions of chromium(III) complexes for Adamson to expound his empirical rules[147] to codify this area of photochemistry. A general pattern for photoreactions of cobalt(III) complexes has been slower to emerge, principally owing to the difficulties attendant on characterizing primary photoproducts of redox processes, since cobalt(II) is such a labile centre. However, a model based on known antibonding properties of excited states has recently been shown both to rationalize Adamson's empirical rules for chromium(III) complexes[148] and to apply to the photochemistry of cobalt(III) [and rhodium(III)] complexes.

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[138] P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, 1973, **77**, 2049.

[139] A. F. Vaudo, E. R. Kantrowitz, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, *J. Amer. Chem. Soc.*, 1972, **94**, 6655.

[140] M. Ionescu, H. Kelm, and H. F. Wasgestian, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1097.

[141] L. Moggi, N. Sabbatini, and O. Traverso, *Mol. Photochem.*, 1973, **5**, 11.

[142] S. D. Malone and J. F. Endicott, *J. Phys. Chem.*, 1972, **76**, 2223.

[143] M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, 1972, **94**, 1805.

[144] G. Ferraudi and J. F. Endicott, *J. Amer. Chem. Soc.*, 1973, **95**, 2371.

[145] M. Wrighton, H. B. Gray, G. S. Hammond, and V. Miskowski, *Inorg. Chem.*, 1973, **12**, 740.

[146] M. Wrighton and D. Bredesen, *Inorg. Chem.*, 1973, **12**, 1707.

[147] A. W. Adamson, *J. Phys. Chem.*, 1967, **71**, 798.

[148] J. I. Zink, *J. Amer. Chem. Soc.*, 1972, **94**, 8039.

Photoreactions of these complexes have been, in the author's words, 'shown to depend on the spectrochemical splitting parameter *Dq* and on the energies of the donor orbitals of the ligands and the metal *d*-orbitals in a simple and predictable way'.[149] Indeed this model has been found to be satisfactory for a wide range of octahedral transition-metal complexes,[23] while a similar model has been developed which applies not only to octahedral but also to square-planar complexes.[24]

3 Aquation: Chromium(III) Complexes

Several general features of substitution at chromium(III) have already been mentioned in the first section of this chapter. The use of activation volumes and of transition enthalpies in the assignment of substitution mechanisms is discussed there, as is evidence which suggests the operation of a mechanism with some associative character at certain chromium(III) complexes, but of a *D* [S_N1(lim)] mechanism at others.

Unidentate Leaving Groups.—*Ammonia Loss.* Kinetic studies of the aquation of chromium(III)–ammine–ligand complexes are often more complicated than those of analogous cobalt(III) complexes. Whereas for the cobalt(III) complexes aquation generally results only in replacement of the non-ammine ligand(s) by water, for many chromium(III) complexes aquation involves parallel or consecutive loss of ammonia as well as of other ligands. This is illustrated by several recently reported examples. Thus aquation of $[Cr(NH_3)_5(NO_3)]^{2+}$ yields *cis*-$[Cr(NH_3)_4(OH_2)(OH)]^{2+}$ and both isomers of $[Cr(NH_3)_3(OH_2)(OH)_2]^+$ as well as some $[Cr(NH_3)_5(OH)]^{2+}$.[150] Aquation of $[Cr(NH_3)_5(O_2CR)]^{2+}$ with $R = CCl_3$ gives only $[Cr(NH_3)_5(OH_2)]^{3+}$, but aquation of the related complexes with $R = CHCl_2$, CH_2Cl, or CH_3 yields $[Cr(NH_3)_4(OH_2)(O_2CR)]^{2+}$. Logarithms of rate constants for aquation of these complexes correlate with ligand pK_a values.[151] Aquation of $[Cr(NH_3)_4(ox)]^+$ leads entirely to ammonia loss[152] in four kinetically distinct stages;[153] earlier work had shown that $[Cr(en)_2(ox)]^+$ and $[Cr(trien)(ox)]^+$ aquate by chromium–nitrogen bond breaking. The $[Cr(en)_2(OH_2)(CH_2\text{-}2\text{-}py)]^{2+}$ cation also loses ethylenediamine quickly; subsequent chromium–carbon bond breaking in the $[Cr(OH_2)_5(CH_2\text{-}2\text{-}py)]^{2+}$ intermediate takes place much more slowly. Aquation of the isomeric complex $[Cr(en)_2(OH_2)(CH_2\text{-}3\text{-}py)]^{2+}$, however, takes place by parallel chromium–nitrogen and chromium–carbon bond-breaking pathways.[154] Kinetic parameters for the displacement of ammonia in aquation of chromium(III)–ammine complexes are listed in Table 7.[150–155]

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[149] J. I. Zink, *Inorg. Chem.*, 1973, **12**, 1018.

[150] G. Guastalla and T. W. Swaddle, *J.C.S. Chem. Comm.*, 1973, 61.

[151] E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, *Inorg. Chem.*, 1972, **11**, 1746.

[152] D. A. House, *Acta Chem. Scand.*, 1972, **26**, 2847.

[153] M. B. Davies, J. W. Lethbridge, and M. S. Mirrlees, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3354.

[154] C. T. Loo, L.-Y. Goh, and S. H. Goh, *J.C.S. Dalton*, 1972, 585.

[155] R. Davies and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 2432.

Table 7 *Kinetic parameters for ammonia loss from chromium*(III)*-ammine complexes*

Complex	k/s^{-1} (*temperature*/°C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Conditions*	*Ref.*
$[Cr(NH_3)_5(NO_3)]^{2+}$	1.6×10^{-3} (25)[a]	—	—	0.1M-NH_4ClO_4 (pH = 6)	150
$[Cr(NH_3)_5(O_2\cdot CHCl_2)]^{2+}$	1.7×10^{-3} (70)	24.7 ± 0.6	$+1\pm2$		
$[Cr(NH_3)_5(O_2C\cdot CH_2Cl)]^{2+}$	5.9×10^{-3} (70)	25.3 ± 0.5	-5 ± 2	0.1—0.01M-$HClO_4$	151
$[Cr(NH_3)_5(O_2C\cdot CH_3)]^{2+}$	2×10^{-2} (70)	19 ± 1	—		
$[Cr(NH_3)_4(ox)]^{+}$[b]	20.9×10^{-5} (35)[c]	—	—	0.5M-$HClO_4$	155
	7.5×10^{-5} (35)[c]	—	—	0.1M-$HClO_4$	155
	2.25×10^{-5} (34.8)	—	—	0.025M-$HClO_4$	152
	7.7×10^{-5} (50)	—	—	0.01M-$HClO_4$	153
$[Cr(NH_3)_3(OH_2)(ox)]^{+}$[b]	1.28×10^{-5} (34.8)	—	—	0.025M-$HClO_4$	152
	6.1×10^{-5} (50)	—	—	0.01M-$HClO_4$	153

[a] Parallel nitrate loss is characterized by a rate constant of 0.8×10^{-3} s^{-1}. [b] Note that aquation rates are strongly pH-dependent for these two complexes. [c] Estimated from the kinetics of reaction of this complex with chromium(II).

Halides. The loss of halide from *cis*- and from *trans*-$[Cr(NH_3)_4(OH_2)X]^{2+}$, with X = Br or I, is stereospecific, with complete retention of configuration as is usual at chromium(III). Activation parameters for these reactions[156] are listed in Table 8. The loss of the first halide from *trans*-$[Cr(pn)_2X_2]^+$, with X = Cl or Br, is a first-order process, and again goes with retention of configuration. The rate constant for bromide loss is larger (3.62×10^{-4} s^{-1} at 25 °C) than that for chloride loss (2.08×10^{-5} s^{-1} at 25 °C). This rate-constant difference is determined by the activation energies rather than by the activation entropies (Table 8). The kinetic pattern for the next stage in the aquation is less simple, for isomerization and chromium–nitrogen bond breaking take place in parallel with loss of halide from the *trans*-$[Cr(pn)_2(OH_2)X]^{2+}$ intermediate.[157] Some very qualitative observations on chloride loss from the $[CrCl_6]^{3-}$ anion are made in a paper reporting the preparation and hydrolysis of the $[Co(NH_3)_6]^{3+}$ salt of this new hexachlorochromium(III) anion.[158]

Table 8 *Activation parameters for aquation of halogeno-chromium*(III) *complexes*

Complex	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Conditions*	*Ref.*
cis-$[Cr(NH_3)_4(OH_2)Br]^{2+}$	20.2	−9.5	$HClO_4$–$NaClO_4$ I = 1.00	156
trans-$[Cr(NH_3)_4(OH_2)Br]^{2+}$	21.6	−9.4		
cis-$[Cr(NH_3)_4(OH_2)I]^{2+}$	20.2	−4.9		
trans-$[Cr(NH_3)_4(OH_2)I]^{2+}$	20.9	−6.7		
trans-$[Cr(pn)_2Cl_2]^+$	23.9	+0.1	0.1F-HNO_3	157
trans-$[Cr(pn)_2Br_2]^+$	22.3	+0.5	0.3F-HNO_3	

The rate laws for aquation of the complexes $[Cr(OH_2)_5X]^{2+}$, where X = Cl, Br, I, NCS, or NO_3, include acid-dependent and acid-independent terms. Transition enthalpies (ΔH_T, the enthalpy difference between transition state and products) have been determined for the acid-independent path of these aquations. The ΔH_T values cover a range of 6.4 kcal mol^{-1}. The size of this range and the order of values within it both suggest that the leaving group is less solvated and less dissociated from the chromium than in aquations of cobalt(III)–ammine–halide complexes.[10]

Oxoanions. Aquation of the four nitrito-chromium(III) complexes listed in Table 9, in acid solution (pH < 1), follows the rate law

$$-\mathrm{d}[\text{complex}]/\mathrm{d}t = \{k_1[H^+] + k_2[H^+]^2\}[\text{complex}]$$

This rate law is the same as that established for $[Co(NH_3)_5(ONO)]^{2+}$ aquation. Rate constants, obtained using stopped-flow techniques, and activation parameters are reported in Table 9. All of these reactions proceed with retention of configuration. The mechanism involves nitrogen–oxygen bond cleavage

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[156] W. W. Fee, W. G. Jackson, and P. D. Vowles, *Austral. J. Chem.*, 1972, **25**, 459.

[157] M. C. Couldwell and D. A. House, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 947; *Inorg. Chem.*, 1972, **11**, 2024.

[158] H. H. Eysel, *Z. anorg. Chem.*, 1972, **390**, 210.

in ligand-protonated derivatives $[CrL_5(ONOH)]^{n+}$ and $[CrL_5(ONOH_2)]^{(n+1)+}$. The low value of the activation enthalpy for aquation of *cis*-$[Cr(NH_3)_4(NCS)(ONO)]^+$ is attributed to neighbouring-group participation between the nitrite and the thiocyanate,[159] specifically between the lone pair on the thiocyanate nitrogen and the incipient leaving NO^+ unit {*cf.* thiocyanate catalysis of aquation of $[Co(NH_3)_5(ONO)]^{2+}$ (ref. 160)}.

The rate law for aquation of the newly characterized phosphito-complex $[Cr(OH_2)_5(O_3PH_2)]^{2+}$ is

$$-d[\text{complex}]/dt = k_1[H^+][\text{complex}]$$

and thus of the same form as that established for aquation of the hypophosphito-complex $[Cr(OH_2)_5(O_2PH_2)]^{2+}$. Rates of aquation of complexes CrX^{2+} correlate with the pK_a values of the respective acids HX for X = N_3, CN, F, or H_2PO_3, but not for X = H_2PO_2. This suggests that, whereas aquation of the hypophosphito-complex involves phosphorus–oxygen bond breaking, aquation of the phosphito-complex involves chromium–oxygen bond breaking.[161]

Other Leaving Groups. The complexes $[Cr(NH_3)_5(N_3)]^{2+}$,[162] $[Cr(NH_3)_5(O_2CCCl_3)]^{2+}$,[151] $[Cr(OH_2)_5(p\text{-}SC_6H_4NH_3)]^{3+}$,[163] and $[Cr(OH_2)_5(SCH_2CH_2NH_3)]^{3+}$ (ref. 164) all aquate in aqueous solution according to the rate law

$$-d[\text{complex}]/dt = \{k_0 + k_1[H^+]\}[\text{complex}] \qquad (5)$$

In each case the k_1 term can be assigned to a pathway in which rapid pre-equilibrium protonation of the complex is followed by rate-determining aquation. The k_0 term of equation (5) could arise from one of two kinetically equally likely paths, the separation either of HL^+ from $[Cr(OH_2)_4(OH)]^{2+}$ or of L from $[Cr(OH_2)_6]^{3+}$. Correlation of kinetic results for aquation of several such chromium(III) complexes of ligands derived from weak acids indicates that it is the former path, involving the separation of HL^+, which operates when the pK_a of HL^+ is greater than about 2.[165] Kinetic parameters for these aquations are collected together in Table 10. Some associative character is suggested for both pathways in the aquation of the azido-complex.[162] The aquation of $[Cr(OH_2)_5(p\text{-}SC_6H_4NH_3)]^{3+}$ only follows the rate law of equation (5) under anaerobic conditions; in the presence of oxygen there is autocatalysis, possibly involving oxidation of the co-ordinated ligand to a labile co-ordinated free radical.[163]

Interest is increasing in aquations in which the leaving group is uncharged. This has been mentioned earlier in this chapter in connection with cobalt(III) complexes and dimethyl sulphoxide as a leaving group. The aquation of

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[159] T. C. Matts, P. Moore, D. M. W. Ogilvie, and N. Winterton, *J.C.S. Dalton*, 1973, 992.
[160] D. E. Klimek, B. Grossman, and A. Haim, *Inorg. Chem.*, 1972, **11**, 2382.
[161] L. S. Brown and J. N. Cooper, *Inorg. Chem.*, 1972, **11**, 1154.
[162] C. Chatterjee and P. Chaudhuri, *Indian J. Chem.*, 1971, **9**, 1132.
[163] L. E. Asher and E. Deutsch, *Inorg. Chem.*, 1972, **11**, 2927.
[164] L. E. Asher and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 1774.

Table 9 *Kinetic parameters for aquation of nitrito-chromium*(III) *complexes;* k_1 *and* k_2 *are defined by the rate law cited in the text,* $\Delta H_1^{\ddagger}$ *and* $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$ *and* $\Delta S_2^{\ddagger}$ *are derived from the respective* k_1 *and* k_2 *values. Rate constants are quoted at 25 °C*[a]

Complex	10^2k_1/ l mol^{-1} s^{-1}	$\Delta H_1^{\ddagger}$/ kcal mol^{-1}	$\Delta S_1^{\ddagger}$/ cal deg^{-1} mol^{-1}	10^2k_2/ l^2 mol^{-2} s^{-1}	$\Delta H_2^{\ddagger}$/ kcal mol^{-1}	$\Delta S_2^{\ddagger}$/ cal deg^{-1} mol^{-1}
trans-$[Cr(NH_3)_4Cl(ONO)]^+$	2.59	20.3±0.3	+6±1	6.27	14.7±0.2	−12±1
cis-$[Cr(NH_3)_4(NCS)(ONO)]^+$	12.7	15.3±0.1	−8.4±0.2	86.1	11.9±0.1	−16.7±0.2
cis-$[Cr(NH_3)_4(OH_2)(ONO)]^{2+}$	5.9	—	—	12.9	—	—
cis-$[Cr(en)_2(NCS)(ONO)]^+$	13.7	—	—	45.3	—	—

[a] Earlier kinetic results for aquation of a variety of nitrito-chromium(III) complexes are tabulated in ref. 159.

Table 10 *Kinetic parameters for aquation of chromium*(III) *complexes; subscripts* 0 *and* 1 *refer to kinetic pathways defined by equation* (5) *in the text*

Complex	k_0/s^{-1} (*temperature*/°C)	$\Delta H_0^{\ddagger}$/ kcal mol^{-1}	$\Delta S_0^{\ddagger}$/ cal deg^{-1} mol^{-1}	k_1/l mol^{-1} s^{-1} (*temperature*/°C)	$\Delta H_1^{\ddagger}$/ kcal mol^{-1}	$\Delta S_1^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
$[Cr(NH_3)_5(N_3)]^{2+}$	1.4×10^{-5} (70)	26.3±1.1	−5	2.3×10^{-4} (70)	24.1±0.2	−6	162
$[Cr(NH_3)_5(O_2CCCl_3)]^{2+}$	4.9×10^{-4} (70)	21.5±0.9	−11	2.0×10^{-3} (70)	21.6±4.1	—	151
$[Cr(OH_2)_5(p\text{-}SC_6H_4NH_3)]^{3+}$	4.0×10^{-6} (25)	29.8±0.7	+17	1.1×10^{-5} (25)	23.6±0.7	−2	163
$[Cr(OH_2)_5(SCH_2CH_2NH_3)]^{3+}$	4.5×10^{-5} (25)	27.6±0.4	+14	1.3×10^{-4} (25)	20.6±0.3	−7	164

$[Cr(OH_2)_5(p\text{-}SC_6H_4NH_3)]^{3+}$, discussed in the previous paragraph, involves a formally uncharged leaving group, though in fact this leaving group is a zwitterion. 3-Picoline is a truly uncharged leaving group; the kinetics of aquation of $[Cr(OH_2)_5(3\text{-picoline})]^{3+}$ indicate a rate law

$$-\mathrm{d}[\text{complex}]/\mathrm{d}t = \{k_0 + k_{-1}[H^+]^{-1}\}[\text{complex}]$$

This is a common form of rate law for aquations of aquo-chromium(III) complexes. Activation enthalpies are greater than 30 kcal mol^{-1} for both aquation routes for this 3-picoline complex.[165]

The kinetics of aquation of the $[Cr(OH_2)_5(N_3)]^{2+}$ cation over the range $10^{-3}M < [HClO_4] < 1M$ have previously been examined. Now the kinetic pattern over the range $1M < [HClO_4] < 11M$ has been established, both to try to find the pK of the co-ordinated azido-ligand in this complex and to see if a correlation of reactivity with Hammett h_0 values exists. The rate law in these relatively strong perchloric acid media is

$$\frac{-\mathrm{d}[\text{complex}]}{\mathrm{d}t} = \frac{(ka_W + k^1)h_0}{K_1 + h_0}[\text{complex}]$$

where a_W is the water activity, h_0 the Hammett acidity constant, and K_1 the protonation constant for the complex, which could be independently determined by spectrophotometry. The established rate law was interpreted in terms of parallel S_N1 and S_N2 pathways; the N_3H ligand should be a good leaving group, facilitating dissociative aquation of the protonated form of the complex.[166]

Rates of aquation of *cis*-$[Cr(ox)_2(OH_2)(NCS)]^{2-}$ are independent of pH in the range $3 < pH < 4$. The activation parameters, derived from rate constants measured over the commendably lengthy temperature range of 25—55 °C, are $\Delta H^{\ddagger} = 20.1 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -13.1 \pm 1.2$ cal deg^{-1} mol^{-1}. On the basis of the rather flimsy evidence available, the authors tentatively suggest an I_d mechanism.[167] Activation enthalpies for aquation (pyridine or acetate loss) of the complexes *trans*-$[Cr(ox)_2(py)_2]^-$, *trans*-$[Cr(ox)_2(OH_2)(OAc)]^{2-}$, and *trans*-$[Cr(ox)_2(OH)(OAc)]^{3-}$ are 27.7, 16.3, and 8.4 kcal mol^{-1} respectively. These values correlate with the overall charges on the complexes.[168]

Multidentate Leaving Groups.—Three previously published papers have reported kinetic parameters for the aquation of the *cis*-$[Cr(mal)_2(OH_2)_2]^-$ anion. They agreed tolerably well on the activation enthalpy for this reaction, but reported very different rate constants. Now a fourth paper on the kinetics of this aquation, which follows the rate law

$$-\mathrm{d}[cis\text{-}Cr(mal)_2(OH_2)_2^-]/\mathrm{d}t = k[cis\text{-}Cr(mal)_2(OH_2)_2^-][H^+]$$

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[165] M. Orhanovic and M. Avdagic, *Inorg. Chem.*, 1973, **12**, 492.
[166] J. C. Templeton and E. L. King, *J. Amer. Chem. Soc.*, 1971, **93**, 7160.
[167] K. R. Ashley and S. Kulprathipanja, *Inorg. Chem.*, 1972, **11**, 444.
[168] M. Casula, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, 1972, **11**, 1062.

states that the value of k at 45 °C is 7.22×10^{-4} l mol^{-1} s^{-1}, and that the activation parameters are $\Delta H^{\ddagger} = 21.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5$ cal deg^{-1} mol^{-1}. A comparison of these results with the known kinetics of isomerization of the *trans*-isomer of the $[Cr(mal)_2(OH_2)_2]^-$ anion indicates that the mechanism of aquation of this *trans*-isomer involves isomerization followed by aquation of the *cis*-isomer thus produced.[169] Whereas the anions $[Cr(ox)_3]^{3-}$ and $[Cr(mal)_3]^{3-}$ aquate to *cis*-diaquo-products, the analogous methylmalonato-anion $[Cr(Me\ mal)_3]^{3-}$ aquates to the *trans*-diaquo-product. As the rate of *cis*→*trans* isomerization for $[Cr(Me\ mal)_2(OH_2)_2]^-$ is less than the rate of aquation of $[Cr(Me\ mal)_3]^{3-}$, the latter must give the *trans*-diaquo-product directly. The mechanism proposed is fast attack of two water molecules on the product of dissociation of a protonated intermediate $[Cr(LL)_2(LLH)]^{2-}$.[170] The kinetics of aquation of *cis*- and of *trans*-$[Cr(Me\ mal)_2(OH_2)_2]^-$ to $[Cr(Me\ mal)(OH_2)_4]^+$ indicate a rate law in each case of

$$-d[Cr(Me\ mal)_2(OH_2)_2^-]/dt = \{k_0 + k_1[H^+]\}[Cr(Me\ mal)_2(OH_2)_2^-]$$

Composite activation parameters are reported, and a similar aquation mechanism to that for *cis*-$[Cr(mal)_2(OH_2)_2]^-$ is suggested.[171]

Aquation of the newly characterized complex cation $[Cr(bigH)_2(ox)]^+$ results in the successive loss of the two biguanide ligands. The rate constant for loss of the first biguanide ligand is 14.2×10^{-3} s^{-1} at 40 °C and that for loss of the second ligand is 5.06×10^{-3} s^{-1} at 40 °C. The activation parameters for the two steps are $\Delta H^{\ddagger} = 18.5$ and 18.9 kcal mol^{-1} and $\Delta S^{\ddagger} = -8.4$ and -18.4 cal deg^{-1} mol^{-1} respectively. There is little evidence from which to deduce the mechanisms for the two steps, but an S_N2ca mechanism for each is tentatively suggested, principally from the derived activation enthalpy values.[172]

Aquation of $[Cr(en)_2(ox)]^+$ also results in loss of the ethylenediamine rather than of the oxalate ligand. The principal aim of the authors was to demonstrate the usefulness of ion-exchange techniques backed up by atomic absorption spectroscopy in elucidating kinetics and mechanisms of reactions of inorganic complexes in solutions of low concentrations. In the present case they were able to show that the principal reaction pathway involves the loss of the two ethylenediamine ligands in four kinetically distinct stages. Rate constants are given for all four stages; from the published results it is possible to estimate that for aquation of the $[Cr(en)(ox)(OH_2)_2]^+$ cation $\Delta H^{\ddagger} = 19.9 \pm 2.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16$ cal deg^{-1} mol^{-1}.[173] Other instances of loss of ethylenediamine or of triethylenetetramine on aquation of appropriate chromium(III) complexes have already been mentioned in connection with similar ammonia

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[169] M. J. Frank and D. H. Huchital, *Inorg. Chem.*, 1972, **11**, 776.
[170] J. C. Chang, *J. Inorg. Nuclear Chem.*, 1972, **34**, 221.
[171] J. C. Chang, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2417.
[172] D. Banerjea and S. S. Gupta, *Z. anorg. Chem.*, 1973, **397**, 215.
[173] M. B. Davies, J. W. Lethbridge, and O. Nor, *J. Chromatog.*, 1972, **68**, 231.

loss. A further example of chromium–nitrogen bond breaking in aquation of a triethylenetetramine complex is provided by the kinetic study of the stepwise aquation of 1,2,3-$[Cr(trienH)(OH_2)_2(N_3)]^{3+}$ to $[Cr(trienH_3)(OH_2)_5]^{6+}$. Here the first step is the breaking of one chromium–trien bond; the second step, *viz.* the aquation of $[Cr(trienH_2)(OH_2)_3(N_3)]^{4+}$, consists of parallel loss of azide and breaking another chromium–trien bond. All of these reactions are acid-catalysed, so it is difficult to extract individual rate constants and non-composite activation parameters from observed rate constants. However, the authors have succeeded in unravelling the rate constants at 60 °C, 3F-$HClO_4$ and have displayed them effectively on a reaction scheme diagram.[174] Rate constants for three steps in the dechelation of *N*-(2-hydroxyethyl)ethylenediamine from chromium(III) in strongly basic solution have been determined at 25 °C. These rate constants are independent of the pH.[175]

Effects of Non-leaving Ligands.—The effects of various bidentate nitrogen ligands on the ease of aquation of *trans*-$[Cr(LL)_2Cl_2]^+$ cations are illustrated by the kinetic parameters cited in Table 11. This Table includes recently reported results and, for comparative purposes, the kinetic parameters for aquation of the *trans*-$[Cr(en)_2Cl_2]^+$ cation,[176] on which reactivity comparisons in this area are generally based. Ring-size effects are illustrated by comparing the results for the complex where $(LL)_2$ = $(pn)_2$[157] and $(LL)_2$ = (en)(pn)[177] with those for the complex where $(LL)_2$ = $(en)_2$.[176] Replacement of $(en)_2$ by $(bipy)_2$ results in much slower loss of chloride.[178] In some cases similar comparisons are available for analogous bromo-complexes (Table 12).[157,179] A discussion of the reactivities of *cis*- and *trans*-$[M(LL)_2Br_2]^+$, with M = Cr or Co and LL = en or pn, suggested that the mechanism of aquation of the chromium complexes was predominantly dissociative, but with a small degree of associative character.[179]

Stereochemical and kinetic studies of the stepwise aquation of the $[Cr(CN)_6]^{3-}$ and $[Cr(CN)_5(NO)]^{3-}$ anions have indicated that the cyano-ligand has a strong *trans*-labilizing effect in this type of complex. Hence it seemed an attractive idea to study this postulated effect in the simplest member of this group, the $[Cr(OH_2)_5(CN)]^{2+}$ cation. Unfortunately accurate kinetic studies of substitution reactions of this complex were ruled out by the observation that aquation and anation processes occur at comparable rates.[14] The strong *trans* effect of iodide complexed to chromium(III)[13] is mentioned in the section on mixed and non-aqueous solvents below.

Two examples of *cis*-ligand labilization by oxoanion ligands have already

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[174] S. C. Tang, S. Lum, D. A. Kamp, R. L. Wilder, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3177.

[175] R. K. Wharton and A. G. Sykes, *J.C.S. Dalton*, 1972, 2404.

[176] D. J. MacDonald and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1961, **18**, 219.

[177] M. C. Couldwell, D. A. House, and H. K. J. Powell, *Inorg. Chem.*, 1973, **12**, 627.

[178] Yu. I. Bratushko and Yu. P. Nazarenko, *Russ. J. Inorg. Chem.*, 1972, **17**, 241.

[179] N. A. Maes, M. S. Nozari, and J. A. McLean, *Inorg. Chem.*, 1973, **12**, 750.

Table 11 *Effects of non-leaving ligands on the aquation of chloro-chromium*(III) *complexes*

Complex	$10^5k/s^{-1}$ (*temperature*/°C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Conditions*	*Ref.*
trans-$[Cr(en)_2Cl_2]^+$	2.2 (25)	22.7	−5	0.1F-HNO_3	176
trans-$[Cr(pn)_2Cl_2]^+$	2.08 (25)	23.9	+0.1	0.1F-HNO_3	157
trans-$[Cr(en)(pn)Cl_2]^+$	1.93 (25)	22.8±0.3	−3.6±0.5	0.4F-HNO_3	177
trans-$[Cr(en)(pn)(OH_2)Cl]^{2+}$[a]	0.31 (25)	21.9±1.0	−12.3±2.0	1.0F-HNO_3	177
trans-$[Cr(bipy)_2Cl_2]^+$	11.8 (80)	23.8±0.9	−10	pH≃3.9	178

[a] Aquation of *trans*-$[Cr(en)(pn)(OH_2)Cl]^{2+}$ results in both Cr—Cl and Cr—N bond breaking (*cf.* discussion earlier in text); the results quoted here refer to the replacement of the chloride only as they are derived from measurements of $+d[Cl^-]/dt$.

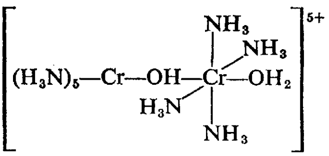
Table 12 *Effects of non-leaving ligands on the aquation of bromo-chromium*(III) *complexes*

Complex	$10^5k/s^{-1}$ (25 °C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Conditions*	*Ref.*
trans-$[Cr(en)_2Br_2]^+$	32.6	21.8	+1	0.1N-HNO_3	179
trans-$[Cr(pn)_2Br_2]^+$	36.2	22.3	+0.5	0.3F-HNO_3	157
	39.2	21.3±0.9	−2.7±3.0	0.1N-HNO_3	179
cis-$[Cr(en)_2Br_2]^+$	230	18.6±0.9	−8.3±3.0	0.01N-HNO_3	179
cis-$[Cr(pn)_2Br_2]^+$	257	18.8±1.2	−7.4±3.6	0.1N-HNO_3	179
cis-$[Cr(pn)_2(OH_2)Br]^{2+}$[a]	16	—	—	0.4N-$HClO_4$	179
cis-$[Cr(NH_3)_4(OH_2)Br]^{2+}$	8.0	20.2	−9.5	I = 1.0 ($HClO_4$, $NaClO_4$)	156
trans-$[Cr(NH_3)_4(OH_2)Br]^{2+}$	1.0	21.6	−9.4	I = 1.0 ($HClO_4$, $NaClO_4$)	156

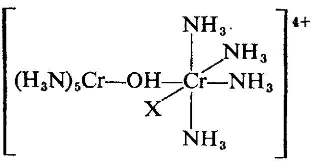
[a] Aquation of the *trans*-isomer involves both Cr—Br and Cr—N bond breaking [*cf.* the chloro-analogue (Table 11)].

been mentioned in the section on ammonia as leaving ligand.* These concerned aquation of the carboxylato-complexes $[Cr(NH_3)_5(O_2CR)]^{2+}$, with R = CH_3, CH_2Cl, or $CHCl_2$,[151] and of the nitrato-complex $[Cr(NH_3)_5(NO_3)]^{2+}$.[150] As the authors of the latter paper believe that substitution at chromium(III) is often associative in character, they propose that this *cis*-activation involves the intermediacy of a transient bidentate nitrato-complex, whose formation involves the easing out of a *cis*-ammonia by the incoming nitrato oxygen in an associative seven-co-ordinate transition state. Such behaviour might also occur in similar compounds containing potentially bidentate oxoanion ligands. This would explain the failure to prepare $[Cr(NH_3)_5(SO_4)]^+$ salts, and some features of aquation of nitrito-chromium(III) complexes (p. 191).[150]

Bridged Dichromium Complexes.—Aquation of the hydroxo-bridged complex (20) in acidic aqueous solution yields *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ and $[Cr(NH_3)_5(OH_2)]^{3+}$. The reaction follows first-order kinetics, and the rate constant is independent of pH in the range $0.2M < [HClO_4] < 0.7M$. The activation enthalpy is reported as 27.0 ± 0.5 kcal mol^{-1}; the activation entropy is $+8.8$ cal deg^{-1} mol^{-1}.[180] The products of aquation of the bridged dichromium complexes (21) and (22) are the $[Cr(NH_3)_5(OH_2)]^{3+}$ and *cis*-$[Cr(NH_3)_4(OH_2)X]^{2+}$ cations. Again the rates of aquation of these two complexes are independent of pH – it is interesting to note that whereas aquation rates of μ-hydroxo-dicobalt(III) complexes generally vary markedly with pH, the only μ-hydroxo-dichromium(III) complex so far observed to show a pH-dependence of aquation rates is the $[(phen)_2Cr(OH)_2Cr(phen)]^{4+}$ cation.[101] For complex (21) activation parameters for aquation are quoted as $\Delta H^{\neq} = 23.12 \pm 0.59$ kcal mol^{-1} and $\Delta S^{\neq} = -3.46 \pm 1.82$ cal deg^{-1} mol^{-1}, and for complex (22). $\Delta H^{\neq} = 16.92 \pm 1.50$ kcal mol^{-1} and $\Delta S^{\neq} = -7.78 \pm 4.47$ cal deg^{-1} mol^{-1}.[181]



(20)



(21) X = F

(22) X = NCS

* A third recent example of such *cis* labilization is provided by the (formation) reactions of edta with $[Cr(OH_2)_6]^{3+}$ and with carboxylato-complexes $[Cr(OH_2)_5(O_2CR)]^{2+}$. In the latter cases, the observed faster rates of replacement of water have been ascribed to an analogous *cis* anchimeric effect to that operating in the ammine aquations mentioned (M. V. Olson, *Inorg. Chem.*, 1973, **12**, 1416). This type of anchimeric effect has been observed previously, as for example in the rapid aquation of *O*-nitrito-chromium(III) complexes [T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1971, 1632].

[180] H. N. Po and H. Enomoto, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2581.

[181] H. N. Po, Y.-H. Chung, and S. R. Davis, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2849.

The kinetics of sulphate exchange with two μ-sulphato-dichromium(III) complexes[182] are reported in the ligand-exchange section of this chapter (p. 247), and the photoaquation of μ-hydroxo-dichromium complexes at the appropriate later stage in this section.

Mixed and Non-aqueous Solvents.—Studies of solvolyses of chromium(III) complexes in mixed aqueous solvents are particularly fruitful when kinetic studies can be complemented by n.m.r. studies of the solvation shell of the complexes.[183] The latest application of this approach has been to the solvolysis of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ in aqueous acetonitrile. The kinetic pattern for thermal solvolysis does not correlate with the concentration, mole fraction, or activity of the water, but correlates well with the variation of the solvent-shell composition established by n.m.r. This is best interpreted in terms of a mechanism in which an encounter equilibrium between complex and solvent is treated as distinct from the subsequent interchange aquation step. As usual, the pattern of photochemical aquation differs from the above behaviour in thermal aquation, since the excited state in photochemical aquation has a much longer lifetime.[184] Rates of solvolysis of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ in alcohols (pure, not aqueous mixtures) decrease in the order methanol > ethanol > propanol.[185] In all these cases aquation results solely in displacement of the thiocyanate, but in solvolysis of [Cr(*m*-xylidine)$_2$(NCS)$_4$]$^-$ in aqueous ethanol there is parallel replacement of *m*-xylidine and of thiocyanate. It is suggested that the former is replaced by ethanol and the latter by water, though there seems to be insufficient product investigation to prove this hypothesis unequivocally.[186] Similarly the solvolysis of the $[Cr(py)_2(NCS)_4]^-$ anion in acetone–water mixtures results in parallel loss of pyridine and of thiocyanate. Monitoring the rate of liberation of thiocyanate ion permits the separation of the overall observed rate of solvolysis into thiocyanate-loss and pyridine-loss components. The variation of these separated rate constants with solvent composition has been interpreted in terms of an associative mechanism for the replacement both of thiocyanate and of pyridine. Again the lack of product-analysis figures leaves the reader in some doubt as to which ligand is replaced by which solvent. The composite activation parameters for these solvolyses vary little with solvent: $24.6 < \Delta H^{\ddagger} < 25.3$ kcal mol^{-1} and $-10.8 < \Delta S^{\ddagger} < -5.4$ cal deg^{-1} mol^{-1}.[187] A review of the solvolysis of complexes of this [Cr(amine)$_2$(NCS)$_4$]$^-$ type lists 47 references.[188]

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[182] S. Indubala and D. Ramaswamy, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2055.

[183] See, *e.g.*, p. 162 of Volume 2 of this Report.

[184] V. S. Sastri, R. W. Henwood, S. Behrendt, and C. H. Langford, *J. Amer. Chem. Soc.*, 1972, **94**, 753.

[185] A. Lodzinska and P. Kita, *Roczniki Chem.*, 1972, **46**, 815 (*Chem. Abs.*, 1972, **77**, 144 256a).

[186] J. Zsakó, V. Voiculescu, I. Ganescu, and A. Popescu, *Rev. Roumaine Chim.*, 1972, **17**, 1977.

[187] J. Zsakó, D. Oprescu, C. Várhelyi, and I. Ganescu, *Russ. J. Inorg. Chem.*, 1972, **17**, 1705.

[188] G. Thomas, *Wiss. Z. Martin-Luther-Univ., Halle-Wittenberg, Math. Naturwiss. Reihe*, 1970, **19**, 93 (*Chem. Abs.*, 1971, **75**, 67 886k).

In dimethyl sulphoxide solutions of *cis*- and of *trans*-$[Cr(en)_2Br_2]^+$ both isomerization and solvolysis are important:

$$\underset{trans}{\overset{cis}{\upharpoonleft\!\downharpoonright}}\ [Cr(en)_2Br_2]^{2+} \rightleftharpoons \underset{trans}{\overset{cis}{\upharpoonleft\!\downharpoonright}}\ [Cr(en)_2(DMSO)Br]^{2+} \rightleftharpoons \underset{trans}{\overset{cis}{\upharpoonleft\!\downharpoonright}}\ [Cr(en)_2(DMSO)_2]^{3+}$$

All of these processes are thought to be dissociative in character, with ion-pairing having a significant effect on reactivities.[189] The analogous chloride system is in fact slightly more complicated, for *trans*-$[Cr(en)_2(DMSO)Cl]^{2+}$ undergoes solvolysis by parallel reactions involving the displacement of chloride or of ethylenediamine. It still remains to measure DMSO exchange rates before a complete kinetic picture and discussion of these systems can be presented.[190] Another investigation conducted in DMSO was that of the reaction of $[Cr(CN)_5(NO)]^{3-}$ with alkyl halides, which induce solvolysis to $[Cr(DMSO)_5(NO)]^{2+}$.[191] E.s.r. spectroscopy provided information on the intermediates involved in this five-step solvolysis sequence; the reaction pattern and methods of investigation are very similar to those for the earlier-studied aquation of the $[Cr(CN)_5(NO)]^{3-}$ anion.[192] The mechanism for the displacement of the cyanide by DMSO is suggested, on the basis of kinetic evidence, to involve attack at the co-ordinated cyanide, and is therefore mentioned in Chapter 5. When solvolysis of $[Cr(OH_2)_5I]^{2+}$ is conducted in dimethyl sulphoxide–water mixtures, the dimethyl sulphoxide proves an invaluable stereochemical label to provide definitive support for the specifically *trans*-labilizing effect of iodide first proposed on the basis of experiments on this complex in aqueous solution.[13]

That logarithms of rate constants for aquation of cobalt(III)–chloride complexes in aqueous–organic mixed solvents correlate with Grunwald–Winstein solvent Y values is now well established.[193] A similar correlation has now been found for aquation of several chromium(III)–chloride complexes, *viz.* $[Cr(NH_3)_5Cl]^{2+}$, *cis*-$[Cr(en)_2Cl_2]^+$, and *trans*-$[Cr(OH_2)_4Cl_2]^+$. The slopes (m) of the correlation plots are markedly less than those for similar cobalt(III) complexes. This difference might arise from a marked degree of associative character to the aquation at chromium(III) – (approximate) m values for S_N2 organic solvolyses are less than the value of m defined for S_N1 solvolyses of t-butyl chloride. It has been suggested that the slightly larger size, and hence perhaps slightly lower degree of solvation, of the chromium(III) than of the cobalt(III) complexes, might contribute to the lower m values for the former complexes. This explanation seems unlikely in the light of reported m values for rhodium(III) and for iridium(III) complexes which are as high as those for their cobalt(III) analogues. An attempt to extend this Grunwald–Winstein

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[189] D. A. Palmer and D. W. Watts, *Inorg. Chim. Acta*, 1972, **6**, 197.

[190] D. A. Palmer and D. W. Watts, *Inorg. Chim. Acta*, 1972, **6**, 515.

[191] D. C. McCain, *Inorg. Chim. Acta*, 1971, **5**, 611.

[192] See p. 170 of Volume 1 of this Report.

[193] See, *e.g.*, C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228; J. Burgess, *J. Chem. Soc. (A)*, 1970, 2703; J. Burgess and M. G. Price, *ibid.*, 1971, 3108.

treatment of solvolysis rates in mixed aqueous solutions to aquation of chromium(III)–thiocyanate complexes was unsuccessful.[194]

pH Variation.—There are two ways in which variation of pH produces a variation in aquation rates for chromium(III) complexes. The first operates for complexes with ligands which can be protonated; here the variation of rate with pH reflects the different reactivities of the protonated and unprotonated forms of the complex and the equilibrium constant relating them. The second operates for aquo-chromium(III) complexes, where the variation of rate with pH arises from the differing reactivities of the complex and of its conjugate base.

The rate law for aquations of complexes containing ligands which can be protonated is usually

$$-\mathrm{d[complex]/d}t = \{k_0 + k_1[\mathrm{H^+}]\}[\mathrm{complex}] \qquad (6)$$

Complexes whose aquation kinetics conform to this pattern include $[Cr(NH_3)_5(N_3)]^{2+}$,[162] $[Cr(NH_3)_5(O_2CCCl_3)]^{2+}$,[151] and $[Cr(OH_2)_5(p\text{-}SC_6H_4NH_3)]^{3+}$.[163] Rate constants for these complexes have been listed in Table 10. The rate law for aquation of $[Cr(OH_2)_5(O_3PH_2)]^{2+}$ corresponds to equation (6) with $k_0 = 0$;[161] that for aquation of several nitrito-chromium(III) complexes has terms in $[H^+]$ and in $[H^+]^2$.[159]

Rate laws for aquation of aquo-chromium(III) contain terms in $[H^+]^{-1}$ when aquation of the conjugate base makes a significant contribution to the overall aquation reaction. Thus the rate laws for aquation of *cis*- and *trans*-$[Cr(en)_2(OH_2)Cl]^{2+}$, of $[Cr(NH_3)_4(OH_2)Cl]^{2+}$,[195] and of $[Cr(OH_2)_5(3\text{-picoline})]^{3+}$ (ref. 165) are

$$-\mathrm{d[complex]/d}t = \{k_0 + k_{-1}[\mathrm{H^+}]^{-1}\}[\mathrm{complex}]$$

Many reported rate laws for aquation of aquo-chromium(III) complexes do not contain the $k_{-1}[H^+]^{-1}$ term. This will generally be the case if the pH range covered by the experiments is entirely in the fairly to strongly acid region {the pK_a of $[Cr(OH_2)_6]^{3+}$ itself is 3.82 (ref. 196)}.

The variation of aquation rate with pH of the $[Cr(OH_2)_5(N_3)]^{2+}$ cation will reflect both ionization of a proton from co-ordinated water and protonation of co-ordinated azide. The most recent kinetic study[166] of aquation of this complex reports the rate law for aquation in 1—11M-$HClO_4$ (see the section on unidentate leaving groups above), where it is the reversible protonation of the azido-ligand which affects rates of aquation.

Catalysis.—In 1965 Langford reported that a linear free-energy plot of logarithms of aquation rate constants against logarithms of stability constants for a series of $[Co(NH_3)_5X]^{2+}$ complexes had a slope of 1.0. This suggested that

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[194] J. Burgess, *J.C.S. Dalton*, 1973, 825.

[195] Yu. I. Bratushko and Yu. P. Nazarenko, *Ukrain. khim. Zhur.*, 1972, **38**, 3 (*Chem. Abs.*, 1972, **76**, 90 609b).

[196] A. G. Sykes, 'Kinetics of Inorganic Reactions', Pergamon, Oxford, 1966, p. 280.

the characteristics of the solvated leaving X^- in the transition state were very similar to those of the product X^-. A similar plot for iridium(III) complexes had a slope of 0.9 and one for chromium(III) complexes a slope of 0.6. This latter low value suggested that the departing halide was less like the product ion in aquation of chromium(III) halide complexes, a conclusion not inconsistent with some degree of associative character, as suggested in earlier sections of this chapter. Although halides might not be good leaving groups from chromium(III), HgX^+ units are likely to be good leaving groups, or, alternatively phrased, mercury(II)-catalysed aquation of chromium(III)–halide complexes is likely to be purely dissociative in mechanism as far as the chromium is concerned. Thus one might expect the linear free-energy plot for mercury(II)-catalysed aquation to have a slope close to 1.0. Such a linear free-energy plot has now been presented, and indeed has a slope of 0.90.[197] However, this result is less clear-cut than it might be, for three reasons. Firstly, the rate constants determined are likely to be composite quantities, each consisting of the equilibrium constant for the formation of a dinuclear Cr—Cl—Hg bridged intermediate and the rate constant for its dissociation. Secondly, the dependence of the observed rate constants for aquation of the iodo-complex on mercury(II) concentration is not as simple as expected. And, thirdly, previously published results for the analogous pseudohalide complex $[Cr(OH_2)_5(NCS)]^{2+}$ do not fit the correlation graph for these halide complexes $[Cr(OH_2)_5X]^{2+}$.

The rate law for these mercury(II)-catalysed aquations of $[Cr(OH_2)_5X]^{2+}$, with X = Cl or Br, is

$$-d[\text{complex}]/dt = \{k_0 + k_{-1}[H^+]^{-1}\}[Hg^{2+}][\text{complex}]$$

Rate constants and activation parameters are reported for both paths for the compounds X = Cl and Br reacting with Hg^{2+}, and for the compound with X = I reacting with $HgCl^+$ or $HgCl_2$.[197] Rate laws and kinetic parameters have also been reported for the mercury(II)-catalysed aquations of *cis*-$[Cr(NH_3)_4(OH_2)X]^{2+}$ with X = Cl, Br, or I, and of *trans*-$[Cr(NH_3)_4(OH_2)X]^{2+}$ with X = Br or I.[156]

The aquation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ is catalysed by iron(III), the rate law being

$$-d[\text{complex}]/dt = \{k_1[Fe^{3+}] + k_2[H^+]\}[\text{complex}]$$

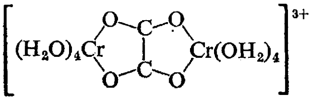
Activation parameters for the path corresponding to the $k_1[Fe^{3+}]$term are $\Delta H^{\ddagger} = 24.2 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 8.9 \pm 1.6$ cal deg^{-1} mol^{-1}. The iron(III) assists the oxalate group to leave by co-ordinating to it, possibly in a unidentate-oxalate intermediate rather than in the starting complex itself.[198] Several examples of metal-ion-catalysed aquation of chromium(III) complexes are included in the general rate constant against stability constant correlation discussed in the section on catalysed aquation of cobalt(III) complexes.[113, 114]

[197] J. P. Birk and C. M. Ingerman, *Inorg. Chem.*, 1972, **11**, 2019 and refs. therein.
[198] S. N. Choi and D. W. Carlyle, *Inorg. Chem.*, 1972, **11**, 1718.

Redox catalysis of aquation of chromium(III) complexes by chromium(II) is a special case of metal-ion-catalysed aquation. The rate law for the redox aquation of $[\mathrm{Cr(OH_2)_5(py)}]^{3+}$ is

$$-\mathrm{d}[\mathrm{Cr(py)}^{3+}]/\mathrm{d}t = k[\mathrm{Cr(py)}^{3+}][\mathrm{Cr}^{2+}][\mathrm{H}^{+}]^{-1}$$

which suggests a hydroxo-bridged inner-sphere mechanism.[199] Activation parameters for this reaction are $\Delta H^{\ddagger} = 20.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.9 \pm 0.6$ cal deg^{-1} mol^{-1}, which may be compared with the activation parameters for mercury(II)-catalysed aquation of similar chromium(III) complexes mentioned above. An oxalate-double-bridge transition state (23) is suggested for the chromium(II)-catalysed aquation of $[\mathrm{Cr(ox)(OH_2)_4}]^{+}$. The activation parameters for this catalysed aquation are $\Delta H^{\ddagger} = 11$ kcal mol^{-1} and $\Delta S^{\ddagger} = -26$ cal deg^{-1} mol^{-1}. The rate of this reaction is not a function of the pH, but rates of the chromium(II)-catalysed aquation of *cis*-$[\mathrm{Cr(ox)_2(OH_2)_2}]^{-}$ are pH-dependent. For this complex $\Delta H^{\ddagger} = 12$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24$ cal deg^{-1} mol^{-1} at $[\mathrm{H}^{+}] = 1.0$M.[200] Electrochemical reduction of $[\mathrm{Cr(phen)_3}]^{3+}$ also involves some aquation catalysed by chromium(II) species produced.[201] An e.s.r. study of the kinetics of, and intermediates in, aquation of $[\mathrm{Cr(CN)_5(NO)}]^{3-}$ deals with the catalytic effects of $[\mathrm{Cr(OH_2)_6}]^{3+}$, $[\mathrm{Cu(citrate)}]^{2-}$, and $[\mathrm{Fe(CN)_6}]^{3-}$; the possibility of a redox mode of catalysis is discussed.[202]



(23)

Aquation of the $[\mathrm{Cr(ox)_3}]^{3-}$ anion is enormously accelerated in the presence of surfactants such as octylammonium tetradecanoate or dodecylammonium propionate. This catalytic effect is ascribed to hydrogen-bonding between substrate oxygen and surfactant $\mathrm{RNH_3^+}$ groups. Significantly, hexadecyltrimethylammonium butyrate, where the $\mathrm{R_4N^+}$ group cannot hydrogen-bond to substrate oxygen, does not show this catalytic effect. In benzene–water solvents the reaction is first-order in water concentration, which suggests an associative mechanism for these aquations.[203]

Photochemistry.—The study of the photochemistry of chromium(III) complexes in aqueous solution continues to flourish. It is several years since Adamson stated his empirical rules[204] which effectively summarized the state of knowledge in this area at the time, and which have proved applicable to practically all chromium(III) complex photoreactions investigated sub-

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[199] M. Orhanovic and V. Buthovic, *Inorg. Chim. Acta*, 1972, **6**, 652.
[200] T. Spinner and G. M. Harris, *Inorg. Chem.*, 1972, **11**, 1067.
[201] D. M. Soignet and L. G. Hargis, *Inorg. Chem.*, 1972, **11**, 2921.
[202] A. T. Nikitaev, A. Ya. Sychev, and K. I. Zamaraev, *Russ. J. Inorg. Chem.*, 1972, **17**, 512.
[203] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1973, **95**, 600.
[204] A. W. Adamson, *J. Phys. Chem.*, 1967, **71**, 798.

sequently. However, it has recently become apparent that an isomerization step subsequent to, or associated with, ligand loss is necessary to accommodate some of the observations of stereochemical courses of photoaquation of mixed-ligand chromium(III) complexes. Thus, for example, $[Cr(NH_3)_5X]^{2+}$ cations, with X = Cl, Br, or O_2CR, photoaquate with loss of ammonia, as expected, but produce the *cis*- rather than the *trans*-isomer of $[Cr(NH_3)_4(OH_2)X]^{2+}$. An early report[205] on the photoaquation of the $[Cr(NH_3)_5(NCS)]^{2+}$ cation suggested, rather tentatively, that the product was *trans*-$[Cr(NH_3)_4(OH_2)(NCS)]^{2+}$, but a recent reinvestigation[206] has shown that the product is the *cis*-isomer. Thus the photoaquation of this thiocyanato-complex conforms to the pattern established for photoaquation of other $[Cr(NH_3)_5X]^{2+}$ cations.

Now that Adamson's rules have been firmly established and widely illustrated, efforts are being made to provide a systematic theoretical basis for them and to elucidate the natures of the excited states involved. In the previous volume of this Report an attempt to explain the photoaquation behaviour of chromium(III) complexes in terms of relative metal–ligand bond strengths was mentioned.[207] A more ambitious attempt to relate the observed photochemistry and Adamson's rules to metal–ligand bonding parameters, based on fundamental crystal-field and molecular orbital theory, has now been described. A model is developed in which the change in the strength of the metal–ligand bond on excitation from the ground to the excited state is the matter of central concern; the model assumes a dissociative mechanism for these photoaquations.[208]

Two mechanisms have been put forward to explain the photochemistry of chromium(III) complexes. Their photoreactivity has been ascribed to excitation either to the lowest spin-forbidden excited state, ^2E_g, or to the lowest quartet excited states, $^4T_{2g}$ and $^4T_{1g}$. Several years ago some quenching experiments on the photoaquation of the $[Cr(NH_3)_2(NCS)_4]^-$ anion indicated that a quartet state was at least partially involved.[209] Recently two papers concerning the photochemistry of the $[Cr(CN)_6]^{3-}$ anion, chosen for the known large energy difference between the doublet and quartet states, have provided strong evidence for a quartet state as the photointermediate. Thus the observations that pyrazine and xanthone sensitize the photoaquation of $[Cr(CN)_6]^{3-}$, but that Michler's ketone and $[Ru(bipy)_3]^{2+}$ do not, rule out photoaquation *via* a doublet state.[210] Likewise a comparison of phosphorescence and photolysis of solutions of $[Cr(CN)_6]^{3-}$ in dimethylformamide showed that the photolysis, to $[Cr(CN)_5(DMF)]^{2-}$, could not proceed *via* the same excited state, ^2E_g, as phosphorescence.[211] Both of these investigations led to the implication of the

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[205] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1969, **91**, 1076.
[206] E. Zinato and P. Riccieri, *Inorg. Chem.*, 1973, **12**, 1451.
[207] S. C. Pyke and R. G. Linck, *J. Amer. Chem. Soc.*, 1971, **93**, 5281.
[208] J. I. Zink, *J. Amer. Chem. Soc.*, 1972, **94**, 8039.
[209] S. N. Chen and G. B. Porter, *Chem. Phys. Letters*, 1970, **6**, 41.
[210] N. Sabbatini and V. Balzani, *J. Amer. Chem. Soc.*, 1972, **94**, 7587.
[211] H. F. Wasgestian, *J. Phys. Chem.*, 1972, **76**, 1947.

$^4T_{2g}$ state as the excited state for photolysis. Differences between the photoreactivities of rigid cyclam complexes and the other non-rigid amine and ammine complexes are also claimed to support a quartet photointermediate.[212] It seems that the $^4T_{2g} \rightarrow {}^2E_g$ transformation is relatively easy, at least for [Cr(acac)$_3$].[213] Photoexcitation of [Cr(NCS)$_6$]$^{3-}$ or of [Cr(NH$_3$)$_2$(NCS)$_4$]$^-$ to the $^4T_{2g}$ state is followed either by release of thiocyanate ion and consequent aquation or by non-radiative transition to the ^2E_g state.[214]

The photochemistry of chromium(III) complexes has been usefully collected and collated in a recent review, in which the involvement of the quartet state in these photoreactions is discussed.[215] This review also highlights the domination of chromium(III) photochemistry by solvolysis, generally aquation, reactions. There are relatively few examples of photoracemization and photoisomerization, and, until a report on the photochemistry of [Cr(NH$_3$)$_5$(N$_3$)]$^{2+}$ published this year,[216] no unequivocal examples of photoredox processes.

Quantum yields have been determined for aquation of several complexes of the general formula [Cr(NH$_3$)$_5$L]$^{n+}$, where L = carboxylate (O$_2$CR, with R = CCl$_3$, CHCl$_2$, CHCl$_2$, CH$_3$, or CF$_3$)[151] or halide.[217, 218] Quantum yields for the aquation of amine analogues [Cr(RNH$_2$)$_5$Cl]$^{2+}$, where R = Me or Et, have also been determined.[217] In several cases the estimation of quantum yields is complicated by parallel loss of ammonia or amine and chloride.[217, 218] The relative importance of ammonia loss and of halide loss has been related to their respective crystal-field parameters.[218] Whereas thermal aquation of the ammine–carboxylate complexes results in parallel loss of ammonia or of carboxylate, the photoaquation proceeds entirely by ammonia loss. The quantum yield and mechanism of photoaquation of [Cr(en)$_3$]$^{3+}$ have been described.[219]

The majority of photochemical studies of chromium(III) complexes have to date dealt with mononuclear complexes containing either one or two types of ligand molecule. In order to see whether the general principles evolved for these classes of complex can be extended to more complicated species, an investigation of the *trans*-[Cr(en)$_2$(NCS)Cl]$^+$ cation was conducted. Photoaquation of this complex involves parallel loss of chloride, of thiocyanate, or of ethylenediamine. All three reactions are thought to proceed *via* a quartet excited state, though it is suggested that whereas photosolvolysis of the chloride or thiocyanate involves the ^4E state, photosolvolysis of the ethylenediamine may involve the higher-energy $^4B_2$ state.[220] Thermal reactions of the

[212] A. W. Adamson and C. Kutal, *Mol. Photochem.*, 1973, **5**, 251.

[213] J. T. Yardley and K. J. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 8925.

[214] T. Ohno and S. Kato, *Bull Chem. Soc. Japan*, 1973, **46**, 1602.

[215] A. D. Kirk, *Mol. Photochem.*, 1973, **5**, 127

[216] A. Vogler, *J. Amer. Chem. Soc.*, 1971, **93**, 5912.

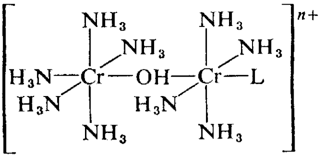
[217] C. H. Langford and L. Tipping, *Canad. J. Chem.*, 1972, **50**, 887.

[218] V. S. Sastri, *Z. phys. Chem. (Frankfurt)*, 1973, **84**, 10.

[219] W. Geis, H. F. Wasgestian, and H. Kelm, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1093.

[220] M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Amer Chem. Soc.* 1972, **94**, 7152.

μ-hydroxo-dichromium(III) complexes (24) and (25) involve cleavage of the hydroxo-bridge, but such cleavage does not occur in photochemical reactions of these complexes. The cation (24) merely isomerizes from the *trans*- to the *cis*-form, and the cation (25) has either the chloride or one ammonia replaced by water.[221]



(24) $L = OH_2; n = 5$

(25) $L = Cl; n = 4$

The role of sensitization in the elucidation of mechanisms of photoaquation has already been alluded to at the beginning of this section. Other papers in which the effect of sensitizing agents on photoreactions of chromium(III) complexes are discussed include one on $[Cr(CN)_6]^{3-}$ plus $[Ru(bipy)_3]^{2+}$,[222] one on $[Cr(ox)_3]^{3-}$ plus again $[Ru(bipy)_3]^{2+}$,[136] and one on $[Cr(NH_3)_5X]^{2+}$, where X = Cl or NCS, plus riboflavin.[223]

4 Aquation: Other Complexes

***d*⁰: Titanium(IV).**—The kinetics of the autocatalytic hydrolysis of hexafluorotitanate(IV) have been examined titrimetrically, at 0 and at 25 °C in aqueous solution. The results were discussed in terms of the establishment of the following equilibria:[224]

$$[TiF_6]^{2-} + 2H_2O \rightleftharpoons [TiF_4(OH)(OH_2)]^- + F^- + HF$$

$$[TiF_4(OH)(OH_2)]^- + H_2O \rightleftharpoons [TiF_3(OH)(OH_2)_2] + F^-$$

d^1: Molybdenum(V).—Photochemical studies of the molybdenum(IV) anion $[Mo(CN)_8]^{4-}$ are common (*cf.* below), but of its molybdenum(V) analogue $[Mo(CN)_8]^{3-}$ they are rare. The photoreduction of this latter anion involves substitution, for the product in neutral or acidic solution is $[Mo(CN)_7(OH_2)]^{3-}$, in alkaline solution $[Mo(CN)_7(OH)]^{4-}$. This hydroxo-anion quickly reacts further to give the $[Mo(CN)_4(O)(OH)]^{3-}$ anion. The suggested mechanism involves a dissociative aquation step followed by electron transfer within a $[Mo(CN)_7(OH_2)]^{3-}\ CN^-$ ion pair.[225]

d^2: Molybdenum(IV).—Yet further studies on the photochemistry of

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[221] P. Riccieri and E. Zinato, *Inorg. Chim. Acta*, 1973, 7, 117.
[222] F. Bolletta, M. Maestri, and L. Moggi, *J. Phys. Chem.*, 1973, **77**, 861.
[223] E. L. Wehry, *J. Amer. Chem. Soc.*, 1973, **95**, 2137.
[224] I. G. Ryss, M. O. Tereshkevich, and V. G. Korovina, *Russ. J. Phys. Chem.*, 1972, **46**, 1334.
[225] G. W. Gray and J. T. Spence, *Inorg. Chem.*, 1971, **10**, 2751.

$[Mo(CN)_8]^{4-}$ solutions deal with the quantum yield of the primary photoaquation reaction.[226] The photoaquation and photoredox processes in the photochemistry of $[Mo(CN)_8]^{4-}$ have been succinctly contrasted in a paper whose main discussion is concerned with the solvated electrons formed during irradiation of aqueous solutions containing this complex ion at internal-charge-transfer and charge-transfer-to-solvent frequencies.[227]

***d^2*: Tungsten(IV).**—The quantum yield for the primary photoaquation process of the $[W(CN)_8]^{4-}$ anion has been determined, *via* polarographic estimation of cyanide liberated and spectrophotometric estimation of the heptacyano-complex produced.[226]

***d^2*: Osmium(VI).**—The hydrolysis of the osmium(VI) esters $OsO_2(OR)_2L_2$, whose rate law for redox formation from osmium tetroxide, cyclohexene-3-carboxylic acid, and (substituted) pyridine has been determined, takes place exclusively by osmium–oxygen bond cleavage. This has been shown by ^{18}O-tracer experiments.[228]

***d^3*: Molybdenum(III).**—The kinetics of the first stage in the aquation of the hexachloromolybdate anion,

$$[MoCl_6]^{3-} \longrightarrow [MoCl_5(OH_2)]^{2-}$$

have been studied at 0 °C. The rate constant for this first-order reaction is $1.33 \times 10^{-4}\ s^{-1}$. Subsequent aquation of $[MoCl_5(OH_2)]^{2-}$ to $[MoCl_4(OH_2)_2]^-$ is much slower than this. One cannot make a direct molybdenum–chromium reactivity comparison here, as only very qualitative information of the aquation of $[CrCl_6]^{3-}$ is available (see Section 3 of this chapter). However, one can observe that this $[MoCl_6]^{3-}$ aquation is a pretty fast substitution process for a d^3 centre.[229]

***d^3*: Rhenium(IV).**—In aqueous solution containing dissolved oxygen, the final product of the aquation of the $[ReCl_6]^{2-}$ or $[ReBr_6]^{2-}$ anions is tetraoxorhenate(VII). The rate-determining step in the reaction sequence is the loss of the first halide ion from the rhenium(IV). Activation parameters for the aquation of the $[ReBr_6]^{2-}$ anion in aqueous solution are $\Delta H^{\neq} = 26.0\ \text{kcal mol}^{-1}$ and $\Delta S^{\neq} = -6\ \text{cal deg}^{-1}\ \text{mol}^{-1}$; the high activation enthalpy reflects both the d^3 configuration of the central cation and its high formal charge of +4. The variation of aquation rate with solvent composition in mixed aqueous solvents hints at a dissociative mechanism. The expected catalysis of aquation by mercury(II) was observed.[230]

***d^4*: Manganese(III).**—The dependence of rates of hydrolysis of trisoxalatomanganate(III) on pH, on oxalate concentration, and on the concentration of added salts suggests that the kinetic pattern is determined by the presence of

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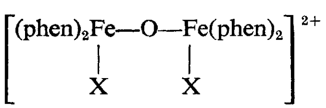
[226] R. P. Mitra, B. K. Sharma, and H. Mohan, *Austral. J. Chem.*, 1972, **25**, 499.
[227] M. Shirom and Y. Siderer, *J. Chem. Phys.*, 1972, **57**, 1013.
[228] L. R. Subbaraman, J. Subbaraman, and E. J. Behrman, *Inorg. Chem.*, 1972, **11**, 2621.
[229] W. Andruchow and J. DiLiddo, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 689.
[230] J. Burgess, R. D. Peacock, and A. M. Petric, *J.C.S. Dalton*, 1973, 902.

three complexes, which decompose at different rates, in equilibrium with each other. These complexes are proposed to be the tris- and bis-oxalato-complexes and a species $[\mathrm{Mn(ox)_2(oxH)(OH_2)}]^{2-}$ containing a unidentate protonated oxalate ligand.[231] The photosolvolysis of the *trans*-$[\mathrm{Mn(ox)_2(OH_2)_2}]^-$ anion in dimethylformamide solution has been probed by visible–u.v. and e.s.r. spectroscopic techniques. Replacement of an oxalate ligand is preceded by electron transfer – in fact it is an oxalate radical $\mathrm{ox}^{\cdot-}$ which leaves from the manganese.[232]

***d^4*: Ruthenium(IV).**—The dependence of the rate of aquation of $[\mathrm{Ru(NO)(OH)Cl_4}]^{2-}$ on pH exhibits the usual pattern of behaviour for a complex containing a ligand whose degree of protonation varies. In this case the inflection in the rate–pH profile comes at a pH of *ca.* 4, with the rate constant at high pH about eight hundred times greater than that at low pH. Surprisingly, the rate–pH profile for $[\mathrm{Ru(NO)Cl_5}]^{2-}$ is of the same shape, but here the rate constant in alkaline solution is only about twice that in strong acid.[233] Some qualitative information pertaining to the kinetics of aquation of the dinuclear $[\mathrm{Ru_2OCl_{10}}]^{4-}$ anion has been published.[234]

***d^5*: Iron(III).**—The primary process resulting from irradiation of an aqueous perchloric acid solution of mono-oxalatoiron(III) is redox decomposition. This behaviour contrasts with the predominant photoaquation reported for the bis- and tris-oxalotoiron(III) complexes.[235] However, the principal photoreaction of the trisoxalato-complex in the presence of $[\mathrm{PdCl_4}]^{2-}$ is again redox decomposition.[236] The products of photochemical hydrolysis of the bridged di-iron complexes (26), with X = Cl, Br, NCS, or $\mathrm{ClO_4}$, include $[\mathrm{Fe(phen)_3}]^{2+}$ and $\mathrm{Fe^{3+}_{aq}}$. From quantum yields and scavenging and flash photolysis experiments it has been deduced that in aqueous solution the first reaction is displacement of X by water. This step is followed by the primary photochemical step, which is iron–oxygen bond breaking. In acetone solution, the primary photochemical process for the compound (26) with X = NCS is iron–thiocyanate bond breaking.[237]



$$\left[\begin{array}{ccc}(\mathrm{phen})_2\mathrm{Fe} & -\mathrm{O}- & \mathrm{Fe}(\mathrm{phen})_2\\ | & & | \\ \mathrm{X} & & \mathrm{X}\end{array}\right]^{2+}$$

(26)

[231] M. Wronska and T. Ernst, *Roczniki Chem.*, 1972, **46**, 643 (*Chem. Abs.*, 1972, **77**, 118 782z).

[232] I. G. Murgulescu, T. Onescu, and S. G. Ionescu, *Rev. Roumaine Chim.*, 1972, **17**, 423.

[233] E. E. Mercer and A. B. Cox, *Inorg. Chim. Acta*, 1972, **6**, 577.

[234] I. P. Alimarin, V. I. Shlenskaya, and Z. A. Kuratashvili, *Russ. J. Inorg. Chem.*, 1973, **18**, 250.

[235] G. D. Cooper and B. A. DeGraff, *J. Phys. Chem.*, 1972, **76**, 2618.

[236] T. V. Lutskina and V. V. Sviridov, *Russ. J. Phys. Chem.*, 1973, **47**, 276.

[237] P. G. David, J. G. Richardson, and E. L. Wehry, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1333.

***d^5*: Ruthenium(III).**—The kinetics of aquation of carboxylato-ruthenium(III) complexes $[Ru(NH_3)_5L]^{2+}$, with L = formate, acetate, propionate, isobutyrate, glycollate, or glycinate, have been studied spectrophotometrically. The rate law for aquation of all these complexes proves to be

$$-\mathrm{d[complex]/d}t = \{k_0 + k_1[\mathrm{H}^+]\}[\mathrm{complex}] \qquad (7)$$

The trend of rate constants, with faster aquation of complexes of the bulkier ligands, is consistent with a dissociative mechanism. On the basis of comparisons of rate constants with those for aquation of the corresponding cobalt(III) complexes, and extrapolations from the results of tracer experiments on aquation of these cobalt(III) complexes, the authors suggest that the k_0 path of equation (7) corresponds to ruthenium–oxygen bond breaking, but that the k_1 path corresponds to oxygen–carbon bond breaking. Activation energies for the k_0 terms lie between 22 and 26 kcal mol^{-1}, which values are similar to those for aquation of the corresponding cobalt(III) and rhodium(III) complexes. Activation energies for the k_1 terms are much lower, between 16 and 22 kcal mol^{-1}. Activation entropies for the k_0 path are between -2 and -11 and for the k_1 path between -6 and -26 cal deg^{-1} mol^{-1}.[238]

There is complete retention of configuration both in the uncatalysed and in the mercury(II)-catalysed aquation of *cis*-$[Ru(en)_2Cl_2]^+$. This situation contrasts with that for similar cobalt(III) complexes, where generally the steric course of mercury(II)-catalysed aquation differs from that for uncatalysed aquation. One presumes that the mercury(II)-catalysed aquation of *cis*-$[Ru(en)_2Cl_2]^+$ is dissociative as far as the ruthenium is concerned; in order to retain the configuration at ruthenium the transition state for this reaction must be square pyramidal rather than trigonal pyramidal.[239]

***d^6*: Rhodium(III).**—Transition enthalpies, which are the enthalpy changes from transition states to respective products, for aquation of $[Rh(NH_3)_5X]^{2+}$, with X = Cl, Br, I, or NCS, correlate with enthalpies of hydration of the leaving groups X^-. The slope of such a correlation plot is intermediate between those for analogous complexes of cobalt(III) and chromium(III). The conclusion drawn is that in the rhodium(III) aquations bond breaking is the main feature in transition-state formation, but that there is a small but significant interaction between the rhodium and the incoming group in the transition state.[9] Yet another paper devoted to the kinetics of aquation of the $[Rh(NH_3)_5Cl]^{2+}$ cation states that its objective is to elucidate the mechanism of this reaction. In fact the authors merely present activation parameters (Table 13), determined at pH = 2, I = 0.1 mol l^{-1} ($LiClO_4$), and over the short temperature range 75—85 °C, and baldly state that the mechanism is I_d.[240] Activation parameters are also reported for aquation of the $[Rh(NH_3)_5(NO_3)]^{2+}$

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[238] A. Ohyoshi, A. Jyo, and N. Shin, *Bull. Chem. Soc. Japan*, 1972, **45**, 2121.
[239] L. A. P. Kane-Maguire, *Inorg. Chem.*, 1972, **11**, 2281.
[240] A. B. Venediktov and A. V. Belyaev, *Russ. J. Inorg. Chem.*, 1972, **17**, 1158.

Table 13 *Activation parameters for the aquation of rhodium*(III) *complexes* $[Rh(NH_3)_5X]^{n+}$

X	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	log *A*	*Ref.*
Uncatalysed				
Cl	25.1 ± 0.4^a	—	11.08	240
NO_3	23.3	−3	—	241
SO_4	21.4	−13.3	—	50
H^+-*catalysed*				
SO_4	28.5	+9.0	—	50
Hg^{2+}-*catalysed*				
Cl	16.1	—	—	240
Cl	16.3	—	—	242
Br	14.4	—	—	242
I	15.3	—	—	243

[a] Activation energy.

(ref. 241) and $[Rh(NH_3)_5(SO_4)]^+$ (ref. 50) cations (Table 13). Aquation of the latter proceeds by acid-catalysed and uncatalysed paths; aquation of the former is thought to be predominantly dissociative in character.

Activation enthalpies[240, 242, 243] for the mercury(II)-catalysed aquation of $[Rh(NH_3)_5X]^{2+}$, where X = Cl, Br, or I, are also included in Table 13. The suggested mechanism involves slow dissociation of an adduct $[Rh(NH_3)_5XHg]^{4+}$ which is in equilibrium with the starting reactants. Both Hg^{2+}- and $HgCl^+$-catalysed aquations of rhodium(III)–halide complexes can be incorporated in the general kinetic *versus* stability-constant correlation for metal-ion catalysis of aquation of halogeno-complexes mentioned in Section 1 of this chapter.[21] Silver(I) is not an efficient catalyst for the aquation of $[Rh(NH_3)_5Cl]^{2+}$.[240] Redox catalysis of substitution at rhodium(III) has been reviewed.[244]

Photochemical aquation of the $[Rh(NH_3)_5Cl]^{2+}$ cation results mainly in replacement of chloride, with only a little replacement of ammonia, by water. For $[Rh(NH_3)_5Br]^{2+}$ loss of bromide and loss of water are of comparable importance, whereas $[Rh(NH_3)_5I]^{2+}$ photoaquates predominantly (>90%) by ammonia loss. Two photochemically excited states are proposed. These, from comparisons of the results of irradiation in the presence and in the absence of biacetyl, must both be triplet states.[245] *trans*-$[Rh(NH_3)_4I_2]^+$, like $[Rh(NH_3)_5I]^{2+}$, gives *trans*-$[Rh(NH_3)_4(OH_2)_2]^{3+}$ as the principal product of photo-aquation. This stereospecificity suggests that the excited state in each case is a

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[241] F. Monacelli and S. Viticoli, *Inorg. Chim. Acta*, 1973, **7**, 231.

[242] S. C. Chan and S. F. Chan, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2311.

[243] A. B. Venediktov and A. V. Belyaev, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1972, 148 (*Chem. Abs.*, 1973, **78**, 62 786e).

[244] R. D. Gillard and B. T. Heaton, *Coordination Chem. Rev.*, 1972, **8**, 149.

[245] T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, 1972, **94**, 278; *J. Phys. Chem.*, 1972, **76**, 1937.

square pyramid with apical iodide.[246] All of the cations *trans*-$[Rh(NH_3)_4Cl_2]^+$, *trans*-$[Rh(en)_2Cl_2]^+$, and *trans*-$[Rh(cyclam)Cl_2]^+$, like $[Rh(NH_3)_5Cl]^{2+}$ mentioned above, photoaquate predominantly by loss of chloride. All three *trans*-dichloro-complexes photoaquate stereospecifically to *trans*-chloro-aquo-products. This photochemical behaviour is assigned to the lowest triplet state.[247] The courses of photoaquation of *cis*-α- and of *cis*-β-$[Rh(trien)Cl_2]^+$ and of *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$ are said to be not inconsistent with Adamson's rules developed for the photochemistry of chromium(III) complexes, despite the difference between the excited states involved.[248] Although most rhodium(III)–ammine– or –amine–chloride complexes photoaquate with predominant loss of chloride, photoaquation of the $[Rh(py)_4Cl_2]^+$ cation leads to replacement of comparable amounts of chloride and of pyridine.[249]

The kinetics of reactions of complexes of the type *trans*-$[Co(dmgH)_2LX]^{n-}$ have been widely studied for many years. A start has now been made on investigating analogous rhodium(III) systems, with the results shown in Table 14.[250–252] Reaction rates decrease somewhat as the proportion of an organic co-solvent, for example ethanol or ethylene glycol, in mixed aqueous solvents increases (selected values are included in Table 14). From the kinetic parameters in water, in aqueous solution in the presence of added salts, and in mixed aqueous solvents, the tentative conclusion is that the mechanism is predominantly dissociative.

Table 14 *Kinetic parameters for the aquation of* trans-$[Rh(dmgH)_2LX]^-$ *anions (X is the leaving group)*

L	X	*Solvent*	10^5k/ s^{-1} (60 °C)	E_a/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
NO_2	Cl	Water	5.6	32.0	+18	250
SO_3H	Cl	Water	11.7	15.8	−29	251
SO_3H	Br	Water	15.4	14.3	−36	252
SO_3H	I	Water	22.1	13.2	−34	252
SO_3H	Cl	57.6% MeOH	4.3	15.5	−32	251
SO_3H	Cl	57.6% Glycol	5.5	17.1	−27	251
SO_3H	Cl	57.6% Dioxan	1.2	15.9	−29	251

The rate law for aquation of $[Rh(ox)_3]^{3-}$, to give $[Rh(ox)_2(OH_2)_2]^-$, is

$$-d[Rh(ox)_3^{3-}]/dt = \{k_1[H^+] + k_2[H^+]^2\}[Rh(ox)_3^{3-}] \qquad (8)$$

The reported activation enthalpies are 25.5 ± 2.0 and 25.9 ± 2.0 kcal mol^{-1} for

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[246] T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, 1972, **94**, 1797.

[247] C. Kutal and A. W. Adamson, *Inorg. Chem.*, 1973, **12**, 1454.

[248] P. M. Gidney, R. D. Gillard, B. T. Heaton, P. S. Sheridan, and D. H. Vaughan, *J.C.S. Dalton*, 1973, 1462.

[249] M. M. Muir and W.-L. Huang, *Inorg. Chem.*, 1973, **12**, 1831.

[250] G. P. Syrtsova and T. S. Bolgar', *Russ. J. Inorg. Chem.*, 1972, **17**, 1585.

[251] G. P. Syrtsova and T. S. Bolgar', *Russ. J. Inorg. Chem.*, 1971, **16**, 1322.

[252] G. P. Syrtsova and T. S. Bolgar', *Russ. J. Inorg. Chem.*, 1972, **17**, 238.

the k_1 and k_2 paths of equation (8) respectively. The activation entropies are -7.8 ± 6.0 (k_1 path) and -2.9 ± 6.0 (k_2 path) cal deg^{-1} mol^{-1}. The suggested reaction sequence involves the successive formation of a transient five-co-ordinate intermediate, of a species $[Rh(ox)_2(\text{unidentate ox})(OH_2)]^{3-}$, and eventually of $[Rh(ox)_2(OH_2)_2]^-$. The first step is a D [S_N1(lim)] process.[12]

d^6: Iridium(III).—An essentially dissociative mechanism, though perhaps with some slight iridium–incoming water interaction in the transition state, is suggested for the aquation of the $[Ir(NH_3)_5(NO_3)]^{2+}$ cation. The activation parameters for this reaction are $\Delta H^{\ddagger} = 26.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4$ cal deg^{-1} mol^{-1}. Rates of reaction decrease on adding perchlorates; this is attributed not to ion-pair formation but to a reduction in water activity.[241] Whereas ion-pairing between a positively charged complex and an anion normally results in an increased rate of aquation for the former, the association of a negatively charged complex with a cation may lead to a reduced rate of aquation of the complex. Such behaviour has been described elsewhere in this Report for the aquation of the *trans*-$[Co(\text{benzylglyoximato})_2(SO_3H)Cl]^-$ anion;[123] it is also the case for aquation of the $[IrBr_6]^{3-}$ anion. Added calcium(II), barium(II), or cadmium(II) reduces the rate of aquation markedly. Ion-association constants (K_{IP}) can be estimated from the dependence of aquation rates on added cation concentrations. For barium(II) $K_{IP} = 530$ l mol^{-1} and for cadmium(II) $K_{IP} = 400$ l mol^{-1}, at 25 °C in 0.1M-$HClO_4$.[253]

Photoaquation of *trans*-$[Ir(py)_2Cl_4]^-$ in neutral aqueous solution results in stepwise loss of the chloride ligands. The trichloro- and dichloro-intermediates and the ultimate product $[Ir(py)_2(OH_2)_4]^{3+}$ were all detected, but no evidence for significant concentrations of $[Ir(py)_2(OH_2)_3Cl]^{2+}$ was obtained. This monochloro-complex must therefore be the most labile member of the series.[254] Quantum yields for photoaquation of iridium(III) and rhodium(III) complexes have been compared for a series of amine–chloride and –bromide complexes. For *trans*-$[Ir(py)_4Cl_2]^+$ parallel loss of chloride and of pyridine was observed.[255]

d^6: Iron(II).—Iron(II) complexes can be either high-spin or low-spin. The former are substitution-labile, the latter inert. In this present section we are concerned only with complexes in the latter class, in which the iron(II) is bonded to ligands with a large crystal-field effect, for example cyanide, 2,2′-bipyridyl, or 1,10-phenanthroline.

The aquation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_5(OH_2)]^{3-}$ is catalysed by mercury(II) and by silver(I). Some details of the mechanisms of these catalysed aquations have been investigated.[256] Further aquation of $[Fe(CN)_5(OH_2)]^{3-}$ to $[Fe(CN)_4(OH_2)_2]^{2-}$ can occur thermally or photolytically. The progress of this

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[253] V. I. Kravtsov, E. G. Sventarnyi, and N. B. Chamaeva, *Russ. J. Inorg. Chem.*, 1971, **16**, 1332.

[254] M. Lamache and F. Larèze, *Compt. rend.*, 1972, **275**, *C*, 115.

[255] M. M. Muir and W.-L. Huang, *Inorg. Chem.*, 1973, **12**, 1930.

[256] A. Žmikić, D. Cvrtila, D. Pavlovic, I. Murati, W. L. Reynolds, and S. Ašperger, *J.C.S. Dalton*, 1973, 1284.

reaction can conveniently be monitored by trapping the product with nitrosobenzene.[257] Conflicting hypotheses concerning the mechanism of photolysis of the nitroprusside anion, $[Fe(CN)_5(NO)]^{2-}$, have been resolved by an investigation of this reaction both in the presence and in the absence of air. Under aerobic conditions nitrite ion can be oxidized to nitrate ion, to complete the reaction sequence:[258]

$$[Fe(CN)_5(NO)]^{2-} \rightleftharpoons [Fe(CN)_5]^{3-} + NO^+$$
$$NO^+ + H_2O \longrightarrow 2H^+ + NO_2^-$$
$$NO_2^- + \tfrac{1}{2}O_2 \longrightarrow NO_3^-$$

The intermediacy of the species $[Fe(CN)_5]^{3-}$ indicates that this is a *D* [S_N1(lim)] mechanism. Other substitution reactions of $[Fe(CN)_5L]^{n-}$ anions which also proceed by a *D* mechanism with generation of the same $[Fe(CN)_5]^{3-}$ intermediate are discussed in Section 7 of this chapter. Kinetics of dissociation of dinuclear iron(II)–cyanide complexes have been followed by u.v.–visible spectroscopy and by polarography.[259] Photoaquation of *cis*- and of *trans*-$[Fe(CNMe)_4(CN)_2]$, with irradiation at either charge-transfer or ligand-field frequencies, results in the formation of $[Fe(CNMe)_2(OH_2)_2(CN)_2]$ as primary product.[260]

Kinetics of aquation of iron(II) complexes of 2,2′-bipyridyl, 1,10-phenanthroline, and their substituted derivatives have been much studied in water, less so in mixed aqueous solvents. Whereas the rate of aquation of $[Fe(4,7\text{-diPh-phen})_3]^{2+}$ in acidic aqueous solution is approximately independent of the nature of the acid added, solutions of this complex in methanol solvolyse at rates which depend markedly on the nature of the acid added.[261] A similar phenomenon has been observed for the aquation of $[Fe(phen)_3]^{2+}$, $[Fe(5\text{-}NO_2\text{-phen})_3]^{2+}$, and $[Fe(4,7\text{-diMe-phen})_3]^{2+}$ in dioxan–water mixtures.[262] These effects have been variously ascribed to the different strengths of the various acids[261] and to ion-pair formation.[262] It is interesting that the rates of aquation of the iron(II) complexes in aqueous dioxan *decrease* as the concentration of acid increases when the acid added is perchloric or sulphuric. As ion pairs between complex cations and simple anions are generally more reactive than the free complexes, the observed rate trend is ascribed here, as in a similar situation involving the complexes $[M(NH_3)_5(NO_3)]^{2+}$, with M = Rh or Ir,[241] to the decrease in water activity on adding electrolytes.[262]

Symmetrical ligands such as phen and bipy will form two identical bonds to a metal cation, so that in aquation of their iron(II) complexes there is a choice of two identical bonds to break in the rate-determining step. If one takes a

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[257] G. Emschwiller, *Rev. Roumaine Chim.*, 1972, **17**, 131; *Compt. rend.*, 1972, **274**, *C*, 1500

[258] R. P. Mitra, B. K. Sharma, and S. P. Mittal, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3919.

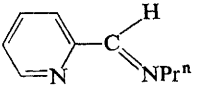
[259] G. Emschwiller, *Colloq. internat. Cent. nat. Rech. sci.*, 1970, 307 (*Chem. Abs.*, 1972, **77**, 106 073f).

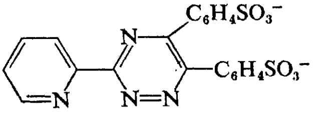
[260] G. Condorelli, L. Giallongo, A. Giuffrida, and G. Romeo, *Inorg. Chim. Acta*, 1973, **7**, 7.

[261] P. Levillain and R. Bourdon, *Bull. Soc. chim. France*, 1972, 3309.

[262] J. Burgess, F. M. Mekhail, and E. R. Gardner, *J.C.S. Dalton*, 1973, 1335.

complex containing an unsymmetrical bidentate ligand, for example the iron(II) complex of ppi (27), the two bonds to the cation are not equivalent and a kinetic pattern corresponding to two parallel processes with different rate constants might be observed. In fact the odd acid dependence of the aquation rate of $[Fe(ppi)_3]^{2+}$, shown in Figure 1(a), suggests that there are two superimposed patterns, Figure 1(b) and (c), which can be assigned to the breaking of the two different metal–ligand bonds.[263] Aquation rates of $[Fe(ppsa)_3]^{2+}$, where ppsa is the bipyridyl-like ligand (28), also vary with pH. Here the


(27)


(28)

situation is more complicated, for there is the possibility of protonating the non-bonding nitrogens of the triazine ring in addition to the normal pH-dependence pattern for aquation of complexes of flexible bipyridyl-like ligands and non-equivalence of the two bonds between iron and each ligand.[264]

Some years ago a mechanism was proposed for aquation of the complex $[Fe(tptz)_2]^{2+}$, where tptz is the terdentate ligand 2,4,6-tri-(2-pyridyl)-1,3,5-

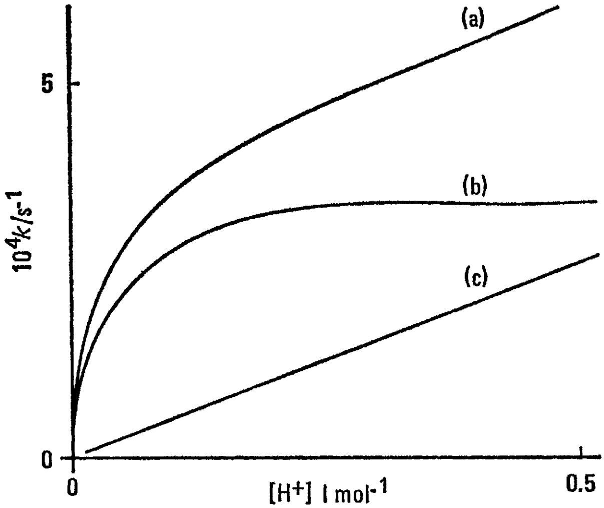


Figure 1 *The dependence of aquation rate constants* (*k*) *on acid concentration for the* $[Fe(ppi)_3]^{2+}$ *cation. Curve* (a) *shows the actual results; curves* (b) *and* (c) *show the hypothetical components*

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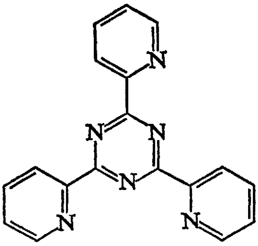
[263] P. Krumholz and E. J. Vichi, Proceedings of the 3rd Symposium on Coordination Chemistry, Debrecen, Hungary, 1970, Vol. 1, p. 357; Vol. 2, p. 195.

[264] E. R. Gardner, F. M. Mekhail, J. Burgess, and J. M. Rankin, *J.C.S. Dalton*, 1973, 1340.

triazine (29).[265] A recent spectroscopic determination of the stability constant for this complex, in which evidence for the existence of a protonated derivative in strong acid was obtained, casts some doubt on the originally proposed aquation mechanism.[266] In this the effect of acid concentration on aquation rates was ascribed solely to the intermediacy of complexes containing bi- or uni-dentate protonated ligands; the intermediacy of species containing terdentate ligands protonated at the unco-ordinating triazine nitrogen or pyridyl nitrogen seems not to have been considered.[265] The recent paper proposes suitable modifications to the original reaction scheme.[266]



(29)

The rate-determining step in the reaction of $[Fe(bipy)_3]^{2+}$, $[Fe(phen)_3]^{2+}$, or $[Fe(terpy)_2]^{2+}$ with peroxodiphosphate is dissociative – the breaking of an iron–nitrogen bond.[267] It has been recognized for some time that these and related iron(II) complexes react with peroxodisulphate by parallel oxidative and dissociative rate-determining steps; the reaction of the $[Fe(ppsa)_3]^{2+}$ cation mentioned above with peroxodisulphate provides a recent example of this behaviour.[264] It is now apparent that any direct oxidation of this type of iron(II) complex with peroxodiphosphate is so slow that reaction proceeds entirely *via* rate-determining dissociation, presumably with subsequent rapid oxidation of the products of dissociation.

d^6: Ruthenium(II).—Earlier investigations have shown that the rates of hydrolysis of the products of reduction of the ruthenium(III) complexes $[Ru(NH_3)_5X]^{2+}$ are fast. It has recently been shown that it is possible to determine the rates of aquation of the ruthenium(II) complexes $[Ru(NH_3)_5X]^+$ by cyclic voltammetry experiments on $[Ru(NH_3)_5X]^{2+}$. The kinetic parameters are shown in Table 15.[268] Cyclic voltammetry has also been used to determine rates of aquation of $[Ru(OH_2)_5Cl]^+$ and of $[Ru(OH_2)_4Cl_2]$. The *cis*- and *trans*-isomers of the latter have very similar rates of aquation, which might be coincidental or might result from concomitant isomerization. The activation

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[265] G. K. Pagenkopf and D. W. Margerum, *Inorg. Chem.*, 1968, **7**, 2514.

[266] F. H. Fraser, P. Epstein, and D. J. Macero, *Inorg. Chem.*, 1972, **11**, 2031.

[267] E. Chaffee, I. I. Creaser, and J. O. Edwards, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1; J. O. Edwards, *Coordination Chem. Rev.*, 1972, **8**, 87.

[268] G. N. Coleman, J. W. Gesler, F. A. Shirley, and J. R. Kuempel, *Inorg. Chem.*, 1973, **12**, 1036.

Table 15 *Kinetic parameters for aquation of ruthenium(II) complexes*

Complex	k/s^{-1} (*temperature*/°C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
$[Ru(NH_3)_5Cl]^+$	6.3 (25)	12 ± 3	-16 ± 6	268
$[Ru(NH_3)_5Br]^+$	5.4 (25)	14 ± 3	-10 ± 6	268
$[Ru(OH_2)_5Cl]^+$	9.0×10^{-4} (23.8)	—	—	269
cis-$[Ru(OH_2)_4Cl_2]$	0.13 (25)	11 ± 1	$+26 \pm 4$	269
trans-$[Ru(OH_2)_4Cl_2]$	0.14 (25)			

parameters reported in Table 15 are thus experimental values for aquation of one or both isomers.[269] In all these cases the activation enthalpy for aquation of ruthenium(II)–chloride complexes is, as would be expected, much lower than for aquation of similar ruthenium(III)–chloride complexes. Activation enthalpies for aquation of the latter lie between 18 and 24 kcal mol^{-1}.[270]

Irradiation of $[Ru(NH_3)_5(py)]^{2+}$ at a charge-transfer band frequency leads to photoaquation of pyridine and of *cis* and *trans* ammonia ligands. The dependence of quantum yields on pH has been estimated for photoaquation of this and other complexes of general formula $[Ru(NH_3)_5L]^{2+}$, with L = benzonitrile, 3-chloropyridine, or 4-methylpyridine. Competitive protonation of an excited state or of an intermediate is proposed.[271]

d^6: Osmium(II).—An i.r. study of the aquation of $[Os(NH_3)_5(N_2)]^+$ showed that the reaction was first-order in complex, and had an activation energy of 35 kcal mol^{-1} and a frequency factor of 4×10^{13}. Aquation is slightly faster in the presence of acid.[272] Subsequent work has revealed some deviation from first-order kinetics. The observed small acceleration as the aquation proceeds has been ascribed to catalysis by the $[Os(NH_3)_5(OH_2)]^{2+}$ produced. This product and the starting material react to form the dinuclear $[(H_3N)_5Os(N_2)Os(NH_3)_5]^{4+}$ cation.[273]

d^6: Platinum(IV).—Photoaquation of the $[PtCl_6]^{2-}$ anion has been the subject of three investigations.[274–276] The principle product is the $[PtCl_5(OH_2)]^-$ anion. The reaction is affected by added chlorine, so a mechanism involving platinum–chloride homolysis to generate a transient platinum(III) species and atomic chlorine was proposed.[274] It subsequently proved possible to build up a spectrum for this intermediate, which was considered to be the $[PtCl_4]^-$ anion.[275] Photoaquation also appears to be inhibited by added chloride,[276] so

[269] P. E. Dumas and E. E. Mercer, *Inorg. Chem.*, 1972, **11**, 531.

[270] C. H. Langford and V. S. Sastri, in 'Reaction Mechanisms in Inorganic Chemistry', ed. M. L. Tobe, M.T.P. International Review of Science, Butterworths, London, 1971, Series 1, Vol. 9, p. 240.

[271] D. A. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Peterson, D. P. McDonald, and P. C. Ford, *J. Amer. Chem. Soc.*, 1972, **94**, 6665.

[272] Yu. P. Myagkov, M. G. Kaplunov, Yu. G. Borod'ko, and A. E. Shilov, *Kinetika i Kataliz*, 1971, **12**, 1158 (*Chem. Abs.*, 1972, **76**, 18 410n).

[273] B. Folkesson, *Acta Chem. Scand.*, 1972, **26**, 4157.

[274] L. E. Cox, D. G. Peters, and E. L. Wehry, *J. Inorg. Nuclear Chem.*, 1972, **34**, 297.

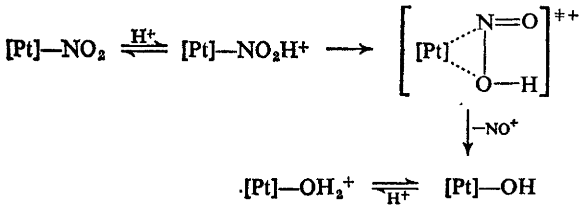
[275] R. C. Wright and G. S. Laurence, *J.C.S. Chem. Comm.*, 1972, 132.

[276] G. A. Shagisultanova, R. M. Orisheva, A. A. Karaban, and S. P. Gorbunova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1646.

platinum–chloride heterolysis may also contribute to the overall photoaquation. Rates of thermal aquation of $[PtCl_6]^{2-}$ have also been reported.[277]

There is evidence for the transitory existence of Br_2^- during the photoaquation of *trans*-$[Pt(NH_3)_4Br_2]^{2+}$ in the presence of bromide. The Br_2^- ion can hardly come directly from the *trans*-complex. It seems more likely to be derived from a *trans*-$[Pt(NH_3)_4Br_2]^{2+}$ Br^- ion-pair. The authors of this report do not believe that platinum(III) species are likely intermediates in the photoaquation either of this complex or of the $[PtBr_6]^{2-}$ anion. However, a redox mechanism involving the intermediacy of platinum(II) and elemental bromine is put forward for the photoaquation of $[PtBr_6]^{2-}$.[278] This view contrasts with an assertion published elsewhere that the photoaquation of $[PtBr_6]^{2-}$ takes place by a non-redox, non-chain process.[274] Copper(II), cobalt(II), nickel(II), iron(III), and chromium(III) are all claimed to act as effective catalysts for the thermal aquation of $[Pt(NH_3)_2Br_4]$ (of unspecified stereochemistry).[279]

In acid solution the $[Pt(NO_2)_6]^{2-}$ anion undergoes both hydrolysis and reduction. The first steps in the reaction sequence are the replacement of two nitrito-ligands to give $[Pt(NO_2)_4(OH_2)_2]$; reduction occurs subsequently.[280] Rates of loss of the first nitrito-ligand from the complexes $[PtL_2Br_2(NO_2)_2]$, where L_2 = bipy, $(py)_2$, or $(PEt_3)_2$, have been determined in aqueous sulphuric acid (1.6—15.4M) and in acetic acid–sulphuric acid mixtures. Treatment of the kinetic results in aqueous sulphuric acid according to the methods of Bunnett or of Zucker and Hammett suggests that water is not incorporated into the transition state. The rate-determining step suggested is the loss of NO^+ from the complex {here [Pt] = $[PtL_2Br_2(NO_2)]$}:[281]



This mechanism parallels that proposed earlier for the aquation of nitritocobalt(III), -rhodium(III), and -iridium(III) complexes in acid media.[282]

5 Base Hydrolysis

All the available kinetic parameters for base hydrolysis of complexes

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[277] S. Yamasaki, T. Kumamaru, and I. Nakamori, *Kyushu Daigaku Kogaku Shuho*, 1971, **44**, 82 (*Chem. Abs.*, 1972, **77**, 66 631c).

[278] P. D. Fleischauer and A. W. Adamson, *Inorg. Chim. Acta*, 1972, **6**, 323.

[279] Yu. A. Makashev, F. Ya. Kul'ba, and R. A. Zlotnikova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1023.

[280] L. K. Shubochkin, E. F. Shubochkina, M. A. Golubnichaya, and L. D. Sorokina, *Russ. J. Inorg. Chem.*, 1972, **17**, 1210.

[281] D. Humphreys and P. J. Staples, *J.C.S. Dalton*, 1973, 897.

[282] B. E. Crossland and P. J. Staples, *J. Chem. Soc.* (*A*), 1971, 2853.

$[M(NH_3)_5X]^{n+}$, where M = Co^{III}, Rh^{III}, Ir^{III}, or Cr^{III}, have been conveniently, if not particularly accessibly, gathered together and tabulated. Activation energies correlate with logarithms of frequency factors for X = halide for all four elements, but complexes containing other ligands X cannot always be included in the halide correlations. Ligand-field effects on reactivity are discussed, as are relationships between activation enthalpies (entropies) and enthalpies (entropies) of solvation of the respective leaving ligands.[283]

Cobalt(III) Complexes.—The operation of an S_N1cb mechanism for base hydrolysis of cobalt(III) complexes containing ammine or amine ligands is now firmly established. It is, however, difficult to determine the pK values for these co-ordinated ligands, for the concentration of conjugate base in equilibrium with the complex is very small at normally accessible pH's. Recent work has suggested that the equilibrium constant for equilibrium proton loss from $[Co(en)_3]^{3+}$ is about 0.6 l mol^{-1}.[284] Rates of base hydrolysis of cobalt(III) complexes are not sensitive to the presence of added singly charged anions, but the addition of doubly charged anions has a significant effect on reactivity. Thus second-order rate constants for base hydrolysis of $[Co(NH_3)_5(OAc)]^{2+}$ *decrease* on adding sulphate or dicarboxylates. The ratios k_2 (ion pair)/k_2 (free complex) lie between 0.16 and 0.51 for the anions investigated, and correlate with the respective ion-association constants.[33]

Kinetic parameters for base hydrolysis of several ammine- or amine-halide complexes are collected in Table 16. Most of these have been determined with

Table 16 *Kinetic parameters for base hydrolysis of cobalt*(III) *ammine- or amine-halide complexes in aqueous solution*

Complex	k_2/l mol^{-1} s^{-1} (*temperature*/°C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
trans-$[Co(NH_3)_4(CN)Cl]^+$	0.035 (0)	23.8	+22	81
trans-$[Co(NH_3)_4(NCS)Cl]^+$	0.048 (0)	29.6	+44	82
cis-$[Co(en)_2(Pr^nNH_2)Cl]^{2+}$	0.273 (0)	23.4	+25	65
cis-$[Co(en)_2(Bu^nNH_2)Cl]^{2+}$	0.295 (0)	23.4	+25	65
cis-$[Co(en)_2(Bu^iNH_2)Cl]^{2+}$	0.387 (0)	23.4	+25	65
cis-$[Co(en)_2(Bu^sNH_2)Cl]^{2+}$	1.55 (0)	23.4	+28	65
cis-$[Co(en)_2(C_6H_{11}NH_2)Cl]^{2+}$	2.5 (0)	—	—	67
cis-$[Co(en)_2(C_6H_{11}NH_2)Br]^{2+}$	8.9 (0)	—	—	67
cis-$[Co(en)_2\{HO(CH_2)_4NH_2\}Cl]^{2+}$ [a]	0.25—0.31 (0)	—	—	70
trans-$[Co(en)_2(OAc)Cl]^+$ [b]	10.8 (25)	22.6 ± 0.5	+22 ± 2	76
π-$[Co(en)(dien)Cl]^{2+}$	360 (25)	—	—	88
$\varkappa$-$[Co(en)(dien)Cl]^{2+}$	47 000 (25)	—	—	88
ω-$[Co(en)(dien)Cl]^{2+}$	7.26 (25)	—	—	88
trans-$[Co(cyclam)(NO_2)Cl]^+$	28 (0)	—	—	39
trans-$[Co(cyclam)(CN)Cl]^+$	0.81 (0)	22.6	+24	81
trans-$[Co(cyclam)(NCS)Cl]^+$ [c]	26 (0)	21.1	+25	82

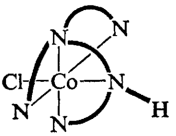
[a] $2 < n < 6$. [b] Product is 20% *cis*, 80% *trans*. [c] In borax-boric acid buffer.

[283] G. C. Lalor, *Rev. latinoamer. Quím.*, 1972, **3**, 100.

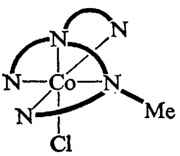
[284] G. Navon, R. Panigel, and D. Meyerstein, *Inorg. Chim. Acta*, 1972, **6**, 299.

the intention of probing sundry non-leaving-ligand effects on reactivity. The favourite non-leaving-ligand comparison, here as in aquation in acid media, is that of $(NH_3)_4$ with $(en)_2$ and with cyclam, which it is now fashionable to discuss in terms of the relative nephelauxetic effects of these ligands.[39, 81, 82] Other non-leaving-ligand effects probed recently include ring-size effects [for ligands $HO(CH_2)_nNH_2$],[70] steric effects (n-, iso-, and sec-butylamines),[65] and the relative reactivities of isomers {previous example plus the π-, κ-, and ω-isomers of $[Co(dien)(en)Cl]^{2+}$}.[65, 88]

The site of deprotonation in the generation of the conjugate base from the complex $[Co(trenen)Cl]^{2+}$ in base hydrolysis of this complex was said to be the nitrogen at position 7 in the trenen ligand [trenen = 4-(2-aminoethyl)-1,4,7,10-tetra-azadecane]. The proton removed is that shown in (30).[285] It was thought that the replacement of this 7-proton in the trenen by a methyl group, which methyl-trenen ligand gives the complex (31), should lead to a much lower rate of base hydrolysis. This turns out not to be the case. The different geometry of the complex, greater steric strain in the ligand, and the proximity of the 7-methyl group to the leaving chloride seem to counterbalance the unfavourable effect of having to remove a proton from some other position of the methyl-trenen ligand.[286]



(30)



(31)

Rates and activation enthalpies for base hydrolysis of the $\alpha\beta R$- and $\alpha\beta S$-isomers of $[Co(tetren)(NCS)]^{2+}$ are remarkably similar. Second-order rate constants at 25 °C are 88.5 and 108 $l\,mol^{-1}\,s^{-1}$ respectively, and the activation enthalpies are 9.6 ± 1.9 and 10.1 ± 2.5 kcal mol^{-1}.[83] The predominant reaction of the *S*-thiocyanato-complex *trans*-$[Co(en)_2(NH_3)(SCN)]^{2+}$ in basic solution is base hydrolysis, with less than 10% isomerization to the *N*-thiocyanato-isomers. Base hydrolysis of $[Co(NH_3)_5(SCN)]^{2+}$ is accompanied by much more isomerization. *S*-Thiocyanato is approximately as good a leaving group as chloride from cobalt(III) in basic solution.[287] The activation enthalpy for base hydrolysis of $[Co(NH_3)_5(S_2O_3)]^+$ is 30.4 kcal mol^{-1}; the activation entropy is 25.7 cal $deg^{-1}\,mol^{-1}$.[288] In dilute alkali, base hydrolysis of $[Co(en)_2(ox)]^+$ gives 100% *cis*-$[Co(en)_2(OH_2)_2]^{3+}$, but in 4M alkali, the product distribution is

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[285] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1969, **8**, 1595.

[286] D. A. Buckingham, M. Dwyer, A. M. Sargeson, and K. J. Watson, *Acta Chem. Scand.*, 1972, **26**, 2813.

[287] D. A. Buckingham, I. I. Creaser, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, 1972, **11**, 2738.

[288] G. C. Lalor, G. A. Neita, and A. N. Newton, *Rev. latinoamer. Quím.*, 1972, **2**, 149.

about 50% *cis*- and 50% *trans*-$[Co(en)_2(OH_2)_2]^{3+}$.[289] Base hydrolysis of complexes $[Co(LLLL)(CO_3)]^+$, where LLLL = a methyl-substituted quadridentate (four nitrogen donor atoms) macrocycle, takes place in two kinetically distinct stages. In the first a unidentate carbonato-intermediate $[Co(LLLL)(OH)(CO_3)]$ is formed.[290]

The α-cis-$[Co(edda)(NH_3)_2]^+$ cation loses ammonia in basic aqueous solution. The reaction follows the usual rate law, first-order in complex and first-order in hydroxide-ion concentration. The activation energy is about 40 kcal mol^{-1}.[291] The kinetics of base hydrolysis have also been reported for the β-*cis*-isomer. The analogous ethylenediamine complex $[Co(edda)(en)]^+$ undergoes isomerization rather than hydrolysis in basic solution.[292]

Cobalt(III)–dimethylglyoxime complexes also undergo base hydrolysis by an S_N1cb mechanism. In the case of base hydrolysis of *trans*-$[Co(dmgH)_2(py)Cl]$ the conjugate base persists long enough for its purple colour to be observed. The equilibrium constant for the formation of this conjugate base* has been evaluated spectrophotometrically as 1545 l mol^{-1}. The rate of chloride release from the conjugate base is between 3 and $4 \times 10^{-4}\ s^{-1}$ at 30 °C in 10% ethanol.[110] An S_N1cb mechanism also operates for base hydrolysis of the *trans*-$[Co(dmgH)_2(NO_2)_2]^-$ anion[294, 295] and for *trans*-$[Co(dmgH)_2(OH_2)(NO_2)]$.[295] Base hydrolysis of $[Co(dmgH)_2(OH_2)(NCS)]$ involves two kinetically significant paths, with a consequently more complicated rate law. Both paths involve the conjugate base $[Co(dmgH)_2(OH)(NCS)]^-$, which undergoes parallel simple aquation and base hydrolysis *via* a further deprotonated conjugate base $[Co(dmgH)(dmg)(OH)(NCS)]^{2-}$. By working at high hydroxide-ion concentration and low temperature the authors were able to isolate the latter path and determine activation parameters of $\Delta H^{\ddagger} = 22.5 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -1.2 \pm 1.1$ cal deg^{-1} mol^{-1}. The contribution of this path to the overall rate at lower hydroxide-ion concentrations could then be subtracted, to permit the estimation of $\Delta H^{\ddagger} = 32.2 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = +28.4 \pm 1.3$ cal deg^{-1} mol^{-1} for the aquation of the $[Co(dmgH)_2(OH)(NCS)]^-$ conjugate-base anion.[296] The kinetic pattern and suggested mechanisms for base hydrolysis of $[Co(dmgH)_2(OH_2)(NCSe)]$ are similar to those just outlined for the equivalent thiocyanato-complex. The activation

* Equilibrium constants for conjugate-base formation from the related complexes $[Co(dmgH)_2(py)Br]$ and $[Co(dmgH)_2(4\text{-}Me\text{-}py)X]$, with X = Cl or Br, have also been estimated (ref. 293).

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[289] M. E. Farago, C. F. V. Mason, and B. A. Page, Proceedings of the 3rd Symposium on Coordination Chemistry, Debrecen, Hungary, 1970, Vol. 1, p. 313; Vol. 2, p. 227.

[290] J. F. Endicott, N. A. P. Kane-Maguire, D. P. Rillema, and T. S. Roche, *Inorg. Chem.*, 1973, **12**, 1818.

[291] K. Kuroda, *Chem. Letters*, 1972, 1153.

[292] K. Kuroda and F. Mohri, *Chem. Letters*, 1972, 719.

[293] V. R. Vijayaraghavan and M. Santappa, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3035.

[294] C. Várhelyi, J. Zsakó, and M. Zsigmond, *Studia Univ. Babes-Bolyai, Ser. Chem.*, 1971, **16**, 53 (*Chem. Abs.*, 1972, **76**, 90 688b).

[295] J. Zsakó, Z. Finta, and C. Várhelyi, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2887.

[296] Z. Finta, C. Várhelyi, and J. Zsakó, *Rev. Roumaine Chim.*, 1973, **18**, 417.

enthalpies for each base-hydrolysis pathway for the selenocyanato-complex are equal, within the limits of experimental uncertainty, to those for the thiocyanato-complex.[297]

In basic solution *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$ undergoes tetramerization:

$$4[Co(NH_3)_4(OH_2)_2]^{3+} + 6OH^- \longrightarrow [Co\{(OH)_2Co(NH_3)_4\}_3]^{6+} + 4NH_3 + 8H_2O$$

This reaction is first-order in monomer. The variation of rate with pH suggests that the rate-determining step is a dissociative reaction of *trans*-$[Co(NH_3)_4(OH)_2]^+$. As the rate-determining step comes so early in the reaction sequence it is impossible to obtain any kinetic information pertaining to dimeric or trimeric intermediates. But it is possible to rule out the dimer $[(H_3N)_4Co(OH)_2Co(NH_3)_4]^{4+}$ as an intermediate, since this μ-dihydroxo-cation gives a precipitate of cobalt hydroxide instantly in media whose pH's fall within the range covered by this investigation of the tetramerization.[298]

Other Complexes.—*Chromium.* The complexes *cis*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$ and *cis*- and *trans*-$[Cr(NH_3)_4(OH_2)Br]^{2+}$ all undergo hydrolysis in basic solution with complete retention of configuration. Rates of base hydrolysis of these complexes are high, for in each case reaction is complete within two minutes of mixing the reagent solutions.[156] The kinetics of base hydrolysis of *trans*-$[Cr(pn)_2Cl_2]^+$ are complicated by the fact that the second chloride is lost more rapidly than the first. However, it is possible to estimate that loss of the first chloride from this complex takes place slightly more rapidly than the similar loss from *trans*-$[Cr(en)_2Cl_2]^+$. The relative reactivities of these pn and en complexes are thus in the same order as those of their cobalt(III) analogues.[299]

The rate law for base hydrolysis of the $[Cr(NH_3)_5(N_3)]^{2+}$ cation is

$$+d[N_3^-]/dt = \{k_1 + k_2[OH^-]\}[Cr(NH_3)_5(N_3)^{2+}]$$

The k_2 term is assigned to an S_N1cb process, the activation parameters for which are $\Delta H^{\ddagger} = 24.9 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = +2.9$ cal deg^{-1} mol^{-1}. The value of k_1 appears greater than expected from known rates of aquation of this complex in acid solution, but the situation is complicated by the possibility of parallel loss of ammonia and of azide.[300]

Iron. The rate law for the reaction of the S-bonded thiocyanato-complex $[Fe(CN)_5(SCN)]^{3-}$ with hydroxide ion suggests two parallel paths. The first is a *D* or $S_N1(lim)$ path, with an $[Fe(CN)_5]^{2-}$ intermediate discriminating between hydroxide ion and thiocyanate ion. The second path is thought to involve the intermediacy either of $[Fe(CN)_5(OH)(SCN)]^{4-}$ or of $[Fe(CN)_5(NCS)]^{3-}$. An S_N1cb process is, of course, precluded here.[301] The reactions of optically

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[297] J. Zsakó, Z. Finta, and C. Várhelyi, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2839.

[298] S. Balt and W. de Kieviet, *Inorg. Chem.*, 1972, **11**, 2251; S. Balt and P. M. Kwantes, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2407.

[299] R. R. Barona and J. A. McLean, *Inorg. Chem.*, 1972, **11**, 1443.

[300] C. Chatterjee and P. Chaudhuri, *Indian J. Chem.*, 1971, **9**, 1132.

[301] J. H. Espenson and S. G. Wolenuk, *Inorg. Chem.*, 1972, **11**, 2034.

active $[Fe(bipy)_3]^{2+}$ or $[Fe(phen)_3]^{2+}$ with hydroxide ion are said to lead to complete loss of optical activity.[302] Rates of reaction of the $[Fe(ppsa)_3]^{2+}$ cation, where ppsa = (28) of Section 4, show the expected dependence on hydroxide-ion concentration but an unexpectedly large sensitivity to the nature of the salt used to maintain constant ionic strength.[303] The base hydrolysis of *cis*- and of *trans*-$[Fe(CNMe)_4(CN)_2]$ is a second-order process. Again an S_N1cb mechanism is impossible, so bimolecular nucleophilic attack by the hydroxide at the ion is the proposed mechanism. The activation parameters for the reaction of the *cis*-isomer are $E_a = 28 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = +5.8$ cal deg^{-1} mol^{-1} and for the *trans*-isomer $E_a = 31 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = +17.6$ cal deg^{-1} mol^{-1}.[260]

Ruthenium. The activation enthalpy for base hydrolysis of $[Ru(NO)(OH)Cl_4]^{2-}$ is 24.4 kcal mol^{-1} and that of $[Ru(NO)Cl_5]^{2-}$ is 27.5 kcal mol^{-1}.[233] The overall reaction of the trinuclear cation $[(H_3N)_5Ru\cdot O\cdot Ru(NH_3)_4\cdot O\cdot Ru(NH_3)_5]^{7+}$ in basic solution is a redox process, with the evolution of oxygen, but the rate-determining step is attack of hydroxide ion at the central ruthenium atom, for which the activation enthalpy is 19 kcal mol^{-1}.[304]

Rhodium. Isotope effects on the reactivity of rhodium(III) complexes towards base hydrolysis have been probed by comparing activation parameters for the reactions of the cations $[Rh(ND_3)_5X]^{2+}$ with OD^- in D_2O with the activation parameters for the analogous ^1H systems. Rates of reaction are slightly greater in the deuterium systems than in their respective protium analogues. These different reactivities arise from differences of about 2 kcal mol^{-1} between the respective activation enthalpies and of 5—20 cal deg^{-1} mol^{-1} between activation entropies. The results are interpreted in terms of a fully associative mechanism, with appropriate differences in solvation effects in the initial and transition states.[305] It is somewhat surprising to find the assumption of a fully associative mechanism for these reactions in the light of recent reviews[306] which favour an S_N1 mechanism, possibly with some associative character, for base hydrolysis of rhodium(III)- and of iridium(III)-ammine complexes. However, two recent papers do provide some support for the assumption of an associative mechanism for base hydrolysis of these complexes. The rate laws for the base hydrolysis of $[Rh(NH_3)_5(NO_3)]^{2+}$ (ref. 241) and of $[Rh(NH_3)_5(SO_4)]^{+}$ (ref. 50) are both consistent with an S_N1cb or with an S_N2cb mechanism. The activation entropies for the base hydrolysis of these complexes are +26 and +10 cal deg^{-1} mol^{-1} respectively. As these values are markedly less positive than those for base hydrolysis of the analogous cobalt(III) complexes, it is said that an S_N2cb mechanism may operate for the rhodium(III) complexes, and for their iridium(III) analogues (see below). The

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[302] G. Nord, *Acta Chem. Scand.*, 1973, **27**, 743.

[303] E. R. Gardner, F. M. Mekhail, J. Burgess, and J. M. Rankin, *J.C.S. Dalton*, 1973, 1340.

[304] J. E. Earley and T. Fealy, *Inorg. Chem.*, 1973, **12**, 323; J. E. Earley and H. Razavi, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 331.

[305] S. C. Chan and S. F. Chan, *J. Inorg. Nuclear Chem.*, 1972, **34**, 793.

[306] See, *e.g.*, C. H. Langford and V. S. Sastri, ref. 270, pp. 243—4.

activation enthalpies for base hydrolysis of the $[Rh(NH_3)_5(NO_3)]^{2+}$ and $[Rh(NH_3)_5(SO_4)]^+$ cations are 27.5 and 24.5 kcal mol^{-1} respectively.

The rate law, rate constants, and activation parameters have been established for the base hydrolysis of the *trans*-$[Rh(en)_2(OH)I]^+$ cation. It appears from these results that the intrinsic kinetic *trans* effect of a hydroxo-ligand is very similar to that of chloride in this type of rhodium(III) complex.[307] Base hydrolysis of *cis*-$[Rh(bipy)_2Cl_2]^+$ or of its phen analogue is normally very slow, but is considerably catalysed by the presence of reducing agents such as ethanol or hydrazine.[308] This behaviour is reminiscent of substitution at *trans*-$[Rh(py)_4Cl_2]^+$.[309]

Iridium. Activation parameters have been determined for the base hydrolysis of $[Ir(NH_3)_5X]^{2+}$, where X = Cl, Br, or NO_3 (Table 17). Base-hydrolysis rates for the iridium(III)–halide complexes $[Ir(NH_3)_5X]^{2+}$ increase in the order X = I < Br < Cl, in contrast to the opposite order of reactivity for the analogous cobalt(III) series. For the rhodium(III) complexes $[Rh(NH_3)_5X]^{2+}$ rates of base hydrolysis are approximately equal for the three compounds with X = Cl, Br, or I. For all three series the highest activation enthalpy is observed for the iodo-complex, so the various rate trends noted are determined by the activation entropies. Indeed activation entropies correlate with entropies of hydration of the leaving ligands for base hydrolysis both of the $[Ir(NH_3)_5X]^{2+}$ and the $[Rh(NH_3)_5X]^{2+}$ series of complexes.[310] Base hydrolysis of $[Ir(NH_3)_5(NO_3)]^{2+}$ may have an S_N2cb mechanism, since the activation entropy for this reaction is very different from that for base hydrolysis of $[Co(NH_3)_5(NH_3)]^{2+}$.[241] The photochemistry of *trans*-$[Ir(py)_2Cl_4]^-$ in basic solution has been described.[254]

Table 17 *Kinetic parameters for base hydrolysis of* $[Ir(NH_3)_5X]^{2+}$ *cations in aqueous solution*

X	k_2/l mol^{-1} s^{-1} (25 °C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
Cl[a]	4.83×10^{-8}	33.7	+18.9	310
Br[a]	2.15×10^{-8}	35.2	+22.3	310
NO_3[b]	1.9×10^{-6}	31.0	+19	241

[a] Extrapolated to zero ionic strength. [b] $I = 1.0$ mol l^{-1} ($NaClO_4$).

6 Formation

In this section, formation reactions at inert transition-metal centres are discussed, with cations arranged in order of increasing number of *d* electrons.

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[307] A. J. Poë and C. P. J. Vuik, *J.C.S. Dalton*, 1972, 2250.

[308] P. M. Gidney, R. D. Gillard, and B. T. Heaton, *J.C.S. Dalton*, 1972, 2621.

[309] See, *e.g.*, ref. 244 of Section 4 for a review of redox catalysis of substitution at rhodium(III).

[310] G. C. Lalor and T. Carrington, *J.C.S. Dalton*, 1972, 55.

Formation reactions of mixed aquo–ligand as well as of hexa-aquo-complexes are included. Formation reactions at labile cations are discussed in Chapter 4 of this Part.

d^2: Vanadium(III).—From time to time there are suggestions that formation reactions at hexa-aquovanadium(III), as at other d^2, d^1, and d^0 centres where there is at least one vacant t_{2g} orbital, occur by a mechanism having some associative character. However, a definitive demonstration of associative anation at vanadium(III) has yet to be reported. The most recent reference to present some evidence for an associative formation involving vanadium(III) deals with the kinetics of oxalato-complex formation.[311]

d^3: Chromium(III).—The rate law for the reaction of $[Cr(NH_3)_5(OH_2)]^{3+}$ with azide, over the pH range 3.4—4.3, has been interpreted as indicating parallel reactions of the azide ion with $[Cr(NH_3)_5(OH_2)]^{3+}$ itself and with its conjugate base $[Cr(NH_3)_5(OH)]^{2+}$. Activation parameters for the former path are $\Delta H^{\ddagger} = 25.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = +3.0$ cal deg^{-1} mol^{-1} and for the latter path are $\Delta H^{\ddagger} = 32.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = +6.4$ cal deg^{-1} mol^{-1}. The operation of an S_N1 *IP* mechanism is proposed for both paths.[312]

The kinetics of formation of oxalato-complexes both from $[Cr(OH_2)_6]^{3+}$ (refs. 313, 314) and from mixed ligand–aquo-chromium(III) complexes[172, 315] have been investigated. Some of the results of a detailed study of the kinetics of formation of the mono-, bis-, and tris-oxalato-complexes from $[Cr(OH_2)_6]^{3+}$, as a function of oxalate concentration, pH, temperature, and ionic strength, are given in Table 18.[313] Second-order rate constants for each step in this

Table 18 *Kinetic parameters for the formation of oxalato-chromium*(III) *complexes*

Reactant	10^5k/ l mol^{-1} s^{-1} (*temperature*/ °C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Conditions*	*Ref.*
$[Cr(OH_2)_6]^{3+}$	4 (25)	26.6	+7.4	pH = 2.7; I = 1.0M	313
$[Cr(OH_2)_4(ox)]^{+}$	53 (25)	32.2	−0.6		
$[Cr(OH_2)_2(ox)_2]^{-}$	14 (25)	21.7	−10.0		
$[Cr(NH_3)_5(OH_2)]^{3+}$	62 (50)	26.4[a]	+8.6[a]	3<pH<4: I = 1.0M (HClO$_4$)	315
$[Cr(bigH)_2(OH_2)_2]^{3+}$	660 (25)	20.2	−1.1	I = 1.0M	172

[a] Estimated activation parameters for the formation interchange process within the $[Cr(NH_3)_5(OH_2)]^{3+}$ ox^{2-} or $[Cr(NH_3)_5(OH_2)]^{3+}$ Hox^{-} ion pairs.

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[311] R. C. Patel and H. Diebler, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1035.
[312] D. Banerjea and S. Sarkar, *Z. anorg. Chem.*, 1972, **393**, 301.
[313] C. Schenk, H. Stieger, and H. Kelm, *Z. anorg. Chem.*, 1972, **391**, 1.
[314] C. Schenk and H. Kelm, *J. Coordination Chem.*, 1972, **2**, 71.
[315] O. Nor and A. G. Sykes, *J.C.S. Dalton*, 1973, 1232.

reaction sequence increase with increasing pressure (Scheme 1) (25 °C, pH = 2.7). The rate-determining step is, in the light of this evidence, stated to be bimolecular attack of HC_2O_4 at the chromium(III).[314] However, a comparison of the rate of reaction between $[Cr(NH_3)_5(OH_2)]^{3+}$ and oxalate with the rates of reaction between this cation and other ligands suggests that the first step is a dissociative interchange. The observed product of this reaction of $[Cr(NH_3)_5(OH_2)]^{3+}$ with oxalate is $[Cr(NH_3)_4(ox)]^{+}$ – there is no evidence for a significant build-up of the likely intermediate $[Cr(NH_3)_5(ox)]^{+}$. The chelation step, from the penta-ammine to the tetra-ammine complex, must therefore be relatively rapid. This step may well have considerable associative character, encouraged by the forced proximity of the potentially chelating oxygen of the unidentate oxalate and the chromium.[315] Activation parameters for the reaction of $[Cr(bigH)_2(OH_2)]^{3+}$ with oxalate, to give the previously uncharacterized complex $[Cr(bigH)_2(ox)]^{+}$, are quoted in Table 18. The limited evidence available is consistent with an I_d (S_N1ip) mechanism.[172]

$$\begin{tikzcd}
{[Cr(OH_2)_6]^{3+}} \arrow[d, "{+\ ox^{2-}}"', "{\Delta V^{\ddagger} = -2.2\ cm^3\ mol^{-1}}"] \\
{[Cr(OH_2)_4(ox)]^{+}} \arrow[d, "{+\ ox^{2-}}"', "{\Delta V^{\ddagger} = -8.2\ cm^3\ mol^{-1}}"] \\
{[Cr(OH_2)_2(ox)_2]^{-}} \arrow[d, "{+\ ox^{2-}}"', "{\Delta V^{\ddagger} = -10.0\ cm^3\ mol^{-1}}"] \\
{[Cr(ox)_3]^{3-}}
\end{tikzcd}$$

Scheme 1

The rate law for the reactions of *cis*-$[Cr(ox)_2(OH_2)_2]^{-}$ with bipy or phen (LL) is

$$-d[cis\text{-}Cr(ox)_2(OH_2)_2^{-}]/dt = \{k_1 + k_2[LL]\}[cis\text{-}Cr(ox)_2(OH_2)_2^{-}]$$

As the value of k_1 is the same for LL = bipy or phen, this pathway is assigned a dissociative mechanism. Some associative character is ascribed to the k_2[LL] path, although the observed activation enthalpies $\Delta H_2^{\ddagger}$ (bipy) = 19.8 kcal mol^{-1} and $\Delta H_2^{\ddagger}$ (phen) = 20.8 kcal mol^{-1} are surprisingly high compared with $\Delta H_1^{\ddagger}$ = 11.5 kcal mol^{-1} for the k_1 path.[316]

In aqueous ethylene glycol mixtures (mole fraction of glycol up to 0.9) the primary solvation shell of Cr^{3+} consists of six water molecules, one unidentate glycol plus five water molecules, or one bidentate glycol plus four water molecules. Interconversion of the last two species is relatively fast compared with the rate of formation of the monoglycol solvate from $[Cr(OH_2)_6]^{3+}$. The disparity in the various rates here is less than in the $[Cr(NH_3)_5(OH_2)]^{3+}$ plus

[316] D. Banerjea and J. Roy, *Z. anorg. Chem.*, 1973, **399**, 115.

oxalate system discussed in an earlier paragraph, and it has proved possible to elucidate the rate laws governing the formation and decomposition not only of the bidentate glycol species $[Cr(OH_2)_4(glycol)]^{3+}$ but also of the unidentate glycol species $[Cr(OH_2)_5(glycol)]^{3+}$. The formation of this latter complex from $[Cr(OH_2)_6]^{3+}$ has an activation enthalpy of 25.2 kcal mol^{-1}. The chelation step,

$$[Cr(OH_2)_5(glycol)]^{3+} \longrightarrow [Cr(OH_2)_4(glycol)]^{3+} + H_2O$$

has an activation enthalpy of 15.3 kcal mol^{-1}.[317]

Rates of reaction of mono- and di-nuclear aquo-chromium(III) species with edta have been measured.[318] The operation of an anchimeric *cis* effect in the reactions of $[Cr(OH_2)_5(O_2CR)]^{2+}$ cations with edta has already been mentioned (see footnote on p. 200).

The reaction of *cis*-$[Cr(en)_2(DMSO)_2]^{3+}$ with chloride ion, in dimethyl sulphoxide solution, is some thirty times faster than the reaction of this complex with bromide ion. This reactivity difference can be ascribed to the relative values of the ion-association constants between this cation and the incoming chloride or bromide.[190]

***d*^{3}: Molybdenum(III).**—A preliminary study of the kinetics of the reaction of the recently characterized aquomolybdenum(III) ion with thiocyanate suggests a second-order rate constant of about 10 l mol^{-1} s^{-1}. This reaction rate is about a million times greater than that for hexa-aquochromium(III) plus thiocyanate. Such a difference in reactivity may betoken a much more associative mechanism* for the reaction at the aquomolybdenum(III) cation – the trend at least is in the right direction for this. However, the possibility that the high rate may arise from redox catalysis by traces of some other oxidation state of molybdenum should be borne in mind unless unequivocally eliminated by subsequent work.[319]

***d*^{5}: Iron(III).**—In anation reactions involving cationic complexes and anions it is always impossible to distinguish kinetically between an S_N1 (lim) or *D* and an $S_N1$ip or I_d mechanism – and often difficult to distinguish between these and an associative (S_N2) mechanism. With anation reactions between

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* Since the preparation of the manuscript for this chapter, a rate constant for the reaction of aquomolybdenum(III) with thiocyanate differing by a factor of *ca.* 40 from that claimed in reference 319 has been reported. However, the mechanism for the reaction of aquomolybdenum(III) with thiocyanate and with chloride does indeed, from several pieces of evidence, appear to be associative in character (Y. Sasaki and A. G. Sykes, *J.C.S. Chem. Comm.*, 1973, 767). Inconsistencies of kinetic parameters in this area are none too surprising in view of disagreements over the physical properties of various purported preparations of solutions containing monomeric aquomolybdenum(III) (Y. Sasaki and A. G. Sykes, *J.C.S. Chem. Comm.*, 1973, 767; A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 3287; and ref. 319).

[317] H. B. Clonis and E. L. King, *Inorg. Chem.*, 1972, **11**, 2933.

[318] J. Geher-Glucklich and M. T. Beck, *Acta Chim. Acad. Sci. Hung.*, 1971, **70**, 235, 247 (*Chem. Abs.*, 1972, **76**, 18 320h, 18 423u).

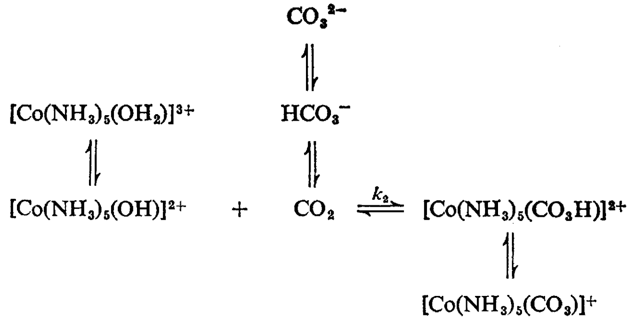
[319] K. Kustin and D. Toppen, *Inorg. Chem.*, 1972, **11**, 2851.

anionic complexes and anions the situation is simpler, as at least pre-equilibrium formation of ion pairs can be ruled out. Thus in the classic system of anion substitution at $[Co(CN)_5(OH_2)]^{2-}$ the operation of an S_N1 (lim) or *D* mechanism has been unequivocally established. Recently the kinetics of substitution at $[Fe(CN)_5(OH_2)]^{2-}$, using thiocyanate ion as entering group, have been investigated. The results are less clear-cut than for the cobalt analogue. The most satisfactory conclusion from these results and information on base hydrolysis of $[Fe(CN)_5(SCN)]^{3-}$ is that anation at $[Fe(CN)_5(OH_2)]^{2-}$ is associative. Transition states $[Fe(CN)_5(OH_2)(SCN)]^{3-}$ and $[Fe(CN)_5(OH)(SCN)]^{4-}$ are proposed; the latter is postulated from a term at $[H^+]^{-1}$ in the rate law.[301] The formation of $[Fe(CN)_5(SCN)]^{3-}$ from the dinuclear complex $[Fe_2(CN)_{10}]^{4-}$ takes place in two kinetically distinct stages. The postulated intermediate could be formed *via* the plausible mechanism of thiocyanate attack at the less stable iron–nitrogen end of one of the two bridging cyano-groups in the dimer:[301]

$$[(NC)_4Fe(CN)_2Fe(CN)_4]^{4-} + NCS^- \longrightarrow [(NC)_5Fe(CN)Fe(CN)_4(SCN)]^{5-}$$

***d^6*: Cobalt(III).**—Kinetic studies of formation reactions from aquocobalt(III) are understandably rare. However, the kinetics of formation of both the mono- and bis-salicylato-complexes can be monitored before the redox reaction to cobalt(II) supervenes. Rate laws and rate constants at 25 °C have been established.[320]

The kinetics of formation of $[Co(NH_3)_5(CO_3)]^+$ from $[Co(NH_3)_5(OH_2)]^{3+}$ and carbon dioxide have been examined in the pH range 7—9. These results, considered in relation to the known kinetic pattern for the aquation of the carbonato-complex, suggest the reaction scheme outlined below (Scheme 2).*



$$\begin{tikzcd}
 & & CO_3^{2-} \arrow[d, shift left] & \\
{[Co(NH_3)_5(OH_2)]^{3+}} \arrow[d, shift left] & & HCO_3^- \arrow[u, shift left] \arrow[d, shift left] & \\
{[Co(NH_3)_5(OH)]^{2+}} \arrow[u, shift left] & + & CO_2 \arrow[u, shift left] \arrow[r, shift left, "k_2"] & {[Co(NH_3)_5(CO_3H)]^{2+}} \arrow[l, shift left] \arrow[d, shift left] \\
 & & & {[Co(NH_3)_5(CO_3)]^+} \arrow[u, shift left]
\end{tikzcd}$$

Scheme 2

*H^+ omitted from Scheme 2 for clarity.

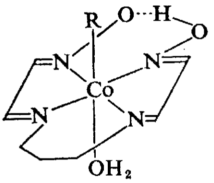
[320] R. G. Sanberg, J. J. Auborn, E. M. Eyring, and K. O. Watkins, *Inorg. Chem.*, 1972, **11** 1952.

The actual formation step is the reaction of carbon dioxide itself with the conjugate base of the penta-ammine–aquo-complex. For this process the second-order rate constant (k_2 in Scheme 2) is 2.2×10^2 l mol^{-1} s^{-1} at 25 °C; the activation parameters are $\Delta H^{\ddagger} = 15.3 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = +3.6 \pm 3.0$ cal deg^{-1} mol^{-1}.[321] The activation parameters for the reaction of $[Co(NH_3)_5(OH_2)]^{3+}$ with the neutral ligand glycine are $\Delta H^{\ddagger} = 27.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = +5.2$ cal deg^{-1} mol^{-1}. The mechanism suggested is one of dissociative interchange following a pre-equilibrium association between the reactants. A dissociative mechanism is supported by the similarity of the activation enthalpy for this reaction with those for water exchange and azide reaction with $[Co(NH_3)_5(OH_2)]^{3+}$, which are 26.6 kcal mol^{-1} and 26.9 kcal mol^{-1} respectively.[322] The *cis*- and *trans*-isomers of $[Co(NH_3)_4(OH_2)(OH)]^{2+}$ react with ammonia at approximately the same rates in 8M-NH_3 solution to produce the $[Co(NH_3)_5(OH)]^{2+}$ cation.[323] Activation parameters for the reaction of $[Co(tren)(OH_2)_2]^{3+}$ with bromide ion are reported to be $\Delta H^{\ddagger} = 25.2 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0.19 \pm 1.1$ cal deg^{-1} mol^{-1} in aqueous solution ($I = 2.0$M). The rate law is consistent with a dissociative interchange or with a bimolecular (S_N2) mechanism; the principle of microscopic reversibility is invoked to rule out the latter.[324]

The kinetics of replacement of the water ligand of alkylaquo-1,3-bis(biacetyl monoximeimino)propanatocobalt(III) (32) by a variety of anionic and uncharged nitrogen ligands conform to one of two patterns. For thiocyanate, azide, ammonia, piperidine, or morpholine as incoming group, there is a simple rate law consistent with dissociative replacement, but for reaction with imidazole, benzylamine, pyridine, or 4-methylpyridine, the rate law is

$$\text{Rate} = k[(32)][L]/(k^1 + [L])$$

This rate law is consistent with a *D* or with an ion-pair mechanism. The latter seems improbable as the incoming group is uncharged. The former is also unacceptable as the limiting rates for the various entering groups are widely different. The feature which is common to all these entering groups, and which distinguishes them from the first group of entering ligands (*viz.* thiocyanate *etc.*), is their aromaticity. It is therefore suggested that the aromatic bases



(32)

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[321] E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Amer. Chem. Soc.*, 1973, **95**, 4169.
[322] D. Banerjea and J. Roy, *Z. anorg. Chem.*, 1973, **400**, 89.
[323] E. G. A. M. Bohte and S. Balt, *Rec. Trav. chim.*, 1973, **92**, 826.
[324] K. Kuo and S. K. Madan, *Inorg. chim. Acta*, 1973, **7**, 110.

react by an 'ion-pair' type of mechanism, but that the associated intermediate here involves π-association between the aromatic entering group and the conjugated part of the complex rather than the electrostatic association of an ion pair.[325]

Much effort has been devoted to the determination of kinetic parameters for the displacement of water from compounds of the general formula $[Co(dmgH)_2(L)(OH_2)]^{n+}$.[94, 326–330] Activation parameters for a number of such reactions are quoted in Table 19. The variation of substitution rate with the nature of L, when L is thiourea or one of its derivatives, is consistent with a dissociative mechanism.[327] From the present[328, 329] and earlier results one can place ligands L in the following *trans*-labilizing order in this type of complex:

Table 19 *Activation parameters for the replacement of water in* trans-$[Co(dmgH)_2(L^1)(OH_2)]^{n+}$ *by an incoming ligand* L^2 *in aqueous solution*

L^1	L^2	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	log *A*	*Ref.*
tu	tu	19.2	−19	—	326
etu	etu	15.5	−20	—	327
tmtu	tmtu	16.8	−20	—	327
py	py	16.6	—	6.7	328
NO_2^-	py	13.6	—	5.8	328
OH_2	py	11.9	—	4.9	328
NH_3	Cl^-	34.3	—	18.6	94
Cl	tu	11.9	−30	—	330
Br	tu	12.5	−28	—	330
I	tu	13.4	−26	—	330

$$SO_3^{2-} \sim tu \gg OH^- \sim S_2O_3^{2-} > OH_2 > NO_2^- > py$$

The variation of rates and activation parameters with solvent composition has been examined, for complexes with L = (substituted) thiourea, in mixed aqueous solvents containing up to 50% ethanol, 50% propan-2-ol, and 30% dioxan. Some illustrative values are listed in Table 20. The variation of kinetic parameters with solvent composition, in particular plots of logarithms of rate constants against reciprocal dielectric constants, is said to be consistent with the dissociative mechanism one would expect for complexes containing such strong *trans*-labilizing groups as thiourea and its substituted derivatives.[326, 327]

The rate law for the formation of the newly prepared μ-selenato-μ-amido-complex (33) from (34) is

$$\text{Rate} = k_f[(33)][SeO_4^{2-}][H^+] \qquad (9)$$

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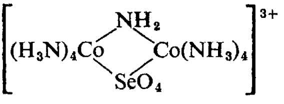
[325] G. Tauzher, R. Dreas, G. Costa, and M. Green, *J.C.S. Chem. Comm.*, 1973, 413.
[326] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1972, **17**, 1576.
[327] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1972, **17**, 1435.
[328] N. M. Samus' and T. S. Luk'yanets, *Russ. J. Inorg. Chem.*, 1972, **17**, 390.
[329] J. E. Earley and J. G. Zimmerman, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 687.
[330] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1973, **18**, 232.

Table 20 *Kinetic parameters for the replacement of water in* trans-$[Co(dmgH)_2(L^1)(OH_2)]^+$ *by an incoming ligand* L^2 *in aqueous and in mixed aqueous solution*

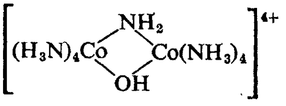
$L^1 = L^2$	*Solvent*	$10^5k^a/s^{-1}$	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
tu	Water	6.7	19.2	−19	326
	50% EtOH	4.3	18.4	−19	
	50% Pr^iOH	4.0	21.2	−18	
etu	Water	14^b	15.5	−20	327
	50% EtOH	10.8	18.0	−19	
	50% Pr^iOH	8.9	17.0	−21	
	30% dioxan	1.3	17.0	−21	

[a] At 40 °C. [b] By extrapolation.

The value of k is 1.35×10^{-2} l^2 mol^{-2} s^{-1} at 25 °C. The activation parameters are $\Delta H^{\ddagger} = 18.2 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.3 \pm 0.9$ cal deg^{-1} mol^{-1}. Selenate reacts at about the same rate as sulphate with (34); both of these oxo-anions react much more rapidly than do bromide or chloride. There is no evidence that ion-pair formation between (34) and selenate makes an appreciable contribution to the observed kinetics.[104] The reaction of the μ-hydroxo-cation (35) with thiocyanate follows a rate term analogous to that in equation (9) above. Here $k_f = 3 \times 10^{-3}$ l^{-2} mol^{-2} s^{-1} at 25 °C, and the activation parameters are $\Delta H^{\ddagger} = 10.9 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -25.8 \pm 2.2$ cal deg^{-1} mol^{-1}. The products include equal amounts of the $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ cations.[101]



(33)



(34)

$$[(H_3N)_5Co—OH—Co(NH_3)_5]^{5+}$$

(35)

An attempt to study the kinetics of condensation of *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$ and *fac*-$[Co(NH_3)_3(OH_2)_3]^{3+}$ was not fruitful, since there proved to be too much decomposition and loss of ammonia.[331] However, a study of the tetramerization of *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$ did prove successful.[298]

The rate of formation of the ternary complex from *NN*-diaceticanthra-anilatocobalt(III) and nitrite ion is a function of pH, with a maximum velocity at pH 2.5. The activation energy is 22.1 kcal mol^{-1} and the probability factor is 1.17×10^{20}, which corresponds to an activation entropy of about +35 cal deg^{-1} mol^{-1}.[332]

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[331] G. Schwarzenbach, J. Boesch, and H. Egli, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2141.

[332] C. Dragulescu, R. Kuzman-Anton, and P. Tribunescu, *Bul. stiint. teh. Inst. Politeh. Timisoara, Ser. chim.*, 1970, **15**, 137 (*Chem. Abs.*, 1973, **78**, 76 342u).

d^6: Rhodium(III).—It is usually impossible to distinguish kinetically between a fully dissociative mechanism with a five-co-ordinate intermediate and a dissociative mechanism involving interchange within an ion pair for a reaction between a cationic complex and an anionic ligand. However, in the particular case of an aquo-complex there may be useful additional information derived from the pH-variation of reaction rates. Such is the situation for the formation of *trans*-$[Rh(OH_2)_4Cl_2]^+$ from $[Rh(OH_2)_5Cl]^{2+}$, where a decision in favour of an S_N1(lim) mechanism is possible. Details of the lengthy argument involved are given in an appendix to this paper.[333] A *D* mechanism had earlier been suggested for the reaction of $[Rh(OH_2)Cl_5]^{2-}$ with anionic ligands, where ion-pairing seems unlikely. In the light of this build-up of evidence for the operation of a *D* mechanism in substitution at rhodium(III), earlier kinetic results[334] on the reaction of $[Rh(OH_2)_6]^{3+}$ with chloride have now been reinterpreted in terms of a *D* mechanism.[333]

Rate constants and activation parameters for the chloride anation of $[Rh(dmgH)_2(NO_2)(OH_2)]$ have been determined from kinetic results obtained for the reversible aquation of the $[Rh(dmgH)_2(NO_2)Cl]^-$ anion. For the reaction of $[Rh(dmgH)_2(NO_2)(OH_2)]$ with chloride, $\Delta H^{\ddagger} = 12.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -25$ cal deg^{-1} mol^{-1}.[250] The reported activation enthalpy seems surprisingly low for substitution at rhodium(III); previously determined activation enthalpies for reactions of complexes of the type $[Rh(LL)_2(L)(OH_2)]^{n+}$ with chloride or bromide ions fall within the range 23.8—32.0 kcal mol^{-1}.[335]

d^6: Platinum(IV).—The rate law for the reactions of $[Pt(OH_2)_2Br_4]$ and of $[Pt(OH_2)Br_5]^-$ with bromide is

$$\text{Rate} = \{k_1[Br^-] + k_2[Br^-]^2\}[Pt^{IV}]$$

Some pre-equilibrium association between bromide ion and platinum(IV) complex is invoked to account for the k_2 term. A redox cycle involving platinum(II) intermediates is thought not to be important in these systems.[336] This point of view contrasts with that expressed by some earlier authors – for instance the redox mechanism proposed for halide-substitution reactions of *trans*-$[Pt(en)_2Cl_2]^{2+}$ and related compounds.[337]

Kinetic parameters for the reactions of *trans*-$[Pt(NH_3)_4(OH)Cl]^{2+}$ and of *trans*-$[Pt(en)_2(OH)Cl]^{2+}$ with chloride ion have been obtained as a by-product of an investigation of the oxidative addition of chlorine to platinum(II) complexes. For the bis-ethylenediamine complex an activation enthalpy of only 1 kcal mol^{-1} is suggested; the activation entropy is -34 cal deg^{-1} mol^{-1}.[338] There has been a parallel study of the analogous bromo-system.[339]

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[333] M. J. Pavelich and G. M. Harris, *Inorg. Chem.*, 1973, **12**, 423.
[334] K. Swaminathan and G. M. Harris, *J. Amer. Chem. Soc.*, 1966, **88**, 4411.
[335] A. J. Poë and K. Shaw, *J. Chem. Soc. (A)*, 1970, 393.
[336] L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 1971, **5**, 643.
[337] A. J. Poë and D. H. Vaughan, *J. Amer. Chem. Soc.*, 1970, **92**, 7537.
[338] M. M. Jones and K. A. Morgan, *J. Inorg. Nuclear Chem.*, 1972, **34**, 259.
[339] K. A. Morgan and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1972, **34**, 275.

***d^6*: Ruthenium(II).**—The replacement of the water ligand of the $[Ru(NH_3)_5(OH_2)]^{2+}$ cation by each of a wide variety of ligands, including ammonia, substituted pyridines, acetonitrile, benzonitrile, and imidazole, follows the rate law[340, 341]

$$-d[Ru(NH_3)_5(OH_2)^{2+}]/dt = k[Ru(NH_3)_5(OH_2)^{2+}][L]$$

in weakly acidic aqueous solution. At low pH's the conjugate acids of some of the ligands cited may also react, leading to a rate law of the type[341]

$$-d[Ru(NH_3)_5(OH_2)^{2+}]/dt = \{k[py] + k'[pyH^+]\}[Ru(NH_3)_5(OH_2)^{2+}]$$

The value of k varies only slightly with the nature of the incoming ligand L, which suggests a D [S_N1(lim)] rather than an A (S_N2) mechanism for these reactions. However, the small variation of k with the nature of the incoming ligand does correlate, if one omits ligands where steric hindrance may affect reactivity, with ligand basicities for the series of substituted pyridines.[340] The observed effects of steric hindrance on reactivity support a D mechanism. Thus the very much slower rate of formation of the 2,6-lutidine complex compared with that of the pyridine complex (the ratio of rates is $5 \times 10^{-4} : 1$) can readily be explained in terms of very unequal competition between 2,6-lutidine and water, but more equal competition between pyridine and water, for the $[Ru(NH_3)_5]^{2+}$ intermediate.[341] The activation parameters for these reactions are $\Delta H^{\ddagger} = 15.1$—$16.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7$ to -13 cal deg^{-1} mol^{-1}. The values for the various entering groups are equal within experimental uncertainty, and moreover are very close to those reported[342] for the reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with nitrogen or with nitrous oxide. This similarity of activation parameters for a wide range of entering ligands provides yet more support for the hypothesis of a D mechanism.[340, 341] As kinetic information is also available on the aquation of some of the $[Ru(NH_3)_5(L)]^{2+}$ complexes formed in these reactions, it is possible to estimate the equilibrium constants for the reactions

$$[Ru(NH_3)_5(OH_2)]^{2+} + L \rightleftharpoons [Ru(NH_3)_5(L)]^{2+} + H_2O \qquad (10)$$

where L = ammonia or pyridine. From this information it can be estimated that the ruthenium–pyridine bond is more stable, to the extent of *ca.* 5 kcal mol^{-1}, than the ruthenium–ammonia bond – a difference which can be ascribed mainly to the additional π-bonding in the former case.[341] Interestingly, enthalpies of reaction for several processes of the type shown as equation (10) above have recently been determined[343] and are thus available for comparison with the kinetic parameters for the reactions discussed in this paragraph.

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[340] R. J. Allen and P. C. Ford, *Inorg. Chem.*, 1972, **11**, 679.
[341] R. E. Shepherd and H. Taube, *Inorg. Chem.*, 1973, **12**, 1392.
[342] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 6170.
[343] G. D. Watt, *J. Amer. Chem. Soc.*, 1972, **94**, 7351.

The novel feature of the reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with the *N*-methylpyrazinium ($nmpz^+$) ion is the employment of a cationic entering group. The kinetic pattern is complicated by the existence of a parallel redox reaction, but the anation reaction appears to involve two steps:

$$[Ru]\text{–}OH_2^{2+} + nmpz^+ \underset{K}{\rightleftharpoons} \text{intermediate} \xrightarrow{k_1} [Ru]\text{–}nmpz^{3+}$$

The activation parameters for the second step are $\Delta H^{\neq} = 18.4$ kcal mol^{-1} and $\Delta S^{\neq} = -10$ cal deg^{-1} mol^{-1}. The thermodynamic parameters for the preliminary equilibrium are $\Delta H = -5.7$ kcal mol^{-1} and $\Delta S = -17$ cal deg^{-1} mol^{-1}. This negative entropy change is reasonable in the light of the expected changes in solvation involved in the association of a uni- and a bi-positive species.[344]

7 Ligand Exchange and Replacement

Solvent Exchange.—Kinetic parameters for water exchange at some d^3 and d^6 complexes of formula $[ML_5(OH_2)]^{3+}$ are given in Table 21. A comparison of activation volumes for water exchange at the three complexes $[M(NH_3)_5(OH_2)]^{3+}$, with M = Co,[345] Cr,[5] or Rh,[5] suggests that the mechanism is dissociative at cobalt(III) but associative at chromium(III) or at rhodium(III). The operation of an associative mechanism in this rhodium(III) case gains further support from the lower activation enthalpy compared with that for water exchange with the analogous cobalt(III) complex. An attempt to distinguish between an I_a and an A mechanism for water exchange with $[Cr(NH_3)_5(OH_2)]^{3+}$ foundered on the overlarge standard error in the determined value of $\partial V^{\neq}/\partial p$. A distinction between an I_d and a D mechanism for water exchange with $[Co(NH_3)_5(OH_2)]^{3+}$ was sought by comparing this reaction with that of water exchange at $[Co(MeNH_2)_5(OH_2)]^{3+}$.[346] The results are consistent with those from an earlier study of acid and base hydrolysis of $[Co(RNH_2)_5Cl]^{2+}$ complexes.[347] There is some indication that an intermediate $[Co(RNH_2)_5]^{3+}$ may be slightly less evanescent than $[Co(NH_3)_5]^{3+}$.

Table 21 *Kinetic parameters for water exchange at* $[ML_5(OH_2)]^{3+}$ *cations*

M	L	k_{25}/s^{-1}	$\Delta V^{\neq}$/ cm^3 mol^{-1}	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal deg^{-1} mol^{-1}	*Ref.*
Co	NH_3	6×10^{-6}	$+1.2 \pm 0.2$	26.6 ± 0.3	$+6.7 \pm 1.0$	345
Cr	NH_3	5.2×10^{-5}	-5.8 ± 0.2	23.2 ± 0.5	0 ± 1.6	5
Rh	NH_3	0.84×10^{-5}	-4.1 ± 0.4	24.6 ± 0.3	-0.8 ± 1.1	5
Co	$MeNH_2$	1.1×10^{-4}	—	—	—	346

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[344] H. E. Toma and J. M. Malin, *J. Amer. Chem. Soc.*, 1972, **94**, 4039.
[345] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.
[346] A. G. Shaver and M. Parris, *Canad. J. Chem.*, 1973, **51**, 1392.
[347] D. A. Buckingham, B. M. Foxman, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 1790.

The dependence of the rate of DMSO exchange with $[\mathrm{Cr(DMSO)_6}]^{3+}$ in dimethyl sulphoxide–nitromethane solvent mixtures suggests, at first sight, a dissociative mechanism. However, activation volumes for solvent exchange at chromium(III) complexes suggest an associative mechanism for these processes. The apparent contradiction has been tentatively resolved by postulating a unique solvation site in $[\mathrm{Cr(DMSO)_6}]^{3+}$, in which one DMSO molecule undergoes preferential exchange.[348]

Ligand Exchange: Unidentate.—The rates of halide exchange with $[\mathrm{Ru(NH_3)_5X}]^{2+}$, with X = Cl, Br, or I, are independent of free-halide concentration (at least over the range $0.02 < [\mathrm{X^-}] < 0.12\mathrm{M}$), of pH, and of ionic strength. Activation energies are 20.0 ± 0.5 kcal mol^{-1} for the chloro-, 23.2 ± 0.9 kcal mol^{-1} for the bromo-, and 30 ± 1 kcal mol^{-1} for the iodo-complex. The mechanism suggested in each case is rate-determining formation of an aquo-intermediate $[\mathrm{Ru(NH_3)_5(OH_2)}]^{3+}$, followed by rapid anation. Reactivity trends for these three halogeno-complexes are said to be consistent with an associative aquation step; reactivity trends for halide exchange at $[\mathrm{M(NH_3)_5X}]^{2+}$, with M = Ru, Rh, or Ir, are as expected from crystal-field effects on an associative rate-determining step.[349] The two iodide ligands *trans* to each other in *mer*-$[\mathrm{Pt(NH_3)_3I_3}]^+$ undergo rapid exchange, but the third iodide undergoes exchange at a rate too low to be detected.[350]

The rate law for ^{18}O-exchange between *trans*-$[\mathrm{Re(en)_2O_2}]^+$ and water is

$$\text{Rate} = \{k_0 + k_1[\mathrm{enH_2^{2+}}] + k_2[\mathrm{en}] + k_3[\mathrm{OH^-}]\}[\mathrm{Re(en)_2O_2^+}]$$

Activation energies for the various paths are 30.4 kcal mol^{-1} for the k_0 term, 30.5 for the k_1 term, 18.1 for the k_2 term, and 24.2 for the k_3 term.[351] The rate law for ^{18}O-exchange between *trans*-$[\mathrm{Re(CN)_4O_2}]^{3-}$ and water is

$$\text{Rate} = k_1[\mathrm{Re(CN)_4(O)(OH)^{2-}}] + k_x[\mathrm{Re(CN)_4O_2^{3-}}]$$

In the presence of an excess of cyanide, $k_x = k_2[\mathrm{CN^-}]^{-0.90}$; in the absence of added cyanide, $k_x = k_3[\mathrm{OH^-}]^{+0.22}$. At 35 °C $k_1 = 3.42 \times 10^{-2}\ \mathrm{s^{-1}}$; the corresponding activation enthalpy is 23.3 ± 0.3 kcal mol^{-1}. In acid solution oxygen exchange is facilitated by the protonation of one of the oxo-ligands. In basic solution cyanide displacement and consequent labilization of an oxo-ligand are proposed. Easy displacement of cyanide is not an unreasonable postulate in the light of the known ease of cyanide exchange at this complex. Rate laws and kinetic parameters are also reported for oxygen exchange between water and the newly characterized dinuclear $[\mathrm{(NC)_4ORe\cdot O\cdot ReO(CN)_4}]^{4-}$ anion.[352]

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[348] C. H. Langford, R. Scharfe, and R. Jackson, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1033.

[349] T. Shinohara, T. Yamada, N. Takebayashi, S. Hiraki, and A. Ohyoshi, *Bull. Chem. Soc. Japan*, 1972, **45**, 3081.

[350] Yu. N. Kukushkin, M. A. Kuz'mina, and V. V. Sibirskaya, *Radiokhimiya*, 1971, **13**, 914 (*Chem. Abs.*, 1972, **76**, 90 670q).

[351] L. B. Kriege and R. K. Murmann, *J. Amer. Chem. Soc.*, 1972, **94**, 4557.

[352] D. L. Toppen and R. K. Murmann, *Inorg. Chem.*, 1973, **12**, 1611.

The kinetics of cyanide exchange at $[Fe(CN)_5(py)]^{3-}$ have been studied, in the presence and in the absence of added pyridine, by $^{14}CN^-$ tracer techniques. The proposed mechanism here, as in similar substitution reactions of $[Fe(CN)_5(L)]^{3-}$ complexes (*cf.* Sections 4 and 5 of this chapter), is S_N1(lim). The transient $[Fe(CN)_5]^{3-}$ intermediate seems to contain two types of cyanide ligand of different labilities; it does not seem possible to distinguish between the two possibilities of four labile and one inert cyanide or three labile and two inert cyanides. Cyanide ion seems much more labile in $[Fe(CN)_5(py)]^{3-}$ than in $[Fe(CN)_5(NO)]^{2-}$ or in $[Fe(CN)_6]^{4-}$. This high reactivity is explained by facile loss of cyanide from the $[Fe(CN)_5]^{3-}$ intermediate, itself more easily generated from $[Fe(CN)_5(py)]^{3-}$ than from the other two complexes.[353]

Ligand Replacement: Unidentate by Unidentate.—A dissociative mechanism is proposed for the replacement of nitrito- or of thiocyanato-ligands in *trans*-$[Co(dmgH)_2(NO_2)_2]^-$ and in *trans*-$[Co(dmgH)_2(NCS)_2]^-$ respectively by thiourea. Thiocyanate is replaced much more rapidly than nitrite from these cobalt(III) centres.[354] Substitution at bisdimethylglyoximatocobalt(III) complexes can be catalysed by cobalt(II) complexes. This has been demonstrated by the elucidation of the rate law for the cobalt(II)-catalysed reaction of *trans*-$[Co(dmgH)_2(PPh_3)(NO_2)]$ with pyridine:

$$\text{Rate} = k_2[\text{Co}^{\text{III}}(\text{dmgH})_2(\text{PPh}_3)(\text{NO}_2)][\text{Co}^{\text{II}}(\text{dmgH})_2(\text{PPh}_3)]$$

The absence from this rate law of a term in the concentration of pyridine is explained by rapid conversion of the cobalt(II) complex into $[Co^{II}(dmgH)_2(py)]$, followed by a rate-determining inner-sphere electron- and ligand-transfer step.[355] Ligand-exchange reactions

$$[\text{Co(baen)(L)}_2]^- + [\text{Co(baen)(L}')_2]^- \rightleftharpoons 2[\text{Co(baen)(L)(L}')]^-$$

where baen = *NN'*-ethylenebis(acetylacetoneiminate) and L and L′ are amino-acids, here acting as unidentate (N-bonded) ligands, are fast on the n.m.r. time-scale.[356] The solvolysis of the $[Co(NH_3)_5Cl]^{2+}$ cation in liquid ammonia, to produce $[Co(NH_3)_6]^{3+}$, has, in view of its similarity to aquation, already been mentioned in Section 2 of this chapter.[111]

Rates of replacement of chloride in *trans*-$[Rh(NH_3)_4Cl_2]^+$ by bromide, iodide, or hydroxide have been determined, and compared with the rates of analogous reactions of *trans*-$[Rh(en)_2Cl_2]^+$. Substitution at the tetra-ammine complex is about twice as fast as at the bisethylenediamine complex. This rate difference is reflected in a small difference in activation enthalpies. That for reaction of the tetra-ammine complex with bromide ion is 24.11 ± 0.39 kcal mol^{-1} and that for the bisethylenediamine complex with bromide ion is

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[353] B. Jezowska-Trzebiatowska, A. Keller, and J. Ziolkowski, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1972, **20**, 655.

[354] N. M. Samus', A. S. Dimoglo, and G. A. Konunova, *Issled. Khim. khelatnykh Soedinenii*, 1971, 65 (*Chem. Abs.*, 1972, **77**, 118 807m).

[355] L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, 1972, **11**, 2050.

[356] Y. Fujii, *Bull. Chem. Soc. Japan*, 1972, **45**, 3084.

24.81 ± 0.56 kcal mol^{-1}. In the light of the reported standard errors, one can only claim at a fairly low confidence level that these activation enthalpies do differ significantly – the small difference can be attributed to solvation effects. The activation entropies are the same, at -9.2 ± 1.1 cal deg^{-1} mol^{-1} for the $(NH_3)_4$ compound and -8.7 ± 1.6 for the $(en)_2$ compound. The independence of substitution rates of the nature and concentration of the incoming ligand indicates a dissociative mechanism.[357] Indeed rates of substitution at several rhodium(III)- and iridium(III)-ammine or amine–chloride complexes have been found to be independent of nature and concentration of the incoming group, at concentrations usually employed in such kinetic studies. However, when low concentrations of incoming ligand are used – radiochemical monitoring of kinetics is easier than spectrophotometric under such conditions – rates of ligand substitution decrease with decreasing concentration of entering ligand.[358] The rate *versus* ligand-concentration profile is consistent with either an ion-pairing or an S_N1(lim) (D) mechanism. The variation of hypothetical ion-pairing constants, derived from the kinetic results, with solvent composition and with the nature of the incoming anion disfavours an ion-pairing mechanism. An S_N1(lim) mechanism is both consistent with the kinetic pattern and an attractive hypothesis in view of other recent demonstrations of the operation of this mechanism in substitution at rhodium(III) complexes (*cf.* refs. 11 and 12 in Section 1 of this chapter). The kinetics of the reactions of *cis*-α-$[Rh(trien)Cl_2]^+$ with bromide, iodide, or azide have been monitored, and the results discussed in terms of ligand replacement *via* an aquo-intermediate, whose rate-determining formation is followed relatively rapidly by anation by the incoming nucleophile.[248]

Catalysis of substitution reactions of rhodium(III) complexes by reducing agents has in the past few years become a well-documented subject. *trans*-$[Rh(py)_4Cl_2]^+$ was one of the earlier examples of rhodium(III) complexes undergoing redox-catalysed substitution. Recent work has shown similar catalysis in the reactions of *trans*-$[RhL_4X_2]^+$, with L = a 3- or 4-substituted pyridine, or quinoline, and X = Cl or Br, with a variety of incoming ligands, including fluoride, azide, thiocyanate, and nitrite.[359] The intermediacy of rhodium(I) species is postulated here, and in the hydrazine-catalysed reaction of *cis*-$[Rh(bipy)_2Cl_2]^+$ or its phen analogue with cyanide ion.[308] Ethanol is not a sufficiently strong reducing agent to generate rhodium(I) species from $[Rh(trien)Cl_2]^+$ and does not catalyse substitution of this complex, but stronger reducing agents do catalyse such substitution.[248]

Substitution reactions involving platinum(IV) complexes are usually strongly catalysed by platinum(II) complexes.[360] It is only recently that a similar situation has been described for palladium complexes; the vastly greater amount of

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[357] A. J. Poë and M. V. Twigg, *Canad. J. Chem.*, 1972, **50**, 1089.

[358] See, *e.g.*, J. Burgess, E. R. Gardner, and F. M. Mekhail, *J.C.S. Dalton*, 1972, 487 and refs. therein.

[359] A. W. Addison, K. Dawson, R. D. Gillard, B. T. Heaton, and H. Shaw, *J.C.S. Dalton*, 1972, 589.

[360] W. R. Mason, *Coordination Chem. Rev.*, 1972, **7**, 241.

information on the platinum systems may be ascribed to the much more convenient reaction rates thereof. Rate laws have now been determined for the reaction of *trans*-$[Pd(en)_2Cl_2]^{2+}$ with bromide ion and of *trans*-$[Pd(en)_2Br_2]^{+}$ with chloride ion, in both cases in the presence of $[Pd(en)_2]^{2+}$. For both reactions there is a term $k[Pd^{IV}][X^-][Pd^{II}]$ in the rate law, which demonstrates that a similar redox substitution path operates for palladium(IV) as for platinum(IV). In the case of the reaction of the dichloro-complex with bromide ion there is a second term in the rate law, $k'[Pd^{IV}][Br^-]$, ascribed to reductive attack by bromide ion. For the reaction of the dibromo-complex with chloride, the second term in the rate law involves only $[Pd^{IV}]$, indicating a simple dissociative rate-determining step. These differences in rate laws and chemistry between the two reactions are understandable in terms of the difference between the reducing powers of the bromide and chloride anion, and the expected difference between palladium(IV)–bromide and palladium(IV)–chloride bond strengths. Activation parameters for the various constituent reactions are reported. Most of these are composite quantities, except for the dissociative reaction of the dibromo-complex, where the observed activation parameters are $\Delta H^{\ddagger} = 14 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9 \pm 6$ cal deg^{-1} mol^{-1}.[361]

Four papers on ligand-replacement reactions of compounds $[Fe(CN)_5L]^{3-}$, as well as a paper on aquation of $[Fe(CN)_5(NO)]^{2-}$ and one on cyanide-ion exchange with $[Fe(CN)_5(py)]^{3-}$ mentioned earlier (ref. 258 of Section 4 and ref. 353 of this section respectively), have one feature in common, the intermediacy of $[Fe(CN)_5]^{3-}$. All these reactions therefore proceed by a limiting S_N1 (or D) mechanism. The kinetic pattern can be illustrated by reference to one case, that of the reaction of $[Fe(CN)_5(PhNO)]^{3-}$ with cyanide ion.[362] The dependence of reaction rate on cyanide-ion concentration is shown in Figure 2, the dependence of reciprocal rate constant on reciprocal cyanide-ion concentration in Figure 3. The kinetic behaviour thus depicted can in general arise from an ion-pairing or an S_N1(lim) mechanism, of which the former can be eliminated in the present reaction of the $[Fe(CN)_5(PhNO)]^{3-}$ anion with anionic cyanide. Similar systems include the reaction of $[Fe(CN)_5(py)]^{3-}$ with cyanide ion[363] and those of $[Fe(CN)_5(NO)]^{2-}$ with hydroxylamine, hydrazine, or ammonia.[364] An S_N1(lim) mechanism has also been proposed for the reactions of $[Fe(CN)_5L]^{3-}$, where L = pyridine, 4-methylpyridine, pyridine-4-carboxamide, 4,4′-bipyridyl, or pyrazine, with the *N*-methylpyrazinium cation. Here of course ion-pairing is possible, but the operation of an S_N1(lim) mechanism here too both seems likely and is indeed confirmed by some ancillary results involving pyrazine as replacing ligand. Moreover, the assign-

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[361] W. R. Mason, *Inorg. Chem.*, 1973, **12**, 20.

[362] D. Pavlović, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1973, 602.

[363] B. Jezowska-Trzebiatowska, A. Keller, and J. Ziolkowski, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1972, **20**, 649.

[364] L. Dozsa, I. Szilassy, and M. T. Beck, *Magyar Kém. Folyóirat*, 1973, **79**, 45 (*Chem. Abs.*, 1973, **78**, 140 852q).

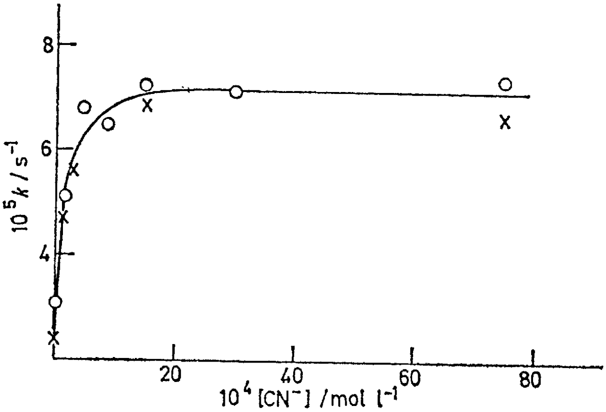


Figure 2 *Cyanide-ion dependence of the rate of replacement of* PhNO *by* CN$^-$ *ion in* 0.00015M-$Na_3[Fe(CN)_6(PhNO)]$ *at* 50 °C; *in the absence* (×) *and presence* (○) *of* 0.01M-$NaClO_4$

(Reproduced from *J.C.S. Dalton*, 1973, 602)

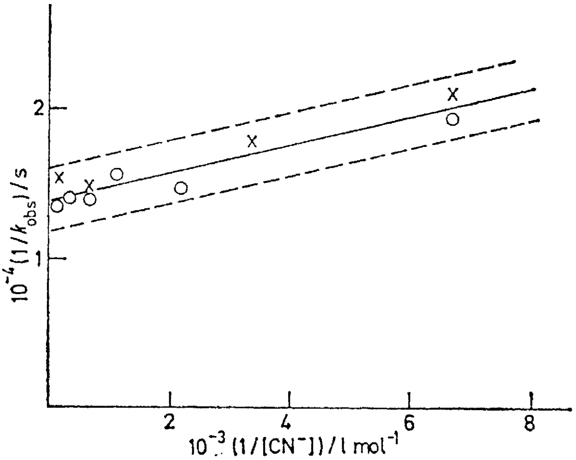


Figure 3 *Plot of* $1/k_{obs}$ *against* $1/[CN^-]$ *for the reaction of the* $[Fe(CN)_5(PhNO)]^{3-}$ *anion with cyanide; data are from Figure* 2. *The broken lines show the* 95 % *confidence limits*

(Reproduced from *J.C.S. Dalton*, 1973, 602)

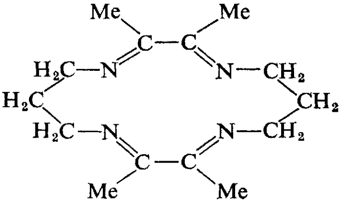
Table 22 *Kinetic parameters for reactions of low-spin iron*(II) *complexes* $[Fe(CN)_5L]^{n-}$ *with incoming ligands* L′

L	L′	k[d]/s^{-1} (*temperature*/°C)	$\Delta H^{\neq}$/ kcal mol^{-1}	$\Delta S^{\neq}$/ cal deg^{-1} mol^{-1}	*Ref.*
PhNO	CN$^-$	7×10^{-5} (50)	—	—	362
py	CN$^-$	—	15.3[a]	—	363
py	mpz$^+$[b]	11.0×10^{-4} (25)	24.8 ± 0.5	$+11\pm2$	365
4-Me-py	mpz$^+$	11.5×10^{-4} (25)	24.0 ± 0.5	$+9\pm2$	
4-CONH$_2$-py	mpz$^+$	7.3×10^{-4} (25)	26.0 ± 0.5	$+14\pm2$	
4,4′-bipy	mpz$^+$	6.2×10^{-4} (25)	26.5 ± 0.5	$+16\pm2$	
pz[c]	mpz$^+$	4.2×10^{-4} (25)	26.4 ± 0.5	$+14\pm2$	

[a] Activation energy. [b] mpz$^+$ = methylpyrazinium cation. [c] pz = pyrazine.
[d] These rate constants are the limiting values reported at high concentrations of incoming ligand L′.

ment of a dissociative mechanism is supported by the positive activation entropy found.[365] Some kinetic parameters for substitution at $[Fe(CN)_5L]^{n-}$ complexes have been collected together in Table 22.

The complex *trans*-$[Fe(LLH)_2(py)_2]$, with LL = diphenylglyoximate, reacts with carbon monoxide in chlorobenzene solution. The determined rate law, the positive activation entropy, and the variation of the rate constant where the py ligands are replaced by their *p*-methyl or *m*-chloro-derivatives, are all consistent with a limiting S_N1 (D) mechanism for these reactions[366] as for those of the $[Fe(CN)_5L]^{n-}$ complexes discussed in the previous paragraph. Preparative and equilibrium studies have been made of the complex $[Fe(tim)(NCMe)_2]^{2+}$, where tim is the quadridentate macrocyclic ligand (36) derived from 1,3-diaminopropane and 2,3-butanedione. These studies suggest that kinetic studies of reactions of this complex could provide information on novel substitution reactions of iron(II), for example the (reversible) replacement of the acetonitrile ligand by carbon monoxide.[367]



(36)

E.s.r. spectroscopy has been used to monitor the stepwise displacement of bromide from the $[Mo^{V}OBr_5]^{2-}$ anion by dimethyl phosphite, in tetrahydrofuran solution. Rate laws and activation parameters were determined for each

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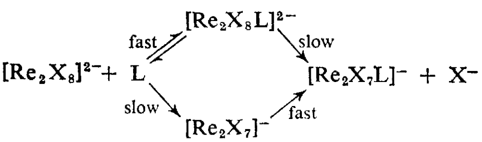
[365] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.
[366] L. Vaska and T. Yamaji, *J. Amer. Chem. Soc.*, 1971, **93**, 6673.
[367] D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Amer. Chem. Soc.*, 1973, **95**, 5152.

step. Displacement of the first bromide ligand does not follow a simple kinetic pattern, but both the rate laws and the activation entropies (between -8 and -19 cal deg^{-1} mol^{-1}) suggest an associative mechanism for the subsequent displacement steps. Activation enthalpies lie within the range 18.7—21.2 (with uncertainties of between 1.1 and 2.0) kcal mol^{-1}.[368]

Rate laws and rate constants have been determined for the reactions of the dinuclear rhenium(III) complexes $[Re_2X_8]^{2-}$ with thiourea or tris-n-butylphosphine in methanol. The kinetic pattern suggests the reaction sequence shown in Scheme 3. The reaction of $[Re_2Br_8]^{2-}$ with chloride ion was also studied.[369]



Scheme 3

The reaction of $[Ru(NH_3)_6]^{3+}$ with nitric oxide, which yields $[Ru(NH_3)_5(N_2)]^{2+}$,[370] is discussed in the chapter on reactions of co-ordinated ligands (Chapter 5 of this Part).

Ligand Replacement: Multidentate by Unidentate.—Kinetic results on the reaction of the cydta complex of manganese(III), which in alkaline solution is $[Mn(cydta)(OH)]^{2-}$, with cyanide ion indicate the following reaction sequence:

$$[Mn(cydta)(OH)]^{2-} + CN^- \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [Mn(cydta)(CN)]^{2-} + OH^-$$

$$[Mn(cydta)(CN)]^{2-} + CN^- \xrightarrow{k_2} [Mn(cydta)(CN)_2]^{3-}$$

$$[Mn(cydta)(CN)_2]^{3-} + 4CN^- \xrightarrow{\text{fast}} [Mn(CN)_6]^{3-} + cydta^{4-}$$

Activation energies are 11.3 ± 0.5 kcal mol^{-1} for the k_1 reaction and 14.1 ± 0.4 kcal mol^{-1} for the k_2 reaction. Both the kinetic pattern and the activation energies are markedly different from similar previously studied nickel(II) and cobalt(II) systems.[371] The reaction of $[Ni(edds)]^{2-}$ with cyanide ion follows fourth-order kinetics, first-order in nickel complex and third-order in cyanide. This behaviour parallels that reported previously for reactions of other aminocarboxylatonickel(II) chelates with cyanide ion.[372] In these reactions, and in the reactions of $[Ni(ttha)]^{4-}$ with cyanide,[373] there is strong kinetic

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[368] G. Y. S. Lo and C. H. Brubaker, *J. Coordination Chem.*, 1972, **2**, 5.

[369] M. J. Hynes, *J. Inorg. Nuclear Chem.*, 1972, **34**, 366.

[370] S. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, 1972, **94**, 686.

[371] R. E. Hamm and J. C. Templeton, *Inorg. Chem.*, 1973, **12**, 755.

[372] G. K. Pagenkopf, *J. Coordination Chem.*, 1972, **2**, 129.

[373] V. Stará and M. Kopanica, *Coll. Czech. Chem. Comm.*, 1972, **37**, 2882.

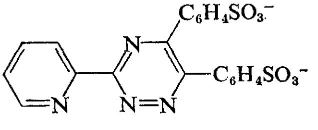
evidence for the intermediacy of ternary (mixed) complexes *en route* to the $[Ni(CN)_4]^{2-}$ product.

Ligands such as phen and bipy appear to withdraw enough electron density from the vicinity of the iron atom in compounds of the type $[Fe(LL)_3]^{2+}$ to permit bimolecular nucleophilic attack. Such attack by cyanide and by hydroxide at complexes where LL = bipy, phen, or one of their substituted derivatives is fairly well established by now. Similar nucleophilic attack by these two ions has now been demonstrated for the complex with LL = ppsa (37). Activation parameters were determined for cyanide attack at this complex;[264] they have also been obtained for the attack of cyanide at $[Fe(bipy)_3]^{2+}$.[374] Activation parameters for cyanide attack at these and at other iron(II) complexes are collected together in Table 23. A little information is available on the kinetics of the reaction between $[Fe(4,7\text{-diPh-phen})_3]^{2+}$ and cyanide in methanol solution.[261]

Table 23 *Activation parameters for cyanide attack at low-spin iron*(II) *complexes* $[Fe(LL)_3]^{2+}$

LL	*Solvent*	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
bipy	Water	23.0	+9	374
ppsa (37)	Water	25.2	+12	264
phen	Water	20	−3	378
sb (38)	95% MeOH	20.4	+10	[a]

[a] From J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc.* (*A*), 1971, 44.



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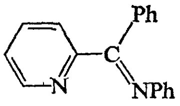

(38)

Contradictory reports have appeared on the stereochemical course of the reaction between the $[Fe(phen)_3]^{2+}$ cation and cyanide ion. On the one hand optical inversion is reported – the first report of inversion at octahedral iron(II)[375,376] – while on the other hand a total loss of optical activity is claimed.[377] The earliest reference to the kinetics of the reaction of $[Fe(phen)_3]^{2+}$ with cyanide reported[378] the rate law to be

$$-\mathrm{d}[\mathrm{Fe(phen)}_3^{2+}]/\mathrm{d}t = \{k_1 + k_2[\mathrm{CN}^-]\}[\mathrm{Fe(phen)}_3^{2+}]$$

[374] J. Burgess, *J.C.S. Dalton*, 1972, 1061.

[375] R. D. Archer, L. J. Suydam, and D. D. Dollberg, *J. Amer. Chem. Soc.*, 1971, **93**, 6837.

[376] R. D. Archer, L. J. Kluss, and V. M. Marganian, Proceedings of the 3rd Symposium on Coordination Chemistry, Debrecen, Hungary, 1970, Vol. 1, p. 291; Vol. 2, p. 191.

[377] G. Nord, *Acta Chem. Scand.*, 1973, **27**, 743.

[378] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706.

The mechanisms suggested to explain the observed optical activity changes indicate that the rate law may be somewhat more complicated than this. However, mundane obstacles in the form of low solubilities of reactants and of product prevent the extension of the kinetic experiments to sufficiently high cyanide-ion concentrations to confirm or modify the original rate law.[376]

The iron atom in $[Fe(mnt)_3]^{2-}$ is formally iron(IV). The study of the reaction of this complex with triphenylarsine oxide thus represents an investigation of substitution kinetics at a novel metal centre. The reaction is in fact both substitution and redox, with the available evidence not sufficiently ample to enable a firm mechanism to be proposed.[379]

Ligand Replacement: Unidentate by Multidentate.—Some kinetic information is available on the reactions of $[Ni(CN)_4]^{2-}$ with the multidentate aminocarboxylate ligands edds[372] and ttha.[373] In both cases the displacement of cyanide was of secondary interest to the reverse reactions, which have already been mentioned in the previous section on the replacement of multidentate by unidentate ligands.

The reactions of $[Fe(bipy)_2(CN)_2]$ and of an analogous Schiff-base complex with phen link this section to the next. The ultimate product is $[Fe(phen)_3]^{2+}$ in both cases; both the unidentate cyanide and the bidentate bipy or Schiff base are replaced by phen. The rate-determining step appears to be iron–bipyridyl or iron–Schiff base bond dissociation. This must generate a high-spin intermediate which rapidly gives $[Fe(OH_2)_6]^{2+}$, which in turn reacts relatively quickly with the excess of phen present to give $[Fe(phen)_3]^{2+}$. Logarithms of reaction rates in mixed aqueous solvents correlate well with Grunwald–Winstein solvent Y values. The slopes (m) of the correlation graphs are about

Table 24 *References to kinetic studies of the replacement of multidentate ligands by other multidentate ligands*

Complex[a]	*Incoming ligand*[a]	*Ref.*
Nickel(II)–asp	cal	381
–dien	cal	381
–dien	edta, hedta	382
–edma	edta, hedta	382
–glu	cal	381
–ida	cal	381
–nta	cal	381
–tetren	ttha	383
Cobalt(II)–nta	cal	381
Copper(II)–mq	edta	384
Zinc(II)–dto	aminocarboxylates	385
–nta	dto, mnt	385
Zirconium(IV)–xyl	edta	386
Hafnium(IV)–xyl	edta	386

[a] For abbreviations see list at start of this volume.

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[379] J. K. Yandell and N. Sutin, *Inorg. Chem.*, 1972, **11**, 448.

0.2 and zero for the bipy and Schiff-base compounds respectively. That the logarithms of rate constants against Y values plots are linear, for a variety of co-solvents for $[Fe(bipy)_2(CN)_2]$, is suggestive of a dissociative reaction. No useful conclusions can be drawn from the smallness of the m values as the atoms separating, *viz.* iron and nitrogen, are so different from those separating in the reference organic system (for t-butyl chloride solvolysis, $m = 1.00$ by definition).[380] These substitution reactions may prove of interest to kineticists with a physical chemical bias, for they provide examples of reactions between uncharged species; such reactions are relatively rare in aqueous solution chemistry of inorganic complexes.

Ligand Replacement: Multidentate by Multidentate.—References to kinetic studies of reactions which involve simple replacement of multidentate ligands by other multidentate ligands are listed in Table 24.[381–386] Closely related investigations include an e.s.r. study of ligand-replacement reactions in the system $[Cu(dtp)_2]$–$[Cu(dtp)(dtc)]$–$[Cu(dtc)_2]$, for which rate constants and activation parameters are available,[387] and a qualitative study of the yttrium(III)–hexafluoroacetylacetone–trifluoroacetylacetone system.[388]

Rate laws and rate constants have been obtained for the amino-acid-catalysed replacement of oligopeptides, for example triglycine or tetraglycine, from their copper(II) complexes by edta. There is steric hindrance to the direct approach of edta to these copper(II)–oligopeptide complexes. The amino-acid can approach more readily and thus start the peeling-off of the oligopeptide from the copper, eventually giving an intermediate in which the approach of the edta to the central copper atom is no longer hindered.[389]

It had been hoped that the reaction of $[MoO_3(dien)]$ with oxine, to yield the known compound $[MoO_2(OH)_2(oxine)]^-$, would be amenable to kinetic study, to provide rate and mechanism data pertaining to substitution at octahedral molybdenum(VI). Sadly the proposed investigation proved impossible, as $[MoO_3(dien)]$ was found to be extensively hydrolysed in aqueous solution.[390]

An understanding of multidentate ligand-replacement reactions is helped by knowledge of dissociation mechanisms for these chelates. Recent studies resulting in kinetic or mechanistic information on the dissociation of amino-carb-

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[380] J. Burgess, *J.C.S. Dalton,* 1972, 203.

[381] M. Kodama, T. Sato, and S. Karasawa, *Bull. Chem. Soc. Japan*, 1972, **45**, 2757.

[382] M. Kodama, M. Hashimoto, and T. Watanabe, *Bull. Chem. Soc. Japan*, 1972, **45**, 2761.

[383] V. Stará and M. Kopanica, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3545.

[384] K. Haraguchi and S. Ito, *Nippon Kagaku Kaishi*, 1972, 2082 (*Chem. Abs.*, 1973, **78**, 34 388h).

[385] R. G. Pearson and D. G. DeWit, *J. Coordination Chem.*, 1973, **2**, 175.

[386] L. I. Budarin, R. B. Suchkova, and K. B. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1971, **16**, 989.

[387] B. S. Prabhananda, S. J. Shah, and B. Venkataraman, *Proc. Indian Acad. Sci.*, 1972, **76A**, 231 (*Chem. Abs.*, 1973, **78**, 140 832h).

[388] N. Serpone and R. Ishayek, *Inorg. Chem.*, 1971, **10**, 2650.

[389] G. R. Dukes and D. W. Margerum, *Inorg. Chem.*, 1972, **11**, 2952.

[390] R. S. Taylor, P. Gans, P. F. Knowles, and A. G. Sykes, *J.C.S. Dalton*, 1972, 24.

Table 25 *References to kinetic and mechanistic studies of dissociation of multidentate aminocarboxylato-complexes*

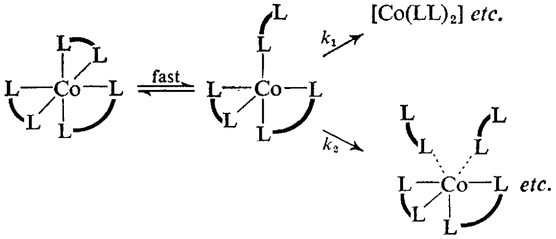
Ligand	*Cation*	*Ref.*
cydta	Cd^{2+}, Pb^{2+}	391
dtpa	Cd^{2+}	391
dtpa	Pb^{2+}	391, 392
dtpa	UO_2^{2+}	393
edta	Cu^{2+}, La^{3+}, Yb^{3+}	394
edta	Er^{3+}, Eu^{3+}, Nd^{3+}, Pr^{3+}	395
gedta	Cd^{2+}, Ni^{2+}, Zn^{2+}	396
pdta	Cd^{2+}, Zn^{2+}	397

oxylate complexes are summarized in Table 25.[391-397] The converse chelate-formation reactions seem less studied; the first step in the oxidation of dtpa by cerium(IV) is the formation of the 1 : 1 complex between these species.[398]

Ligand Exchange: Multidentate.—Exchange of acac with $[Co(acac)_3]$ takes place just sufficiently faster than decomposition of the complex for the kinetics of acac exchange to be monitored. The rate law is

$$\text{Rate} = \{k_1 + k_2[\text{acacH}]\}[\text{Co(acac)}_3] \qquad (11)$$

Composite activation energies have been obtained from the temperature dependence of k_0, where $k_0 = k_1 + k_2[\text{acacH}]$. These activation energies are 18 kcal mol^{-1} in toluene, 21 kcal mol^{-1} in chlorobenzene, and 25 kcal mol^{-1} in anisole. Comparisons of these kinetic results with those for racemization of this complex, and for isomerization and inversion of $[Co(bzac)_3]$, suggest that the k_1 term of equation (11) relates to rate-determining dissociation of a five-co-ordinate intermediate, and the k_2 term to associative attack by the incoming acetylacetone at the same intermediate (Scheme 4).[399]



Scheme 4

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[391] T. Fujisawa and N. Tanaka, *Nippon Kagaku Zasshi*, 1971, **92**, 962 (*Chem. Abs.*, 1972, **76**, 63 982m).
[392] P. Letkeman and J. B. Westmore, *Canad. J. Chem.*, 1972, **50**, 3821.
[393] T. T. Lai and C. S. Wen, *J. Inorg. Nuclear Chem.*, 1972, **34**, 709.
[394] T. Ryhl, *Acta Chem. Scand.*, 1972, **26**, 3955.
[395] T. Ryhl, *Acta Chem. Scand.*, 1973, **27**, 303.
[396] M. Kodama and N. Oyama, *Bull. Chem. Soc. Japan*, 1972, **45**, 2169.
[397] D. L. Rabenstein and B. J. Fuhr, *Inorg. Chem.*, 1972, **11**, 2430.
[398] S. B. Hanna, R. K. Hessley, W. R. Carroll, and W. H. Webb, *Talanta*, 1972, **19**, 1097.
[399] K. Saito and M. Murakami, *Bull. Chem. Soc. Japan*, 1972, **45**, 2472.

Ligand exchange with $[In(CF_3COCHCOR)_3]$ complexes has been monitored by ^{19}F n.m.r. spectroscopy. ^{19}F n.m.r. was preferred to ^1H n.m.r. as chemical shifts are larger for the former nucleus; n.m.r. methods are preferable to radiochemical as separation problems are avoided. However, the estimation of rate constants from n.m.r. spectra is only possible over a narrow range of rates, and in this present study it was only possible to set limits to exchange rates in benzene and in DMSO. In di-isopropyl ketone it was possible to determine rates of exchange for the complexes with R = Me, Bu^i, Ph, 2-naphthyl, and 2-thienyl. In all cases the reaction was first-order in complex concentration, zero-order in added free ligand {contrast $[Co(acac)_3]$ above}. A mechanism involving rate-determining reaction of a five-co-ordinate intermediate is proposed. Such an intermediate should be easy to generate, as many compounds of indium(III) with co-ordination numbers lower than six are known. Conversely the great reluctance of indium(III) to assume a co-ordination number greater than six is used by the authors to argue against an associative mechanism.[400] One feels compelled to comment that a similar argument applied in organic chemistry leads to an erroneous conclusion about the frequency of occurrence of S_N2 reactions at carbon.

Kinetics of exchange of edta with two of its rare-earth complexes have been described – for La^{3+} [401] and for Lu^{3+}.[402] In the former case, catalysis by hydroxide ion was observed. Rates and mechanisms of ligand exchange for pdta and eddda complexes of Cd^{2+}, Zn^{2+}, and Pb^{2+} have been derived from n.m.r. line-broadening observations. On the basis of these ligand-exchange results and earlier kinetic data it is possible to establish the mechanisms of complex formation for these and related complexes.[403]

The rate law for ligand exchange at $[Nd(tren)_2]^{3+}$ in acetonitrile solution, established by n.m.r. line-broadening techniques, is

$$\text{Rate} = k_2[\text{Nd(tren)}_2^{3+}][\text{tren}]$$

At 25 °C, $k_2 = 58\ \text{l mol}^{-1}\ \text{s}^{-1}$; the activation parameters are $\Delta H^{\ddagger} = 10.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -15$ cal deg^{-1} mol^{-1}. As models show that it is impossible for an incoming tren molecule to get anywhere near the Nd atom of $[Nd(tren)_2]$ when both tren ligands are quadridentate, the mechanism proposed is of the attachment of the incoming tren to the neodymium after at least one of the original tren ligands has become partially unwrapped from the metal atom.[404]

Sulphate exchange with the μ-sulphato-dichromium complexes (39) and (40) has been monitored by ^{35}S labelling. Rates depend on pH:

$$k_{\text{obs}} = k_1 + k'[\text{H}^+]^{-1}$$

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[400] G. M. Tanner, D. G. Tuck, and E. J. Wells, *Canad. J. Chem.*, 1972, **50**, 3950.

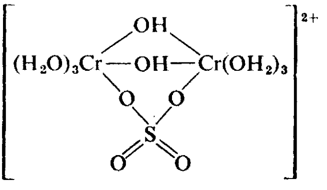
[401] T. Ryhl, *Acta Chem. Scand.*, 1972, **26**, 4001.

[402] K. B. Yatsimirskii, E. D. Romanenko, and L. I. Budarin, *Doklady Akad. Nauk S.S.S.R.*, 1972, **202**, 1140 (*Chem. Abs.*, 1972, **76**, 132 033s).

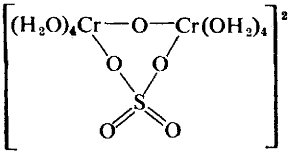
[403] B. J. Fuhr and D. L. Rabenstein, *Inorg. Chem.*, 1973, **12**, 1868.

[404] M. F. Johnson and J. H. Forsberg, *Inorg. Chem.*, 1972, **11**, 2683.

The activation energies for both processes are 22.2 kcal mol^{-1}.[182]



(39)



(40)

8 Metal Exchange and Displacement

References to kinetic studies of the displacement of one metal cation from its complex with a multidentate ligand by another metal cation are listed in Table 26.[405-412] In general these reactions proceed either by dissociation of the initial complex, followed by complex formation between the now free ligand and the displacing cation, or through an intermediate or intermediates in which both cations are bonded simultaneously to the multidentate ligand. Both mechanisms have been demonstrated in a study of reactions of iron(III) complexes of aminocarboxylate ligands with indium(III). The hedta and egta complexes appear to react *via* rate-determining dissociation of the ligand from

Table 26 *Kinetic studies of the displacement of cations from multidentate ligand complexes*

Complex[a]	*Displacing cation*	*Ref.*
Magnesium(II)–edta	Nickel(II)	408
Lead(II)–edta, –hedta, –cydta, –dtpa	Nickel(II)	409
Nickel(II)–R_2dtc	Copper(II)	411
–edda	Copper(II)	412
Copper(II)–ttha	Nickel(II)	406
Zinc(II)–cydta, edta	Indium(III)	410
Indium(III)–ttha	Nickel(II), gallium(III)	407
Iron(III)–dtpa, –egta, –hedta	Indium(III)	405

[a] For ligand abbreviations see list at start of this volume.

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[405] T. Nozaki, K. Kasagu, and K. Koshiba, *Nippon Kagaku Kaishi*, 1972, 568 (*Chem. Abs.*, 1972, **76**, 145 394k).

[406] M. Kopanica and V. Stará, *Coll. Czech. Chem. Comm.*, 1972, **37**, 80.

[407] Tran Chuong Huyen and M. Kopanica, *Coll. Czech. Chem. Comm.*, 1972, **37**, 2874.

[408] Z.-F. Lin and M.-C. Wu, *J. Chinese Chem. Soc.* (*Taipei*), 1971, **18**, 195 (*Chem. Abs.*, 1972, **76**, 131 978s).

[409] T. Nozaki, K. Kasuga, and N. Kagawa, *Nippon Kagaku Kaishi*, 1973, 718 (*Chem. Abs.*, 1973, **79**, 10 367v).

[410] T. Takahashi, T. Koiso, and N. Tanaka, *Nippon Kagaku Zasshi*, 1973, 64 (*Chem. Abs.*, 1973, **78**, 89 038z).

[411] R. R. Scharfe, V. S. Sastri, and C. L. Chakrabarti, *Canad. J. Chem.*, 1972, **50**, 3384.

[412] R. K. Steinhaus and R. L. Swann, *Inorg. Chem.*, 1973, **12**, 1855.

the iron(III), whereas the dtpa complex reacts *via* rate-determining formation of a dinuclear iron–dtpa–indium intermediate.[405] Rate-determining formation of a dinuclear intermediate is also reported for the reaction of the copper(II)–ttha complex with nickel(II),[406] and for the reactions of indium(III)–ttha with gallium(III) or with nickel(II).[407] An analogous mechanism is implied for the reaction of magnesium(II)–edta with nickel(II).[408] Whereas the lead(II)–dtpa complex reacts with nickel(II) only *via* a dinuclear intermediate, the lead(II)–edta, –hedta, and –cydta complexes all react with nickel(II) by parallel dissociative and bimolecular pathways.[409] The different kinetic patterns for reaction of the edta and cydta complexes of zinc(II) with indium(III) are ascribed to the different sizes and stereochemistries of the two ligands.[410] Different mechanisms for ligand- or cation-replacement reactions involving edta and cydta have been noted in earlier volumes of this Report – cydta complexes show a greater tendency to react by a fully dissociative mechanism. Ligand stereochemistry and bulk are also important in determining the reactivity of substituted bisdithiocarbamato-nickel(II) complexes towards copper(II). The observed variation of rate with nature of ligand was interpreted as favouring attack by the copper at a sulphur rather than at a nitrogen atom of the co-ordinated dithiocarbamate. The variation of the rates of these reactions with the nature of the solvent was also determined, though detailed mechanistic conclusions could not be drawn.[411]

A general rate law has been established for the exchange of cerium(III) with several of its polyaminocarboxylate complexes, over a range of pH's.[413] Rates of exchange of cobalt(II) with its bisbenzenediamine complexes have been investigated. In formamide solution, the rate constant at 35 °C is 1.0×10^{-7} l mol^{-1} s^{-1} for the benzene-1,2-diamine complex; exchange rates for the 1,3- and 1,4-isomers are very much lower. At first sight this is surprising, as the 1,2-ligand is bidentate, the others unidentate. However, polymeric complexes, which may well be unreactive, are conceivable for the 1,3- and the 1,4-benzenediamines.[414] Rates of isotopic cation exchange have been measured, at 20 °C in a 1 : 1 chloroform–ethanol solvent mixture, for 8-mercaptoquinoline (thio-oxine) complexes of a range of 2+ and 3+ cations.[415] The remaining references to cation exchange at multidentate ligand complexes are of only fringe interest, for they deal with extensions of kinetic studies of lanthanide(III) exchange with edta complexes from homogeneous solution to heterogeneous systems, specifically with the kinetics of exchange of lanthanide(III) cations between cation-exchange resins and aqueous solutions containing edta[416] or nta.[417]

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[413] C. I. Balcombe and B. Wiseall, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2859.

[414] B. R. Mannar and P. R. Naidu, *J. Inorg. Nuclear Chem.*, 1972, **34**, 379.

[415] Yu. A. Bankovskii, O. Veveris, L. Pelekis, and A. Pelne, *Latv. P.S.R. Zinat. Akad. Vestis, kim. Ser.*, 1972, 689 (*Chem. Abs.*, 1973, **78**, 62 769b).

[416] M. G. Yashkarova, L. I. Martynenko, and V. I. Spitsyn, *Russ. J. Inorg. Chem.*, 1972, **17**, 115.

[417] N. D. Mitrafanova, L. I. Martynenko, and I. N. Perova, *Russ. J. Phys. Chem.*, 1973, **47**, 189.

9 Isomerization and Racemization

General.—The subject of isomerization and racemization has been reviewed at length (176 pages; 359 references).[418] Several authors have discussed rearrangements in octahedral complexes, often concentrating on tris-chelate complexes, in general, geometrical, topological, and symmetry terms.[419–422]

Cobalt(III) Complexes.—Specific rate constants [$k_f + k_b$ of equation (12)] and derived composite activation parameters have been determined for the isomerization

$$cis\text{-}[Co(en)_2(OAc)_2]^+ \underset{k_f}{\overset{k_b}{\rightleftharpoons}} trans\text{-}[Co(en)_2(OAc)_2]^+ \qquad (12)$$

The activation enthalpy of 28.5 kcal mol^{-1} is in the expected region for a cobalt(III) substitution process. It is interesting that the equilibrium constant for equation (12) appears to be invariant with temperature; in other words the enthalpy change for reaction (12) is very close to zero.[48] Rates of isomerization of $[Co(en)_2(OAc)_2]^+$ in dimethyl sulphoxide, both in the absence and in the presence of added acetate, have been measured. An increase in rate on adding acetate is ascribed to the formation of more reactive ion-pairs.[423] In chloroform solution, the rate constant for *trans*-$\rightleftharpoons$*cis*-$[Co(acac)_2(N_3)_2]^-$ is approximately 4×10^{-4} s^{-1} at 35 °C; for $[Co(acac)_2(NO_2)_2]^-$ the rate of isomerization is less, *ca.* 8×10^{-6} s^{-1} at 35 °C.[424]

Isomerization of $[Co(en)(NH_3)_3(OH)]^{2+}$ and of $[Co(en)(NH_3)_2(OH)_2]^+$ has been extensively studied by spectrophotometry in dilute aqueous solution. Recent kinetic results for the former isomerization obtained by the use of ^{59}Co n.m.r. spectroscopy, in concentrated solutions, are consistent with the early spectrophotometric results. The $[Co(en)(NH_3)_2(OH)_2]^+$ cation exists in three isomeric forms. The observed isomerization paths and their respective rate constants, also obtained by ^{59}Co n.m.r. spectroscopy, are shown in Table 27. The proposed mechanism for these isomerizations involves reversible dissociation of one end of the ethylenediamine ligand from the cobalt. Isomerization of *mer*- or *fac*-$[Co(en)(NH_3)_3(OH)]^{2+}$ was not detected, even after

Table 27 *Isomerization of* $[Co(en)(NH_3)_2(OH)_2]^+$

Isomerization process	10^6k/s^{-1} (25 °C)	*Ref.*
trans → *cis,cis*	35	425
cis,cis → *trans*	43	
cis,trans → *cis,cis*	10	

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[418] N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, 1972, **17** (part 2), 391.

[419] W. G. Klemperer, *J. Amer. Chem. Soc.*, 1972, **94**, 6940; *Inorg. Chem.*, 1972, **11**, 2668; *J. Chem. Phys.*, 1972, **56**, 5478.

[420] S. S. Eaton and G. R. Eaton, *J. Amer. Chem. Soc.*, 1973, **95**, 1825.

[421] J. I. Musher, *Inorg. Chem.*, 1972, **11**, 2335.

[422] A. T. Balaban, *Rev. Roumaine Chim.*, 1973, **18**, 841.

[423] A. W. Chester, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 167.

[424] L. J. Boucher and D. R. Herrington, *Inorg. Chem.*, 1972, **11**, 1772.

Table 28 *Isomerization and racemization of* $[Co(en)_2(OH_2)_2]^{3+}$

Reaction	*Conditions*	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
cis inversion	dil. acid	29.2	+8.1	289
cis→*trans*		29.4	+13.4	
trans→*cis*		28.0	+12.1	
trans→*cis*	10M-HClO$_4$	25.5	+12.8	

90 days at 25 °C or 30 minutes at 80 °C.[425] Rates of *cis*$\rightleftharpoons$*trans* isomerization of $[Co(NH_3)_4(OH_2)_2]^{3+}$, $[Co(NH_3)_4(OH_2)(OH)]^{2+}$, and $[Co(NH_3)_4(OH)_2]^{+}$ are all about a hundred times faster than those for the analogous bisethylenediamine analogues. It is interesting that the aquo-hydroxo-complex is the most reactive both in the tetra-ammine and in the bisethylenediamine series.[426] Activation parameters for isomerization and racemization of $[Co(en)_2(OH_2)_2]^{3+}$ have been reported, in dilute and in concentrated perchloric acid (Table 28). The difference in activation parameters between the two acid concentrations is due to protonation of one of the water ligands, to give an OH_3^+ ligand, in 10M-HClO$_4$.[289] Activation parameters for the isomerization of κ-[Co(dien)(en)-$(OH_2)]^{3+}$ to the π-form, in 1M-HClO$_4$, are $E_a = 29.7 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = +7.4 \pm 3.6$ cal deg^{-1} mol^{-1}.[88]

Semi-empirical calculations suggest a barrier of 5—7 kcal mol^{-1} to ring inversion in compounds $[M(en)_3]^{n+}$. This implies too rapid inversion for n.m.r. monitoring of inversion rates. However, the replacement of the nitrogen protons of ethylenediamine by alkyl groups might be a possible means of lowering ring inversion rates sufficiently for them to be estimated from n.m.r. spectra. Indeed n.m.r. spectra of the pseudo-tetrahedral $[Co(tmeda)(NO)_2]^+$ cation, newly prepared and characterized as its tetraphenylboronate salt, show that the rate of inversion of the tmeda (*NNN'N'*-tetramethylethylenediamine) chelate ring is 113 s^{-1} at the coalescence temperature of −90 °C, in [$^2H_6$]-acetone.[427] One hopes that an estimate of the barrier to chelate ring inversion in an octahedral M^{n+}–tmeda complex will soon be forthcoming. Barriers to ring inversion in $[M(pn)_3]^{n+}$ have been calculated to be *ca.* 7 kcal mol^{-1}, very similar to those for the analogous $[M(en)_3]^{n+}$ cations (see above).[428] This low barrier is consistent with earlier n.m.r. observations of rapid conformational inversion for $[M(pn)_3]^{n+}$ complexes.[429] It has been argued that in the racemization of *trans*-$[Co(dien)_2]^{3+}$ the two rings do not invert simultaneously.[430] Rate constants for mutarotation, with respect to the secondary nitrogen centre, have been determined for the $[Co(trien)(gly)]^{2+}$ cation.[431]

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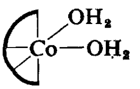
[425] F. Yajima, Y. Koike, T. Sakai, and S. Fujiwara, *Inorg. Chem.*, 1972, **11**, 2054.
[426] S. Balt, *Rec. Trav. chim.*, 1972, **91**, 1026; E. G. A. M. Bolte and S. Balt, *ibid.*, 1973, **92**, 826.
[427] K. G. Caulton, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 533.
[428] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1972, **11**, 156.
[429] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1970, **9**, 1807.
[430] G. H. Searle and F. R. Keene, *Inorg. Chem.*, 1972, **11**, 1006.
[431] R. J. Dellaca, V. Janson, W. T. Robinson, D. A. Buckingham, L. G. Marzilli, I. E. Mazwell, K. R. Turnbull, and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1972, 57.

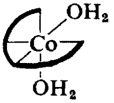
There are two *cis*-isomers of $[Co(trien)(OH_2)_2]^{3+}$, the α- (41) and the β- (42) forms. Both the α- and the β-forms isomerize to a mixture of α- and β-isomers; there is no isomerization to the *trans*-form. The rate of isomerization is equal to the rate of racemization for the α-isomer over the pH range ($1 < pH < 3$) investigated; a term in $[H^+]^{-1}$ in the rate law is ascribed to parallel reaction of the hydroxoaquo-complex $[Co(trien)(OH_2)(OH)]^{2+}$. It proved impossible to study the isomerization of the β-isomer spectrophotometrically as the spectroscopic change involved was too small. Racemization of this β-isomer follows the rate law

$$\text{Rate} = k[\text{complex}][H^+]^{-1}$$

over the pH range 1—3, indicating that it is in fact only the hydroxoaquo-species which racemizes. Some activation parameters have been estimated, and a number of possible pathways for isomerization and for racemization discussed in detail.[432] The isomerization of α-$[Co(trien)(CO_3)]^+$ to the β-form is thought to proceed by an intramolecular twist which may be preceded by the dissociation of one oxygen of the carbonato-ligand. The rate of isomerization is very close to that for inversion in $[Co(en)_2(CO_3)]^+$, which is reasonable in view of the inversions at nitrogen which are needed to turn the α-isomer of $[Co(trien)(CO_3)]^+$ into the β-form.[433]



(41)



(42)

Kinetic parameters for racemization of the cobalt(III) and iron(II) complexes of the sexidentate ligand tptame (43), derived from 1,1,1-tris(aminoethyl)-ethane and pyridine-2-aldehyde, have been determined by n.m.r. spectroscopy. N.m.r. spectra of the $[Co(tptame)]^{3+}$ cation, in dimethyl sulphoxide solution over the temperature range 80—120 °C, indicate an activation energy of 10.1 kcal mol^{-1} for racemization. The ligand can only bond to a cation in a *cis* configuration, so there is no confusion with isomerization. An intermolecular mechanism for racemization seems unlikely for a complex containing a sexidentate ligand, especially one such as tptame which consists effectively of three bipyridyl units. Intramolecular racemization could occur *via* a no-bond-breaking twist or *via* an intermediate containing the ligand in a quinquedentate form. There are two reasons for disliking the latter mechanism. The first is that bond-breaking in this type of complex is generally much slower than the observed rate of racemization. The second is that, by analogy with the aquation of similar complexes in acid solution, one would expect a pH-dependence of the rate of racemization – such a pH-dependence is not observed. Thus a purely

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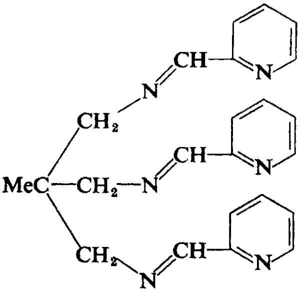
[432] G. H. Searle and A. M. Sargeson, *Inorg. Chem.*, 1973, **12**, 1014.
[433] T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, 1973, **12**, 488.

intramolecular twist mechanism is preferred; a trigonal-prismatic transition state for this should be fairly readily accessible from the ground state.[434]



(43)

The tris-α-isopropyl- and tris-α-isopropenyl-tropolonatocobalt(III) complexes are stereochemically non-rigid, and indeed represent the first examples of such behaviour in this type of cobalt complex. The mechanism of inversion involves a trigonal twist. The activation enthalpies are 15.6 and 16.2 kcal mol^{-1} and the activation entropies are +4.8 and +5.4 cal deg^{-1} mol^{-1} respectively for inversion of the *trans*-compounds. This inversion is apparent from the temperature variation of the n.m.r. spectra at low temperatures; at higher temperatures *cis*$\rightleftharpoons$*trans* isomerization of these complexes can be monitored by n.m.r.[435] Intramolecular rearrangements of these tristropolonato-complexes take place very much more rapidly than those of tris-β-diketone complexes. Whereas the tropolonato-complexes rearrange by a twist mechanism, the β-diketone complexes rearrange through intermediates containing a unidentate ligand.[436] Trisdithiocarbamatocobalt(III) complexes are also stereochemically non-rigid. The dibenzyl-substituted complex has a barrier intermediate between those of the tristropolonato- and those of the tris-β-diketone complexes.[437]

Rates of racemization of the edta and pdta complexes of cobalt(III) in acid aqueous solution depend on the pH, as there is equilibrium protonation of the ligands. The rate law for racemization of the pdta complex is simple, with a first-order term in hydrogen-ion concentration. Activation parameters for the racemization of this pdta complex, determined in 0.53M-KNO_3 over the temperature range 120—140 °C, are $\Delta H^{\ddagger}$ = 37.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = +14.8 cal deg^{-1} mol^{-1}. The racemization of the cobalt(III)–pdta complex is catalysed by traces of its cobalt(II) analogue.[438]

[434] S. O. Wandiga, J. E. Sarneski, and F. L. Urbach, *Inorg. Chem.*, 1972, **11**, 1349.

[435] S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 6411.

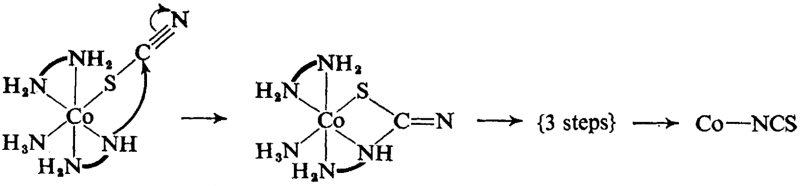
[436] S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1973, **95**, 1116.

[437] L. H. Pignolet, D. J. Duffy, and L. Que, *J. Amer. Chem. Soc.*, 1973, **95**, 295.

[438] H. Ogino, M. Takahashi, and N. Tanaka, *Bull. Chem. Soc. Japan*, 1973, **46**, 178.

The kinetics of racemization of the $[Co(ox)_3]^{3-}$ anion in the presence of perchloric, hydrochloric, or sulphuric acid are consistent with an *A*1 mechanism. Some features of this acid catalysis do not correspond with metal-ion-catalysed racemization of this complex, which may mean that different mechanisms are involved. An obvious difference would be between an intramolecular twist involving no metal–ligand bond breaking on the one hand, and a mechanism with a unidentate oxalato-complex as intermediate on the other.[439]

Tracer studies have shown that the isomerization of *trans*-$[Co(en)_2(NH_3)(SCN)]^{2+}$ to the *N*-thiocyanato-linkage isomer in basic aqueous solution is intramolecular. The detailed mechanism may involve an 'intimate' ion pair which does not exchange its thiocyanate with the thiocyanate in solution, a species in which the thiocyanate is π-bonded to the cobalt, or intramolecular attack of a deprotonated amine nitrogen at the thiocyanate carbon (Scheme 5).[287] Aquation of $[Co(NH_3)_5(\text{sulphamate})]^{2+}$ is preceded by isomerization of the starting complex to an equilibrium mixture of N- and O-bonded isomers. The specific rate constant for approach to equilibrium is $1.1 \times 10^{-3}\ s^{-1}$ at 25 °C; composite activation parameters are $\Delta H^{\ddagger} = 24.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 10.9$ cal deg^{-1} mol^{-1}. Inability to estimate the equilibrium constant satisfactorily precludes the separation of these kinetic parameters into their forward and backward components.[47]



Scheme 5

N.m.r. spectra of solutions of alkylcobaloxime dimers, in methylene chloride or in bromobenzene, show that there is environmental exchange of the dimethylglyoxime methyl groups. Activation enthalpies are between 13 and 14 kcal mol^{-1}, and activation entropies are between +25 and +26 cal deg^{-1} mol^{-1}. These large, positive activation entropies suggest dissociative processes. As the concentration of free monomer in these solutions is known to be undetectably small, a mechanism in which the two cobalt centres have to be separated to a great distance, in order to permit motion of the dimethylglyoxime methyl groups, seems most plausible.[440]

Chromium(III) Complexes.—The effects of alkali-metal cations and of tetra-alkylammonium cations on the rate of racemization of the $[Cr(ox)_3]^{3-}$ anion are ascribed to pre-equilibrium ion-pairing, with parallel rate-determining racemization of the ion pair and of the free complex. The magnitudes of the

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[439] A. L. Odell, R. W. Olliff, and D. B. Rands, *J.C.S. Dalton*, 1972, 752.

[440] A. W. Herlinger and T. L. Brown, *J. Amer. Chem. Soc.*, 1972, **94**, 388.

ion-pairing constants are fairly small: for the tetraethylammonium cation, K_{IP} = 26±5 at 25 °C.[441] Rate constants for the isomerization *trans*-→*cis*-$[Cr(ox)_2(OH_2)_2]^-$ have been evaluated over the pressure range 1—2500 atm at 25 °C, and over the temperature range 15—40 °C at 1 atm, in aqueous methanol and aqueous dioxan. As the proportion of methanol increases (5% intervals) up to 50%, the activation enthalpy increases from 18.1 to 20.5 kcal mol^{-1} and the activation entropy changes from -15 to -10 cal deg^{-1} mol^{-1}. Similarly as the proportion of dioxan increases (5% intervals) up to 50%, the activation enthalpy increases to 20.8 kcal mol^{-1} and the activation entropy changes again to -10 cal deg^{-1} mol^{-1}. The activation volume remains essentially constant at -16 ± 1 cm^3 mol^{-1} over all the solvent mixtures studied, though it is reduced to -9.8 cm^3 mol^{-1} when the isomerization is catalysed by calcium nitrate, and further reduced to -5.4 cm^3 mol^{-1} when the catalyst is perchloric acid. The mechanism seems to involve chelate ring opening and the participation of a water molecule in the transition state.[442] Comparisons of the kinetics of *trans*→*cis* isomerizations of $[Cr(mal)_2(OH_2)_2]^-$, $[Cr(mal)_2(OH_2)(OH)]^{2-}$, and $[Cr(mal)_2(OH)_2]^{3-}$ with those for the analogous oxalato-complexes suggest that the mechanisms for the two types of complex are different. Whereas the oxalato-complexes isomerize by dissociation of one end of an oxalate ligand, the malonato-complexes are thought to isomerize by way of dissociation of a water ligand.[168] The effects of lithium perchlorate, lithium nitrate, and sodium perchlorate on rates of isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ have been compared.[443]

The isomerization of 1,2,6(*mer*)-$[Cr(trienH)(OH_2)_2(N_3)]^{3+}$ to the 1,2,3(*fac*)-isomer is catalysed by acids. It is difficult to accommodate the rate–pH profile in a simple rate law. In 3F-$HClO_4$ the activation enthalpy derived from observed rate constants at 15, 20, and 25 °C is 25.4 kcal mol^{-1}.[174] Isomerizations of *cis*- and of *trans*-$[Cr(en)_2Br_2]^+$ and their solvolysis products in dimethyl sulphoxide have already been alluded to in the chromium(III) solvolysis section (see Section 3).[189]

Activation parameters have been determined for *cis*→*trans* and for *trans*→*cis* isomerization of $[Cr(tfac)_3]$, both in toluene and in 1,2,4-trimethylbenzene solution. The kinetic parameters are considerably more sensitive to the nature of the solvent than are the equilibrium constants.[444]

Photoracemization of $[Cr(phen)_3]^{3+}$ can be studied at 350 nm with negligible interference from photoaquation. Some information on the nature of excited states can be gleaned from the effects of additives, for example iodide, which quenches both the racemization and the phosphorescence of this complex.[445] Photochemical and thermal inversion of $[Cr(acac)_3]$ have been compared.[446]

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[441] A. L. Odell and D. Shooter, *J.C.S. Dalton*, 1972, 135.

[442] E.-G. Conze, H. Stieger, and H. Kelm, *Chem. Ber.*, 1972, **105**, 2334.

[443] M. J. Frank and D. H. Huchital, *Inorg. Chem.*, 1972, **11**, 776.

[444] R. Fontaine, C. Pommier, and G. Guiochon, *Bull. Soc. chim. France*, 1972, 1685.

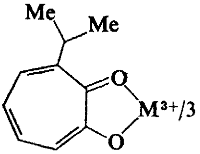
[445] N. A. P. Kane-Maguire and C. H. Langford, *J. Amer. Chem. Soc.*, 1972, **94**, 2125.

[446] K. L. Stevenson, *J. Amer. Chem. Soc.*, 1972, **94**, 6652.

Intramolecular Rearrangements of Tris-chelate Complexes.—The kinetics and mechanisms of such rearrangements of cobalt(III) and of chromium(III) complexes have already been discussed at appropriate points in the previous two sections.

One of the simplest bidentate ligands is the oxalate anion. Racemization of its tris-chelates of cobalt(III)[439] and chromium(III)[441] have already been mentioned; racemization of its rhodium(III) tris-chelate has also been studied recently. The similarity of the kinetic parameters for racemization and for inner-oxygen exchange of $[Rh(ox)_3]^{3-}$ suggests a close similarity of mechanism. A common five-co-ordinate intermediate is proposed, whose lifetime is sufficient for inner⇌outer oxygen exchange or for racemization to take place.[12]

Rearrangements in tris-α-isopropyl- (44) and tris-α-isopropenyl-tropolonato-complexes of several metal(III) cations have been probed by n.m.r. spectroscopy. Two intramolecular processes are likely for these tris-chelates of unsymmetrical ligands, $\Delta \rightleftharpoons \Lambda$ inversion and *cis*⇌*trans* isomerization. Both processes can be seen in the variable-temperature n.m.r. spectra of the aluminium(III), gallium(III), and cobalt(III) complexes, the $\Delta \rightleftharpoons \Lambda$ inversion taking place, probably by a trigonal twist mechanism, at a lower temperature than the *cis*⇌*trans*. Only isomerization could be detected from the vanadium(III) and manganese(III) complexes, only $\Delta \rightleftharpoons \Lambda$ inversion for the germanium(IV) derivative $[Ge(\alpha\text{-}Pr^i\text{-tropolonate})_3]^+$. The rhodium(III) and ruthenium(III) complexes are stereochemically rigid at the temperatures accessible in this investigation.[435, 436] The determination of the crystal structure of tristropolonatoaluminium(III) provides useful stereochemical background information to the discussion of rearrangement processes in this type of compound.[447]



(44)

Two intramolecular processes are evident from variable-temperature n.m.r. studies of CD_2Cl_2 or $C_6D_5NO_2$ solutions of $[Ru\{Me(PhCH_2)dtc\}_3]$. At low temperatures the $\Delta \rightleftharpoons \Lambda$ inversion can be monitored and at higher temperatures rotation about the ligand carbon–nitrogen bonds can be observed.[437] Similar observations are reported for CD_2Cl_2 solution of $[Fe(MePhdtc)_3]$; the detailed dependence of the ^1H n.m.r. spectrum on temperature shows that the low-temperature inversion process takes place by a trigonal twist mechanism.[448] This iron(III) complex has a lower barrier to inversion than the ruthenium(III) complex cited in the previous sentence.[437] Two intramolecular processes,

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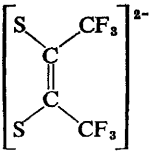
[447] E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1972, **94**, 8046.
[448] M. C. Palazzotto and L. H. Pignolet, *J.C.S. Chem. Comm.*, 1972, 6.

again inversion and carbon–nitrogen bond rotation, are evident in the variable-temperature n.m.r. spectra of CD_2Cl_2 solutions of the iron(IV) chelate $[Fe\{Me(PhCH_2)dtc\}_3]^+$. The barrier to $\Delta \rightleftharpoons \Lambda$ inversion is probably lower for the iron(IV) derivative than for the iron(III), whereas the barrier to rotation about the carbon–nitrogen bonds in the dtc ligands appears to be higher for the iron(IV) compound.[449] The barrier to inversion for iron(III)-substituted dtc complexes is lower than that for the iron(II) complex $[Fe(dtc)_2(phen)]$. For all of these iron(IV), iron(III), and iron(II) complexes the predominant pathway for rearrangement is a trigonal twist. $[Co\{(PhCH_2)(PhCH_2)dtc\}_3]$ is also stereochemically non-rigid, and again the mechanism of inversion is thought to be a trigonal twist. $[Rh\{(PhCH_2)(PhCH_2)dtc\}_3]$ is rigid at least up to 200 °C in $C_6D_5NO_2$ solution.[450]

Closely related to the compounds discussed in the previous paragraph are the mixed-ligand tris-chelates $[Fe(R^1R^2dtc)_2(mnt)]$. For the compounds with $R^1 = R^2 =$ Et and with $R^1 =$ Me, $R^2 =$ Ph there are again two intramolecular processes whose rates are within the n.m.r. time-scale – and again the processes are a lower-temperature inversion and a higher-temperature rotation about ligand carbon–nitrogen bonds. This behaviour is similar to that established earlier for complexes $[Fe(R^1R^2dtc)_2(tfd)]$, where tfd = (45). The activation parameters for inversion of $[Fe(Et_2dtc)_2(mnt)]$ are $\Delta H^{\ddagger} = 8.6 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.4 \pm 5.0$ cal deg^{-1} mol^{-1} and those for rotation about the carbon–nitrogen bond are $\Delta H^{\ddagger} = 12.5 \pm 2.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5.5 \pm 6.0$ cal deg^{-1} mol^{-1}, in CD_2Cl_2 solution.[451] The temperature dependence of n.m.r. spectra of diamagnetic M^{II} and M^{III} complexes of dialkyldithiocarbamate ligands has been the subject of detailed discussion.[452] The activation parameters for racemization of the iron(II) complex of the sexidentate ligand tptame (43), in D_2O solution, are $E_a = 18.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = +1$ cal deg^{-1} mol^{-1}. Interestingly this activation energy is much higher than that for racemization of the analogous cobalt(III) complex (see above).[434]

An example of a full kinetic study of a related tetrakis-chelate complex is afforded by the intramolecular rearrangement of $[Zr(h^3\text{-allyl})_4]$, details of which belong in the organometallic section of this Report.[453]



(45)

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[449] D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, 1972, **11**, 2843.

[450] M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, and L. H. Pignolet, *J. Amer. Chem. Soc.*, 1973, **95**, 4537.

[451] L. H. Pignolet, R. A. Lewis, and R. Holm, *Inorg. Chem.*, 1972, **11**, 99.

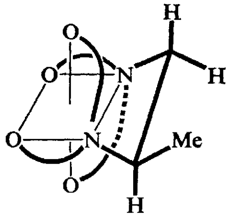
[452] R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, 1972, **11**, 2435.

[453] J. K. Krieger, J. M. Deutch, and G. M. Whitesides, *Inorg. Chem.*, 1973, **12**, 1535.

Miscellaneous.—Isomerization of [MoO$_2$(dipivaloylmethanato)$_2$] is definitely intramolecular, but it is not possible to choose between a purely non-dissociative twist and a mechanism in which one or both of the bidentate ligands undergoes partial dissociation to become unidentate. The activation energy for this isomerization is 17.0 kcal mol^{-1}; the frequency factor is e$^{12.56}$.[454] Interconversion of isomers of octahedral molybdenum(v) complexes of the type MoOL$^1_2$L$^2_2$X is fast.[455]

trans to *cis* Isomerization of [Ru(NH$_3$)$_4$(NO)(OH)]$^{2+}$ is extremely slow, as is the reverse reaction in acidic or neutral solution. However, the half-life for isomerization of the *cis*- to the *trans*-isomer is a few minutes in aqueous ammonia at around 100 °C.[456]

Over a decade ago it was reported that the (−)$_{546.1}$-isomer of the rhodium(III)-D(−)-pdta complex lost its optical activity on irradiation with u.v. light, but that the optical activity returned on keeping the solution in the dark. These observations were interpreted in terms of sexidentate and quinquedentate forms of the chelate.[457] Now as a result of an extensive study, using the techniques of u.v.–visible and n.m.r. spectroscopy and circular dichroism, it is suggested that the pdta ligand remains sexidentate throughout, and that the observed changes can be attributed to conformational isomerization of the ligand, (46)$\rightleftharpoons$(47). The difference in energy between these isomers appears to be about 3 kcal mol^{-1}; equilibrium is established in a few minutes at room temperature.[458]



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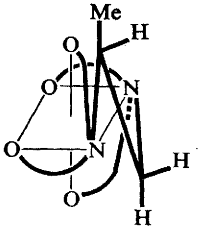

(47)

Racemization of some macrocyclic Schiff-base complexes of nickel(II) is reported to involve inversion of both asymmetric secondary nitrogen atoms; activation parameters are reported.[459] The *mer*→*fac* isomerization of [Ni(oxine)$_3$]$^-$ is facile in methanol–chloroform solvent mixtures.[460]

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[454] T. J. Pinnavaia and W. R. Clements, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1127.

[455] I. N. Marov, V. K. Belyaeva, Yu. N. Dubrov, and A. N. Ermakov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1561.

[456] S. Pell and J. N. Armor, *Inorg. Chem.*, 1973, **12**, 873.

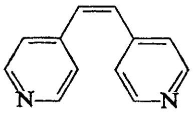
[457] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 1961, **83**, 2610.

[458] G. L. Blackmer, J. L. Sudmeier, R. N. Thibedeau, and R. M. Wing, *Inorg. Chem.*, 1972, **11**, 189.

[459] E. Sledziewska, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1972, **20**, 49 (*Chem. Abs.*, 1972, **76**, 145 355y).

[460] Y. Yamamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 331.

The only significant photoreaction of the ruthenium(II)-4-stilbazole (stb) complexes $[Ru(bipy)_2(stb)_2]^{2+}$ and $[Ru(bipy)_2(stb)Cl]^+$ is *cis* ⇌ *trans* [(48) ⇌ (49)] isomerization of the 4-stilbazole ligand.[461]



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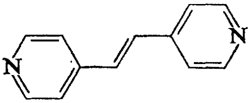
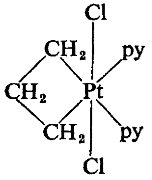
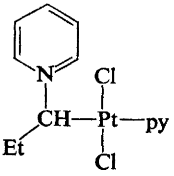


(49)

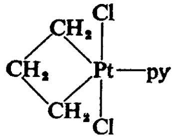
The redox isomerization of the platinum(IV) compound (50) to the platinum(II) compound (51), in benzene solution, is thought to be dissociative in mechanism. The intermediate (52), which can either re-form (50) or undergo platinum–carbon bond cleavage, is suggested.[462]



(50)



(51)



(52)

Interest continues in stereochemical rigidity of six- and eight-co-ordinate metal compounds containing unidentate ligands. Barriers to stereochemical rearrangement of seventeen iron(II) and eleven ruthenium(II) compounds of formulae MH_2L_4 and $MH_2L_3L^1$, where L = a phosphine, phosphite, phosphinite, or phosphonite, and L^1 = CO or PhCN, have been estimated from 220 MHz ^1H and ^{31}P n.m.r. spectroscopy. The $\Delta G^{\ddagger}$ values are higher for the ruthenium compounds than for the iron compounds, and are relatively insensitive to steric and electronic differences between ligands. Two possible mechanisms for these rearrangements are discussed in detail, the shift of hydrogen from an occupied to a vacant 'tetrahedral' face and the simultaneous shift of two hydrogens from face to edge situations to give an approximately D_{2d} transition state.[463] Barriers to rearrangement of eight-co-ordinate compounds MH_4L_4 are consistently higher for M = W than for M = Mo.[464,465] Intramolecular rearrangement of nine-co-ordinate MH_6L_3 is, not surprisingly, too fast to monitor by n.m.r. spectroscopy.[465] Eight-co-ordinate MoH_4L_4

[461] P. P. Zarnegar, C. R. Bock, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1973, **95**, 4367.
[462] R. D. Gillard and M. F. Pilbrow, *J.C.S. Dalton*, 1973, 102.
[463] P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 75.
[464] B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J.C.S. Chem. Comm.*, 1972, 34.
[465] P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 1467.

compounds are thus non-rigid, $[Mo(CN)_8]^{4-}$ may be non-rigid,[466] and now a recent ^{13}C n.m.r. investigation of $[Mo(Bu^tNC)_4(CN)_4]$ has given results which are consistent both with the existence of just one isomer or with a rapid interconversion between two isomers (at least down to −47 °C in chloroform solution).[467]

10 Co-ordination Numbers Greater than Six

All of the kinetic studies of substitution and related reactions of inert metal complexes with co-ordination numbers greater than six reported in the present volume are concerned with eight-co-ordinate complexes. The relevant references are collected together in Table 29. It is likely that the co-ordination numbers of the lanthanide and actinide cations whose complexes are mentioned in Sections 7 and 8 of this chapter are greater than six, but as knowledge of the precise co-ordination number in each case is lacking, these are not included in Table 29.

Table 29

Co-ordination number	*Compound*	*Reaction*	*Ref.*
8	$[Mo(CN)_8]^{3-}$	Substitution and photoreduction	225
8	$[Mo(CN)_8]^{4-}$	Photoaquation	226, 227
8	$[Mo(CN)_8]^{4-}$	Rearrangement	466
8	$[Mo(Bu^tNC)_4(CN)_4]$	Rearrangement	467
8	$[MoH_4L_4]$	Rearrangement	464, 465
8	$[W(CN)_8]^{4-}$	Photoaquation	226
8	$[WH_4L_4]$	Rearrangement	464, 465
8	$[Nd(tren)_2]^{3+}$	Ligand exchange	404

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[466] E. L. Muetterties, *Inorg. Chem.*, 1965, **4**, 769.
[467] M. Novotny, D. F. Lewis, and S. J. Lippard, *J. Amer. Chem. Soc.*, 1972, **94**, 6961.

4

Labile Metal Complexes

BY D. N. HAGUE

1 Introduction

The layout of this chapter is similar to, but not identical with, that of the corresponding chapter of Volume 2: the topics covered are complex formation between unsubstituted metals and unidentate ligands, complex formation between unsubstituted metals and multidentate ligands, and the effect of bound ligands. The first two parts are subdivided into sections on the main-group metals, nickel(II) (still by far the most popular labile metal for mechanistic investigations), other bivalent transition metals, and, finally, metals of valency three and higher. The discussion sections of many papers centre around the dissociative-interchange mechanism proposed by Eigen. This mechanism, the salient features of which were described in Chapter 1 of Part III of Volume 1 of these Reports, is referred to in several ways in the literature, but the designation I_d (dissociative interchange) of Langford and Gray[1] appears to have been particularly popular during the period under review. Perhaps this terminology will gradually replace the collection of sometimes rather misleading names which have been used to date for this increasingly successful mechanistic model.

Three brief reviews have appeared during the review period. Two of these, by Wilkins[2] and Alimarin,[3] were plenary lectures at international conferences and the third, on nickel(II), forms part of a general mechanistic review[4] on the trio nickel, palladium, and platinum.

2 Complex Formation involving Unsubstituted Metal Ions: Unidentate Ligands and Solvent Exchange

Main-group Ions.—The ultrasonic absorption of magnesium sulphate has been measured[5] in a solvent of 37% by weight dioxan–water and the results have been discussed in the context of previous ultrasonic work with the sulphates of Mg^{2+} and Mn^{2+}. The importance of specific solvent effects in the formation of

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[1] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1965.

[2] R. G. Wilkins, *Pure Appl. Chem.*, 1973, **33**, 583.

[3] I. P. Alimarin, *Pure Appl. Chem.*, 1973, **34**, 1.

[4] A. Peloso, *Coordination Chem. Rev.*, 1973, **10**, 123.

[5] F. H. Fisher, *J. Phys. Chem.*, 1972, **76**, 1571.

these complexes is confirmed and it is pointed out how measurements of this type can be used to discriminate between the conflicting sets of multistate parameters which have been used to rationalize ultrasonic absorption in aqueous solutions. The pressure-jump and shock-wave methods have been used[6] to follow the formation of magnesium trifluoroacetate in methanol. The rate and activation parameters are compared with those known for the solvent-exchange process and it is concluded that the release of co-ordinated methanol from the inner co-ordination sphere of the metal ion is the rate-determining process.

Nickel(II).—By virtue of its neutral charge and the similarity of its size and structure to those of water, NH_3 has held a particularly important position in the mechanistic investigations of complex formation in aqueous solution. Thus, when interpreted in the light of the dissociative mechanism, the formation rate constant for the 1 : 1 ammonia complexes of Ni^{II} has been found to be in excellent agreement with the solvent-exchange data obtained from n.m.r. measurements (which have, incidentally, recently been up-dated[7]). The application of the ammonia results to reactions involving larger ligands containing amine nitrogen groups is complicated by the uncertain influence of steric and inductive effects resulting from substitution on the nitrogen atoms. Rorabacher and Melendez-Cepeda have studied[8] the reaction of the hexa-aquonickel(II) ion with several amines and have found that increasing alkyl substitution significantly decreases the formation rate constant of the 1 : 1 complexes and slightly increases the dissociation rate constant (Table 1).

Table 1 *Rate and equilibrium constants*[a] *for* 1 : 1 *complexes of nickel*(II) *with alkylamines*

Ligand (L)	$k_f/10^3$ l mol^{-1} s^{-1}	k_d/s^{-1}	log K_1
NH_3	4.48	7.1	2.80
$MeNH_2$	1.31	7.7	2.23
$EtNH_2$	0.865	13.3	1.81
Pr^iNH_2	0.605	16.8	1.56
Me_2NH	0.332	11.3	1.47

[a] Data are from ref. 8 and refer to 25 °C and ionic strength 1.0M ($HLClO_4$).

Whereas the former trend is readily attributable to steric effects, the latter trend is in apparent contradiction to anticipated inductive effects; moreover, it is in disagreement with the results of earlier studies which had indicated a direct relationship between the complex-dissociation rate constants and the acid dissociation constants of the ligand for the nickel complexes of a series of related ligands. Another interesting aspect of these results (Table 1) is that the

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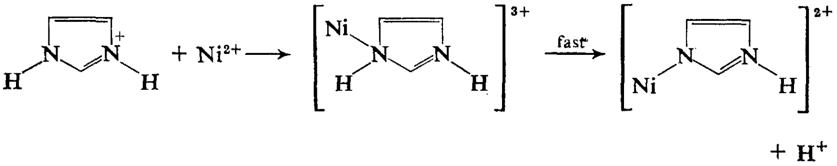
[6] P. Fischer, H. Hoffmann, and G. Platz, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1060.

[7] J. W. Neely and R. E. Connick, *J. Amer. Chem. Soc.*, 1972, **94**, 3419, 8646.

[8] D. B. Rorabacher and C. A. Melendez-Cepeda, *J. Amer. Chem. Soc.*, 1971, **93**, 6071.

trend in complex stability constant does not parallel k_d, as is so often the case, but is primarily dependent on the formation rate constant. The magnitude of the trend in k_f suggests that very large steric effects are to be expected for ligands in which secondary and tertiary nitrogen donor atoms carry bulky alkyl substituents.

The pressure dependence of the reaction of Ni^{2+}_{aq} with NH_3 has been studied[9] in greater detail and the pH dependence of the nickel–imidazole reaction has been followed by Letter and Jordan.[10] The complexing of nickel(II) by imidazole is unusual in that the protonated as well as the unprotonated form of the ligand reacts. For most unidentate ammonia- and pyridine-type ligands, protonation removes the only non-bonded electron pair on the ligand and the protonated form is not reactive. However, for imidazole one electron pair is essentially non-bonding even in the protonated form and can be used for complexation (Scheme 1).



Scheme 1

Rate constants were evaluated for the reaction of both the protonated and unprotonated forms (see Table 8, p. 275). Wilkins and co-workers have also studied[11] the Ni^{2+}–imidazole system but have been unable to explain the discrepancies between their results and those of Letter and Jordan.

Rorabacher has extended[12] his experiments on the effect of solvent on the nickel–ammonia reaction. The solvent used was a water–methanol mixture (varying in composition in the range 0—99% methanol) and, in an attempt to minimize inner-sphere effects so that the influence of the bulk solvent could be isolated, the quinquedentate ligand *N*-hydroxyethylethylenediamine *NN'N'*-triacetate (heedta) was complexed to the Ni^{II} ion, leaving a single co-ordination site available for solvent–ammonia exchange. (The reaction being studied was therefore

$$NiZS + NH_3 \underset{k_f}{\overset{k_d}{\rightleftharpoons}} NiZ(NH_3) + S$$

where Z and S represent molecules of heedta and solvent, respectively. Although this technically involves complex formation at a substituted metal ion and therefore belongs in Section 4, we have chosen to report the results

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[9] E. F. Caldin, M. W. Grant, and B. B. Hasinoff, *J.C.S. Faraday I*, 1972, **68**, 2247.

[10] J. E. Letter and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 2692.

[11] J. C. Cassatt, W. A. Johnson, L. M. Smith, and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1972, **94**, 8399.

[12] F. R. Shu and D. B. Rorabacher, *Inorg. Chem.*, 1972, **11**, 1496.

Table 2 *Rate and equilibrium constants*[a] *for the* $[\mathrm{Ni(heedta)(NH_3)}]^-$ *complex in methanol–water mixtures*

[MeOH]/Wt%	$k_f/10^3\ \mathrm{l\ mol^{-1}\ s^{-1}}$	$k_d/\mathrm{s^{-1}}$	$\log K$
0	0.78	6.2	2.097
25	0.79	6.3	2.097
50	1.37	7.5	2.263
65	1.58	8.0	2.299
70	2.19	9.8	2.348
80	3.11	12.8	2.384
90	3.63	25.0	2.161
95	4.04	34.8	2.064
99	4.39	48.0	1.96

[a] Data are from ref. 12 and refer to 25 °C and ionic strength 0.3M ($\mathrm{NaClO_4}$).

here because the authors themselves have discussed them in the context of the mechanism of substitution at the bare metal ion.) The results show that both k_f and k_d increase as the methanol content of the solvent is increased (Table 2), which is in marked contrast to their behaviour for the corresponding reactions of $\mathrm{Ni^{2+}}$ with $\mathrm{NH_3}$[13] and bipy.[14] The authors conclude that the earlier studies were, in fact, largely influenced by inner-sphere effects and that the variation in k_f with solvent composition can be interpreted consistently in terms of a dissociative mechanism without invoking matrix (bulk solvent) effects. (This does, of course, assume that the inner-sphere influence exerted by heedta does not greatly alter the relative preference of $\mathrm{Ni^{II}}$ for water over methanol as a ligand.) In contrast, it is suggested that the dissociation process is markedly affected by the nature of the bulk solvent.

The kinetics of reaction between nickel(II) and chloride,[15] acetate (and mono-, di-, and tri-chloroacetate),[16] and trithiocarbonate[17] in methanol have also been discussed in terms of the normal dissociative mechanism. The values of k_f, which decrease by a factor of about three on passing from acetate to trichloroacetate, are found[16] to be proportional to the basicity of the incoming ligand (the values for *p*-nitrobenzoate also fall on the linear plot of k_f *versus* $\mathrm{p}K_a$ of the ligand). It is argued that the inductive effect of the chlorine atoms tends to withdraw charge from the carboxylate group, thus affecting the tendency of the anion both to accept a proton ($\mathrm{p}K_a$) and to form an outer-sphere complex with a metal ion (K_{os} and therefore k_f). The fact that *p*-nitrobenzoate behaves in a similar way suggests that steric factors are unimportant within this series of reactions.

If a dissociative-interchange mechanism is assumed for the reaction of nickel(II) and substituted dithiocarbamates, a calculated value for the rate-

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[13] W. J. MacKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, 1971, **93**, 4379.

[14] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2190, 2198, 2207; H. P. Bennetto, *ibid.*, p. 2211.

[15] F. Dickert, P. Fischer, H. Hoffmann, and G. Platz, *J.C.S. Chem. Comm.*, 1972, 106.

[16] F. Dickert and R. Wank, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1028.

[17] R. J. Matthews and J. W. Moore, *Inorg. Chim. Acta*, 1972, **6**, 359.

determining solvent-loss process which is 10—50 times smaller than the measured value for the solvent-exchange process is calculated on the basis of the measured[18] values of k_f and the usual estimates of K_{OS}. Such a difference is not easily accommodated since the mechanism requires that complex-formation rate constants (suitably adjusted) should fall below solvent-exchange rate constants by only a statistical factor which accounts for the number of outer-sphere sites. (This has been estimated to be a matter of a factor of 5—10 only.) Langford and co-workers therefore conclude[18] that these results (together with previous results for the reaction of nickel with bipy, murexide, and CNS^- in DMSO) reflect either a new mechanism or, as they put it, 'failure of the simplistic Fuoss–Eigen equation' (for K_{OS}). Dickert and Hoffmann[19] have used pressure methods to study the nickel–thiocyanate and –chloride reactions in DMSO and have concluded that, on the contrary, the results are perfectly consistent with the 'normal' mechanism; the source of the disagreement with Langford and Tsiang[20] is simply that the latter workers, in their stopped-flow studies, were observing the formation not of the monothiocyanato-complex but rather of some other species. Evidently this is a matter for further investigation.

The reaction between nickel(II) and pyridine has been measured[21] in DMSO and acetonitrile; this was part of an investigation with a series of ligands, many of them bidentate, and the results will be discussed in Section 3. Two n.m.r. studies of the exchange of acetonitrile on nickel(II) have been reported, one[22] using ^{14}N linewidths and the other[23] using both the ^1H and ^{14}N signals, but the agreement between them is not very good (Table 3). Lincoln and West[23] discuss the origins of the apparent discrepancies between the two sets of kinetic data. Frankel has used n.m.r. to follow[24] the ligand-exchange kinetics of nickel(II) with DMF in DMF–nitromethane mixed solvents. As was found

Table 3 *Kinetic parameters for the exchange of acetonitrile on bivalent metal ions* (25 °C)

M^{2+}	*Nucleus*	k_{ex}/s^{-1}	$\Delta H^{\ddagger}_{ex}$/kcal mol^{-1}	$\Delta S^{\ddagger}_{ex}$/cal mol^{-1} K^{-1}	*Ref.*
Co^{2+}	^{14}N	2.7×10^5	8.79	−4.2	22
Co^{2+}	^{14}N	$(3.2\pm0.3)\times10^5$	11.4 ± 0.5	5.0 ± 2.0	27
Co^{2+}	^1H	$(3.5\pm0.5)\times10^5$	11.4 ± 0.5	5.2 ± 2.2	27
Ni^{2+}	^{14}N	1.45×10^4	9.44	−7.8	22
Ni^{2+}	^{14}N	$(2.0\pm0.3)\times10^3$	16.4 ± 0.5	12.0 ± 1.9	23
Ni^{2+}	^1H	$(3.6\pm0.6)\times10^3$	14.2 ± 2.1	5.5 ± 4.0	23

[18] R. R. Scharfe, V. S. Sastri, C. L. Chakrabarti, and C. H. Langford, *Canad. J. Chem.*, 1973, **51**, 67.

[19] F. Dickert and H. Hoffmann, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 1320.

[20] C. H. Langford and H. G. Tsiang, *Inorg. Chem.*, 1970, **9**, 2346.

[21] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1973, **12**, 113.

[22] V. K. Kapur and B. B. Wayland, *J. Phys. Chem.*, 1973, **77**, 634.

[23] S. F. Lincoln and R. J. West, *Austral. J. Chem.*, 1973, **26**, 255.

[24] L. S. Frankel, *Inorg. Chem.*, 1971, **10**, 2360.

to be the case in previous studies[25] with DMSO, the ligand-exchange parameters are independent of the composition of the mixed solvent. This finding, coupled with the fact that the solvation shell is not pure DMF (actually, nitromethane is preferred), clearly supports the so-called D mechanism (which requires a five-co-ordinate intermediate of comparatively long lifetime) over the dissociative-interchange (I_d) mechanism in this case, as with DMSO.

Transition Metals M^{2+} (except Ni^{2+}).—A preliminary report has appeared[26] on the kinetics of the reaction between Cr^{2+} and several aliphatic radicals in water in which compounds containing chromium–carbon bonds are formed. The rate constants (Table 4) indicate that the reactions are fast but not diffusion controlled. The order of reactivity of the radicals towards $[Cr(H_2O)_6]^{2+}$ (namely, $\dot{C}H_2COOH > \dot{C}H_2OH > Me\dot{C}HOH > Me_2\dot{C}OH > Me\dot{C}HOEt$) is the same as that of the spin density of the unpaired electron on the α carbon atom calculated from the hyperfine splitting constants measured by e.s.r., suggesting that the mechanism of the reactions has some associative character. The authors conclude that the magnitude of the variation in k_f is too great to be explained purely in terms of steric hindrance.

Table 4 *Rate constants*[a] *for the formation of chromium–carbon bonds*

Reacting radical	k/l mol^{-1} s^{-1}
$\dot{C}H_2CO_2H$	2.5×10^8
$\dot{C}H_2OH$	1.6×10^8
$Me\dot{C}HOH$	7.9×10^7
$Me_2\dot{C}OH$	5.1×10^7
$Me\dot{C}HOEt$	3.4×10^7

[a] Data are from ref. 26. All solutions were saturated with Ar and contained 0.25—0.50M of the organic solute, 10^{-4}—10^{-3}M $[Cr(H_2O)\ ]^{2+}$, and 0.1—1.0M $HClO_4$.

The kinetics of the formation and dissociation of manganese(II), iron(II), and cobalt(II) chlorides have been measured in methanol and it is concluded[6, 25] from the existence of an isokinetic relationship that the release of methanol from the first co-ordination sphere of the metal is the rate-limiting process.

With Co^{2+}, as with Ni^{2+}, the agreement between the acetonitrile-exchange data obtained in two independent studies[22, 27] (Table 3) is not good. West and Lincoln point out[27] that the kinetic parameters for the exchange of acetonitrile on bivalent metal ions exhibit trends in which k_{ex} decreases and ΔH_{ex} increases from Mn^{2+} to Ni^{2+}. Similar trends are observed for solvent exchange on these metal ions in ammonia, methanol, and water, suggesting a similar exchange mechanism in all four solvents. The observed trend in $\Delta H^{\ddagger}_{ex}$ is that

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[25] L. S. Frankel, *Chem. Comm.*, 1969, 1254; *Inorg. Chem.*, 1971, **10**, 814.

[26] H. Cohen and D. Meyerstein, *J.C.S. Chem. Comm.*, 1972, 320.

[27] R. J. West and S. F. Lincoln, *Inorg. Chem.*, 1972, **11**, 1688.

predicted for water exchange by crystal-field calculations in which a dissociative mechanism involving a square-pyramidal transition state is assumed.

The volume of activation of the reaction between cobalt(II) and NH_3 in water has been measured.[9]

Diebler and Rosen have measured[28] the kinetics of formation of the 1 : 1 complexes of copper(II) with imidazole and ammonia in water and have obtained values (5.7×10^8 and 2.0×10^8 l mol^{-1} s^{-1}, respectively, at 25 °C) which they consider to be typical for the reactions of this metal with simple, neutral ligands. They consider the rate constants for the corresponding reactions with en and bipy (4×10^9 and 4×10^7 l mol^{-1} s^{-1}, respectively) and conclude that the first of these is abnormally high (because the second amino-group of en can assist the first water-loss process by the internal conjugate-base mechanism) whereas the second is abnormally low (because of the steric effect associated with the rotation about the C—C bond linking the two rings in bipy). In any event, they point out that there is no correlation between k_f for the four neutral ligands and their basicities.

The ultrasonic absorption of aqueous solutions of copper chloroacetate has been reported.[29]

Metals of Valency Three and Higher.—The n.m.r. technique has been used to study the chloride exchange at the tetrachlorogallate(III) ion in concentrated hydrochloric acid[30] and at $Me(ClCH_2)Si(Cl)NMe_2$ in CH_2Cl_2.[31] In the latter case it was possible to show that the exchange proceeded with inversion of configuration at silicon.

The acid-independent term in the rate expression for complex formation of hexa-aquoiron(III) has been attributed to reactions (1) and (2),

$$[Fe(H_2O)_6]^{3+} + L^- \longrightarrow [Fe(H_2O)_5L]^{2+} + H_2O \qquad (1)$$

$$[Fe(OH)(H_2O)_5]^{2+} + HL \longrightarrow [Fe(H_2O)_5L]^{2+} + H_2O \qquad (2)$$

where L^- and HL represent, respectively, the unprotonated and protonated forms of the incoming ligand. Since these reactions are kinetically equivalent, it has proved rather difficult to say which, in a particular case, is the more important. The present view is that, for ligands of low basicity such as Cl^- or Br^-, the major contribution to the rate constant is that associated with reaction (1) (there being but little dependence on the nature of the ligand) whereas for ligands of higher basicity, such as the substituted phenols, reaction (2) dominates. For incoming ligands of intermediate basicity, such as acetate and the chloroacetates, the uncertainty remains. A temperature-variation study on the reaction of Fe^{III} with acetate has been reported[32] and the results support the view that the dominant component of the acid-independent reaction

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[28] H. Diebler and Ph. Rosen, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1031.
[29] S. Harada, Y. Tsuji, and T. Yasunaga, *Bull. Chem. Soc. Japan*, 1972, **45**, 1930.
[30] S. F. Lincoln, A. Sandercock, and D. R. Stranks, *J.C.S. Chem. Comm.*, 1972, 1069.
[31] S. Distefano and H. Goldwhite, *J.C.S. Chem. Comm.*, 1972, 1195.
[32] R. N. Pandey and W. MacF. Smith, *Canad. J. Chem.*, 1972, **50**, 194.

involves $FeOH^{2+}$ and $MeCO_2H$ reacting by a dissociative-interchange mechanism. On this assumption, the activation enthalpy for reaction (2) with L as acetate is 11.1 ± 2.2 kcal mol^{-1}. The nature of the acid-dependent reactions remains unresolved.

The influence of lithium, potassium, and caesium nitrates on the kinetics of the reverse reaction (*i.e.* the aquation of Fe^{III}) have been reported[33] in the case of $L^- = Cl^-$. Although no specific cationic effects are predicted by the theory of salt effects, it is found that the acid-independent and the acid-dependent pathways are affected in opposite directions. The latter pathway is thought to involve $[FeOHCl]^+$ and the observed salt effects are tentatively ascribed to the influence of water structure.

$$[Fe(H_2O)_5Cl]^{2+} \rightleftharpoons [Fe(H_2O)_4ClOH]^+ + H^+ \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + Cl^-$$

Complex formation between iron(III) and ten phenols has been studied[34] and it has been confirmed that the reaction rate is acid-independent in the pH range 0—2. A mechanism for the aquation of the iron(III)–phenol complex is proposed in which a proton transfers intramolecularly from a co-ordinated water molecule to a phenolate ion:

$$[Fe(OH_2)_5A]^{2+} \longrightarrow [Fe(OH_2)_4(OH),AH]^{2+}$$

The kinetics and mechanism of the reaction of iron(III) with thiocyanate have received further attention.[35]

Further ultrasonic absorption data have been reported on aqueous solutions of the nitrates[36] and sulphates[37] of four of the lanthanides, but the nature of the overall complexation mechanism remains uncertain. It appears[37] that the deuterium isotope effect observed when D_2O is substituted for H_2O as the solvent is not a function of the solvated cation alone, but rather of the cation–ligand complex.

Preliminary stopped-flow work on the reaction between $[Mo(H_2O)_6]^{3+}$ and NCS^- in 1M-toluene-*p*-sulphonic acid yielded[38] a second-order rate constant for complex formation of 10 ± 2 l mol^{-1} s^{-1}. This value is unexpectedly high but can possibly be rationalized by invoking an S_N2-type mechanism (the possibility has not been excluded, however, that a process other than substitution is involved).

Wide-line n.m.r. spectra of ^{17}O and ^{35}Cl have been obtained[39] for complex oxovanadium(IV) species in hydrochloric acid solution over a wide range of

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[33] R. Koren and B. Perlmutter-Hayman, *Inorg. Chem.*, 1972, **11**, 3055.
[34] K. Nakamura, T. Tsuchida, A. Yamagishi, and M. Fujimoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 456.
[35] S. Funahashi, S. Adachi, and M. Tanaka, *Bull. Chem. Soc. Japan*, 1973, **46**, 479.
[36] H. B. Silber, N. Scheinin, G. Atkinson, and J. J. Grecsek, *J.C.S. Faraday I*, 1972, **68**, 1200.
[37] J. Reidler and H. B. Silber, *J. Phys. Chem.*, 1973, **77**, 1275.
[38] K. Kustin and D. Toppen, *Inorg. Chem.*, 1972, **11**, 2851.
[39] A. H. Zeltmann and L. O. Morgan, *Inorg. Chem.*, 1971, **10**, 2739.

concentrations and temperatures. Line-broadening attributable to paramagnetic species is interpreted in terms of equilibria (3) and (4), in which only equatorial ligands have been included.

$$[VO(H_2O)_4]^{2+} + Cl^- \rightleftharpoons [VO(H_2O)_3Cl]^+ + H_2O \qquad (3)$$

$$[VO(H_2O)_3Cl]^+ + Cl^- \rightleftharpoons [VO(H_2O)_2Cl_2] + H_2O \qquad (4)$$

Rate constants and activation energies are obtained for exchange of both $H_2{}^{17}O$ and $^{35}Cl^-$ between the complexes and bulk solvent (Table 5). In each case the exchange process is best represented as H_2O-dependent and the rate equations used to evaluate the data incorporate the activity of water, referred to unity at infinite dilution.

Table 5 *Kinetic parameters*[a] *for the exchange of* Cl^- *and* $H_2{}^{17}O$ *on oxovanadium*(IV) *species*

Complex	*Ligand*	k/s^{-1}	E_A/kcal mol^{-1}
$[VO(H_2O)_4]^{2+}$	$H_2{}^{17}O$	$(5.9 \pm 0.2) \times 10^2$	15 ± 1
$[VO(H_2O)_3Cl]^+$	$H_2{}^{17}O$	$(2.3 \pm 0.6) \times 10^4$	11 ± 1
$[VO(H_2O)_2Cl_2]$	$H_2{}^{17}O$	$(8.5 \pm 0.3) \times 10^5$	10 ± 1
$[VO(H_2O)_3Cl]^+$	Cl^-	$(2.0 \pm 1.6) \times 10^3$	12 ± 2
$[VO(H_2O)_2Cl_2]$	Cl^-	$(2.3 \pm 0.2) \times 10^5$	7 ± 1

[a] Data are from ref. 39 and refer to 27 ± 1 °C.

N.m.r. line-broadening has also been used[40] to measure the kinetics of exchange of glycine on the complex $[VOHGly]^{2+}$ in water; the reaction was found to be zero-order in glycine. The kinetics of formation of the complex $[VOHGly]^{2+}$ (in which the zwitterion of glycine behaves as a unidentate ligand) have also been measured[40] by a stopped-flow method, and the calculated value of K_{OS}, on the I_d mechanism, has been found to be 2.6 l mol^{-1}. With such a large value for K_{OS}, some deviations from first-order behaviour should be noted in the formation data due to incipient saturation of the ion-pair equilibrium. No such deviations are noted and it is therefore concluded that the 'normal' mechanism is not operative. On the other hand, if the outer-sphere process corresponded to the complexation of a protonated glycine in the axial position, the rate of formation would correspond to the product of the axial complexation equilibrium constant and the water-exchange rate in the equatorial position. If the axial formation constant were 0.5 l mol^{-1}, outer-sphere complex formation would be far from complete under the conditions used and the corresponding water-exchange rate constant would have to be increased by a factor of about six over that reported for $[VO(H_2O)_4]^{2+}$ in order to explain the observed rate constant. Such a factor would not be unreasonable but the authors also point out that solvent structure may play a significant role in determining the rate parameters for complex formation and

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[40] H. Tomiyasu, K. Dreyer, and G. Gordon, *Inorg. Chem.*, 1972, **11**, 2409.

conclude that a decision between the various possibilities must await the results of further investigations. Nonetheless, the zero-order dependence of the exchange process on glycine concentration and the fact that the activation parameters for the dissociation of $[VOHGly]^{2+}$ (as calculated from the stopped-flow experiments) and glycine exchange on $[VOHGly]^{2+}$ are not distinguishable experimentally [*i.e.* $\Delta H^{\ddagger}$ (stopped-flow) $= 13.1 \pm 1.5$ kcal mol^{-1}, $\Delta H^{\ddagger}$ (n.m.r.) $= 12 \pm 1$ kcal mol^{-1}; $\Delta S^{\ddagger}$ (stopped-flow) $= -2.4 \pm 2.0$ cal mol^{-1} K^{-1}, $\Delta S^{\ddagger}$ (n.m.r.) $= -3 \pm 1$ cal mol^{-1} K^{-1}] suggest that an S_N1 dissociative mechanism applies.

3 Complex Formation involving Unsubstituted Metal Ions: Multidentate Ligands

Main-group Ions.—There have been several reports dealing with the formation of complexes between the alkali metals and large ring systems such as the crown polyethers. In view of the particular relevance of these studies to the problems of active and passive transport of these ions through biological membranes, they are discussed in Part III.

Kinetic data have been reported[41] for the interaction of Mg^{2+} with six inorganic and nucleoside phosphates, $HP_3O_{10}^{4-}$, ATP^{4-}, CTP^{4-}, $HP_2O_7^{3-}$, ADP^{3-}, and CDP^{3-}. The aim of the study was to determine the effects of the phosphate backbone and the two different ring systems (purine and pyrimidine) on the complexation mechanism. In the case of the inorganic phosphates the data were found to be consistent with the mechanism

$$H_2L \overset{K_a}{\rightleftharpoons} H^+ + HL + M \rightleftharpoons MLH \underset{K_m}{\rightleftharpoons} ML + H^+ \qquad (5)$$

$$HIn \underset{K_{In}}{\rightleftharpoons} H^+ + In^-$$

where all proton-transfer reactions, including that of the indicator HIn, are taken as rapid pre-equilibria. The results (Table 6) are analysed in terms of the normal mechanism with a single rate-determining step involving the expulsion of the first water molecule from the inner hydration sphere of the metal ion;

Table 6 *Rate constants*[a] *for the formation and dissociation of the* 1 : 1 *complexes of* Mg^{2+} *with di- and tri-phosphates*

	k_f/l mol^{-1} s^{-1}	k_d/s^{-1}
MgADP	3.8×10^6	2.3×10^3
MgCDP	3.8×10^6	2.3×10^3
$MgHP_2O_7$	3.85×10^6	2.55×10^3
MgATP	8.7×10^7	7.8×10^2
MgCTP	8.7×10^7	7.8×10^2
$MgHP_3O_{10}$	8.5×10^6	8.5×10^2

[a] Data are from ref. 41 and refer to 15 °C and ionic strength 1M (KNO_3).

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[41] C. M. Frey, J. L. Banyasz, and J. E. Stuehr, *J. Amer. Chem. Soc.*, 1972, **94**, 9198.

the values of the water-exchange rate constant k_{ex} calculated from k_f and the computed outer-sphere stability constant (modified to take into account the known tendency of K^+, the cation of the supporting electrolyte, to complex with polyphosphates) on this basis are in good agreement with the experimentally determined value of *ca.* 10^5 s^{-1}. The mechanism which quantitatively fits the data for all the Mg–nucleotide systems involves the formation of a 1 : 1 complex coupled to the formation of a 2 : 1 complex:

$$\mathrm{HL} \overset{K_a}{\rightleftharpoons} \mathrm{H^+} + \mathrm{L} + 2\mathrm{M} \underset{k_{1f}}{\rightleftharpoons} \mathrm{ML} + \mathrm{M} \underset{k_{2f}}{\rightleftharpoons} \mathrm{M_2L} \qquad (6)$$

$$\mathrm{HIn} \underset{K_{In}}{\rightleftharpoons} \mathrm{H^+} + \mathrm{In^-}$$

The rate-determining step in the formation of both complexes again appears to be water loss from the inner hydration shell of the metal, and the adenine and cytosine nucleotides of a given charge type exhibit the same kinetic behaviour (Table 6).

A shock-wave apparatus has been used[42] to follow the reaction of Mg^{2+} with malonate and tartrate in water. The results are analysed in terms of the three-step mechanism

$$\mathrm{Mg^{2+}} + \mathrm{L^{2-}} \underset{K_0}{\rightleftharpoons} \mathrm{MgH_2OL} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{Mg{-}L} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \mathrm{MgL} \qquad (7)$$

and it is suggested that in both cases the ring-closure step (k_2) is significantly slower than that involving dissociation of the singly bound intermediate Mg—L (k_{-1}). The values of k_2 for malonate and tartrate at 20 °C are calculated as, respectively, 1.6×10^5 and 1.8×10^5 s^{-1} and that of k_{-1} is 6×10^5 s^{-1} for both (assuming k_1 to be 3×10^5 s^{-1} for both); values of k_{-2} are estimated to be 3×10^4 and 8×10^3 s^{-1}.

Dynamic n.m.r. methods have been used[43] to determine the average lifetimes of the magnetically non-equivalent methylenic protons of the acetate groups in 1,3-propylenediaminetetra-acetate complexes of zinc and cadmium; it is proposed that these lifetimes are a measure of the rates of partial dissociation of the complexes. The kinetics have been reported[44, 45] for the interaction between zinc and glycine.

Nickel(II).—Cavasino has extended his temperature-jump studies on the reaction of nickel(II) with anionic bidentate ligands by investigating[46] the behaviour of this metal towards methyl- and n-butyl-malonic acids. The kinetic data obtained for both dicarboxylic acids were consistent with the

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[42] G. Platz and H. Hoffmann, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 491.

[43] D. L. Rabenstein and B. J. Fuhr, *Inorg. Chem.*, 1972, **11**, 2430.

[44] J. A. Miceli and J. E. Stuehr, *Inorg. Chem.*, 1972, **11**, 2763.

[45] M. W. Grant, *J.C.S. Faraday I*, 1973, **69**, 560.

[46] G. Calvaruso, F. P. Cavasino, and E. DiDio, *J.C.S. Dalton*, 1972, 2632.

following reaction scheme:

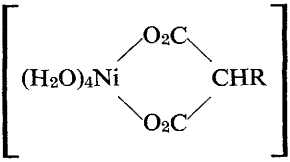
$$\begin{array}{lll} & \mathrm{O_2C{\cdot}CHR{\cdot}CO_2^{2-}} \underset{K_0}{\overset{\text{very fast}}{\rightleftharpoons}} [\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2}] & (8) \\ [\mathrm{Ni(H_2O)_6}]^{2+} + & \quad +\mathrm{H^+} \downarrow\uparrow -\mathrm{H^+} & \\ & \mathrm{HO_2C{\cdot}CHR{\cdot}CO_2^-} \underset{K_0'}{\overset{\text{very fast}}{\rightleftharpoons}} [\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2H}]^+ & (9) \end{array}$$

$$[\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2}] \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{H_2O} + [\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)}] \quad (10)$$

$$[\mathrm{(H_2O)_6Ni,O_2C{\cdot}CHR{\cdot}CO_2H}]^+ \underset{k_1'}{\overset{k_{-1}'}{\rightleftharpoons}} \mathrm{H_2O} + [\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2H)}]^+ \quad (11)$$

$$[\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2H)}]^+ \underset{k_{\mathrm{H}}}{\overset{k_{-\mathrm{H}}}{\rightleftharpoons}} \mathrm{H^+} + [\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)}] \quad (12)$$

$$[\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)}] \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \mathrm{H_2O} +$$



(13)

The products of reactions (8) and (9) (R = Me or Bu^n) represent outer-sphere complexes and reaction (12) is a proton-transfer process which probably involves the solvent as acceptor. According to this mechanism, two reactions contribute significantly to the formation of the nickel monochelate complex in the acidity range investigated, namely the reactions of the nickel(II) ion with the dianionic ligand $[\mathrm{O_2C{\cdot}CHR{\cdot}CO_2}]^{2-}$ and with the corresponding conjugate acid $[\mathrm{HO_2C{\cdot}CHR{\cdot}CO_2}]^-$. The rate constants for the various steps are shown in Table 7 and it will be seen that, for both ligands, the rate constant (k_2) for ring closure is larger by a factor of 13—16 than that (k_{-1}) for dissociation of the unprotonated monochelate $[\mathrm{(H_2O)_5Ni(O_2C{\cdot}CHR{\cdot}CO_2)}]$. The implication of this is that chelate ring closure contributes negligibly to the rate-limiting process when the pH is higher than *ca.* 4. The authors conclude, likewise, that the rate-limiting step in the other reaction pathway is water substitution at the metal and that the behaviour of nickel(II) towards methyl- and n-butylmalonic acids (and, by analogy, malonic acid itself[47]) is 'normal'. In particular, there appears to be no significant difficulty in closing the six-membered chelate

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[47] F. P. Cavasino, *J. Phys. Chem.*, 1965, **69**, 4380.

rings. A similar conclusion has been reached[48] by Petrucci and co-workers on nickel malonate in D_2O. The kinetic data on the reaction of Ni^{2+} with malate[49] and with maleate[50] suggest that water loss is rate limiting here, also.

Volumes of activation have been measured for the reaction of nickel(II) with compound (4)[9] and glycine;[45] the results, which are discussed together with those for cobalt(II), copper(II), and zinc(II) in the next section, provide further support for the validity for the Eigen mechanism in these cases.

Table 7 *Rate constants[a] for the various steps involved in the formation of nickel*(II) *monochelate complexes with methyl- and n-butyl-malonic acids (see text)*

Rate constant	*Methylmalonic acid*	*n-Butylmalonic acid*
$k_2/(k_{-1}+k_2)$	0.93	0.94
k_{-2}/s^{-1}	2.2×10^3	3.9×10^3
k_{-1}/s^{-1}	3.3×10^3	3.1×10^3
k'_{-1}/s^{-1}	1.3×10^4	1.4×10^4
k_2/s^{-1}	4.2×10^4	5.1×10^4

[a] Data are from ref. 46 and refer to 25 °C and ionic strength 0.10M ($NaClO_4$).

To complement their studies[8] on the reaction of Ni^{2+}_{aq} with alkylamines, Rorabacher and co-workers have measured[51] the kinetics of complex formation with a series of *N*-alkyl-substituted ethylenediamines. In addition to the inductive and steric effects observed with the unidentate series, rate enhancements associated with the internal conjugate-base mechanism must be taken into account. However, a comparison of rate constants for the unprotonated and monoprotonated ligands, along with corresponding estimates for en, reveals a uniform decrease in reactivity on going from primary to secondary to tertiary amine nitrogens, *i.e.* the order of relative reactivities towards Ni^{2+}_{aq} is $NH_3 > RNH_2 > R_2NH \gg R_3N$. (This order is clearly established for ethyl substitution and a similar, but less distinct, trend is observed for methyl substitution.) Similarly, the rate of second-bond formation to complete a chelate ring appears to decrease in the case of the diamines on increasing *N*-alkyl substitution. The ultimate result is an apparent shift in the rate-determining step from the first- to the second-bond formation when the substituents become sufficiently large. As a consequence of these observations, the authors make three very interesting generalizations concerning the mechanism of complex formation with large multidentate ligands:

(i) In linear multidentate ligands, such as the straight-chain polyamines, the terminal (primary) donor atoms are much more reactive than the internal

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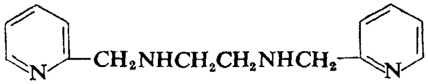
[48] D. Saar, G. Macri, and S. Petrucci, *J. Inorg. Nuclear Chem.*, 1971, **33**, 4227.
[49] S. Harada, K. Amidaiji, and T. Yasunaga, *Bull. Chem. Soc. Japan*, 1972, **45**, 1752.
[50] S. Harada and T. Yasunaga, *Bull. Chem. Soc. Japan*, 1973, **46**, 502.
[51] T. S. Turan and D. B. Rorabacher, *Inorg. Chem.*, 1972, **11**, 288.

(secondary) donor atoms to the extent that the reaction path involving first-co-ordinate-bond formation with a terminal donor atom represents the predominant reaction route.

(ii) For branched multidentate ligands such as edta and analogous ligands involving both primary and tertiary donor atoms, the reaction path involving first-co-ordinate-bond formation to a primary (terminal) donor atom predominates to such an extent that it represents the only kinetically significant route to the final complex ion even when the terminal donor atoms are so weak that the rate-determining step is shifted to the point of second-co-ordinate-bond formation (closure of the first chelate ring).

(iii) Extrapolation of these conclusions to ligands involving a high degree of steric hindrance, such as the macrocyclic ligands, suggests that these species will be very slow to react and, considering the large potential energy barriers to internal rotation, will probably involve a shift in the rate-determining step to the point of second-bond formation even when all donor atoms may be classified as 'strong'.

Further reports on the kinetics of multidentate-ligand substitution have appeared[52] and it has been shown[53] that the reaction of Ni^{2+} with (1) involves an initial and rate-determining bond formation to a pyridine nitrogen. Rate constants have been reported for the reaction of Ni^{2+}_{aq} with glycyl-L-leucine and L-leucylglycine[54] and with α-alanine, β-alanine, ida, aspartic acid, and iminodipropionic acid;[55] sterically controlled ring closure is invoked with the latter series.



(1)

The histidine molecule is a potentially terdentate ligand in aqueous solution and the evidence suggests that all three co-ordination positions are used when this species binds to Ni^{2+}_{aq}. With the aim of establishing the sequence of binding steps in the nickel(II)–histidine system, Letter and Jordan have studied[10] the kinetics of the reaction of nickel with histidine, histidine methyl ester, and imidazole. The results (Table 8) suggest that the first (slow) step in the binding of both histidine and its methyl ester involves the ring nitrogen (Scheme 2). In the case of histidine (but not the ester) the carboxy-group chelates as a third (rapid) step. It is interesting to note that, although imidazole itself reacts in both its protonated and unprotonated forms (see above), histidine only binds in the neutral form, in which one proton has been removed from the

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[52] M. Kodama, T. Sato, and S. Karasawa, *Bull. Chem. Soc. Japan*, 1972, **45**, 2757, 2761.

[53] R. K. Steinhaus and Z. Amjad, *Inorg. Chem.*, 1973, **12**, 151.

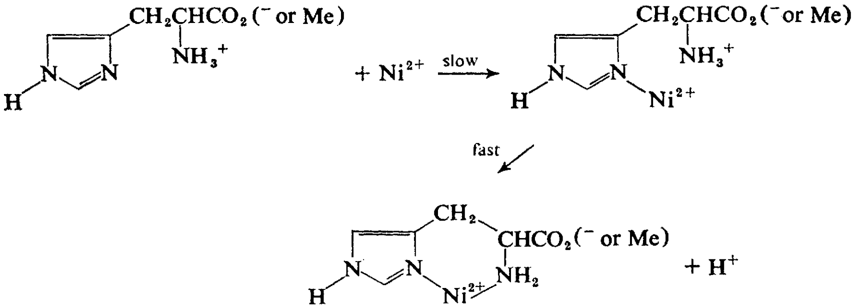
[54] R. F. Pasternack, L. Gipp, and H. Sigel, *J. Amer. Chem. Soc.*, 1972, **94**, 8031.

[55] R. F. Pasternack, M. Angwin, L. Gipp, and R. Rheingold, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2329.

Table 8 *Rate constants*[a] *for complex formation with nickel*(II)

Ligand	*Species*	*Rate constant*/ $\mathrm{l\,mol^{-1}\,s^{-1}}$
Imidazole	H_2L^+	4.0×10^2
	HL	3.2×10^3
Histidine	HL	2.2×10^3
Histidine methyl ester	HL^+	6.0×10^2
	L	2.6×10^3

[a] Data are from ref. 10 and refer to 23.7 °C and ionic strength 0.10M (KNO_3).



Scheme 2

imidazole ring. The rate constants for all species are 'normal' in that they show the type of dependence on charge predicted for the Eigen mechanism.

In a study designed to investigate the effect of the presence on a ligand of one or more protons on the mechanism of complex formation with nickel(II), Wilkins and co-workers have published[11] a list of 13 rate constants for derivatives of imidazole, 2,2′-bipyridine, and 1,10-phenanthroline and for cysteine, penicillamine, chelidamic acids, and pyridine-2-aldoxime. As expected, if the proton is far removed from potential reaction sites it has little effect but if it blocks a binding position, as in bipyH^+ and particularly phenH^+, it has a much larger effect on k_f. Frequently, however, the effect of the proton appears to be merely to reduce K_{os} (and therefore k_f) by increasing the positive charge on the ligand (*cf.* Table 8).

The low rate constant for the reaction of Ni^{2+}_{aq} with (2) has been ascribed[56] to internal hydrogen-bond formation, whereas for (3)[57] and 2-(2-aminoethyl)-pyridine[58] the lower rate constants for the protonated form as compared with the neutral form have been attributed to reductions in K_{os}. The factor-of-three difference in the rate constants at 25 °C for Ni^{2+} + proline (3.4×10^4 $\mathrm{l\,mol^{-1}\,s^{-1}}$) and hydroxyproline ($1.2\times10^4\,\mathrm{l\,mol^{-1}\,s^{-1}}$) has been ascribed[59] to

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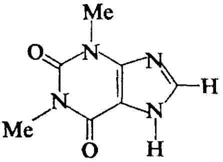
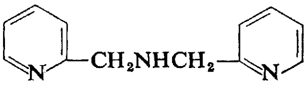
[56] K. Kustin and M. A. Wolff, *J.C.S. Dalton*, 1973, 1031.
[57] C. D. Hubbard, *Inorg. Chem.*, 1971, **10**, 2340.
[58] C. D. Hubbard and W. Palaitis, *Inorg. Chem.*, 1973, **12**, 480.
[59] K. Kustin and S.-T. Liu, *J.C.S. Dalton*, 1973, 278.



(2)



(3)

hydrogen-bond formation between co-ordinated water molecules of the metal ion and the hydroxy-group of the latter ligand.

Cock, Cottrell, and Boyd have studied the formation of 1 : 1 (and 1 : 2) complexes of nickel(II) with terpyridine in DMSO and have critically compared[60] their results with those in the literature. Some of the discrepancies among the published data in various solvents can apparently be attributed to differences in the nature of the species present in the various studies. {It appears, for example, that $[Ni(terpy)Cl(DMSO)_2]^+$ is the major nickel-containing species at high concentrations whereas at lower concentrations the chloride ion is replaced by a third DMSO molecule.} The authors compare the relative merits of the I_d and D (involving a five-co-ordinate intermediate of significant lifetime) mechanisms for reactions of $[Ni(DMSO)_6]^{2+}$ and conclude that there is no compelling reason to discard the former. The fact that the values of K_{os} calculated from measured complex-formation and solvent-exchange rate constants are usually lower than those predicted by the Fuoss equation need not surprise us in view of the fact that the only solvent property taken into account by the Fuoss equation is the bulk dielectric constant, which is, of course, highly inappropriate for interactions between species which are separated by distances as small as 5 Å. The lower rates observed in DMSO, relative to those in water, are entirely due to the activation-entropy term; indeed, the activation enthalpies are higher in water than in DMSO. The release of structured solvent in the bulk liquid during the activation process will increase both the entropy and energy of activation, and these effects will be largest in solvents, like water, which are known to form rigid solvation structures. Thus, the mere fact that the absolute value of K_{os}, required for the reaction to be interpreted in terms of the I_d mechanism in DMSO, is lower than that calculated from the Fuoss equation, whereas it agrees with the predicted value in water, seems to be no reason for discarding the I_d mechanism in the former case.

Chattopadhyay and Coetzee[21] have measured the rate constants and activation parameters for the reaction of nickel(II) with pyridine, bipy, phen, and terpy in acetonitrile and in DMSO, for terpy in methanol and in ethylene glycol, and for bipy in ethanol–water and t-butyl alcohol–water mixtures in order to investigate further the role of the solvent in complex formation with nickel. They introduce a dimensionless parameter R, given by $R = 4k_f/(3K_{os}k_{ex})$, which they use as a criterion of whether a particular reaction is

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[60] P. A. Cook, C. E. Cottrell, and R. K. Boyd, *Canad. J. Chem.*, 1972, **50**, 402.

'normal'. (This R is not unlike the n of Bennetto and Caldin.[14]) If substitution is 'normal' (*i.e.* the dissociative-interchange I_d mechanism is operative) R will have a value near unity; in addition, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for ligand substitution should be similar to those for solvent exchange. Table 9 shows their results for k_f, R, $\Delta H^{\ddagger}_f$, $\Delta\Delta H^{\ddagger}$ ($\equiv \Delta H^{\ddagger}_f - \Delta H^{\ddagger}_{ex}$), $\Delta S^{\ddagger}_f$, and $\Delta\Delta S^{\ddagger}$ ($\equiv \Delta S^{\ddagger}_f - \Delta S^{\ddagger}_{ex}$), and it will be seen that it is possible to draw the following conclusions: (i) rate constants and activation parameters for ligand substitution depend strongly on the nature of the solvent and, in acetonitrile and DMSO, on the nature of the ligand as well; (ii) the value of R (at 25 °C) for pyridine seems reasonably 'normal' in acetonitrile and in DMSO, as it is in water; (iii) in contrast to the situation in water and methanol, values of R for the multidentate ligands are significantly smaller than unity in DMSO; (iv) in sharp contrast to the situation in DMSO, the properties of multidentate ligands in acetonitrile generally deviate from those in water and methanol in the opposite direction. The value of R for phen is $\gg 1$ and those of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ for all multidentate ligands are significantly negative; (v) values of R, $\Delta\Delta H^{\ddagger}$, and $\Delta\Delta S^{\ddagger}$ vary by as much as factors of 4.5×10^3, 14 kcal mol^{-1}, and 29 cal mol^{-1} K^{-1}, respectively.

Chattopadhyay and Coetzee discuss[21] their observations in the light of the papers by Bennetto and Caldin[14] and conclude that, in DMSO, substitution by pyridine proceeds by an I_d mechanism in which solvent exchange is rate limiting (as in water) but that with the multidentate ligands (such as bipy[14] and terpy)[60] the rate-determining step may well be ring closure. There is evidence that, near 120 °C with this solvent, nickel(II) loses its ability to discriminate among the four ligands. The same result is found with acetonitrile at about 65 °C for the ligands pyridine, bipy, and terpy, but the behaviour with phen is significantly different. The authors offer a tentative explanation for this, suggesting that 1,10-phenanthroline (in particular) undergoes a specific interaction with the polarized acetonitrile molecules in the primary solvation shell of the metal in a manner analogous to that invoked in the internal conjugate-base mechanism (which was proposed to explain the abnormally high reaction rate of ethylenediamine in aqueous solution). However, they also point to the fact that the values of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ are negative for the multidentate ligands in acetonitrile whereas they are positive for pyridine, and emphasize the need for more work, particularly with other unidentate ligands having different steric requirements, before much can be said about what constitutes 'normal' substitution in acetonitrile.

The results obtained[21] in mixed solvents essentially confirm those previously reported[14] for bipyridine. With increasing methanol content of methanol–acetonitrile mixtures, all observations are consistent with the gradual replacement of acetonitrile by methanol in the primary solvation sphere of the metal. For alcohol–water mixtures the activation parameters show the typical near-compensation, with marked extrema at the water-rich end of the composition range (see Figure). With increasing molecular size of the alcohol, the extrema in $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ (normalized with respect to corresponding values in pure water) become larger and sharper and occur at progressively lower alcohol

Table 9 *Comparison of rate constants and activation parameters*[a] *for ligand substitution at nickel*(II) *with those for solvent exchange (see text)*

Solvent	*Ligand*	k_{ex} or k_f[b]	*R*	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
Water	water	3×10^4	—	10.8	—	−2	—
	py	*ca.* 4×10^3	*ca.* 0.6	*ca.* 11	*ca.* 0	*ca.* −5	*ca.* −3
	bipy	2.26×10^3	0.33	11.7±0.2	+0.9	−4	−2
	terpy	1.49×10^3	0.22	12.3±0.1	+1.5	−3	−1
	phen	4.14×10^3	0.61	11.5±0.3	+0.7	−4	−2
Methanol	methanol	1.0×10^3	—	15.8	—	+8	—
	bipy	9.4×10	0.25	—	—	—	—
	terpy	4.6×10	0.12	16.8±0.5	+1.0	+5	−3
	phen	2.4×10^2	0.65	—	—	—	—
Ethylene glycol	ethylene glycol	4×10^3	—	—	—	—	—
	terpy	9.6	0.006	14.0±0.4	—	−7	—
Acetonitrile	acetonitrile	2.8×10^3	—	11.7	—	−4	—
	py	8.3×10^2	0.39	14.7±0.4	+3.0	+4	+8
	bipy	4.1×10^3	1.9	6.5±0.2	−5.2	−20	−16
	terpy	2.2×10^3	1.0	8.4±0.3	−3.3	−15	−11
	phen	5.0×10^4	23	4.7±0.2	−7.0	−21	−17
Dimethyl sulphoxide	dimethyl sulphoxide	7.5×10^3 (?)	—	8 (?)	—	−14 (?)	—
	py	*ca.* 2×10^3	*ca.* 0.5	*ca.* 4	*ca.* −4	*ca.* −30	*ca.* −16
	bipy	6.9×10	0.02	12.6±0.1	+5	−8	+6
	terpy	2.5×10	0.006	15.0±0.7	+7	−2	+12
	phen	3.5×10^2	0.08	8.3±0.3	0	−19	−5

[a] From ref. 21. [b] Units: s^{-1} at 25 °C for k_{ex}, l mol^{-1} s^{-1} at 25 °C for k_f.

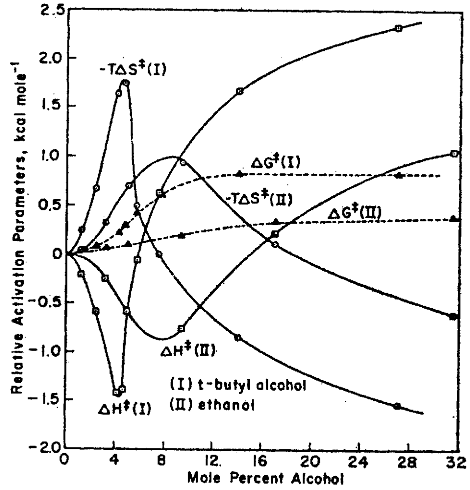


Figure *Activation parameters for the reaction of nickel*(II) *with* 2,2′-*bipyridine in water–ethanol and water–t-butyl alcohol mixtures, normalized with respect to those in pure water* (298 K).
(Reproduced by permission from *Inorg. Chem.*, 1973, **12**, 113)

content. The extrema cannot be attributed to dramatic changes in solvation of nickel(II) since, for the two larger alcohols at least, it is very probable that the primary solvation sphere contains only water at 9% and 4.5% alcohol, respectively. The authors agree with the previous conclusion[14] that the initial progressive decrease in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is consistent with a transition state characterized by passage of a solvent molecule from the disordered region adjacent to the primary solvation sphere into a medium which is both stiffer and more ordered than pure water itself. They do, however, emphasize that, although this simple model accounts for the properties of water-rich solvent mixtures, it fails to account for substantial differences in the behaviour of bipyridine and ammonia in methanol-rich mixtures. It seems, therefore, that in alcohol–water mixtures the composition of the inner sphere, the steric requirements of the ligand, and the structure of the solvent all play a significant role.

The reaction between Ni^{2+} and 1,10-phenanthroline in ethanol has been studied in some detail by Sanduja and Smith. They find[61] that sodium perchlorate has a significant effect on the kinetics whereas tetrabutylammonium perchlorate does not (Table 10). If ion-pairing between Ni^{2+} and ClO_4^- is occurring to a significant degree, the kinetic activity of the ion pairs must be close to that of free Ni^{2+}. The apparent depressive effect of Na^+ was unexpected but the authors suggest that it might be connected with the formation of associates

[61] **M. L. Sanduja and W. MacF. Smith,** ***Canad. J. Chem.,*** **1972, 50, 3861.**

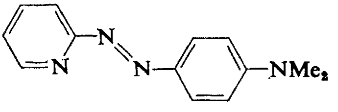
Table 10 *Rate constants*[a] *for the formation of* $[Ni(phen)]^{2+}$ *in ethanol at* 25 °C

Added electrolyte	*Ionic strength*/M	$[Ni^{II}]/10^{-3}M$	$[phen]_0/10^{-5}M$	$k_f/10^3\ l\ mol^{-1}\ s^{-1}$
None	0.006	2.0	2.0	31.3 ± 3.1
None	0.006	2.0	5.0	32.7 ± 5.6
None	0.012	4.0	2.0	29.8 ± 2.9
Tetrabutyl-ammonium perchlorate	0.050	2.0	2.0	29.2 ± 1.8
Sodium perchlorate	0.050	2.0	2.0	13.7 ± 0.7

[a] Data are from ref. 61.

between Na^+ and phen. The rate constant at 25 °C is consistent with a dissociative-interchange mechanism, given the rate constant for ethanol exchange on nickel, but the value of $\Delta H^{\ddagger}$ for complex formation (15.9 ± 1.0 kcal mol^{-1}) is about 5 kcal mol^{-1} higher than that reported for ethanol exchange. However, the authors feel that the agreement is no worse than can be expected in view of the wide range of activation parameters quoted by different workers for many exchange reactions and conclude that the I_d mechanism applies for the reaction $[Ni(EtOH)_6]^{2+}$ + phen.

Transition Metals M^{2+} (except Ni^{2+}).—The volumes of activation for the reaction of several bivalent cations with NH_3[9] and with the bidentate ligands pada (4)[9] and the glycinate[45] mono-anion have been measured. The values of



(4)

$\Delta V_f^{\ddagger}$ (Table 11) are remarkably similar for all of the systems studied – a result which is consistent with there being a common rate-determining step which does not involve the ligands. The authors discuss their data in terms of the dissociative-interchange mechanism and note that the measured function $\Delta V_f^{\ddagger}$ is in reality a composite quantity, the sum of the volume of reaction for formation of the outer-sphere complex (ΔV°_{OS}) and the volume of activation for water loss, $\Delta V^{\ddagger}_{H_2O}$. Evidence from the literature suggests that ΔV°_{OS} is zero for the neutral ligands and -3 cm^3 mol^{-1} for the glycine mono-anion, and the values of $\Delta V^{\ddagger}_{H_2O}$ calculated on this basis are given in Table 11. The values for Co^{2+} and Ni^{2+} for different ligands are the same within experimental error (the error limits quoted being regarded as conservative estimates), as would be expected if the rate-determining step in the reaction were the stretching of the metal ion—water oxygen bond. It is likely that the extent of stretching differs from one metal ion to the other, as is suggested by the difference between the ΔV_{H_2O} values for copper and zinc; the hydrated cupric ion, for example, is not

Table 11 *Volumes of activation*[a] *for reactions of* Co^{2+} *and* Ni^{2+} *in water at* 25 °C (*see text*)

System	$\Delta V_f^{\ddagger}$/cm³ mol⁻¹	$\Delta V_{H_2O}^{\ddagger}$/cm³ mol⁻¹
$Co^{2+}+NH_3$	4.8 ± 0.7	4.8 ± 0.7
$Co^{2+}+(4)$	7.2 ± 0.2	7.2 ± 0.2
$Co^{2+}+Gly^-$	8 ± 2	5 ± 2
$Ni^{2+}+NH_3$	6.0 ± 0.3	6.0 ± 0.3
$Ni^{2+}+(4)$	7.7 ± 0.3	7.7 ± 0.3
$Ni^{2+}+Gly^-$	10 ± 1	7 ± 1
$Cu^{2+}+Gly^-$	12 ± 1	9 ± 1
$Zn^{2+}+Gly^-$	7 ± 1	4 ± 1

[a] From refs. 9 and 45.

octahedral, because of Jahn–Teller distortion, and it is quite possible that changes in the metal–water distances other than in that bond being stretched also occur in the formation of the transition state. As Grant points out,[45] it would be interesting to see whether volumes of activation can be used diagnostically to distinguish between reactions in which water substitution is rate limiting and those in which some other step, such as ring closure, has become rate limiting.

Sterically controlled ring closure is invoked[55] in the formation of six-membered chelate rings with Co^{2+}, Ni^{2+}, and Cu^{2+} (the ligands used being α-alaninate, β-alaninate, iminodiacetate, aspartate, and iminodipropionate), whereas the low values of k_f for the reaction of these metals with L-hydroxyproline compared with that with L-proline are attributed[59] to hydrogen-bond formation between co-ordinated water molecules of the metal ion and the hydroxy-group of the ligand. Co^{2+} reacts with (3) about ten times as rapidly as it does with terpy.[57] It is concluded,[54] from the fact that the rate constants for the formation of the complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} with glycyl-L-leucine and L-leucylglycine are generally about a factor of ten less than those for the α-amino-acids of the same formal charge, that only ion pairs in which the amino end of the peptide is in proximity to the inner co-ordination sphere of the metal lead to the reaction (*i.e.* the ion pairs in which the carboxylate end of the molecule are in proximity to the metal–water sheath do not yield the complex).

Acidic solutions (pH 1—5) of copper(II)–adenosine triphosphate yield ultrasonic attenuation spectra[62] consisting of three maxima. The overall reaction which fits the data best is

$$Cu^{2+} + H_2ATP^{2-} \rightleftharpoons CuHATP^{-} + H^{+}$$

The shortest relaxation time (*ca.* 2×10^{-9} s) is attributed to penetration of the inner hydration sphere of the metal by the ligand. The next slower process (*ca.* 1×10^{-8} s) is then due to chelate ring closure of the species formed in the faster

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[62] R. S. Brundage, R. L. Karpel, K. Kustin, and J. Weisel, *Biochim. Biophys. Acta*, 1972, **267**, 258.

step. The lowest frequency peak (< 2 MHz) is taken to be either a characteristic of aqueous Cu^{2+} (similar to that already observed with, for example, $CuSO_4$) or to be due to formation of another complex species such as CuH_2ATP. On the assumption that formation of copper(II) complexes follows the established pattern of nickel(II), values of 8.8×10^8 and 6.3×10^7 s^{-1}, respectively (at 25 °C and ionic strength 0.1—0.8M), are obtained as the rate constants for water elimination and sterically controlled ring closure.

The kinetics of the formation and dissociation of the copper(II) complex of adenosine have been determined[63] at low pH; the complex is formed between Cu^{2+} and the adenine base. At high pH, only the dissociation of the complex, in which the metal is bridged with ribose hydroxy-groups, could be followed. The suggestion[28] that the formation of copper(II) complexes with bipy and en does not involve rate-determining water substitution has been discussed in Section 2 and the results of other studies with copper(II) are considered in Section 4 (*cf.* Table 16, p. 290).

Rate constants and activation parameters for the formation and dissociation of complexes of manganese(II) with phen, bipy, and terpy have been measured,[64] at low temperatures in anhydrous methanol, by the stopped-flow method. The values of $\Delta H^{\ddagger}_{f}$ (Table 12) are significantly larger than the activation enthalpy

Table 12 *Kinetic data*[a] *for the formation and dissociation of manganese*(II) *complexes in methanol*

Complex	$\log(k_f$/l mol^{-1} $s^{-1})$	$\Delta H^{\ddagger}_{f}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{f}$/cal mol^{-1} K^{-1}	log (k_d/s^{-1})	$\Delta H^{\ddagger}_{d}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{d}$/cal mol^{-1} K^{-1}
$[Mn(phen)]^{2+}$	4.95	10.6±0.4	−0.4±1.6	1.15	13.5±0.3	−8.2±0.9
$[Mn(bipy)]^{2+}$	4.24	11.7±0.1	0.1±0.1	1.57	13.4±0.5	−6.4±1.9
$[Mn(terpy)]^{2+}$	3.72	12.8±1.0	+1.3±3.9	1.33	13.7±0.6	−18±2

[a] From ref. 64; 25 °C and ionic strength 0.2M ($NaClO_4$).

associated with solvent exchange at Mn^{2+} in methanol (6.2 kcal mol^{-1}) and the authors suggest that this could be rationalized in terms of sterically controlled substitution (ring closure), at least for bipy and terpy. In the case of the unflexible ligand phen the rationalization is less convincing unless there is a considerable distortion in the bonding of one end of this ligand to a metal ion, which would presumably show up in studies with other metals and in other solvents. In any event, the data for all three ligands are not in accord with the dissociative-interchange mechanism.

Metals of Valency Three and Higher.—The kinetics of the formation of complexes of gallium(III), indium(III), and thallium(III) with semi-xylenol orange (5; shown in the form H_3SXO^-) in acid solution have been reported.[65] The

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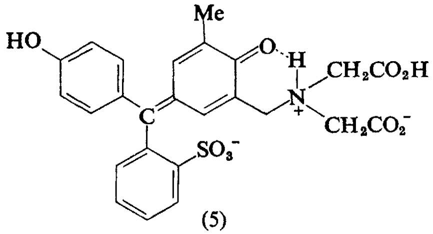
[63] G. Boivin and M. Zador, *Canad. J. Chem.*, 1972, **50**, 3117.

[64] D. J. Benton and P. Moore, *J.C.S. Chem. Comm.*, 1972, 717; *J.C.S. Dalton*, 1973, 399.

[65] Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Fujimoto, *Bull. Chem. Soc. Japan*, 1972, **45**, 1417.



(5)

results are interpreted in terms of a two-step mechanism:

$$\mathrm{M^{III}} + \mathrm{SXO} \underset{K_p}{\rightleftharpoons} \mathrm{M^{III}\cdots SXO} \quad \text{(fast)}$$

$$\mathrm{M^{III}\cdots SXO} \underset{\vec{k}}{\overset{\overleftarrow{k}}{\rightleftharpoons}} \mathrm{M^{III}SXO} \quad \text{(slow)}$$

The reaction of each of the three metal species M^{3+}, MOH^{2+}, and $M(OH)_2^+$ with the five ligand species H_6SXO^{2+}, H_5SXO^+, H_4SXO, H_3SXO^-, and H_2SXO^{2-} was considered, and it was concluded that, for all three metals, reaction (14) represents a major pathway. The rate constants for reaction (14)

$$\mathrm{MOH^{2+}} + \mathrm{H_3SXO^-} \longrightarrow \text{complex} \qquad (14)$$

at 25 °C are: Ga^{III} 1.1×10^3 l mol^{-1} s^{-1} (ionic strength 0.1M), In^{III} 5.0×10^6 l mol^{-1} s^{-1} (0.1M) and 2.2×10^6 l mol^{-1} s^{-1} (2.0M), and Tl^{III} 5.3×10^5 l mol^{-1} s^{-1} (2.0M). Thus, the order of reactivity towards H_3SXO^- is $InOH^{2+} > TlOH^{2+} > GaOH^{2+}$. The possibility that the rate-limiting step involves cleavage of the internal hydrogen bond of (5) is discussed.

The second-order rate constants for complex formation with vanadium(III) (Table 13) show a significant ligand dependence. Both the large spread of values of k_f and the fact that k_f reflects the basicity of the incoming ligand have led Patel and Diebler[66] to support the suggestion that the substitution mechanism at V^{3+} has an appreciable degree of S_N2 character.

The kinetics of the reaction of iron(III) with acetylacetone have been studied in detail by Sutin and co-workers.[67] The keto (HK) and enol (HE) tautomers

Table 13 *Kinetic data*[a] *for complex formation with* V^{3+} *in water* (25 °C)

Ligand	k_f/l mol^{-1} s^{-1}	$\Delta H_f^\ddagger$/kcal mol^{-1}
SCN^-	1.1×10^2	7.6
$HC_2O_4^-$	1.3×10^3	—
Cl^-	$\leqslant 3$	>11.2
Br^-	$\leqslant 10$	>11.8
HN_3	0.4	—

[a] From ref. 66.

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[66] R. C. Patel and H. Diebler, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1035.

[67] D. P. Fay, A. R. Nichols, and N. Sutin, *Inorg. Chem.*, 1971, **10**, 2096.

of acetylacetone both react by parallel acid-independent and acid-dependent pathways. If these paths are ascribed to the reactions of Fe^{3+} and $FeOH^{2+}$, respectively [equations (15)—(18)], then the kinetic data give $k_{15} = 0.29$,

$$Fe^{3+} + HK \underset{k_{15}}{\overset{k_{-15}}{\leftrightarrows}} FeE^{2+} + H^{+} \tag{15}$$

$$Fe^{3+} + HE \underset{k_{16}}{\overset{k_{-16}}{\leftrightarrows}} FeE^{2+} + H^{+} \tag{16}$$

$$FeOH^{2+} + HE \underset{k_{17}}{\overset{k_{-17}}{\leftrightarrows}} FeE^{2+} \tag{17}$$

$$FeOH^{2+} + HK \underset{k_{18}}{\overset{k_{-18}}{\leftrightarrows}} FeE^{2+} \tag{18}$$

$k_{16} = 5.2$, $k_{17} = 4.4 \times 10^{7}$, and $k_{18} = 5.4\ \mathrm{l\ mol^{-1}\ s^{-1}}$. [If instead of equation (17) the inverse acid path for the reaction of the enol tautomer is interpreted to be

$$Fe^{3+} + E^{-} \underset{k_{19}}{\overset{k_{-19}}{\leftrightarrows}} FeE^{2+} \tag{19}$$

then $k_{19} = 8 \times 10^{8}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, which is very much larger than the rate constants for complex formation of Fe^{3+} with other singly charged anions; this indicates that the reactants in the inverse acid path are correctly formulated as $FeOH^{2+}$ and HE {equation (17)}.] Both k_{16} and the ratio k_{17}/k_{16} (*ca.* 10^{7}) are close to the 'normal' values for substitution at iron(III) and it therefore seems that the sterically controlled substitution mechanism which has been invoked[68] in the corresponding reaction with copper(II) is not operative here. The reactions of Fe^{3+} and $FeOH^{2+}$ with the keto tautomer HK are too slow for water release from the metal ions to be rate determining. Moreover, the ratio k_{18}/k_{15} is only *ca.* 20 (in contrast to the value of k_{17}/k_{16} of *ca.* 10^{3}) and the rate constant for the reaction of HK with Cu^{2+} is only *ca.* 10^{2} times larger than that for the reaction with Fe^{3+} (in contrast to the customary factor of *ca.* 10^{5}). It had been proposed[68] that the first step in the reaction between copper(II) and the keto tautomer of acetylacetone involves the formation of the intermediate (6) in which the metal ion is bound to both keto-groups. In terms of this mechanism, the cupric ion acts as an electron sink and the rate-determining step involves the slow, metal-ion-catalysed proton release from (6). To some extent the results of the study with iron are consistent with this interpretation. However, the simple electrostatic picture would predict a larger value of k_{HK} for the more highly charged Fe^{3+} (k_{15}) than for either Cu^{2+} or $FeOH^{2+}$ (k_{18}) but this is not observed. It is concluded[67] that other factors, such as the stability of the precursor complexes [*e.g.* (6)], are also important in determining the rate of the reaction of the keto tautomer of acetylacetone.

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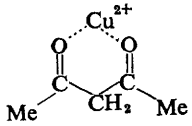
[68] R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, 1970, **9**, 39.



(6)

The fact that the rate constant for the reaction of $FeOH^{2+}$ with H_2nta^- is 20 times that for reaction with SCN^- is ascribed[35] to the operation of the internal conjugate-base mechanism of Rorabacher.

The formation of complexes between the vanadyl cation and malonate, oxalate, L-tartrate, and racemic tartrate has been studied[69] by the pressure-jump technique. Three relaxation times were found for the first two systems; in the case of malonate they were attributed to the formation of the complexes $[(VOOH)_2mal]$, $[VO(mal)]$, and $[VO(mal)_2]^{2-}$, whereas in the case of oxalate they were attributed to the formation of $[VO(ox)]$ and the two isomeric complexes $[VO(ox)_2]^{2-}_{ax}$ and $[VO(ox)_2]^{2-}_{eq}$. The two relaxation times for the tartrate systems were ascribed to the formation of $[VO(tar)]$ or $[VO(tarH)]^+$ and $[VO(tar)]_2$. It was also found that the formation of the dimer takes place stereospecifically such that no mixed complex (VO–L-tar–VO–D-tar) is formed.

The rate constants for the formation of the murexide complexes of Ho^{3+}, Dy^{3+}, Tb^{3+}, and Gd^{3+} in 50% aqueous ethanol differ very little from those obtained in water and it is suggested[70] that ligand effects are important in these systems.

The kinetics of the formation of the 'brown' plutonium(IV)–hydrogen peroxide complex have been investigated[71] and the following rate law found:

$$\mathrm{d[complex]/d}t = [H_2O_2][Pu^{IV}]^2\{k_2[H^+]^{-1} + k_3[H^+]^{-2}\}$$

The values of k_2 and k_3 and their activation parameters were determined but it was impossible to distinguish between two likely reaction mechanisms, namely (20)—(24) and (25)—(29).

$$Pu^{4+} + H_2O \rightleftharpoons PuOH^{3+} + H^+ \quad \text{(fast)} \tag{20}$$

$$Pu^{4+} + PuOH^{3+} \rightleftharpoons [Pu_2OH]^{7+} \quad \text{(fast)} \tag{21}$$

$$2PuOH^{3+} \rightleftharpoons [Pu_2(OH)_2]^{6+} \quad \text{(fast)} \tag{22}$$

followed by

$$[Pu_2OH]^{7+} + H_2O_2 \longrightarrow [Pu(OO)(OH)Pu]^{5+} + 2H^+ \quad \text{(slow)} \tag{23}$$

and

$$[Pu_2(OH)_2]^{6+} + H_2O_2 \longrightarrow [Pu(OO)(OH)Pu]^{5+} + H^+ + H_2O \quad \text{(slow)} \tag{24}$$

$$Pu^{4+} + H_2O_2 \rightleftharpoons [Pu^{4+}\text{—}H_2O_2] \quad \text{(fast)} \tag{25}$$

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[69] H. Hoffmann and W. Ulbricht, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 1052.
[70] J. L. Bear and C. T. Lin, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2368.
[71] A. Ekstrom and A. McLaren, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1009.

or

$$\mathrm{PuOH^{3+} + H_2O_2 \rightleftharpoons [PuOH^{3+}—H_2O_2]} \quad \text{(fast)} \qquad (26)$$

followed by

$$\mathrm{[Pu^{4+}—H_2O_2] + PuOH^{3+} \longrightarrow [Pu(OO)(OH)Pu]^{5+} + 2H^+} \quad \text{(slow)} \qquad (27)$$

or

$$\mathrm{[PuOH^{3+}—H_2O_2] + Pu^{4+} \longrightarrow [Pu(OO)(OH)Pu]^{5+} + 2H^+} \quad \text{(slow)} \qquad (28)$$

and

$$\mathrm{[PuOH^{3+}—H_2O_2] + PuOH^{3+} \longrightarrow [Pu(OO)(OH)Pu]^{5+} + H^+ + H_2O} \quad \text{(slow)} \qquad (29)$$

4 The Effect of Bound Ligands

Bivalent Metals M^{2+} in Water.—There exists a fairly extensive literature on the thermodynamics of the formation of mixed-ligand and 1 : 2 complexes but it is difficult in most cases to make more than a very approximate estimate of the stability constants for such a compound. Tanaka has proposed[72] a method, based on mechanistic considerations, for predicting the formation constant of a mixed-ligand complex. The rate of dissociation of the ligand L from a mixed-ligand complex MAL is assumed to be inversely proportional to the Brønsted basicity and the electron-donating ability of L and proportional to the electron-donating ability of the remaining ligand A. The logarithmic formation constant of MAL is then given by

$$\log K^{\mathrm{L}}_{\mathrm{MAL}} = \log K^{\mathrm{L}}_{\mathrm{ML}} + (\log K_{\mathrm{os(MA,L)}} - \log K_{\mathrm{os(M,L)}}) + \log\left(\frac{\text{number of } \mathrm{H_2O} \text{ in MA}}{\text{number of } \mathrm{H_2O} \text{ in M}}\right) + \sum^{I}\sum^{J} \delta_{ij}\mathrm{X}_i(\mathrm{A})\mathrm{Y}_j(\mathrm{L})$$

where $K^{\mathrm{L}}_{\mathrm{ML}}$ is the stability constant of ML, $K_{\mathrm{os(MA,L)}}$ and $K_{\mathrm{os(M,L)}}$ the outer-sphere formation constants for [MA,L] and [M,L], respectively, δ_{ij} the effect of the donor atom X_i in the ligand A on the donor atom Y_j in the ligand L, and $\mathrm{X}_i(\mathrm{A})$ and $\mathrm{Y}_j(\mathrm{L})$ the number of the donor atoms X_i in A and Y_j in L, respectively. The equation therefore allows us to predict $\log K^{\mathrm{L}}_{\mathrm{MAL}}$ (and $\log K^{\mathrm{L}}_{\mathrm{ML_2}}$) from the known value of $\log K^{\mathrm{L}}_{\mathrm{ML}}$. The author has used the formation constants for various nickel complexes involving amines and aminocarboxylates to calculate δ_{ij} for amine nitrogens and carboxylates. Thus, for example, δ_{NN} (the effect of an amine nitrogen in A or L on an amine nitrogen in the second ligand L) = -0.25 and δ_{ON} (the effect of a carboxylate in A or L on an amine

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[72] M. Tanaka, *J. Inorg. Nuclear Chem.*, 1973, **35**, 965.

nitrogen in the second ligand L) = δ_{NO} (the effect of an amine nitrogen in A or L on a carboxylate in the second ligand L) = +0.11 and, consequently, a 1 : 1 complex involving amine nitrogen as a donor atom gives rise to a less stable mixed complex with a ligand involving amine nitrogen(s) but a more stable mixed complex with a ligand involving carboxylate(s). The technique appears to have been very successful[72] for mixed complexes of nickel(II) in which steric interference is absent; it will be interesting to see whether it can be extended to include other metals.

Another communication has appeared[73] in which the mechanistic approach has been used as a basis for discussing the stabilities of mixed-ligand complexes of nickel(II). The title of the article is 'Mechanistic analysis of environmentally important mixed-ligand complex formation; Ni^{2+} as an example', and it must be particularly gratifying in these cost- and environment-conscious days for those who are responsible for the allocation of public funds to see that the study of inorganic reaction mechanisms has its wider implications.

Hunt and co-workers have reported[74] unusual water-exchange behaviour in the nickel(II) and copper(II) complexes of tren. Among the considerable number of Ni^{II} complexes this group has studied in recent years by means of ^{17}O n.m.r., only one apparent exchange rate for bound water in the partly substituted species has been observed in a given case. For the Ni^{II}–tren species, however, two distinct rates were observed. (A similar result has apparently been obtained[75] for the Ni^{II}–nta system.) This can be rationalized if the structure of this compound in water is *cis*-octahedral $[Ni(tren)(H_2O)_2]^{2+}$, in which the two water molecules have different environments, being *trans* to a tertiary and to a primary nitrogen, respectively. The two rate constants are, at 25 °C, 8.2×10^5 and *ca.* 9×10^6 s^{-1} with activation enthalpies of, respectively, 8 ± 1 and 8 ± 1.5 kcal mol^{-1}. The lower exchange rate is approximately that predicted on the basis of the other studies of nickel(II) bound to aliphatic amine ligands.

The case of Cu^{II}–tren is particularly interesting because only a single, relatively slow exchange process is observed. This has a rate constant (25 °C) of 2.5×10^5 s^{-1} and $\Delta H^{\ddagger}$ of 10.4 ± 0.3 kcal mol^{-1} – rate parameters more akin to those found typically with nickel(II) than with copper(II). The structure of the Cu^{II}–tren complex in aqueous solution is uncertain but it is suggested[74] that the co-ordination number of the metal is five.

Grant, Dodgen, and Hunt have expanded[76] their previous preliminary communication on the structure and water-exchange characteristics of the nickel(II)–edta complex and Melvin, Rablen, and Gordon have measured[77] the rates of formation of the phen, bipy, and terpy complexes of Ni^{2+}_{aq}, $[Ni(en)]^{2+}$, $[Ni(dien)]^{2+}$, and $[Ni(en)_2]^{2+}$ in water. As had been found in previous work,

[73] C. H. Langford, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 679.

[74] D. P. Rablen, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1972, **94**, 1771.

[75] J. Vriesenga and R. E. Connick, personal communication, quoted in ref. 74.

[76] M. W. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1971, **93**, 6828.

[77] W. S. Melvin, D. P. Rablen, and G. Gordon, *Inorg. Chem.*, 1972, **11**, 488.

the co-ordination of ethylenediamine or diethylenetriamine to nickel(II) substantially increases the rate of substitution at the metal ion. Although the rates of water exchange on the substituted metal increase regularly, it is apparent (Table 14) that these increases are not reflected as dramatically in the rates of ligand substitution. The authors use the data in Table 14 to evaluate K_{OS} on the assumption that the dissociative-interchange mechanism applies. Finding that it varies from 0.005 to 0.065 l mol^{-1}, they suggest that this should not be taken as an indication that a change in mechanism has occurred but, rather, that it merely reflects the tenuous assumptions made and the approximations used in the calculation. If this is so, and the interchange mechanism is correct here, it is clear that the actual rate of water exchange on a metal-ion complex cannot be inferred from its rate of ligand substitution.

Table 14 *Summary*[a] *of second-order substitution rate constants*[b] *for nickel*(II) *at* 25 °C

Ligand	$[Ni(H_2O)_6]^{2+}$	$[Ni(en)]^{2+}$	$[Ni(dien)]^{2+}$	$[Ni(en)_2]^{2+}$
phen	2.95	9.5	22.6	9.3
bipy	1.61	5.0	11	8.4
terpy	1.52	—	7.7	—
NH_3	2.8	12	43	—
H_2O[c]	0.44	4.40	18	54.5

[a] From ref. 77. [b] 10^3 l mol^{-1} s^{-1}. [c] First-order water-exchange rate constants/10^5 s^{-1}.

Further evidence that the number of aliphatic nitrogen atoms in the inner co-ordination sphere of nickel(II) can have a larger influence on ternary complex formation than the charge on the substituted metal ion has been provided[78] by a study with pyridine-2-azo-*p*-dimethylaniline (4). The rate constants and activation parameters were measured (Table 15) for the reaction of this neutral bidentate ligand with a series of seven substituted nickel species, bearing charges ranging from -3 to $+2$, in which the number of binding nitrogen atoms ranged from 0 to 4. The general pattern obtained with NH_3 is also found with (4) (Table 15) except that, in the latter case, the values of k_f^s for $[Ni(trien)]^{2+}$ and $[Ni(tren)]^{2+}$ are significantly lower than for NH_3. (k_f^s is the rate constant for the formation of the complex; it incorporates a statistical correction for the reduced number of water molecules on the substituted-metal species compared with the hexa-aquo-ion.) This is rationalized in terms of a contribution by ring closure to the rate-limiting process for these two species with the bidentate ligand. With minor fluctuations, $\Delta S_f^{\ddagger(s)}$ (the activation entropy for formation of the complex which has been adjusted in a similar way to the rate constant) is constant at *ca.* 0 cal mol^{-1} K^{-1} and the increase in k_f^s along the series is reflected largely in a decrease in $\Delta H_f^{\ddagger}$. A similar trend has been noted for the exchange parameters k_{ex} and $\Delta H_{ex}^{\ddagger}$ but no absolute correlation has been established.

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[78] M. A. Cobb and D. N. Hague, *J.C.S. Faraday I*, 1972, **68**, 932.

Table 15 *Kinetic data*[a] *for the formation of nickel*(II) *complexes in water* (*see text*)

System	k_f^s/l mol^{-1} s^{-1}	$\Delta H_f^\ddagger$/kcal mol^{-1}	$\Delta S_f^{\ddagger(s)}$/ cal mol^{-1} K^{-1}
Ni^{2+} + (4)	1.4×10^3	13.6	+1
Ni^{2+} + NH_3	2.8×10^3	—	—
$[Ni(TP)]^{3-}$ + (4)	4.0×10^3	14.1	+5
[Ni(ida)] + (4)	1.3×10^4	12.6	+3
[Ni(ida)] + NH_3	5.0×10^3	—	—
[Ni(mida)] + (4)	5.4×10^3	13.1	+3
$[Ni(nta)]^-$ + (4)	1.3×10^4	12.4	+2
$[Ni(nta)]^-$ + NH_3	1.4×10^4	—	—
$[Ni(dien)]^{2+}$ + (4)	9.4×10^4	10.3	−1
$[Ni(dien)]^{2+}$ + NH_3	7.8×10^4	—	—
$[Ni(trien)]^{2+}$ + (4)	7.5×10^4	8.8	−7
$[Ni(trien)]^{2+}$ + NH_3	1.0×10^6	—	—
$[Ni(tren)]^{2+}$ + (4)	5.5×10^4	9.8	−4
$[Ni(tren)]^{2+}$ + NH_3	2.0×10^6	—	—

[a] From ref. 78.

The rate constants for the reaction of $[Ni(nta)(H_2O)_2]^-$ with various ligands in their neutral and protonated forms have been reported,[11] as has that for the formation of the bis-complex of nickel(II) with the purine base theophylline.[56] Rate constants have also been reported for the formation of bis-complexes of cobalt(II), nickel(II), and copper(II) with L-proline,[59] L-hydroxypyroline,[59] glycyl-L-leucine,[54], L-leucylglycine,[54] α-alanine,[55] β-alanine,[55] iminodiacetic acid,[55] iminodipropionic acid,[55] and aspartic acid.[55]

It has been established that ternary complexes of copper(II) frequently have a high thermodynamic stability compared with the corresponding binary complexes. This is especially true of mixed-ligand complexes containing bipy or another aromatic ligand when the donor atoms of the second ligand are oxygens. As part of their programme of investigating the origin of this effect Pasternack *et al.*[79] have measured the rate constants for the reaction of $[Cu(bipy)]^{2+}$ with ethylenediamine and α- and β-alanine. The rate constants for attack by the zwitterion form of the amino-acids are zero, within experimental error, and those for en, α-alaninate, and β-alaninate are, respectively, $(2.0\pm0.4)\times10^9$, $(1.0\pm0.2)\times10^9$, and $(3.4\pm0.7)\times10^8$ l mol^{-1} s^{-1} at 25 °C. These are all comparable to k_f for the respective binary system and the results can be interpreted as providing some evidence for an S_N2 mechanism.

Sharma and Leussing have also studied[80, 81] the formation of ternary complexes of copper(II) and have concluded that the reactions are associative (S_N2) in character. Rates of formation and dissociation in Cu^{II}–serinate-(ser^-)–L systems have been investigated,[80] where L is ethylenediamine (en) or histamine (hm). The values, given in Table 16, are classified into three categories depending on the nature of the complex-formation reaction: (*a*) solvent

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[79] R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, 1972, **11**, 276.
[80] V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, 1972, **11**, 138.
[81] V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, 1972, **11**, 1955.

Table 16 *Forward and backward rate constants*[a] *for* Cu^{II}*–serinate–ethylenediamine–histamine complexes*

Reaction no.	*Reaction*	*Forward rate constant/* $l\ mol^{-1}\ s^{-1}$	*Backward rate constant/* s^{-1}
(*a*) *Solvent-substitution reactions*			
1	$Cu^{2+} + ser^- \rightleftharpoons [Cu(ser)]^+$	1.8×10^9	4.8×10
2	$[Cu(ser)]^+ + ser^- \rightleftharpoons [Cu(ser)_2]$	2.8×10^8	1.00×10^2
3	$Cu^{2+} + serH^{\pm} \rightleftharpoons [Cu(serH)]^{2+}$	1.2×10^3	2.4×10^2
7	$[Cu(en)]^{2+} + en \rightleftharpoons [Cu(en)_2]^{2+}$	3.6×10^9	6.1
9	$Cu^{2+} + hm \rightleftharpoons [Cu(hm)]^{2+}$	2.6×10^9	1.4
11	$[Cu(hm)]^{2+} + hm \rightleftharpoons [Cu(hm)_2]^{2+}$	5.6×10^8	2.8×10^2
12	$[Cu(en)]^{2+} + ser^- \rightleftharpoons [Cu(en)(ser)]^+$	6.2×10^8	1.2×10^2
20	$[Cu(hm)]^{2+} + ser^- \rightleftharpoons [Cu(hm)(ser)]^+$	1.1×10^8	1.3×10
(*b*) *Solvent-substitution accompanied by release of a proton to solvent*			
4	$[Cu(serH)]^{2+} \rightleftharpoons [Cu(ser)]^+ + H^+$	1.9×10^2 [b]	1.8×10^4
6	$Cu^{2+} + enH^+ \rightleftharpoons [Cu(en)]^{2+} + H^+$	1.7×10^5	5.6×10^4
8	$[Cu(en)]^{2+} + enH^+ \rightleftharpoons [Cu(en)_2]^{2+} + H^+$	6.3×10^4	5.4×10^5
10	$Cu^{2+} + hmH^+ \rightleftharpoons [Cu(hm)]^{2+} + H^+$	7.1×10^4	1.4×10^5
(*c*) *Ligand substitution accompanied by transfer of a proton from entering to leaving ligand*			
14	$[Cu(ser)_2] + enH^+ \rightleftharpoons [Cu(en)(ser)]^+ + serH$	8.3×10^6	8.3×10^4
22	$[Cu(ser)_2] + hmH^+ \rightleftharpoons [Cu(hm)(ser)]^+ + serH$	1.1×10^5	3.2×10^3

[a] From ref. 80. [b] In s^{-1}.

substitution; (*b*) solvent substitution with transfer of a proton to solvent; and (*c*) ligand substitution (other than solvent) with transfer of a proton from the entering to the leaving ligand. (It is interesting to note that these authors find evidence for the reaction of Cu^{II} with both the zwitterion and neutral forms of Hser.) Many aspects of the results are discussed in the original paper[80] but here we shall confine our discussion to reactions 12, 20, and 2 (Table 16). Electrostatic differences between the first two reactions

$$[Cu(en)]^{2+} + ser \rightleftharpoons [Cu(en)(ser)]^+ \qquad (k_{12} = 6.2 \times 10^8\ l\ mol^{-1}\ s^{-1})$$

and

$$[Cu(hm)]^{2+} + ser^- \rightleftharpoons [Cu(hm)(ser)]^+ \qquad (k_{20} = 1.1 \times 10^8\ l\ mol^{-1}\ s^{-1})$$

and the last

$$[Cu(ser)]^+ + ser^- \rightleftharpoons [Cu(ser)_2] \qquad (k_2 = 2.8 \times 10^8\ l\ mol^{-1}\ s^{-1})$$

can be corrected through their effects on K_{os}. Using the Fuoss equation and assuming an approach distance of 5 Å, the ratios of the rate constants for the reactions $M^{2+} + L^- \rightarrow ML^+$ and $M^+ + L^- \rightarrow ML$ are calculated to be

2.4 : 1. The ratios $k_{12} : k_{20} : k_2$ are observed to be 2.2 : 0.39 : 1. Thus, if k_2 is taken to be 'normal', the rate constant for the reaction of ser$^-$ with $[Cu(en)]^{2+}$ is also consistent with 'normal' substitution whereas the presence of the bulky histamine molecule leads to a relatively low rate constant. Furthermore, k_{-20} {the rate constant for the dissociation of ser$^-$ from $[Cu(hm)(ser)]^+$} is also substantially lower than the rate constant for the dissociation of this ion from the other serinato-complexes (k_{-1}, k_{-2}, k_{-12}), which all have the same value to within a factor of two. This rate reduction may indicate steric hindrance between the co-ordinated histamine molecule and an entering water molecule. In a dissociative mechanism for ligand substitution bulky non-leaving ligands appear to enhance the rate. The opposite effect shown here by histamine suggests that an associative mechanism holds for Cu^{II} substitution. Further evidence for this conclusion has been obtained[81] from the copper(II)–ethylenediamine–histamine system.

The glycine complex of cobalt(II)–bipy, like that of copper(II)–bipy, has a comparatively high stability constant relative to the bis-glycinate of the metal. It has been shown[82] that this can be attributed to a lower dissociation rate constant for the former (55 s^{-1} at 25 °C) than for the latter (330 s^{-1}), the formation rate constants being rather similar (1.6×10^6 and 2.0×10^6 l mol^{-1} s^{-1}, respectively).

The activation parameters have been reported[83] for the formation and dissociation of the 1 : 1 complexes between magnesium and manganese(II) and 8-hydroxyquinoline (oxine) and of the ternary complexes between oxine and the Mg^{II} and Mn^{II} complexes of five charged multidentate ligands. The results strengthen the previous conclusion that the first ligand has comparatively little influence on the kinetics of the reaction of magnesium with a second ligand. With manganese(II), however, the presence of adenosine 5′-triphosphate and polytriphosphate (but not adenosine 5′-diphosphate) in the inner co-ordination sphere of the metal has a large retarding effect on subsequent complex formation. The origin of this effect remains uncertain but it has been demonstrated[84] that it is not associated with a large decrease in the water exchange rate at $[Mn(atp)_{aq}]^{2-}$. (The matter is discussed in greater detail in Part III.)

On the other hand, it has been found[85] that the remaining water molecules in $[Mn(nta)_{aq}]^-$ {and also $[Mn(edta)_{aq}]^{2-}$, in which the metal is seven-co-ordinate} are considerably more labile than they are in hexa-aquomanganese. The magnitude of the labilizing effect of edta is roughly the same as that found[76] for the nickel(II) complex but, whereas in the nickel case there appears to be a significant decrease in $\Delta H^{\ddagger}_{ex}$, it appears that $\Delta S^{\ddagger}_{ex}$ is mainly affected with manganese(II). Nitrilotriacetate has a larger labilizing effect than edta on manganese(II) [though not on nickel(II)] and it is possible that this is associated

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[82] R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, 1972, **11**, 420.

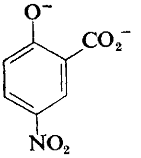
[83] D. N. Hague, S. R. Martin, and M. S. Zetter, *J.C.S. Faraday I*, 1972, **68**, 37.

[84] M. S. Zetter, H. W. Dodgen, and J. P. Hunt, *Biochemistry*, 1973, **12**, 778.

[85] M. S. Zetter, M. W. Grant, E. J. Wood, H. W. Dodgson, and J. P. Hunt, *Inorg. Chem.*, 1972, **11**, 2701.

with the presence of a tertiary nitrogen in the former ligand. No direct evidence was obtained for the kinetic non-equivalence of the water molecules [contrast the result for nickel(II)][75] although the authors do not exclude the possibility that an averaging process is occurring. It is pointed out that if the exchange data[85] are used to compute K_{os} for the outer-sphere complexes formed between $[Mn(nta)_{aq}]^-$ and the protonated and de-protonated forms of oxine from the measured[84] rate constants for complex formation two very low values are obtained (*ca.* 0.001 and 0.01 $l\,mol^{-1}$, respectively). In the case of the anion, one might suspect a charge effect but the value of K_{os} is also anomalously low for the neutral species (possibly even more so than for the anion). If ring closure with replacement of a more slowly exchanging water were rate determining for the substitutions, this should have been detected in the exchange experiment, and one is therefore left with the conclusion that some kind of concerted process involving the incoming (and possibly the bound) ligand is operative in complex formation at manganese(II).

The kinetics of formation of mixed complexes between magnesium and 5-nitrosalicylate (7) have been reported.[86] The results are compared with those



(7)

of the oxine study[84] and it is suggested that the complex-formation data can be rationalized in terms of the normal dissociative model provided the *local* charge densities on the metal ion and the co-ordinating atom of the incoming ligand are considered rather than the overall charges. Certainly, the use of the overall charges in the Fuoss equation does not predict sensible values of K_{os}.

The octahedral–square planar interconversion of the nickel(II) complex of 1,4,8,11-tetra-azaundecane (2,3,2-tet) has been studied[87] in water. The mechanism is assumed to be a two-step one [equations (30) and (31), in which L represents 2,3,2-tet]. On this basis and applying the steady-state approximation to the intermediate $[NiL(H_2O)]^{2+}$ the authors calculate a value of

$$[NiL]^{2+} + H_2O \underset{k_1}{\rightleftharpoons} [NiL(H_2O)]^{2+} \tag{30}$$

$$[NiL(H_2O)]^{2+} + H_2O \rightleftharpoons [NiL(H_2O)_2]^{2+} \tag{31}$$

$(5.6 \pm 0.3) \times 10^4\ l\,mol^{-1}\,s^{-1}$ for k_1 (at 23 °C) and $20 \pm 2\ kJ\,mol^{-1}$ and $-48.6 \pm 5\ J\,mol^{-1}\,K^{-1}$, respectively, for the associated activation enthalpy and entropy.

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[86] G. R. Cayley and D. N. Hague, *J.C.S. Faraday I*, 1972, **68**, 2259.

[87] K. J. Ivin, R. Jamison, and J. J. McGarvey, *J. Amer. Chem. Soc.*, 1972, **94**, 1763.

There have been several reports concerning studies of ligand-exchange reactions involving multidentate ligands. For example, Margerum and co-workers have found[88] that the reaction between copper–triglycine and edta is catalysed by the released triglycinate ion and they have shown that this autocatalysis reaction proceeds through the copper bis-triglycine complex, which is attacked more readily by edta^{4-} than is the mono-complex. The substitution of phen for trien in the complex $[Ni(trien)]^{2+}$ involves[89] the initial rapid formation of the mixed-ligand intermediate followed by a slow reaction which is first-order in this intermediate $[Ni(trien)(phen)]^{2+}$ and zero-order in phen. Other multidentate-ligand studies involving nickel(II) and copper(II) include those detailed in refs. 90—95.

Metals of Valency Three and Higher in Water.—An interesting aspect of a recent[96] pulse radiolysis study on the oxidation of ferrous sulphate solutions concerns the formation of the iron(III)–sulphate (inner sphere) complex. Reactions (32) and (33),

$$[Fe(H_2O)_6]^{3+},HO_2^- + SO_4^{2-} \rightleftharpoons [Fe(H_2O)_6]^{3+},HO_2^-,SO_4^{2-} \quad (32)$$

$$[Fe(H_2O)_6]^{3+},HO_2^-,SO_4^{2-} \longrightarrow [Fe(SO_4)aq]^+ + HO_2^- \quad (33)$$

represent steps in the I_d mechanism given by the overall equation

$$[Fe(H_2O)]^{3+},HO_2^- + SO_4^{2-} \longrightarrow Fe^{3+}SO_4^{2-} + HO_2^-$$

The forward rate constant for reaction (32) is greater than 4×10^6 l mol^{-1} s^{-1} (not unexpectedly) and that for reaction (33) is of the order of 10^4 s^{-1}; the equilibrium constant for (32) is 83 ± 20 l mol^{-1}. Since the inner-sphere sulphato-ferric complex is formed only slowly ($k_f = 4 \times 10^3$ l mol^{-1} s^{-1}) with hydrated ferric ions, it is evident that the presence of the hydroperoxide ion in the outer sphere accelerates the entry of sulphate into the inner sphere. The authors suggest that this may be associated with the partial neutralization by HO_2^- of the positive charge on the ferric ion.

Two problems of continuing interest in lanthanide chemistry are the mechanisms of complex formation in aqueous and other media and the question of whether the solvation-number change in the middle of the series is a function of the cation alone. Previous relaxation measurements have suggested that the spectroscopic and kinetic data for $Er(NO_3)_3$ could only be explained by invoking a solvation-number change in mixed solvents. A preliminary communication[97] on the ultrasonic absorbance of aqueous-

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[88] G. R. Dukes, G. K. Pagenkopf, and D. W. Margerum, *Inorg. Chem.*, 1971, **10**, 2419.
[89] R. K. Steinhaus and J. A. Boersma, *Inorg. Chem.*, 1972, **11**, 1505.
[90] M. Kopanica and V. Stará, *Coll. Czech. Chem. Comm.*, 1972, **37**, 80.
[91] V. Stará and M. Kopanica, *Coll. Czech. Chem. Comm.*, 1972, **37**, 2882.
[92] V. Stará and M. Kopanica, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3545.
[93] J. C. Lockhart and W. J. Mossop, *J.C.S. Dalton*, 1973, 19.
[94] J. C. Lockhart and W. J. Mossop, *J.C.S. Dalton*, 1973, 662.
[95] J. D. Carr and J. Vasiliades, *Inorg. Chem.*, 1972, **11**, 2104.
[96] G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J.C.S. Faraday I*, 1973, **69**, 1079.
[97] J. Reidler and H. B. Silber, *J.C.S. Chem. Comm.*, 1973, 354.

methanolic solutions of the nitrate and chloride of erbium indicates differences for the two anions. The authors suggest that only outer-sphere complexes are formed with the chloride, and that the solvation-number change found with the nitrate (but not the chloride) therefore does depend on the nature of the ligand.

Further evidence for a change in co-ordination number on traversing the lanthanide series has been presented for the edta[98,99] and bisdiglycolate[100] complexes in water, though the properties of the monoglycolates,[100] malonates,[101] and hydrogen malonates[101] do not seem to be consistent with such a change. It has been found[102] that the rate constant for the formation of the bisacetato-complex of dysprosium(III) is significantly larger than that of the monoacetato-complex.

Kinetic and thermodynamic studies on the reaction of oxine with the octahedral complex trioxo(diethylenetriamine)molybdenum(VI), [MoO_3(dien)], in aqueous solution, give almost identical results[103] to those reported previously for the reaction of oxine with molybdate, MoO_4^{2-}, and the authors conclude that [MoO_3(dien)] is extensively hydrolysed under the conditions they use, to give molybdate and free protonated diethylenetriamine. The rate constants for the formation of 1 : 1 and 1 : 2 complexes of molybdate with catechol have also been reported.[104]

Reactions in Non-aqueous Solvents.—N.m.r. studies on five co-ordinate complexes with identical ligands indicate that the barriers to intramolecular exchange are very low (*ca.* 5 kcal mol^{-1}), although it has been reported[105] that the ion $[Co(CNCMe_3)_5]^+$ is stereochemically rigid at -30 °C. Muetterties has recently shown[106] that reaction (34) has a relatively low activation energy

$$[Co(CNCMe_3)_5]^+ \rightleftharpoons [Co(CNCMe_3)_4]^+ + CNCMe_3 \qquad (34)$$

in dichloromethane or THF and has suggested that the four-co-ordinate complexes are key intermediates in solution reactions of cobalt(I) isocyanides.

The interconversion between octahedral $[Co(py)_4Br_2]$ and tetrahedral $[Co(py)_2Br_2]$ in nitromethane has also been studied[107] by n.m.r. The kinetic data are found to be consistent with the following mechanism, in which reaction (35) equilibrates rapidly compared with reaction (36).

$$^{oct}[Co(py)_4Br_2] \rightleftharpoons [Co(py)_3Br_2] + py \qquad (35)$$

$$[Co(py)_3Br_2] \rightleftharpoons {}^{tet}[Co(py)_2Br_2] + py \qquad (36)$$

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[98] T. Ryhl, *Acta Chem. Scand.*, 1972, **26**, 3955, 4001; 1973, **27**, 303.
[99] R. H. Betts and R. H. Voss, *Canad. J. Chem.*, 1973, **51**, 538.
[100] I. Grenthe and H. Ots, *Acta Chem. Scand.*, 1972, **26**, 1217, 1229.
[101] L. Dellien, *Acta Chem. Scand.*, 1973, **27**, 733.
[102] M. Doyle and H. B. Silber, *J.C.S. Chem. Comm.*, 1972, 1067.
[103] R. S. Taylor, P. Gans, P. F. Knowles, and A. G. Sykes, *J.C.S. Dalton*, 1972, 24.
[104] K. Kustin and S.-T. Liu, *J. Amer. Chem. Soc.*, 1973, **95**, 2487.
[105] R. B. King and M. S. Saran, *Inorg. Chem.*, 1972, **11**, 2112.
[106] E. L. Muetterties, *J.C.S. Chem. Comm.*, 1973, 221.
[107] R. D. Farina and J. H. Swinehart, *Inorg. Chem.*, 1972, **11**, 645.

^{14}N magnetic resonance and spectrophotometric data indicate[108] the presence of both [Co(trien)(MeCN)]$^{2+}$ and [Co(trien)(MeCN)$_2$]$^{2+}$ {in addition to [Co(MeCN)$_6$]$^{2+}$, [Co$_2$(trien)$_3$]$^{4+}$, and [Co(trien)$_2$]$^{2+}$} in acetonitrile solutions of cobalt(II)–trien and it is found that the lability of MeCN in the first co-ordination sphere is $>10^3$ times that of MeCN in the first co-ordination sphere of [Co(MeCN)$_6$]$^{2+}$ at 258 K. It appears that, in contrast to Me$_6$tren [which causes cobalt(II) to exhibit five-co-ordination in all complexes so far reported], trien imparts similar stabilities to cobalt(II) complexes exhibiting five- and six-co-ordination, and that the ligands which complete the occupancy of the first co-ordination sphere are of considerable importance in determining the co-ordination number of cobalt(II) in the complex.

Proton n.m.r. has been used[109] to measure the exchange rate of methanol from *cis* and *trans* co-ordination sites of [Co(NCS)(MeOH)$_5$]$^+$. It is concluded that the exchange occurs from both types of co-ordination site without internal rearrangement of the complex, and that the *cis* and *trans* exchange rates are equal; in addition, the exchange occurs exclusively between the bulk and bound environments. These results are markedly different from those reported previously for similar systems {*e.g.* [Co(OH$_2$)(MeOH)$_5$]$^{2+}$ and [CoCl(MeOH)$_5$]$^+$ in which the mean lifetime of a methanol molecule in the *trans* site is 0.59 times that for the *cis*}. The reason for the difference is unclear.

The kinetics of exchange of acetonitrile on the complexes of cobalt(II) and nickel(II) with tren and Me$_6$tren have been measured.[110] The two acetonitrile exchange rates observed for the non-equivalent sites on [Ni(tren)(MeCN)$_2$]$^{2+}$ (Table 17) are ascribed to the *cis* (more labile) and *trans* (less labile) positions relative to the tertiary nitrogen of tren by comparison with the Ni—N distances reported in [Ni(tren)(NCS)$_2$]. The kinetic parameters for both sites indicate considerable labilization relative to [Ni(MeCN)$_6$]$^{2+}$, but in the case of the methyl-substituted ligand there is a significant reduction in the exchange rate. Similar trends are observed for cobalt(II).

Table 17 *Kinetic parameters*[a] *for solvent exchange in acetonitrile*

Complex	k_{ex}/s^{-1}	*Temperature*/ °C	$\Delta H^{\ddagger}_{ex}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{ex}$/ cal mol^{-1} K^{-1}
[Ni(tren)(MeCN)$_2$]$^{2+}$	1.65×10^5	25	10.8	1.4
	$\gtrsim 2\times10^6$	−40	—	—
[Ni(Me$_6$tren)(MeCN)]$^{2+}$	$\lesssim 10^2$	80	—	—
[Co(tren)(MeCN)]$^{2+}$	$\gtrsim 2\times10^6$	−40	—	—
[Co(Me$_6$tren)(MeCN)]$^{2+}$	$\lesssim 10^2$	80	—	—

[a] From ref. 110.

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[108] S. F. Lincoln and R. J. West, *Austral. J. Chem.*, 1972, **25**, 469.
[109] J. R. Vriesenga, *Inorg. Chem.*, 1972, **11**, 2724.
[110] R. J. West and S. F. Lincoln, *Inorg. Chem.*, 1973, **12**, 494.

The reaction of $[Ni(NCS)]^+$ with NCS^- in methanol has been studied[111] by a pressure-jump technique and the results are interpreted in terms of the dissociative-interchange mechanism. A larger difference in k_f between acetate and trichloroacetate has been found[16] for the 1 : 2 complexes of nickel(II) in methanol than for the 1 : 1 complexes (see Section 2) and $[Ni(terpy)Cl(DMSO)_2]^+$ is more reactive[60] towards terpy than is $[Ni(DMSO)_6]^{2+}$.

The exchange kinetics of tren with $[Nd(tren)_2]^{3+}$ in acetonitrile indicate that the reaction is first-order with respect to both the complex and the ligand. The proposed[112] mechanism involves the simultaneous partial attachment of the free ligand and the partial unwrapping of co-ordinated tren from the metal ion.

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[111] J. Williams and S. Petrucci, *J. Phys. Chem.*, 1973, **77**, 130.

[112] M. F. Johnson and J. H. Forsberg, *Inorg. Chem.*, 1972, **11**, 2683.

5

Reactions of Co-ordinated Ligands

BY J. BURGESS

1 Aquation of Oxoanion Complexes

It is by now well established that although most aquation reactions of metal complexes in which an oxoanion is formally displaced by water proceed by central metal to oxygen bond breaking, nonetheless a significant number of oxoanion complexes aquate by breaking an element–oxygen bond within the anion, leaving the central metal to oxoanion-oxygen bond intact. A good example of complexes of the latter class are nitrito-complexes of chromium(III), where aquation involves nitrogen–oxygen rather than chromium–oxygen bond breaking.[1] The aquation of the hypophosphito-complex $[Cr(OH_2)_5(O_2PH_2)]^{2+}$ involves phosphorus–oxygen bond breaking, but the aquation of the phosphito-complex $[Cr(OH_2)_5(O_3PH_2)]^{2+}$ involves chromium–oxygen bond breaking.[2] The rate law for aquation of $[Ru(NH_3)_5(RCO_2)]^{2+}$ complexes consists of two terms. One of these is assigned to a mechanism involving carbon–oxygen bond fission, in a protonated derivative. The other term is assigned to ruthenium–oxygen bond fission.[3] A review of aquation of carboxylato-cobalt(III) complexes mentions cases in which carbon–oxygen bond breaking takes place.[4]

2 Solvolysis of Organic Ligands

The main interest centres on the hydrolysis of co-ordinated esters, though interest in peptide hydrolysis appears to be increasing. Experiments are conducted at two levels of inorganic relevance. In one type of study ligand solvolysis is studied for a preformed and characterized metal complex; in the other type one merely observes the effect of added inorganic species on an organic solvolysis. In this latter class of investigation the postulated intermediate complex may not be isolated or characterized. Several examples of the first type of study are discussed in the following paragraphs. Some examples of the second type are briefly mentioned; an example of this type of investigation which covers both ester and peptide hydrolysis is provided by a qualitative

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[1] T. C. Matts, P. Moore, D. M. W. Ogilvie, and N. Winterton, *J.C.S. Dalton*, 1973, 992.
[2] L. S. Brown and J. N. Cooper, *Inorg. Chem.*, 1972, **11**, 1154.
[3] A. Ohyoshi, A. Jyo, and N. Shin, *Bull. Chem. Soc. Japan*, 1972, **45**, 2121.
[4] M. E. Farago, M. A. R. Smith, and I. M. Keefe, *Coordination Chem. Rev.*, 1972, **8**, 95.

study of the effects of $[Co(trien)(OH)(OH_2)]^{2+}$ and of $[Co(dien)Cl_3]$ on hydrolysis rates.[5] Systems which are primarily of biochemical interest are dealt with in Part III of this Report.

Ester Hydrolysis.—Activation parameters for glycine ester hydrolysis, both of the free ester and of esters complexed as $[Co(en)_2(NH_2CH_2CO_2R)]^{3+}$, are listed in Table 1. For the ethyl ester, the observed greater rate of hydrolysis of the co-ordinated ester than of the free ester is a consequence of a much lower activation enthalpy for the former balanced by a smaller unfavourable contribution from $T\Delta S^{\ddagger}$. There are no activation parameters available for hydrolysis of the free methyl ester, but the activation parameters for hydrolysis of the co-ordinated methyl ester are similar to those for the similarly co-ordinated ethyl ester.[6] For the hydrolysis of methyl 2,3-diaminopropionate (Me-dap) the opposite situation obtains, the faster hydrolysis of the ester co-ordinated to copper(II) arising from a favourable $T\Delta S^{\ddagger}$ difference outweighing an unfavourable difference in $\Delta H^{\ddagger}$ values. In this and similar copper(II) and mercury(II) ester complexes the ester is not co-ordinated through its acyl oxygen; rate accelerations are in the region of 10^2—10^3. When the ester is co-ordinated through an acyl oxygen, as in cobalt(III) esters of type (1), a rate acceleration of *ca.* 10^6 is observed for hydrolysis of the co-ordinated ester.[7, 8]

Table 1 *Activation parameters for the hydrolysis of free and co-ordinated esters*

Compound	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
$[Co(en)_2(Me\text{-}gly)]^{3+}$	9.7	−33	6
$[Co(en)_2(Et\text{-}gly)]^{3+}$	9.3	−37	
Et-gly	14.3	−23	
$[Cu(Me\text{-}dap)_2]^{2+}$	13.2	−3	7
Me-dap	11.6	−20	8
Et-thiox/Mg^{2+}	6.3	−24	9
Et-thiox/Pb^{2+}	10.7	−6	
Et-thiox	9.9	−10	

In the previous paragraph we have noted two different systems in which metal-ion catalysis of co-ordinated ester hydrolysis has respectively a lower and a higher activation enthalpy than that for hydrolysis of the free ester. In the case of metal-ion-catalysed hydrolysis of ethyl thio-oxalate ($^-O_2CCOSEt$) it is noteworthy that whereas hydrolysis in the presence of lead(II) has a higher activation enthalpy than hydrolysis of the free ester, hydrolysis in the presence of magnesium(II) has a lower activation enthalpy (Table 1).[9]

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[5] A. Y. Girgis and J. I. Legg, *J. Amer. Chem. Soc.*, 1972, **94**, 8420.

[6] K. Nomiya and H. Kobayashi, *Z. phys. Chem. (Frankfurt)*, 1973, **84**, 206.

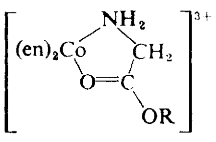
[7] R. W. Hay and P. J. Morris, *J.C.S. Dalton*, 1973, 56.

[8] R. W. Hay and P. J. Morris, *J.C.S. Perkin II*, 1972, 1021.

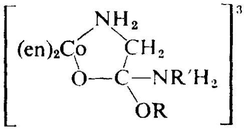
[9] R. J. Angelici and D. B. Leslie, *Inorg. Chem.*, 1973, **12**, 431.

Base hydrolysis of the methyl 6-aminohexanoate ester complex *cis*-$[Co(en)_2\{NH_2(CH_2)_5CO_2Me\}Cl]^{2+}$ takes place in two stages. In the first step chloride ion is displaced, with a second-order rate constant of 13 l mol^{-1} s^{-1} at 25 °C. The second step is base hydrolysis of the co-ordinated ester, for which the second-order rate constant is 0.22 l mol^{-1} s^{-1} at 25 °C. This ester hydrolysis rate is only slightly larger than that for the free ester, which is 0.148 l mol^{-1} s^{-1}. This small difference between rates of hydrolysis of free and complexed ester is the result of the large distance between the cobalt(III) cation and the actual reaction site in the molecule.[10]

All oxygen and nitrogen bases appear to act as specific nucleophiles towards esters in complexes of the type (1). Such complexes therefore also undergo aminolysis. In organic chemistry there are many ester-aminolysis reactions whose mechanism is not known, as it is generally impossible to decide between a concerted or an addition–elimination process for these. There has as yet been no unequivocal demonstration of the generation of an intermediate adduct to confirm the operation of the latter mechanism. However, it has recently proved possible to design a co-ordinated ester complex in which conditions are favourable for the detection of such an intermediate. A substrate containing (1) has a highly activated acyl ester centre and a poor leaving group. When $[Co(en)_2(isopropylglycinate)]^{3+}$ is treated with the ethyl ester of glycine, in dimethyl sulphoxide solution, it is possible to follow the kinetics of formation and of decomposition of the expected co-ordinated ester-aminolysis intermediate (2).[11] The rate laws and rate constants for these reactions, and some of the properties of the intermediate, have been established.[12] Reactions of α-ketocarboxylato-complexes $[Co(NH_3)_5(O_2CCOR)]^{2+}$ with hydroxylamine or with semicarbazide provide further similar instances of co-ordinated ligand reactions.[13]



(1)



(2)

The catalytic effect of nickel(II) on hydrolysis rates of the salicyl and phenyl esters of pyridine-2,6-dicarboxylic acid is ascribed to the intermediacy of a 1 : 1 complex between the ester and the nickel(II). Rates of hydrolysis and of reaction with hydroxide are reported.[14] Kinetic and equilibrium studies have

[10] R. W. Hay, R. Bennett, and D. J. Barnes, *J.C.S. Dalton*, 1972, 1524.

[11] D. A. Buckingham, J. Dekkers, A. M. Sargeson, and M. Wein, *J. Amer. Chem. Soc.*, 1972, **94**, 4032.

[12] D. A. Buckingham, J. Dekkers, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1973, **95**, 4173.

[13] G. Occupati and L. Pratt, *J.C.S. Dalton*, 1973, 1699.

[14] R. Breslow and C. McAllister, *J. Amer. Chem. Soc.*, 1971, **93**, 7096.

been undertaken of the role of nickel(II)–amino-acid complexes in the hydrolysis of esters of amino-acids. There is marked stereoselectivity in some of these reactions.[15]

Catalysis of ester hydrolysis by metal cations is not restricted to esters of organic acids. Both magnesium(II) and zinc(II) cause marked rate enhancements of hydrolysis of phosphate diesters. Here there is parallel hydrolysis of the free ester and of its metal complex under the conditions examined.[16]

Peptide Hydrolysis.—Copper(II) catalysis is observed for the hydrolysis of the methyl ester of glycylglycine, but not for the methyl ester of glycylsarcosine. This can be simply explained. Amide deprotonation is a necessary prerequisite for co-ordination to the copper. This can be accomplished for glycylglycine, but glycylsarcosine contains a methyl group rather than a proton on the appropriate nitrogen atom. The first-order dependence of the copper(II)-catalysed hydrolysis of the methyl ester of glycylglycine suggests rate-determining attack of hydroxide at the co-ordinated ester carbon atom. Zinc(II) catalyses the hydrolysis of amino-acid esters, but does not appear to catalyse hydrolysis of dipeptide esters.[17]

Solvolysis of other Organic Ligands.—A co-ordinated nitrile can be hydrolysed to a co-ordinated carboxamide:

e.g. $$[Co(NH_3)_5(NCR)]^{3+} \xrightarrow[aq]{OH^-} [Co(NH_3)_5(NHCOR)]^{2+}$$

For RCN = benzonitrile or 3- or 4-cyanophenol, this hydrolysis in aqueous solution is first-order in hydroxide-ion concentration. The rate enhancement due to the co-ordinated $[Co(NH_3)_5]^{3+}$ moiety is *ca.* 10^6 times. The kinetic parameters for hydrolysis of these co-ordinated nitriles are listed in Table 2.[18] A much greater rate enhancement, this time of at least 10^{15} times, is reported for the mercury(II)-catalysed hydrolyses of $[Co(en)_2\{H_2N(CH_2)_nCN\}Br]^{2+}$, where n = 1 or 2. The rates are first-order in mercury(II) concentration, but

Table 2 *Kinetic parameters for the hydrolysis of co-ordinated nitriles in complexes* $[Co(NH_3)_5(NCR)]^{3+}$ *in basic solution* (*from ref.* 18)

RNC	k_{25}/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
C_6H_5CN[a]	18.8	16.6	+2.7
3-HO·C_6H_4·CN	3.57	15.1	−5.5
4-HO·C_6H_4·CN	0.18	16.3	−7.4

[a] The kinetic parameters for base hydrolysis of unco-ordinated C_6H_5CN are, in 50% aqueous acetone, $k_{25} = 8.2 \times 10^{-6}$ s^{-1}, $\Delta H^{\ddagger}$ = 19.9 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −15.2 cal deg^{-1} mol^{-1}.

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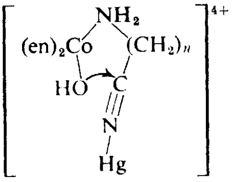
[15] J. R. Blackburn and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1597, 1605, 2421.

[16] J. J. Steffens, E. J. Sampson, I. J. Siewers, and S. J. Benkovic, *J. Amer. Chem. Soc.*, 1973, **95**, 936.

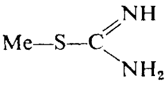
[17] R. Nakon and R. J. Angelici, *J. Amer. Chem. Soc.*, 1973, **95**, 3170.

[18] D. Pinnell, G. B. Wright, and R. B. Jordan, *J. Amer. Chem. Soc.*, 1972, **94**, 6104.

are independent of the pH. The suggested reaction sequence is (i) mercury(II)-assisted removal of bromide, (ii) rapid attachment of water to the cobalt, and (iii) mercury(II)-assisted nucleophilic attack by bound hydroxide at the nitrile (3) to generate the amide complex.[19] Methylisothiourea (4) hydrolyses more rapidly when co-ordinated to platinum(II).[20]



(3) n = 1 or 2



(4)

Kinetic parameters have been determined and discussed for copper(II)-catalysed solvolyses of a range of terdentate (donor atoms ONS) and quadridentate (donor atoms O_2N_2) Schiff-base complexes of nickel(II), in dimethyl sulphoxide.[21] The rate law for solvolyses of substituted dithiocarbamato (R_2dtc) complexes of nickel(II) in the presence of added copper(II), in such solvents as dimethyl sulphoxide, dimethylacetamide, or acetone, is

$$-\mathrm{d}[\mathrm{Ni(R_2dtc)_2}]/\mathrm{d}t = \{k_1 + k_2[\mathrm{Cu^{2+}}]\}[\mathrm{Ni(R_2dtc)_2}]$$

The k_1 and k_2 terms are assigned to dissociative and associative pathways respectively.[22]

3 Hydrogen Exchange

Rate constants and activation parameters for hydrogen–deuterium exchange at *trans*-$[\mathrm{Co(dien)_2}]^{3+}$ are similar to those for similar complexes of *N*-methylethylenediamine and of tetraethylenepentamine, which suggests a similarity of mechanism. This paper contains a brief but useful review of racemization and hydrogen–deuterium exchange kinetics for this type of complex.[23] The malonate-methylene protons in $[\mathrm{Co(LL)_2(mal)}]^+$, where LL = en or bipy, undergo exchange in D_2SO_4–D_2O. The kinetics of this exchange can be monitored by n.m.r. spectroscopy; rates are first-order in D^+ concentration. Activation parameters are given in Table 3; there is a remarkably large difference between these parameters for the two complexes. The enolization mechanism established for hydrogen–deuterium exchange of edta complexes

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[19] D. A. Buckingham, A. M. Sargeson, and A. Zanella, *J. Amer. Chem. Soc.*, 1972, **94**, 8246.

[20] Yu. N. Kukushkin, V. V. Sibirskaya, S. D. Banzargashieva, and V. N. Shvedova, *Russ. J. Inorg. Chem.*, 1972, **17**, 298.

[21] W. W. Fee, J. D. Pulsford, and P. D. Vowles, *Austral. J. Chem.*, 1973, **26**, 1459; W. W. Fee and J. D. Pulsford, *ibid.*, p. 1475.

[22] W. W. Fee, D. E. McElholum, A. J. McPherson, and D. L. Rundle, *Austral. J. Chem.*, 1973, **26**, 1207.

[23] G. H. Searle and F. R. Keene, *Inorg. Chem.*, 1972, **11**, 1006.

may also operate for these malonate complexes. It proved impossible to extend this investigation to similar ethylmalonate complexes as they aquate too rapidly.[24] Half-lives for hydrogen exchange with a series of complexes $[Co(dmgH)_2L_2]^{n-}$ have been determined by ^1H n.m.r. spectroscopy. The exchange rates decrease in the order L = $MeNH_2$ (k_{20} = 2.5×10^{-5} s^{-1}) > NH_3 (k_{20} = 1.7×10^{-5} s^{-1}) > NO_2^- (no k_{20} as complex decomposes too quickly) > CN^- (k_{20} = 9.6×10^{-7} s^{-1}). The exchange rate for the free ligand at 20 °C is $< 2 \times 10^{-7}$ s^{-1}. The order of reactivities for these complexes correlates inversely with the positions of the ligands in the spectrochemical series.[25]

Table 3 *Activation parameters for hydrogen–deuterium exchange between* $[Co(LL)_2(mal)]^+$ *cations and* D_2SO_4–D_2O (*from ref.* 24)

LL	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
en	27.4 ± 3	$+27 \pm 6$
bipy	18.4 ± 4	-1 ± 5

The pH and temperature dependences of linewidths and chemical shifts for aqueous solutions of $[Ru(NH_3)_6]^{3+}$ have been discussed in terms of proton exchange between complex and solvent. This process is base-catalysed, with an activation enthalpy of 20 kcal mol^{-1} and an activation entropy of +51 cal deg^{-1} mol^{-1}. These activation parameters are presumably composite quantities, as an activation enthalpy as high as 20 kcal mol^{-1} is inconsistent with the very high rates observed. The formation of deprotonated species and ion pairs is proposed, to produce an appropriate multi-stage reaction whose overall activation parameters will include ΔH° and ΔS° terms for the relevant pre-equilibria.[26]

In solutions containing $[Pt(NH_3)_6]^{4+}$ and its conjugate base $[Pt(NH_3)_5(NH_2)]^{3+}$, proton exchange with the solvent takes place predominantly with the latter conjugate base. This proton exchange is fast, and involves one conjugate-base ion and one water molecule (5). Proton transfer in (5) is very fast, having activation parameters of $\Delta H^{\ddagger}$ = 0.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −18 cal deg^{-1} mol^{-1}. The rate-determining step in the overall exchange process is the exchange of water between (5) and bulk solvent.[27] The situation here is very different from that established for proton exchange in the analogous aluminium(III)–water system.[28] *N*-Deuteriation of racemic $[Pt(dimetn)(NH_3)_2]^{2+}$ is slightly faster than that of the *meso*-form. This difference, a factor of about two in rate constant, can be understood in geometrical terms in that the leaving proton is slightly more accessible for removal by a hydroxide ion in the racemic form.[29]

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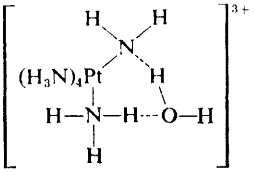
[24] M. E. Farago and M. A. R. Smith, *J.C.S. Dalton*, 1972, 2120.
[25] H. Yoneda, I. Takagi, and Y. Morimoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 3493.
[26] D. Waysbort and G. Navon, *J. Phys. Chem.*, 1973, **77**, 960.
[27] E. Grunwald and D.-W. Fong, *J. Amer. Chem. Soc.*, 1972, **94**, 7371.
[28] E. Grunwald and D.-W. Fong, *J. Amer. Chem. Soc.*, 1969, **91**, 2413.
[29] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 1972, **11**, 124.



(5)

Hydrogen exchange with the acetonylphosphonate anion, $[MeCOCH_2PO_3]^{2-}$, is much accelerated by the presence of magnesium(II). The variation of exchange rate with pH (pD) has been established in the region 5—12. In the acid region rates vary with pH because of equilibrium protonation of the substrate; in the alkaline region rates increase with increasing base concentration owing to attack by OD^-.[30]

4 Oxygen Exchange

Previous studies of the exchange of labelled carbon dioxide between the $[Co(NH_3)_5(CO_3)]^+$ cation and carbonate are to a certain extent inconsistent. By studying the kinetics of ^{18}O exchange between water and dissolved carbonate (CO_3^{2-}–HCO_3^-) on the one hand, and between water and $[Co(NH_3)_5(CO_3)]^+$ on the other, it has now been shown that the earlier proposal[31] that it is the hydration of carbon dioxide which is the rate-determining step in the $[Co(NH_3)_5(CO_3)]^+$–carbonate exchange reaction is correct.[32]

Another ^{18}O exchange which has been subject to rescrutiny is that between $[Co(ox)_3]^{3-}$ and water. At about room temperature, in acid solution, the carbonyl oxygens exchange more rapidly than the carboxy oxygens,[33, 34] but at higher temperatures of *ca.* 55 °C the exchange of the two types of oxygen is kinetically indistinguishable. The activation energy for oxygen exchange with the inner oxygens is 42 kcal mol^{-1}, but with the outer oxygens only 17 kcal mol^{-1}.[34] Earlier discrepancies between reports of six oxygens or twelve oxygens of $[Co(ox)_3]^{3-}$ exchanging with water can probably be attributed to differences in time-scale and in temperature between the various experiments. The present results are compared with those for aquation and for racemization of this complex.

There has been considerable activity over the past few years in the area of oxygen exchange between chromium(III)–oxalate complexes and water.[35] Now a consistent pattern appears to be emerging, as is shown by the discussion of recent work on oxygen exchange with the $[Cr(ox)(OH_2)_4]^+$ cation. In this, as in other chromium(III)- and platinum(II)-oxalate complexes, all the oxalate

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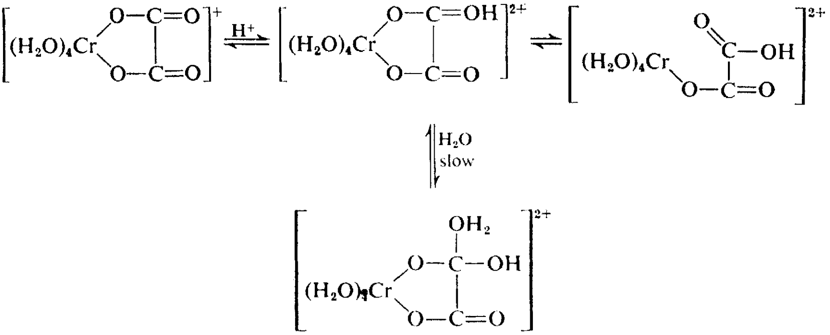
[30] R. Kluger and P. Wasserstein, *J. Amer. Chem. Soc.*, 1973, **95**, 1071, 4473.
[31] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 1968, **90**, 6360.
[32] D. J. Francis and R. B. Jordan, *Inorg. Chem.*, 1972, **11**, 1170.
[33] J. A. Broomhead, I. Lauder, and P. Nimmo, *J. Chem. Soc.* (*A*), 1971, 645.
[34] A. L. Odell and D. B. Rands, *J.C.S. Dalton*, 1972, 749.
[35] See, for example, p. 200 of Vol. 1 and p. 224 of Vol. 2 of this Report.

oxygens exhibit kinetic equivalence. This contrasts with the kinetic inequivalence of the two types of oxalate oxygen demonstrated foı some cobalt(III) (see above) and rhodium(III) complexes. Oxygen exchange with the chromium(III)–oxalate complexes is thought to take place with bidentate oxalate, but the oxygens are rendered equivalent by relatively easy formation and reorganization of a unidentate oxalate species (Scheme 1). Kinetic results for a variety of oxalato-chromium(III) complexes are collected together in the reference under discussion; for the $[Cr(ox)(OH_2)_4]^+$ cation the activation energy for oxygen exchange is 17.1 ± 1.5 kcal mol^{-1}.[36]



Scheme 1

Exchange of ^{18}O between edta and water is catalysed by the presence of metal cations. The catalytic efficiency is strongly dependent on the charge on the cation. The half-life for exchange in the presence of Th^{4+} is 10 min at 100 °C; in the presence of Ca^{2+} it is more than 100 days. There is a ten-fold change in catalytic effect between the two ends of the lanthanide(III) series of cations. The detailed variation of rates with the nature of the Ln^{3+} cation suggests a change from nine-co-ordination to eight-co-ordination in $[Ln(edta)(OH_2)_n]^-$ in the region of holmium. This rate variation is consistent with a gradual change of the ratio of nine- to eight-co-ordinate complexes in this region; the ratios have been estimated from the kinetics and are tabulated in the reference cited.[37]

5 Ligand Rearrangements

Two papers deal with the effect of co-ordinating cations on the case of rotation about carbon–nitrogen bonds in organic molecules. The effect of the variation of oxidation state of the cation on the barrier to rotation has been probed for a series of substituted dithiocarbamato (R_2dtc) complexes of iron. In the iron(II) derivatives $[Fe(R_2dtc)_2(phen)]$ and $[Fe(R_2dtc)_2(bipy)]$, $\Delta G^{\ddagger}$ is *ca.* 8.6 kcal mol^{-1}; in $[Fe^{III}(R_2dtc)_3]$ $\Delta G^{\ddagger}$ is *ca.* 12 kcal mol^{-1}; and in $[Fe^{IV}(R_2dtc)_3]^+$

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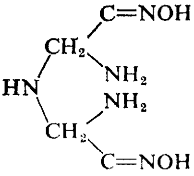
[36] S. G. Gourley and R. M. Milburn, *Inorg. Chem.*, 1972, **11**, 2262.

[37] R. H. Betts and R. H. Voss, *Canad. J. Chem.*, 1973, **51**, 538.

cations $\Delta G^{\ddagger}$ is *ca.* 15 kcal mol^{-1}. In all cases $\Delta G^{\ddagger}$ was determined at 25 °C in CD_2Cl_2 solution. The observed trend can readily be rationalized in terms of the effect of varying the iron–sulphur π-bonding on the carbon–nitrogen bond order in the co-ordinated R_2dtc ligands.[38] The barrier to rotation about carbon–nitrogen bonds in 2,2-iminobis(acetamidoxime) (6) is 10.5 ± 0.3 kcal mol^{-1}. This barrier increases by *ca.* 1 kcal mol^{-1} on co-ordinating (6) to zinc(II) or to magnesium(II). However, the significance of this comparison may well be questioned, as the relevant n.m.r. spectra of the three compounds were obtained in three different solvents.[39]



(6)

6 Other Reactions of Organic Ligands

A large number of M^{2+} and M^{3+} cations catalyse the loss of carbon dioxide from oxaloacetic acid to give pyruvic acid:[40, 41]

$$HO_2CCOCH_2CO_2H \longrightarrow CH_3COCO_2H + CO_2$$

The catalysts include Be^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Y^{3+}, La^{3+}, Gd^{3+}, and Lu^{3+}. The reaction mechanism proposed is the fast formation of a 1 : 1 complex followed by rate-determining loss of carbon dioxide from this complex. The cations thus affect the rate of loss of carbon dioxide in two ways, through the value of the pre-equilibrium complex-formation constant and through the consequences of their electron-withdrawing effect on the actual rate of carbon dioxide loss from the complex. The activation enthalpy is actually higher for the cation-catalysed reaction than for that of free oxaloacetic acid – the observed greater rates in the presence of the cations arise from a large, favourable $T\Delta S^{\ddagger}$ difference. There is a $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ correlation for all these cation-catalysed reactions.[41]

Pyrazole (7) undergoes rather more rapid iodination when it is complexed with nickel(II). The pH-dependence of iodination rates also differs for free pyrazole and its nickel complex. This difference arises from the additional pH-dependent equilibrium between aquo- and hydroxo-ligands on the nickel in the complex.[42] The substituent effect of the —CH_2—Co(dmgH)$_2$py moiety in

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[38] B. L. Edgar, D. J. Duffy, M. C. Palazzotto, and L. H. Pignolet, *J. Amer. Chem. Soc.*, 1973, **95**, 1125.

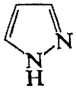
[39] R. E. Cramer and R. DeRyke, *Canad. J. Chem.*, 1973, **51**, 892.

[40] G. Duc and G. Thomas, *Bull. Soc. chim. France*, 1972, 4439.

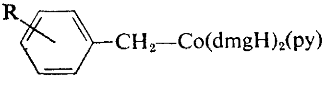
[41] H. Ito, H. Kobayashi, and K. Nomiya, *J.C.S. Faraday I*, 1973, **69**, 113.

[42] J. D. Vaughan and W. A. Smith, *J. Amer. Chem. Soc.*, 1972, **94**, 2460.

electrophilic aromatic substitution lies between those of the methyl and methoxy-groups. This has been established by experiments on the compounds (8), where R = H, 2-Me, or 4-Me.[43]



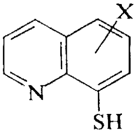
(7)



(8)

Rates of halogenation of co-ordinated acetylacetonate by *N*-halogenosuccinimides have been established for two complexes. Both reactions followed second-order kinetics in chloroform solution at 0 °C. The second-order rate constant for the chlorination of [Co(acac)$_3$] is 7.5×10^{-3} l mol^{-1} s^{-1} and that for the bromination of [Cr(acac)$_3$] is 1.29×10^{-3} l mol^{-1} s^{-1}.[44]

Kinetic parameters are reported for the reaction of nickel(II) complexes of substituted 8-mercaptoquinolines (9) with benzyl bromide and with methyl iodide. Reaction rates were correlated according to the Hammett equation; a ρ value of -2.9 was obtained for both halides, indicating a highly polarized carbon–halide bond. Activation enthalpies lie in the range 10—16 kcal mol^{-1} and activation entropies in the range -28 to -38 cal deg^{-1} mol^{-1}. These negative activation entropies and the Hammett ρ values are both consistent with the postulated template mechanism for these reactions.[45]



(9)

In basic solutions, the following intramolecular ligand condensation between ethylenediamine and co-ordinated nitrile occurs (X = Cl or Br):

$$[Co(en)_2(NH_2CH_2CN)X]^{2+} \longrightarrow [Co(en)\{NH_2CH_2C(NH_2){=}NCH_2CH_2NH_2\}X]^{2+}$$

An *X*-ray structural determination of the product suggests that condensation has taken place at the nitrogen *trans* to the chloride in the starting compound. The first step in the mechanism is deprotonation, shown to be fast in ancillary ^{1}H n.m.r. experiments. Then follows nucleophilic attack at the nitrile carbon atom by the co-ordinated amine. The rate law is

$$-d[Co(en)_2(NH_2CH_2CN)X^{2+}]/dt = k_2[Co(en)_2(NH_2CH_2CN)X^{2+}][OH^-]$$

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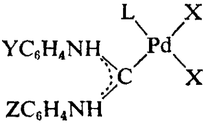
[43] S. N. Anderson, D. H. Ballard, and M. D. Johnson, *J.C.S. Perkin II*, 1972, 311.
[44] G. N. Salaita and L. A. Al-Odeh, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2116.
[45] J. C. Shoup and J. A. Burke, *Inorg. Chem.*, 1973, **12**, 1851.

Rate constants (k_2) at 25 °C are 1.64×10^4 l mol^{-1} s^{-1} for the chloro-complex and 2.36×10^4 l mol^{-1} s^{-1} for the bromo-complex.[46] Another amine–cyanide condensation has been described for palladium(II) complexes. Compounds *cis*-[Pd(*p*-YC_6H_4NC)LX_2], where L = PPh_3 or $AsPh_3$ and X = Cl or Br, react with substituted anilines *p*-$ZC_6H_4NH_2$ in 1,2-dichloroethanes to give (10). The reaction is first-order in complex and first-order in amine. The reactivity trends suggest that the mechanism involves nucleophilic attack of the aniline at the co-ordinated carbon of the *p*-YC_6H_4NC (*cf.* nucleophilic attack by nitrogen compounds at carbon in metal hexacarbonyls). For the reaction in which Y = H, L = PPh_3, and Z = Me, the activation parameters are $\Delta H^{\neq}$ = 9.4 kcal mol^{-1}, $\Delta S^{\neq}$ = −35.1 cal deg^{-1} mol^{-1}. Such a negative value for $\Delta S^{\neq}$ is consistent with a four-centre transition state (11).[47]



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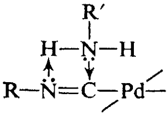


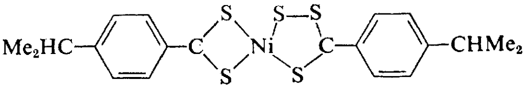
(11)

Isocyanates react with β-keto-imine ligands co-ordinated to copper(II) or to nickel(II) to produce amides. Some qualitative information on rate trends with variation of metal and variation of ligand has been reported.[48]

A plenary lecture at the Third Symposium on Coordination Chemistry, since published,[49] provides an extensive review of the kinetics and mechanisms of a range of reactions of co-ordinated organic compounds. Both substitution, including hydrolysis, and redox reactions are covered.

7 Other Reactions of Inorganic Ligands

Triphenylphosphine removes one sulphur atom from the thiocumato-complex (12), giving triphenylphosphine sulphide, $SPPh_3$. The reaction is second-order, with an activation energy of 7.8 ± 1.0 kcal mol^{-1}.[50]



(12)

The solvolysis of $[Cr(CN)_5(NO)]^{3-}$ in dimethyl sulphoxide is induced by alkyl halides, for example methyl iodide or t-butyl chloride. The mechanism is

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[46] D. A. Buckingham, B. M. Foxman, A. M. Sargeson, and A. Zanella, *J. Amer. Chem. Soc.*, 1972, **94**, 1007.

[47] B. Crociani, T. Boschi, M. Nicolini, and U. Belluco, *Inorg. Chem.*, 1972, **11**, 1292.

[48] J. W. Kenney, J. H. Nelson, and R. A. Henry, *J.C.S. Chem. Comm.*, 1973, 690.

[49] A. E. Martell, Proceedings of the 3rd Symposium on Coordination Chemistry, Debrecen, Hungary, 1970, Vol. 2, p. 125.

[50] J. P. Fackler, J. A. Fetchin, and D. C. Fries, *J. Amer. Chem. Soc.*, 1972, **94**, 7323.

thought to involve successive nucleophilic substitution steps, each followed by loss of the co-ordinated isocyanide so generated. The product is $[Cr(DMSO)_5(NO)]^{2+}$.[51]

Several other references deal with nitric oxide, either as a co-ordinated nitrosyl ligand or as the free molecule reacting with some other co-ordinated ligand. Thus the forward and reverse rate constants and activation parameters have been determined for the reaction of sulphite with nitroprusside:[52]

$$[Fe(CN)_5(NO)]^{2-} + SO_3^{2-} \rightleftharpoons [Fe(CN)_5(NOSO_3)]^{4-}$$

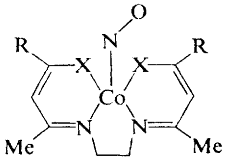
The oxidation of co-ordinated NO to NO_2 was recently reported for an organometallic osmium compound:[53]

$$[Os(CO)_2(NO)(PPh_3)_2]^+ \xrightarrow[RNC]{O_2} [Os(CO)(NO_2)(CNR)_2(PPh_3)_2]^+$$

Shortly afterwards a similar reaction more relevant to the present section was described:[54]

$$[CoL_4(NO)(base)] \xrightarrow{O_2} [CoL_4(NO_2)base]$$

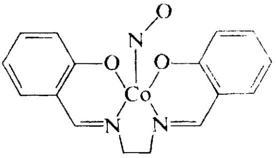
Here L_4 = a quadridentate Schiff base (NNOO ligating atoms) or $(en)_2$, and the base = (substituted) py or an aliphatic amine. A kinetic study[55] of the reaction of [Co(acacen)(NO)] (13) with oxygen in the presence of one of a number of bases, including (substituted) pyridines, imidazole, aliphatic amines, and phosphines, showed that the rate depends on the basicity of the added base except when steric hindrance becomes important, as, for example, when the added base is tricyclohexylphosphine. Rates were also determined for the reactions of [Co(salen)(NO)] (14), [Co(sacsacen)(NO)] (15), [Co(benacen)(NO)] (16), and $[Co(Me_2dtc)_2(NO)]$ (17) with oxygen in the presence of



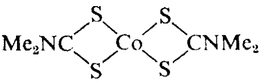
(13) X = O, R = Me

(15) X = S, R = Me

(16) X = O, R = Ph



(14)



(17)

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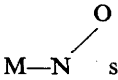
[51] D. C. McCain, *Inorg. Chim. Acta*, 1971, **5**, 611.

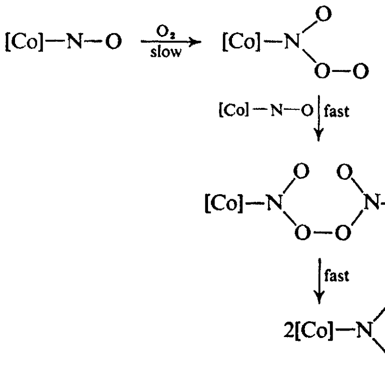
[52] C. Andrade and J. H. Swinehart, *Inorg. Chem.*, 1972, **11**, 648.

[53] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 119.

[54] S. G. Clarkson and F. Basolo, *J.C.S. Chem. Comm.*, 1972, 670.

[55] S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 1973, **12**, 1528.

pyridine or of tributylphosphine. In all cases rates were determined in acetone solution at 25 °C. The rate-determining step is thought to be electrophilic attack by oxygen at the nitrosyl nitrogen {Scheme 2; [Co] represents CoL_4(base)}. It is interesting to contrast these examples of electrophilic attack at nitrogen in a bent  system with established examples of nucleophilic attack at the nitrogen in complexes containing linear M—N—O.[55]



Scheme 2

One of the products of the reaction of $[Ru(NH_3)_5(NO)]^{3+}$ with hydroxide ion is $[Ru(NH_3)_5(NO_2)]^+$. Whereas for the similar reaction of $[Fe(CN)_5(NO)]^{2-}$ with hydroxide to give $[Fe(CN)_5(NO_2)]^{4-}$ there is kinetic and other evidence for a two-step mechanism with $[Fe(CN)_5(NO)(OH)]^{3-}$ as intermediate, there is as yet no evidence for a similar intermediate in the production of $[Ru(NH_3)_5(NO_2)]^+$.[56] The reaction of $[Ru(NH_3)_6]^{3+}$ with nitric oxide is thought, from the results of preliminary kinetic and tracer experiments, to involve attack by the nitric oxide at the NH_2 nitrogen atom of the conjugate base of the starting complex, $[Ru(NH_3)_5(NH_2)]^{2+}$. The product is the ruthenium(II) complex $[Ru(NH_3)_5(N_2)]^{2+}$, so this is a redox reaction as well as a co-ordinated-ligand substitution.[57]

When the reaction

$$\textit{trans}\text{-}[RuCl(NO)(diars)_2]^{2+} + 2N_3^- \longrightarrow [RuCl(N_3)(diars)_2] + N_2 + N_2O$$

was carried out with ^{15}N-labelled nitric oxide in the starting complex, the nitrous oxide produced contained approximately equal amounts of $^{14}N^{14}NO$ and $^{14}N^{15}NO$. Neither $^{15}N^{14}NO$ nor $^{15}N^{15}NO$ was detected amongst the

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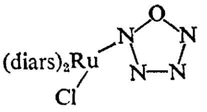
[56] F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.

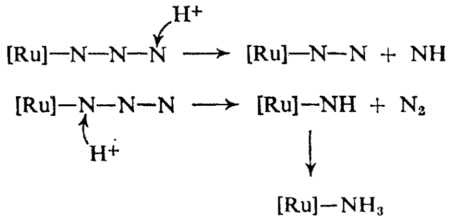
[57] S. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, 1972, **94**, 686.

products. The mechanism which most plausibly accommodates these facts is the formation of the species (18), with subsequent separation and then decomposition of N_4O.[58]



(18)

Co-ordinated Nitrenes.—The complex *trans*-$[RuCl(N_3)(diars)_2]$ reacts in hydrochloric acid to produce approximately equal numbers of molecules of $[RuCl(NH_3)(diars)_2]^+$ and $[RuCl(N_2)(diars)_2]^+$. When this reaction is carried out with ^{15}N-labelled complex containing specifically $Ru(^{15}N^{14}N^{14}N)$, the dinitrogen complex produced contains exclusively $Ru(^{15}N^{14}N)$. This result is consistent with a co-ordinated nitrene ($Ru^{15}N$) intermediate, similar to those previously reported for reactions of ruthenium(III)–azide complexes. However, product and product-distribution comparisons between the ruthenium(II)- and ruthenium(III)–azide plus hydrochloric acid reactions suggest that there must be some difference in mechanism between the complexes of the two different oxidation states. It is therefore proposed that for the *trans*-$[RuCl(N_3)(diars)_2]$ reaction the first step is protonation of the co-ordinated azide, which may occur at either end, followed by a split into N_2 plus NH, which gives an ammonia ligand one way and a dinitrogen ligand the other:*[58]



The reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with hydrazoic acid has as its first step an easy substitution at ruthenium to give $[Ru(NH_3)_5(N_3H)]^{2+}$. This decomposes to $[Ru(NH_3)_5(NH)]^{2+}$ plus dinitrogen. The main interest here, and in other similar cases, is whether this species behaves as an imido (19) or a nitrene (20) derivative. The chemical characteristics of the present intermediate indicate that it acts as an imido-complex.[59]

$$[(H_3N)_5Ru^{IV}(\underset{\cdot\cdot}{\ddot{N}}H)]^{2+} \qquad [(H_3N)_5Ru^{II}(\underset{\cdot\cdot}{\ddot{N}}H)]^{2+}$$

(19) (20)

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* Charges omitted in the interests of clarity.

[58] P. G. Douglas and R. D. Feltham, *J. Amer. Chem. Soc.*, 1972, **94**, 5254.

[59] P. S. Sheridan and F. Basolo, *Inorg. Chem.*, 1972, **11**, 2721.

In contrast, the behaviour of the intermediate $[Ir(NH_3)_5(NH)]^{3+}$ in the reaction of $[Ir(NH_3)_5(N_3)]^{2+}$ with acids in aqueous media suggests that it is a nitrene rather than an imido-complex. The rate law for the reaction of $[Ir(NH_3)_5(N_3)]^{2+}$ with acids indicates that rapid equilibrium protonation is followed by rate-determining reaction of the $[Ir(NH_3)_5(N_3H)]^{3+}$ conjugate acid. From the pH–rate profile, a pK_a value of -2.1 has been estimated for $[Ir(NH_3)_5(N_3H)]^{3+}$. The nitrene intermediate reacts avidly with such anions as HSO_4^- or Cl^-, to produce $[Ir(NH_3)_5(NH_2OSO_3)]^{2+}$ or $[Ir(NH_3)_5(NH_2Cl)]^{2+}$. These species have been characterized, and their hydrolysis to form $[Ir(NH_3)_5(NH_2OH)]^{3+}$ has been studied. The mechanism of these reactions could be S_N2 or S_N1cb in character: there is the customary kinetic ambiguity. The authors prefer S_N2, in the light of the established S_N2 mechanism for hydroxide-ion attack at free NH_2Cl.[60] A primarily preparative pendant to this work concerns the reaction of *trans*-$[Ir(en)_2(N_3)_2]^+$ with concentrated hydrochloric acid, and the subsequent conversion of *trans*-$[Ir(en)_2(NH_2Cl)_2]^{3+}$ into *trans*-$[Ir(en)_2(NH_3)_2]^{3+}$, by the action of hydrogen iodide. This series of reactions appears to be completely retentive of stereochemistry.[61]

Photochemical reactions of the iridium(III) and rhodium(III) complexes $[M(NH_3)_5(N_3)]^{2+}$ result in the production of a co-ordinated nitrene intermediate.[62] In concentrated hydrochloric acid the iridium(III) product is $[Ir(NH_3)_5(NH_2Cl)]^{3+}$, as in the equivalent thermal reaction.[60] These iridium(III) and rhodium(III) complexes thus behave photochemically in a similar manner to hydrazoic acid and to organic azides. Their behaviour contrasts with that of some other transition-metal azide complexes, *e.g.* those of ruthenium(II), where an azido-radical is the photochemical intermediate.[62] One can indeed group transition-metal azide complexes into three groups, with their thermal and photochemical reactions depending on the relative ease of oxidation or reduction (or neither) of the transition-metal centre.[60]

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[60] B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1972, **94**, 3786.

[61] T. R. Weaver, B. C. Lane, and F. Basolo, *Inorg. Chem.*, 1972, **11**, 2277.

[62] J. L. Reed, F. Wang, and F. Basolo, *J. Amer. Chem. Soc.*, 1972, **94**, 7173.

6

Solvent Effects

BY J. BURGESS

In the preceding five chapters of this Part, references to kinetic and mechanistic aspects of reactions of inorganic compounds have been classified and treated according to compound type. This arrangement, convenient though it is from most points of view, does lead to the dispersal of references to the role of the solvent in determining reactivities and mechanisms. Therefore in this present chapter we have gathered together references in which the role of the solvent figures prominently. As Volume 2 of this Report, unlike the first volume, did not contain a chapter specifically devoted to solvent effects, we have included a few of the more important references from Volume 2 in this chapter.

The material of this chapter is arranged in three sections, on reactions in pure (that is single) solvents, in mixed solvents, and in salt solutions. In each section the discussion covers a variety of solvent properties, including fundamental properties such as dielectric constant and composition, empirical solvent parameters such as Grunwald–Winstein Y and Reichardt E_T values, and more qualitative, elusive, or nebulous properties such as solvation and solvent structure. The aim is to provide convenient cross-referencing rather than a detailed and critical treatment. In some cases a less cursory mention will be found in Chapters 1—5 of this Part, or in Part II of Volume 2.

1 Pure Solvents

General.—The very fact that reactants are in solution rather than in the gas phase can have an important effect in determining the mechanism of a reaction. Thus halogen exchange between Lewis acid–base adducts R_3N,BX_3 and boron trihalides BX'_3 in the gas phase proceeds by boron–nitrogen bond breaking, whereas in solution a halogen-bridge mechanism appears to operate in most cases.[1] Polar solvents generally favour heterolytic bond breaking in substitution processes, but for reactions in non-polar solvents the alternative, homolytic, mode of bond breaking may operate. There has recently been considerable interest in mechanisms of the latter type, with several descriptions of inorganic reactions thought to proceed by an S_H2 mechanism. Unequivocal evidence has been presented for such a mechanism for substitution at silicon,[2] and good evidence for such a mechanism at germanium.[2] The first

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[1] B. Benton-Jones and J. M. Miller, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 485.
[2] A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, 1972, **94**, 1384.

examples of S_H2 substitution at a transition-metal centre, specifically at platinum(II), have been reported.[3]

Isotope Effects.—One of the earliest established uses of solvent variation in probing reaction mechanisms was the investigation of solvent isotope effects, especially H *versus* D, on reactivities. This approach continues to be fruitful. Solvent isotope effects on the hydrolysis of substituted benzenesulphonyl chlorides have been studied, and compared with those for similar organic compounds to establish the differences between chloride leaving from sulphur(VI) and from carbon(IV).[4] Although the activation energies for solvolysis of monofluorophosphate (PO_3F^{2-}) in H_2O and in D_2O are the same within (the relatively small) experimental uncertainties, there is an isotope effect of 2.1 for the solvolysis rates. This value supports the proposed mechanism of rapid pre-equilibrium formation of $H_3PO_3F^+$ previous to the solvolysis step.[5]

Rate constants and activation parameters have been determined for *cis*$\rightleftharpoons$*trans* isomerization of the $[Cr(ox)_2(OH_2)_2]^-$ anion in H_2O and in D_2O. The results are discussed in terms of solvent effects in a mechanism involving a trigonal-bipyramidal intermediate containing a unidentate oxalate ligand.[6] The complex $[Co(tren)Cl_2]^+$ is much more reactive than most cobalt(III)–amine–chloride cations. This high reactivity, ascribed to strain in the cobalt–amine part of the cation, is associated with deuterium isotope effects which differ markedly from those observed for reactions of other, 'normal', cobalt(III)–amine–chloride complexes.[7] The different solvating powers of H_2O and D_2O have been invoked to rationalize the difference between the reaction rates of $[Pt(dien)Br]^+$ with 3-cyanopyridine in these two solvents.[8] The results of an investigation of the formation and dissociation of the $[Nd(SO_4)]^+$ cation in H_2O and in D_2O by ultrasonic techniques suggested that solvent loss from the Nd^{3+}_{aq} cation is unlikely to be the rate-determining step in the complexation reaction.[9]

Solvation.—The co-ordinating power of the solvent plays an important part in determining reaction rates for methyl-exchange reactions of *sp*-block-element methyls. Compounds investigated included $GaMe_3$, $InMe_3$, $ZnMe_2$, and $CdMe_2$; the solvents were cyclopentane, toluene, diethyl ether, and triethylamine.[10] Rates of the forward (left→right) component of the equilibrium

$$[Ph_3C][SbCl_6] \rightleftharpoons SbCl_5 + Ph_3CCl$$

are related to solvent donor properties. Specifically, the logarithms of the rate constants correlate linearly, though inversely, with Gutmann donicity

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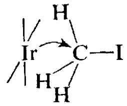
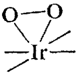
[3] D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 350.
[4] B. Rossall and R. E. Robertson, *Canad. J. Chem.*, 1971, **49**, 1451.
[5] K. W. Min, D. G. Rands, and R. L. Bain, *Inorg. Chem.*, 1972, **11**, 184.
[6] M. W. Rophael and M. A. Malati, *J. Chem. Soc. (A)*, 1971, 1903.
[7] S. G. Zipp and S. K. Madan, *Inorg. Chim. Acta*, 1972, **6**, 401.
[8] S. C. Chan and F. T. Wong, *Z. anorg. Chem.*, 1972, **387**, 120.
[9] H. B. Silber, *Chem. Comm.*, 1971, 731.
[10] J. Soulati, K. L. Henold, and J. P. Oliver, *J. Amer. Chem. Soc.*, 1971, **93**, 5694.

numbers (DN_{SbCl_5}) for six solvents. Results for $PhPOCl_2$ as solvent do not fit this correlation; this deviation was ascribed to the high viscosity of this solvent.[11] Differences between kinetic parameters for exchange between Me_3SbCl_2 and $Me_3SbCl(NO_3)$ in nitromethane and in dichloromethane solutions may arise at least in part from the differing abilities of these two solvents to solvate a possible transition state $[Me_3SbCl^+ \cdots Y^-]^{\ddagger}$.[12]

Gutmann's solvent donor numbers (DN_{SbCl_5}) mentioned in the previous paragraph represent one empirical, thermochemically based parameter for describing solvent effects. Another popular empirical parameter is Reichardt's E_T, based on solvation effects on charge-transfer spectra.[13] The correlation of kinetic results with solvent E_T values has been used in the discussion of the mechanism of oxidative addition of methyl iodide and of oxygen to the iridium(I) complex *trans*-$[IrCl(CO)(PPh_3)_2]$. These two reactions, thought to proceed by S_N2 attack of Ir at carbon (1) and by formation of a three-centred transition state (2) respectively, both give reasonably linear plots of logarithms of rate constants against solvent E_T values. The slopes of the two plots are markedly different, and it is therefore thought that the solvent dependence of rates of oxidative additions may prove a useful diagnostic test for mechanism in this area.[14]



(1)



(2)

Rates of substitution at square-planar complexes are usually sensitive to variation of the nature of the solvent. Both the k_1 and k_2 values for the normal rate law for substitution at such d^8 complexes,

$$-\mathrm{d[complex]/d}t = \{k_1 + k_2[\mathrm{Y}]\}[\mathrm{complex}] \qquad (1)$$

vary with solvent under normal circumstances. A recent example of such a kinetic pattern is provided by the reactions of $[Au(dien - H)Cl]^+$ with thiocyanate, bromide, or nitrate in methanol or in water.*[15] However, in solvents which are particularly poor at solvating such complexes, k_1 and k_2 may no longer vary significantly with solvent. This was demonstrated for the k_1 term several years ago, in the ligand-exchange reaction of $[Pd(acac)_2]$ with acac in benzene, anisole, and 1,2-dichloroethane.[16] More recently a similar insensitivity

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* dien − H = deprotonated dien.

[11] V. Gutman and R. Schmid, *Monatsh.*, 1971, **102**, 1217.

[12] C. G. Moreland and R. J. Beam, *Inorg. Chem.*, 1972, **11**, 3112.

[13] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1.

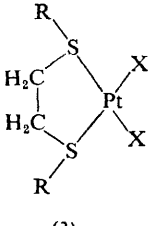
[14] H. Stieger and H. Kelm, *J. Phys. Chem.*, 1973, **77**, 290.

[15] B. I. Peshchevitskii and G. I. Shamovskaya, *Russ. J. Inorg. Chem.*, 1972, **17**, 1386.

[16] K. Saito and M. Takahashi, *Bull. Chem. Soc. Japan*, 1969, **42**, 3462.

of k_2 to solvent has been found for the exchange of ethylene with $[PtCl(acac)(C_2H_4)]$ in chloroform and benzene.[17] In 'pseudo-octahedral' complexes such as $[Pd(Et_4dien)X]^+$ cations, the bulk of the ligand greatly hinders the approach of an incoming ligand Y to the metal, so that the $k_2[Y]$ term in the above rate law becomes negligible. Solvent effects on the k_1 term can then be studied in isolation. The results of an extensive study of substitution reactions of such $[Pd(Et_4dien)X]^+$ cations, with X = Cl, Br, or I, in a range of solvents are reported and discussed in Section 2 of Chapter 2.[18] The rate law for the exchange of acac with $[Be(acac)_2]$ is, despite the difference in geometry of the complex, also as shown in equation (1) above. For this reaction k_1 and k_2 are very solvent sensitive, so that the $k_1 : k_2[acac]$ balance, and thus the predominant reaction pathway, changes according to the nature of the solvent.[19]

It is not possible to discern a general pattern in solvent effects on rates of intramolecular rearrangements from the appropriate papers published during the past three years. In several cases variation of solvent has only a small effect on reaction rate. Examples of this situation include inversion at sulphur in the platinum(II) complexes (3),[20] inversion at phosphorus in the phosphine (4),[21] and rotation about the nitrogen–nitrogen and nitrogen–phosphorus bonds in the hydrazine derivative (5).[22] On the other hand, the activation energy for isomerization of the silyltriazene (6), which involves inversion at nitrogen, varies between 7.7 kcal mol^{-1} in pentane and 19.1 kcal mol^{-1} in ether.[23] Similarly, the difference between the activation energies for isomerization (*cis*⇌*trans*) of $[Cr(tfac)_3]$ in the rather similar solvents toluene and 1,2,4-trimethylbenzene is 3—4 kcal mol^{-1}.[24]



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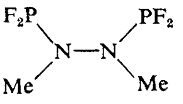
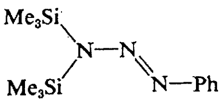


(5)



(6)

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[17] C. E. Holloway and J. Fogelman, *Canad. J. Chem.*, 1970, **48**, 3802.

[18] R. Roulet and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 2101.

[19] A. Barabas, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 775.

[20] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.

[21] H. D. Munro and L. Horner, *Tetrahedron*, 1970, **26**, 4621.

[22] T. T. Bopp, M. V. Havlicek, and J. W. Gilje, *J. Amer. Chem. Soc.*, 1971, **93**, 3051.

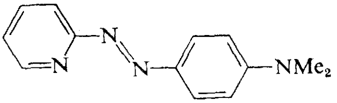
[23] N. Wiberg and H. J. Pracht, *Chem. Ber.*, 1972, **105**, 1392.

[24] R. Fontaine, C. Pommier, and G. Guiochon, *Bull. Soc. chim. France*, 1972, 1685.

Speculation and discussion of the co-ordination numbers of lanthanide cations in various media continue. The effects of a series of Ln^{3+} cations on rates of oxygen exchange between edta and water have been interpreted in terms of a change from a co-ordination number of nine to one of eight in the complexes $[Ln(edta)(OH_2)_n]^-$ about two-thirds of the way along the lanthanide series.[25] Ultrasonic absorption studies on solutions of erbium nitrate and erbium chloride in water–methanol mixtures suggest that a difference in co-ordination number of the erbium cation in nitrate and in chloride media has an effect on kinetic behaviour.[26]

Complex Formation and Solvent Structure.—The Eigen–Wilkins mechanism for the formation of complexes has been comprehensively tested, and found to be valid for a variety of transition- and *sp*-block-metal cations reacting with the majority of ligands in aqueous solution. Outside aqueous solution there is still much testing and discussion of the applicability of this mechanism. Systems studied recently include nickel(II) reacting with py, bipy, phen, or terpy in acetonitrile, dimethyl sulphoxide, methanol, or glycol[27–29] and manganese(II) reacting with bipy, phen, or terpy in methanol.[30] The possibility of ring closure being rate determining for reactions with bipy, phen, or terpy has to be borne in mind, as do the assumptions, particularly concerning the dielectric constant in the immediate vicinity of the reaction centre, on which the estimates of outer-sphere association constants are based. Nevertheless, despite these possible complicating features, the observed kinetic patterns seem to show clear evidence for a significant role for solvent structural properties in determining reactivities.[29] The role of the solvent in such formation reactions has been fully reviewed in Volume 2 of this Report (pp. 201—206).

The kinetics of the reactions of cobalt(II), nickel(II), copper(II), and zinc(II) with pyridine-2-azo-*p*-dimethylaniline [pada (7)] in glycerol solution provide a striking example of the role of the solvent in determining rates of complex formation. The most important feature of the results is the observation that rates of formation vary very little with the nature of the metal cation in glycerol solution, whereas previous studies have shown that rates of formation of pada complexes vary greatly with the cation in aqueous media. It seems that whereas



(7)

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[25] R. H. Betts and R. H. Voss, *Canad. J. Chem.*, 1973, **51**, 538.

[26] J. Reidler and H. B. Silber, *J.C.S. Chem. Comm.*, 1973, 354.

[27] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1973, **12**, 113.

[28] P. A. Cock, C. E. Cottrell, and R. K. Boyd, *Canad. J. Chem.*, 1972, **50**, 402.

[29] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2190, 2198.

[30] D. J. Benton and P. Moore, *J.C.S. Chem. Comm.*, 1972, 717; *J.C.S. Dalton*, 1973, 399.

in water reactivities are 'activation controlled', in other words are determined by the ease of cation–co-ordinated solvent bond breaking, in glycerol rates are 'diffusion controlled' – determined by the comparatively rigid solvent structure. The great decrease in the viscosity of glycerol on warming suggests that the determination of reactivities may change from diffusion control to activation control as the temperature is raised. One should add that the structure of the glycerol solvent is not the only factor which affects the complex formation rates: steric factors and chelate ring formation and dissociation, for the co-ordinated glycerol and for the ligand pada, are also important.[31]

Water is, of course, a solvent with marked and frequently discussed structural features. The majority of recent work on complex formation kinetics in which water is involved has been concerned with mixed solvents, containing smaller or greater amounts of organic components added to modify the structure of the water, and is therefore referenced in the following section. One reaction in aqueous solution in which solvent structure is thought to be an important factor is that of the exchange of glycine with the $[VOH(gly)]^{2+}$ cation. Here there are some deviations from 'normal' kinetic behaviour, which may be ascribed to solvent structural effects.[32]

Other Approaches.—The determination of both kinetic and solubility data can, in favourable systems, permit the separation of solvent effects on reactivities into initial-state and transition-state components. Some interesting mechanistic conclusions have been drawn from such experiments on reactions of tetra-alkyltin compounds with mercury(II) halides and on Menschutkin reactions of primary amines with alkyl halides. In the former case solvent effects on both initial and transition states are important in determining reactivities, whereas in the latter case solvent effects on initial states are of predominant importance. This approach to the diagnosis of reaction mechanisms has been discussed and fully referenced in pp. 112—113 of Volume 1 and pp. 111—112 of Volume 2 of this Report. A similar treatment of the reactions of tetra-alkyl-lead compounds with iodine, in a range of ten solvents, has recently indicated that solvent effects on both the initial and transition states are important factors in determining rates here, as for the tetra-alkyltin reactions mentioned above.[33]

The correlation of reaction rates with dielectric properties is a well-established approach to the diagnosis of mechanism. Most recent examples of this deal with mixed aqueous solvents (see below), but logarithms of second-order rate constants for oxidative addition of methyl iodide or of oxygen to *trans*-$[IrCl(CO)(PPh_3)_2]$ have been found to correlate with the dielectric constant function $(D-1)/(2D + 1)$. However, the correlation of these rate constants with the empirical E_T values for the respective solvents, mentioned above, is better.[14]

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[31] E. F. Caldin and M. W. Grant, *J.C.S. Faraday I*, 1973, **69**, 1648.
[32] H. Tomiyasu, K. Dreyer, and G. Gordon, *Inorg. Chem.*, 1972, **11**, 2409.
[33] M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

2 Mixed Solvents

Kinetic studies in mixed solvents have both advantages and disadvantages compared with those in pure (single) solvents. Whereas many ligand-substitution reactions can be carried out in a range of pure solvents, it is manifestly impossible to study a given solvolysis in more than the one pure solvent. It is thus not possible to study solvent effects on what is probably the most frequently investigated reaction of octahedral complexes, aquation, without having recourse to mixed solvents.

There appear at the present to be three main drawbacks to studying and understanding kinetics of substitution in mixed solvents. The first is that it is often difficult or impossible to know the composition of the immediate environment of the reaction centre. Thus for complex-formation reactions of, say, nickel(II) in solvent mixtures containing water and another solvating solvent such as methanol or ethanol, the reactant distribution $[Ni(OH_2)_x(ROH)_{6-x}]^{2+}$ is in general unknown. However, if the co-solvent is t-butyl alcohol then the hexa-aquo-complex is likely to be the sole component over a wide composition range. Similarly for aquation and other substitution reactions of complexes $[ML_6]^{n+}$ one can monitor the composition of the solvation shell of the complex only in rare cases, for example for those chromium(III) complexes where n.m.r. monitoring of solvation-shell composition has been shown to be possible. Again this problem can be side-stepped by working in mixtures containing one good and one poor solvent.

The second difficulty is that of product distribution. This is well illustrated by the reports of kinetic studies of solvolysis of complexes $[Cr(NCS)_4L_2]^-$, where both solvent components seem to enter the primary co-ordination shell of the chromium(III) during the reaction.[34] The claims that the two components selectively displace the ligands NCS^- or L do not appear to be supported by unequivocal evidence, which would indeed not be easy to obtain.

The third difficulty lies in the imprecise picture and limited physical data available for many solvent mixtures. This is particularly relevant to mixed aqueous solvents, where both inter- and intra-component interactions have such an important effect on the overall structure and properties of the solvent mixtures.

Composition.—The dependence of aquation rate on the concentration of water, using dilute solutions of water in an inert solvent, has not usually proved a satisfactory way of deciding whether the aquation of a particular complex is associative or dissociative in mechanism. However, this approach has recently been applied to the aquation of the $[Cr(ox)_3]^{3-}$ anion in benzene–water solvents containing surfactants. Here a first-order dependence of aquation

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[34] J. Zsakó, I. Ganescu, C. Várhelyi, and A. Popescu, *Z. anorg. Chem.*, 1971, **380**, 216; *Rev. Chim. minérale*, 1970, **7**, 927 (*Chem. Abs.*, 1971, **74**, 91 731f); J. Zsakó, *Studia Univ. Babes-Bolyai, Ser. Chem.*, 1970, **15**, 93 (*Chem. Abs.*, 1970, **73**, 102 471d); J. Zsakó, V. Voiculescu, I. Ganescu, and A. Popescu, *Rev. Roumaine Chim.*, 1972, **17**, 1977; J. Zsakó, D. Oprescu, C. Várhelyi, and I. Ganescu, *Russ. J. Inorg. Chem.*, 1972, **17**, 1705.

rate on water concentration was observed, and interpreted as an indication of an associative mechanism for the aquation of this complex.[35] An associative mechanism has also been proposed for the aquation of [Co(dmgH)$_2$(urea)X], on the basis of both a linear dependence of rate on water concentration and a negative activation entropy.[36] The rate law for the ring closure and attendant halide-expulsion reaction of the *trans*-[Pt(gly)(NH$_3$)X$_2$]$^-$ anion takes the form of a sum of two terms, indicating two parallel reaction paths. One of these terms contains a second-order dependence on water concentration, in several aqueous–organic solvent mixtures. If this reported dependence is not an accidental by-product of the operation of some other effect, a transition state containing two water molecules is indicated for this path.[37] The rate law for racemization of such compounds as chloroethyl-1-naphthylsilane in solvents consisting of an inert major component, such as toluene or carbon tetrachloride, and a racemization-promoting solvent such as dimethyl sulphoxide or dimethylformamide as the minor component is also second-order in the racemization-promoting solvent. Again the participation of two solvent molecules in the transition state is suggested.[38]

Conversely, the rate of catalysed isomerization of platinum(II) complexes in inert solvents is decreased by the addition of polar solvents. The reduction in rate parallels the reciprocal of the concentration of the added polar solvent. Here the effect on the kinetics can be ascribed to competition between the catalyst and the polar solvent at the platinum(II). From these kinetic results one can estimate the solvation number of the platinum(II) complex with respect to the polar solvent. Surprisingly, in most cases this solvation number turns out to be one – only with methanol as added solvent does one get the expected solvation number of two.[39]

Some time ago it was reported that rates of dimethyl sulphoxide exchange with nickel(II) in dimethyl sulphoxide–dichloromethane and dimethyl sulphoxide–nitromethane solvent mixtures were almost independent of solvent composition.[40] Recently, rates of dimethylformamide exchange at nickel(II) in dimethylformamide–nitromethane solvent mixtures have also been found to be remarkably insensitive to solvent-composition variation.[41] Whereas in the dimethyl sulphoxide–dichloromethane solvent mixtures nickel(II) exists as [Ni(DMSO)$_6$]$^{2+}$, in dimethylformamide–nitromethane mixtures the composition of the nickel(II) co-ordination shell varies with solvent composition, with preferential solvation by the nitromethane rather than by the dimethylformamide. These observations are difficult to explain in terms of an I_d

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[35] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1973, **95**, 600.

[36] N. M. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1971, **16**, 1445.

[37] L. M. Volshtein, L. F. Krylova, A. V. Belyaev, and I. G. Luk'yanova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1025.

[38] R. J. P. Corriu and M. Leard, *Chem. Comm.*, 1971, 1086.

[39] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 5243.

[40] L. S. Frankel, *Chem. Comm.*, 1969, 1254.

[41] L. S. Frankel, *Inorg. Chem.*, 1971, **10**, 2360.

mechanism, but are consistent with the intermediacy of a fugitive five-co-ordinate species – in other words with a *D* mechanism. The mechanistic picture is more confused for dimethyl sulphoxide exchange at chromium(III) in dimethyl sulphoxide–nitromethane mixtures,[42] for whereas the variation of exchange rate with solvent composition is consistent with a dissociative mechanism, other studies of solvent exchange at chromium(III) have revealed negative activation volumes and thus indicated an associative mechanism. The suggestion of one unique solvent site in what one would have expected to be a symmetrical octahedral $[Cr(DMSO)_6]^{3+}$ cation is probably a temporary expedient.

Qualitative discussions of the dependence of substitution rates for inorganic complexes on solvent composition in mixed aqueous solvents, and possible mechanistic interpretations thereof, abound. Examples are particularly numerous in the area of bisdioximatocobalt(III) complexes,[43] and have recently appeared for analogous rhodium(III) complexes.[44] Activation parameters, $\Delta V^{\ddagger}$ as well as $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, have been determined for the isomerization of the *trans*-$[Cr(ox)_2(OH_2)_2]^-$ anion in aqueous methanol and in aqueous dioxan. These activation parameters are discussed in terms of a ring-opening mechanism for isomerization[45] (*cf.* ref. 6). Previously reported solvent effects on *cis*$\rightleftharpoons$*trans* isomerization of $[PtL_2X_2]$ complexes have been reinterpreted.[46] Other qualitative reports concerning solvent effects on rates deal with the base hydrolysis of cyanide ion,[47] with oxygen exchange at perrhenate,[48] and with the kinetics of sulphate complexation of magnesium(II) in aqueous dioxan.[49]

Solvation.—The dependence of the reactivity of a complex on the composition of its solvation shell can only rarely be satisfactorily probed. In the case of chromium(III) complexes n.m.r. (and occasionally u.v.–visible) spectroscopy can often reveal the composition of the solvation shell, so that this can be correlated with reaction rates. This treatment was first fully developed for the solvolysis, both thermal and photochemical, of the $[Cr(NCS)_6]^{3-}$ anion in aqueous acetonitrile,[50] as described at some length in Volume 1 of this Report. The approach has subsequently been found useful and informative in investigations of aquation and of isomerization of the $[Cr(ox)_3]^{3-}$ anion in aqueous

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[42] C. H. Langford, R. Scharfe, and R. Jackson, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1033.

[43] G. P. Syrtsova and Nguen Zui Lyong, *Russ. J. Inorg. Chem.*, 1970, **15**, 1414; 1971, **16**, 213; Nguen Zui Lyong and G. P. Syrtsova, *ibid.*, 1971, **16**, 376; and references in the Solvent Variation section of Part II, Chapter 3, Section 2, of this volume.

[44] G. P. Syrtsova and T. S. Bolgar, *Russ. J. Inorg. Chem.*, 1971, **16**, 1322; 1972, **17**, 238, 1585.

[45] E.-G. Conze, H. Stieger, and H. Kelm, *Chem. Ber.*, 1972, **105**, 2334.

[46] D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 1102.

[47] G. H. Wiegand and M. Tremelling, *J. Org. Chem.*, 1972, **37**, 914.

[48] R. K. Murmann, *J. Amer. Chem. Soc.*, 1971, **93**, 4184.

[49] F. H. Fisher, *J. Phys. Chem.*, 1972, **76**, 1571.

[50] L. S. Frankel, *J. Phys. Chem.*, 1969, **73**, 3897; 1970, **74**, 1645; L. S. Frankel, C. H. Langford, and T. R. Stengle, *J. Phys. Chem.*, 1970, **74**, 1376; S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, 1969, **91**, 2236.

dimethyl sulphoxide,[51] and of solvolysis of the *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ anion in aqueous acetonitrile.[52]

Observed reactivities of *trans*-$[PtCl_2(py)_2]$ towards substitution by bromide or thiourea in aqueous (H_2O or D_2O) dimethyl sulphoxide appear to be determined to a considerable extent by solvation of the leaving chloride.[53] Complementarily, the increase in the second-order rate constants for reactions of low-spin iron(II) complexes with cyanide with increasing proportion of organic component in aqueous organic mixtures must at least in part reflect solvation changes around the incoming group as well as those around the complexes.[54]

Dielectric Constant.—Several groups of Russian chemists have for some time used the variation of reaction rates in mixed aqueous solvents with the bulk dielectric constant of the medium to diagnose substitution mechanisms. A good correlation of logarithms of rate constants with reciprocal dielectric constants, or with the function $(D-1)/(2D+1)$, having a markedly negative slope is considered indicative of a dissociative mechanism. An associative mechanism is claimed to be characterized by a very small effect of dielectric constant on rates.* The best correlation between reactivities and dielectric constant functions seems to be obtained for substitutions at bisdioximatocobalt(III) complexes. Thus for the aquation of [Co(α-benzildioximato)$_2$-$(OH_2)Cl]$, the plot of logarithm of rate against reciprocal dielectric constant takes the form of one straight line, for points derived in ethanol–, glycol–, dioxan–, or n-propanol–water mixtures containing up to 50% organic component.[55] A similarly good correlation is reported for aquation of $[Co(dmgH)_2LX]$ anions, with L = semicarbazide or thiosemicarbazide and X = Cl or Br, in a similar range of mixed solvents.[56] Formation reactions, as for example the reaction of $[Co(dmgH)_2(tu)(OH_2)]^+$ with thiourea[57] and of $[Co(dmgH)_2(OH_2)_2]^+$ with substituted thioureas,[58] give good plots of logarithm of reaction rate against reciprocal dielectric constant for aqueous ethanol and aqueous propan-2-ol, but now the aqueous dioxan points lie well away from the aqueous alcohols line. For the aquation of $[Co(dmgH)_2$-(urea)X], where both substrate and leaving group (urea) are uncharged, there is only a very small effect of solvent composition, *i.e.* of dielectric constant, on rates. This is interpreted as indicating an associative mechanism, for which

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* This view contrasts sharply with that expounded in classical texts such as Ingold's 'Structure and Mechanism in Organic Chemistry': see, *e.g.*, pp. 345 *et seq.* of the first edition.

[51] V. S. Sastri and C. H. Langford, *J. Phys. Chem.*, 1970, **74**, 3945.

[52] V. S. Sastri, R. W. Henwood, S. Behrendt, and C. H. Langford, *J. Amer. Chem. Soc.*, 1972, **94**, 753.

[53] R. N. Collins and D. A. Johnson, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1861.

[54] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133; J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc.* (*A*), 1971, 44; E. R. Gardner, F. M. Mekhail, J. Burgess, and J. M. Rankin, *J.C.S. Dalton*, 1973, 1340.

[55] N. M. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1578.

[56] N. M. Samus', O. N. Damaskina, and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1145.

[57] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1972, **17**, 1576.

[58] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1972, **17**, 1435.

there is some flimsy supporting evidence both from the observed negative activation entropy and from the dependence of rate on water concentration.[36]

In contrast with this tidy pattern of reactivities of cobalt(III) complexes, the situation with regard to substitution at platinum(II) and at palladium(II) is much less ordered. Thus for the aquation of *cis*-$[Pt(Me_2NH)_2Cl_2]$,[59] *cis*-$[Pt(Et_2NH)_2Cl_2]$,[60] and *cis*-$[Pt(acetoxime)_2Cl_2]$[60] plots of logarithms of rate constants against reciprocal dielectric constants are linear for each of several aqueous–organic co-solvent mixtures – with methanol, ethanol, glycol, dioxan, or acetone as co-solvent – but the slope of the correlation line differs markedly between different co-solvents. This pattern is attributed to a predominantly dissociative mechanism with a small but important degree of platinum to incoming water bond formation in the transition state. The form of the dependence of aquation rates of *trans*-$[Pd(py)_2Cl_2]$ on reciprocal dielectric constant varies greatly with the nature of the organic cosolvent. Thus in aqueous acetone and aqueous dimethylformamide rates vary little with $1/D$, in aqueous dioxan the plot of $\log k$ against $1/D$ is a good straight line of markedly negative slope [*cf.* cobalt(III) complexes above], and in aqueous methanol the $\log k$ against $1/D$ plot is very curved, nearly semicircular in fact. The plot for aqueous dioxan is described as 'normal'; the departures from this normal behaviour for the other co-solvents are not clearly discussed.[61] Finally, for ring closure in $[Pt(NH_3)(gly)X_2]$ no rate–dielectric constant correlation is claimed. Rather rates were found to be proportional to the square of the water concentration, as discussed in the paragraph on composition above.[62]

Grunwald–Winstein Analysis.—Although the dielectric constant of the medium in the vicinity of the reaction centre undoubtedly plays an important role in determining substitution rates, there are other properties of the solvent, such as its nucleophilicity, which are also of some importance in this connection. This was recognized by Grunwald and Winstein two and a half decades ago, and prompted them to formulate their rate-constant expression

$$\log k/k_0 = mY$$

to correlate rate constants for solvolysis of the typical S_N1 substrate t-butyl chloride with empirical solvent properties. In the equation cited, k is the solvolysis rate constant in a given solvent mixture, k_0 the solvolysis rate constant in the reference solvent, m a reaction parameter fixed as unity for solvolysis of t-butyl chloride, and Y an empirical solvent parameter thereby defined by this equation. So-called mY plots proved useful in differentiating

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[59] V. D. Panasyuk, N. F. Falendysh, and N. A. D'yachenko, *Ukrain. khim. Zhur.*, 1972, **38**, 1218.

[60] V. D. Panasyuk, N. F. Falendysh, and N. A. D'yachenko, *Russ. J. Inorg. Chem.*, 1971, **16**, 1452.

[61] V. D. Panasyuk, T. I. Denisova, and S. K. Rybak, *Russ. J. Inorg. Chem.*, 1972, **17**, 874.

[62] L. M. Volshtein, L. F. Krylova, A. V. Belyaev, and I. G. Luk'yanova, *Russ. J. Inorg. Chem.*, 1972, **17**, 1025.

between dissociative and associative mechanisms in many organic systems, and have subsequently been used in inorganic chemistry. The extensions to inorganic reactions have dealt both with solvolysis of halides of the *sp*-block elements, such as sulphur, phosphorus, and boron (see, *e.g.*, pp. 202—3 of Volume 1), and with aquation of transition-metal complexes, especially those of cobalt(III). Thus *m* values of *ca.* 0.3 have been estimated for a variety of cobalt(III)–chloride complexes (see pp. 150—1 of Volume 2). More recently, linear *mY* plots have been established for the aquation of chloro-chromium(III) complexes; such plots were not obtained for thiocyanato-chromium(III) complexes.[63] For the aquations of the chloro-chromium(III) complexes, *m* values of *ca.* 0.1 were found. This low value, which is not inconsistent with some degree of associative character to aquation at chromium(III) (*cf.* the discussion of this question in Section 3 of Chapter 3), reflects Langford's earlier observations on the lower sensitivity of chromium(III) complexes compared with cobalt(III) complexes with respect to solvent effects on substitution rates.[64]

The mechanism of aquation at another d^3 centre, rhenium(IV), has also been probed by the Grunwald–Winstein method. Plots of logarithms of rate constants for aquation of the hexabromorhenate(IV) anion against solvent *Y* values give one straight line, which includes even a point for aqueous acetic acid. This suggests a dissociative mechanism; the negative *m* value (-0.55) must reflect the very different solvation requirements of the $[ReBr_5]^-$ group as compared with the Me_3C^+ group of t-butyl chloride, and indeed as compared with $[Co(NH_3)_5]^{3+}$.[65] Mercury(II)-catalysed aquation of hexachlororhenate(IV), as of $[Rh(NH_3)_5Cl]^{2+}$, in mixed aqueous solvents is also characterized by a negative *m* value.[65]

Heteroaromatic ligands such as bipy differ greatly from the X^- and HgX^+ leaving groups so far mentioned in this section. Nonetheless the plot of logarithms of rate constants for the reaction of $[Fe(bipy)_2(CN)_2]$ with phen, whose rate-determining step is loss of bipy, against solvent *Y* values is a good straight line for methanol–, ethanol–, and acetone–water mixtures. This plot yields the low value of 0.2 for *m*; an analogous plot for an analogous Schiff-base complex gives an *m* value of zero.[66]

Solvent Structure.—The role of solvent structure in determining rates of formation reactions of dipositive transition-metal cations with such ligands as bipy and terpy has been intensively investigated and discussed for mixed aqueous as well as for non-aqueous solvents (see above). Bennetto and Caldin's work on the reaction of nickel(II) with bipy in methanol–water mixtures[67] was fully reviewed in Volume 2 of this Report (see pp. 201—206 of that volume). As structure modification is more marked in t-butyl alcohol–water than in methanol–water mixtures, the reaction of nickel(II) with bipy has now been

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[63] J. Burgess, *J.C.S. Dalton*, 1973, 825.
[64] C. H. Langford, *Canad. J. Chem.*, 1971, **49**, 1497.
[65] J. Burgess, R. D. Peacock, and A. M. Petric, *J.C.S. Dalton*, 1973, 902.
[66] J. Burgess, *J.C.S. Dalton*, 1972, 203.
[67] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2207.

studied in the first-named mixtures. In alcohol–water mixtures rates of reaction of nickel(II) with bipy are fairly insensitive to solvent composition: it is the activation parameters whose values change markedly with solvent composition. The extrema in plots of activation parameters against solvent composition are, as expected, greatest when t-butyl alcohol is the co-solvent. Thus the difference between the minimum activation enthalpy and that in pure water is *ca.* 0.7 kcal mol^{-1} in methanol–, *ca.* 0.8 kcal mol^{-1} in ethanol–, and 1.5 kcal mol^{-1} in t-butyl alcohol–water mixtures.[27] However, one must add that other authors feel that solvent structural effects are less important than claimed by Bennetto and Caldin and by Chattopadhyay and Coetzee. The results of kinetic studies on nickel(II), both as the hexa-aquo-ion and as a mixed-ligand aquo-complex, with ammonia in methanol–water mixtures have been interpreted in terms of inner-sphere effects being as significant as, or even more important than, bulk solvent structural effects.[68]

Although most of this work on the possible interrelations of solvent structure and reactivities has been concerned with formation at nickel(II), the influence of solvent structure on kinetics has also occasionally been discussed for substitution at other metal centres. A recent example is provided by a study of the kinetics of aquation of $[Fe(phen)_3]^{2+}$, and of some of its ligand-substituted derivatives, in aqueous acetonitrile. The reactivity patterns here can be compared and contrasted with those for the same reactions in t-butyl alcohol–water mixtures and considered in relation to thermochemical and spectroscopic information on inter- and intra-component interactions in these mixed-solvent systems.[69]

The importance of solvent structure in determining reactivity in the formation reaction of hexa-aquonickel(II) with bipy has also been assessed for one wholly non-aqueous mixed-solvent system, that of acetonitrile–methanol.[70]

Stereochemical Labelling.—Several years ago, kinetic studies on substitution at $[Cr(OH_2)_5I]^{2+}$ were discussed in terms of a high *trans* effect of the iodide ligand in this complex. The original kinetic evidence and conclusions were convincing but not absolutely conclusive. Recently kinetic studies in aqueous dimethyl sulphoxide have made ingenious use of the dimethyl sulphoxide as a stereochemical signpost to confirm and amplify the earlier mechanistic hypotheses.[71]

3 Salt Effects

Examples of classical ionic-strength variation and ion-pair formation effects on reactivities of inorganic complexes are legion. However, in some systems the effects of added salts on reactivities cannot be satisfactorily or completely described in such terms, and then recourse may be had to considerations of the

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[68] W. J. MacKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, 1971, **93**, 4379; F. R. Shu and D. B. Rorabacher, *Inorg. Chem.*, 1972, **11**, 1496.

[69] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2351.

[70] H. P. Bennetto, *J. Chem. Soc.* (*A*), 1971, 2211.

[71] D. B. Vanderheiden and E. L. King, *J. Amer. Chem. Soc.*, 1973, **95**, 3860.

effects of the added salts on the structure of the solvent. Effects of added tetra-alkylammonium salts on aqueous systems provide good examples of the consequences of solvent structural modification. Such solvent-structure effects on reaction kinetics have been discussed for three systems recently, the aquation of the monochloroiron(III) cation,[72] the hydrolysis of dichromate,[73] and the exchange of oxygen with nitrate.[74] A related avenue of approach is to consider the effects of added salts on the activity of the water, and the likely kinetic consequences of the assessed variation of water activity with added-salt concentration. These matters are discussed in connection with the kinetics of aquation of the $[Ir(NH_3)_5(NO_3)]^{2+}$ cation in water,[75] and of the $[Fe(X\text{-phen})_3]^{2+}$ cations, with X = H, 5-NO_2, or 4,7-diMe, in aqueous dioxan.[76] In both of these references the main unexpected feature of the observed kinetic pattern proved to be a marked decrease in aquation rates on adding perchlorate. The basic Debye–Hückel theory predicts a very small effect, whether the mechanism be dissociative or associative with uncharged water as incoming group, and ion-pairing in all other studies of added-anion effects on cation reactivities has led to rate increases.

The most spectacular effects of salts on reaction rates are observed in micellar solutions. For instance the presence of anionic surfactants such as dodecyl or tetradecyl sulphate accelerates rates of mercury(II)-catalysed aquation of $[Co(NH_3)_5Cl]^{2+}$ by several orders of magnitude,[77] and polyethylene or polystyrene sulphonates have a similar effect on mercury(II), thallium(III), and silver(I) catalyses of the aquation of the $[Co(NH_3)_5Br]^{2+}$ cation.[78] Cationic surfactants such as the octylammonium or dodecylammonium ions have a dramatic effect on rates of aquation of the $[Cr(ox)_3]^{3-}$ anion.[35] Both anionic and cationic surfactants catalyse the (associative) hydrolysis of the Lewis acid–base adduct Et_3N,SO_3.[79]

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[72] R. Koren and B. Perlmutter-Hayman, *Inorg. Chem.*, 1972, **11**, 3055.
[73] R. Koren and B. Perlmutter-Hayman, *J. Phys. Chem.*, 1972, **76**, 582.
[74] M. I. Valenchuk and M. O. Tereshkevich, *Russ. J. Phys. Chem.*, 1972, **46**, 1650.
[75] F. Monacelli and S. Viticoli, *Inorg. Chim. Acta*, 1973, **7**, 231.
[76] J. Burgess, F. M. Mekhail, and E. R. Gardner, *J.C.S. Dalton*, 1973, 1335.
[77] J.-R. Cho and H. Morawetz, *J. Amer. Chem. Soc.*, 1972, **94**, 375.
[78] N. Ise and Y. Matsuda, *J.C.S. Faraday I*, 1973, **69**, 99.
[79] M. D. Bentley, S. E. Bowie, and R. D. Limoges, *J. Phys. Chem.*, 1971, **75**, 1763.

Part III

REACTIONS OF BIOCHEMICAL INTEREST

By
D. N. HAGUE

1 Introduction

It is proposed to divide this chapter into the same sections as were used in the corresponding part of Volume 2 in this series and, as in the past, we shall concentrate on those papers in which the emphasis has been on the behaviour of the metal. Several papers which are discussed in Chapter 4 of Part II deal with complex formation between labile metal ions and ligands of biological significance (*e.g.* amino-acids); these are not generally referred to again here. A general book on bioinorganic chemistry has at last been published[1] and, in characteristically lucid fashion, Williams has reviewed[2] his and Vallee's 'entatic state' hypothesis in the light of more recent results. Metallo-enzymes have, of course, played an important role in the development of this hypothesis, and the zinc-containing enzyme carboxypeptidase A also features prominently in Lipscomb's Centenary Lecture to the Chemical Society[3] entitled 'Three-dimensional Structures and Chemical Mechanisms of Enzymes'. There has been a general review[4] on 'Metals, Ligands, and Cancer' and a more specific one[5] on the chemistry of complexes related to *cis*-$[Pt(NH_3)_2Cl_2]$ which, following the report of Rosenberg and co-workers[6] of the anti-tumour activity of these compounds, have acquired a considerable general interest. Reviews have also appeared on the inorganic chemistry of vitamin B_{12},[7] nitrogen fixation,[8] molybdenum-containing enzymes,[9] and the evolution of biological iron-binding centres,[10] and the abstracts of papers presented at a conference on metallo-enzymes in 1972 have been published.[11] The eighteen months under discussion have seen the launching of a new journal devoted entirely to bioinorganic chemistry[12] and the introduction of a section in the *Journal of Inorganic and Nuclear Chemistry* for papers of biochemical interest.

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[1] M. N. Hughes, 'The Inorganic Chemistry of Biological Processes', Wiley, London, 1972.

[2] R. J. P. Williams, *Inorg. Chim. Acta Rev.*, 1971, **5**, 137.

[3] W. N. Lipscomb, *Chem. Soc. Rev.*, 1972, **1**, 319.

[4] D. R. Williams, *Chem. Rev.*, 1972, **72**, 203.

[5] A. J. Thomson, R. J. P. Williams, and S. Reslova, *Structure and Bonding*, 1972, **11**, 1.

[6] B. Rosenberg, L. van Camp, J. E. Trosco, and V. H. Manson, *Nature*, 1969, **222**, 385.

[7] J. M. Pratt, 'Inorganic Chemistry of Vitamin B_{12}', Academic Press, London, 1972.

[8] J. Chatt and G. J. Leigh, *Chem. Soc. Rev.*, 1972, **1**, 121.

[9] R. C. Bray and J. C. Swann, *Structure and Bonding*, 1972, **11**, 107.

[10] J. B. Neilands, *Structure and Bonding*, 1972, **11**, 145.

[11] *Biochem. Soc. Trans.*, 1973, **1**, 1—54.

[12] *Bioinorganic Chemistry*, Elsevier, New York.

2 Metal Ion Transport

The transport of Na^+ out of and K^+ into an animal cell against a concentration gradient is catalysed by a (Na^+ + K^+)-activated ATPase. The way in which the cations pass through the cell membrane has not yet been elucidated but a recent review by Schoner[13] summarizes our present knowledge on active transport of these two metals. Studies on ATP hydrolysis have revealed a sodium-dependent phosphorylation of the enzyme protein; the phosphorylated enzyme probably takes part in the transport of the cations through the cell membrane and it appears that this process is associated with a change in the conformation of the enzyme. The energy required for active transport is probably provided by K^+-dependent hydrolysis of the enzyme-bound phosphate. It is uncertain whether carriers are involved in the active transport of the cations but the opinion is expressed that the answer to this question will be provided by further investigations with (Na^+ + K^+)-activated ATPase.

Stein and co-workers[14] have extended a model for glucose transport to include Na^+ and K^+ movement across cell membranes, having been impressed by the similarities in the kinetics of cation and glucose transport. It is postulated that transport occurs by the internal transfer of cations across a protein tetramer embedded in the cell membrane. The protein tetramer can exist in either of two forms of identical energy; transport occurs as a result of the sequential 'flipping' from one conformation to the other. The conformational change results in the interchanging of the affinities of cation-binding sites associated with different subunits of the tetramer with the concomitant hydrolysis of ATP. In another recent study,[15] the potassium for the (Na^+ + K^+)-activated ATPase of erythrocytes was successfully replaced by thallium(I). Since Tl^+ and K^+ are indistinguishable in their fully hydrated states, being equal in charge and size, the observation that the ATPase activity and Na^+ transport were significantly greater in the presence of Tl^+ than K^+ suggested to the authors[15] that the ion–membrane interactions involve the destruction of the hydration sheaths of the cations. The interaction might be of the type encountered in the formation of, for example, the K^+–valinomycin complex, but, since valinomycin is unable to replace the hydration shell of Tl^+ (and the Tl^+–valinomycin complex therefore cannot be formed in aqueous solutions), the nature of the K^+- and Tl^+-binding site of the membrane must involve other types of functional group than those found in valinomycin (*viz.* carbonyl and ether oxygens).

Morf and Simon[16] have used model calculations to investigate the relative effects of several properties of the metal and the ligand on the complexation of alkali-metal and alkaline-earth cations by neutral macrocyclic ligands; factors considered include the co-ordination number of the metal, the dimen-

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[13] W. Schoner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 882.

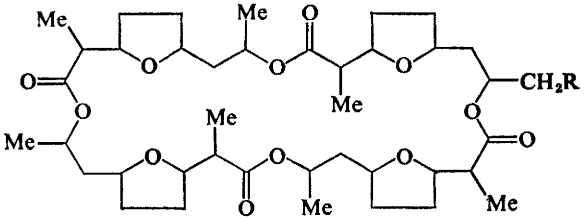
[14] W. D. Stein, W. R. Lieb, S. J. D. Karlish, and Y. Eilam, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 275.

[15] I. A. Skulskii, V. Manninen, and J. Järnefelt, *Biochim. Biophys. Acta*, 1973, **298**, 702.

[16] W. E. Morf and W. Simon, *Helv. Chim. Acta*, 1971, **54**, 2683.

sions of the ligand, steric interactions, and the nature of the solvent. Information is given on the molecular parameters needed to achieve a given ion selectivity. Christensen, Hill, and Izatt[17] have summarized the important factors to be taken into account in any attempt to rationalize the selectivity exhibited by these large molecules and Haynes[18] has given a preliminary report on the use of 1-anilino-8-naphthylsulphonic acid (ANS^-) as a fluorescent indicator for the formation of complexes between cations and valinomycin-type ionophores.

Force–area curves of valinomycin at the air–water interface in the presence of univalent cations suggest[19] that the macrocycle undergoes a rearrangement when it complexes a cation. The observed selectivity order $Rb^+ \geqslant K^+ > Cs^+$ is the same as that found for valinomycin in bilayer conductance and partition experiments. Conformational changes have been shown[20] to occur on the binding of nonactin (1; R = H) to K^+ and it has been confirmed that the metal ion must be stripped of its hydration shell as it enters the nonactin molecule. The loss of hydration energy (*ca.* 80 kcal mol^{-1}) must evidently be compensated by interactions between the cation and its eight co-ordinated oxygen atoms in the complex. It has been shown elsewhere that complex formation is very fast (see below for details) and it is almost certain, on energetic grounds, that stepwise substitution of solvent molecules is essential for this to be so (see also Section 3 of Part II, Chapter 4). Inspection of space-filling models shows[21] that there is room for a hydrated potassium ion inside the central cavity of a nonactin molecule and that, when it is so placed, hydrogen bonds can be formed between its water molecules and the various oxygen atoms of the prospective ligand. The actual complex-formation process therefore probably occurs in a stepwise manner, the removal of successive water molecules being coupled to conformational changes of the ligand and leading to the gradual envelopment of the cation in the central cavity. It may be important in this connection that, as the four ester groups of (1) tilt in the course of complexation, the four unco-ordinated oxygen atoms move to the



(1)

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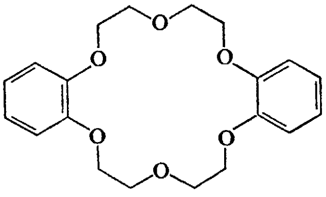
[17] J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, 1971, **174**, 459.
[18] D. H. Haynes, *Biochim. Biophys. Acta*, 1972, **255**, 406.
[19] G. Kemp and C. E. Wenner, *Biochim. Biophys. Acta*, 1972, **282**, 1.
[20] M. Dobler, *Helv. Chim. Acta*, 1972, **55**, 1371.
[21] P. Läuger, *Science*, 1972, **178**, 24.

outside of the molecule. Their role could be to assist complex formation by removing hydrogen-bonded water molecules from the cavity.

The kinetics of the reaction of sodium ions with dibenzo-18-crown-6 (2) in DMF, using ^{23}Na n.m.r. spectroscopy, have been reported.[22] The chemical shifts of ^{23}Na in the solvated sodium and in the complex with (2) are very nearly the same but, because of the lack of cubic symmetry around the metal in the complex, fast quadrupole relaxation causes the linewidth in the latter species to be much greater than in solvated sodium. This enables the rate constant for the exchange process to be determined. The rate constant for the complexation reaction is estimated to be 6×10^7 l mol^{-1} s^{-1} at 25 °C, with an activation energy of 6.5 kcal mol^{-1}. N.m.r. has also been used[23] to measure the kinetics of the binding of five ionophores to K$^+$ in a 80 : 20 by volume methanol–chloroform mixture. The results (Table 1) suggest that the rate of decomplexation at the water–membrane interface is not generally the rate-determining step in the transport reaction sequence. A similar result has been obtained[24] for the reaction between Na$^+$ and several macrocycles in methanol (Table 2). It is interesting to note that the limiting value of the formation rate constant k_f expected for a diffusion-controlled reaction with an uncharged species in methanol is *ca.* 3×10^9 l mol^{-1} s^{-1}. Thus, for monactin



(2)

Table 1 *The rate constants*[a] *for exchange of ionophores and* K$^+$ *in* CH_3OH–$CDCl_3$ (80 : 20 v/v)

Ionophore	k_{on}/l mol^{-1} s^{-1}	k_{off}/s^{-1}
Valinomycin	$>1.1\times10^5$	21 ± 5
Nonactin	$>1.6\times10^5$	32.3 ± 0.6
Monactin	$>1.1\times10^5$	22.9 ± 1.6
Dinactin	$>1.1\times10^5$	21 ± 6
Trinactin	$>0.9\times10^5$	18 ± 5

[a] From ref. 23.

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[22] E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *J. Amer. Chem. Soc.*, 1971, **93**, 7133.

[23] D. H. Haynes, *F.E.B.S. Letters*, 1972, **20**, 221.

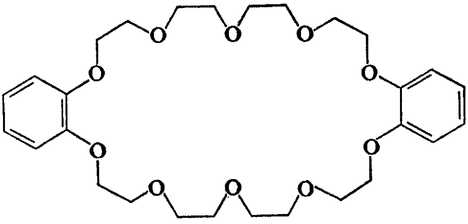
[24] R. Winkler, *Structure and Bonding*, 1972, **10**, 1.

Table 2 *Rate constants*[a] *for the complex formation of* Na^+ *with carriers in methanol*

Carrier	$k_{form}/l\ mol^{-1}\ s^{-1}$	k_{diss}/s^{-1}
Nigericin	$\sim 2\times 10^{10}$	$\sim 2\times 10^{6}$
Monactin	$\sim 2\times 10^{8}$	4×10^{5}
Dinactin	6×10^{7}	5×10^{4}
Trinactin	7×10^{7}	4×10^{4}
Valinomycin	7×10^{6}	5×10^{5}

[a] From ref. 24.

(1; R = Me), dinactin, and trinactin (the latter two molecules are methyl-substituted derivatives of monactin) the reaction rates are only 10—50 times slower than for a diffusion-controlled process. (It is also interesting to note that the value of k_f for the charged-carrier nigericin is, as expected, significantly larger than those for the neutral ligands.)



(3)

The kinetics of the binding of dibenzo-30-crown-10 (3) with univalent cations in methanol are consistent[25] with a two-step mechanism of the type shown in reaction (1), where CR^1, CR^2, and MCR^+ represent, respectively, an

$$CR^1 \xrightleftharpoons{\text{fast}} CR^2 + M^+ \xrightleftharpoons[k_{21}]{k_{12}} MCR^+ \qquad (1)$$

unreactive form of the crown ether, an open configuration of the ether (which is the predominant species in the absence of cations), and the metal complex in which the ether is in a closed configuration.

The rate constants, k_{12}, for the ions studied (Table 3) follow the order $K^+ < Rb^+ \sim Cs^+ \sim Tl^+$. Interestingly, K^+ has the highest hydration energy among these ions; however, Rb^+, Cs^+, and Tl^+ give approximately the same values of k_{12} because of the limitation imposed by diffusion control. The high rate constants suggest that a stepwise mechanism must be involved (see above).

The feasibility of the carrier model for metal-ion transport across biological membranes has been explored by Läuger[21] in terms of the known rate constants for the K^+–valinomycin system. He makes an interesting comparison between the action of a carrier molecule and that of an enzyme. An enzyme

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[25] P. B. Chock, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 1939.

Table 3 *Rate constants*[a] *for complex formation with dibenzo*-30-*crown*-10 *in methanol* [*see reaction* (1)]

M^+	k_{12}/l mol^{-1} s^{-1}	k_{21}/s^{-1}
Na^+	$>1.6\times10^7$	$>1.3\times10^5$
K^+	$(6 \pm 2)\times10^8$	$(1.6 \pm 0.5)\times10^4$
Rb^+	$(8 \pm 2)\times10^8$	$(1.8 \pm 0.4)\times10^4$
Cs^+	$(8 \pm 1)\times10^8$	$(4.7 \pm 0.6)\times10^4$
NH_4^+	$>3\times10^7$	$>1.1\times10^5$
Tl^+	$(8 \pm 1)\times10^8$	$(2.5 \pm 0.3)\times10^4$

[a] From ref. 25; data refer to 25 °C.

reduces the energy barrier which separates the reactants from the products of a chemical reaction; in an analogous way, the function of a valinomycin molecule (for example) consists in reducing the extremely high activation barrier for the transport of an alkali-metal ion across the hydrocarbon interior of a lipid membrane.

3 Metal Complex Formation

The care which must be exercised when choosing a suitable buffer for biochemical studies involving heavy metal ions has been emphasized recently by Dotson,[26] who has characterized a series of complexes between members of the first transition series and the popular buffer tris(hydroxymethyl)aminomethane ('tris'). There are undoubtedly reports of interesting phenomena in the literature that can be attributed to unrecognized complex formation between the metal ion in a biologically active molecule and the buffer or some other supposedly innocent small molecule. (An interesting claim[27] that many of the reports on the behaviour of the zinc-containing enzyme bacterial alkaline phosphatase are erroneous because the experimenters had failed to recognize that the enzyme preparations were contaminated with edta is referred to in greater detail below.)

A kinetic study on the activation of deoxyribonuclease I by magnesium has shown[28] that the activation curve is biphasic (the substrate being the Mg salt of bovine spleen DNA). This indicates that activation occurs at two sites on the protein. Free Mg^{2+} was required for enzyme activity, confirming that a metallo-enzyme as well as a metallo-substrate is necessary for deoxyribonuclease I activity. In contrast, it has been shown[29] that the pyrophosphatase activity of bovine brain alkaline phosphatase depends on Mg^{2+} bound to the enzyme but not on the formation of a magnesium–substrate complex.

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[26] R. L. Dotson, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3131; *Inorg. Nuclear Chem. Letters*, 1973, 9, 215.

[27] H. Csopak, K. E. Falk, and H. Szajn, *Biochim. Biophys. Acta*, 1972, **258**, 466.

[28] L. E. Perlgut and V. Hernandez, *Biochim. Biophys. Acta*, 1972, **289**, 169.

[29] G. Cathala and C. Brunel, *Biochim. Biophys. Acta*, 1973, **315**, 73.

Several papers discuss the proposition[30] that the Mn^{2+}–ATP complex contains a water molecule which is simultaneously co-ordinated to the metal ion and hydrogen-bonded to N-7 of the adenine ring. Zetter, Dodgen, and Hunt[31] were not able to detect two different types of water in this complex by ^{17}O n.m.r. spectroscopy, although they admit that a water molecule which was exchanging either much more rapidly or much more slowly than those observed would not have been detected. The number of bound waters in $[Mn(ATP)aq]^{2-}$ cannot be determined unequivocally from their data but they suggest that there are three rapidly exchanging waters which are, to within a factor of approximately three, kinetically equivalent. It is interesting to note that these water molecules have similar exchange parameters to those bound to the bare metal ion. The origin of the much lower[32] complexation rate constant for the reaction of the oxine mono-anion with $[Mn(ATP)]^{2-}$ than that for the reaction with Mn^{2+}_{aq} is also considered.[31] Evidently, some process other than water exchange is rate limiting and the authors suggest that it might be a change in the binding of the ATP to the metal, such as the dissociation of either the α-phosphate group or the adenine ring or both. No such change occurs on forming the analogous ternary complex of Mg^{2+}, since the ring is not bound to the metal in $[Mg(ATP)]^{2-}$. Hence, they speculate, the interchangeability of Mn and Mg in enzymatic transphosphorylation is more easily rationalized in terms of the structures of the ternary complexes (which are assumed to be similar) than the structures of the binary complexes (which are almost certainly different).

The influence of Mn^{2+} ions on the proton-decoupled ^{13}C n.m.r. spectra of the adenosine monophosphates 2′-AMP, 3′-AMP, and 5′-AMP has been investigated[33] and evidence has been obtained that the metal ion is held near the N-7 position of the base. The line-broadening behaviour is similar for all three mononucleotides and, rather than propose the formation of an intramolecular 1 : 1 complex, which in the case of 2′-AMP and 3′-AMP would involve drastic conformational changes, the authors favour an intermolecular complex in which the metal is bound simultaneously to the phosphate group of one nucleotide and the adenine-ring N-7 of a second nucleotide. The relative shifts produced on the ^{17}O and proton resonances of water in Co^{2+}–ATP and Co^{2+}–CTP solutions are consistent[34] with the model for ATP binding outlined above. The addition of Ni^{2+} to solutions of thiamine pyrophosphate causes shifting and broadening of the proton n.m.r. signals of the thiamine moiety. The results indicate[35] an interaction of the metal ion with both the pyrophosphate group and the N-1′ of the pyrimidine ring. It is proposed that the latter involves a similar outer-sphere interaction through

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[30] T. A. Glassman, C. Cooper, L. W. Harrison, and T. J. Swift, *Biochemistry*, 1971, **10**, 843.
[31] M. S. Zetter, H. W. Dodgen, and J. P. Hunt, *Biochemistry*, 1973, **12**, 778.
[32] D. N. Hague, S. R. Martin, and M. S. Zetter, *J.C.S. Faraday I*, 1972, **68**, 37.
[33] G. Kotowycz and K. Hayamizu, *Biochemistry*, 1973, **12**, 517.
[34] G. P. P. Kuntz, T. A. Glassman, C. Copper, and T. J. Swift, *Biochemistry*, 1972, **11**, 538.
[35] A. A. Gallo, I. L. Harrison, H. Z. Sable, and T. J. Swift, *J. Biol. Chem.*, 1972, **247**, 5913.

hydrogen-bond formation with a molecule of water in the first co-ordination sphere of the metal.

It has been noted[36] that the binding of ATP to $[Cu(bipy)]^{2+}$ results in a significant protection of the former against hydrolysis, whereas the binding of the nucleotide to Cu^{2+} leads to a large increase in hydrolysis rate. The different behaviour of the binary and ternary complexes has been rationalized as follows. Since Cu^{2+} prefers a square-planar co-ordination geometry in aqueous solution, only two positions are left in $[Cu(bipy)]^{2+}$ for the co-ordination of ATP and these are occupied by two of its phosphate groups. Hence, in the mixed complex $[Cu(bipy)(ATP)]^{2-}$ the adenine moiety (and in particular its N-7 atom) cannot participate in further metal binding, as it can in the case of the binary complex $[Cu(ATP)]^{2-}$. This further binding is, presumably, of great importance in the metal-catalysed hydrolysis of ATP. A model for phosphoryl-transfer enzymes has been provided[37] in the zinc-catalysed phosphorylation of 1,10-phenanthroline-2-carbinol by ATP.

The formation of ternary complexes of manganese(II) nucleotides with uridine diphosphate-glucose pyrophosphorylase, formyltetrahydrofolate synthetase, and creatine kinase has been studied[38] by n.m.r. and it has been found[39] in the latter case that structural changes at the active site of the enzyme occur on binding of substrates and competitive inhibitors. Substitution of ligand groups from the protein into the co-ordination sphere of the metal ion is suggested as a possible cause of the changes observed in the e.s.r. spectrum of the enzyme. Evidence has been obtained[40] for the formation of metal-bridged ternary complexes in the Mn^{2+}-activated allosteric enzyme yeast pyruvate kinase, and the formation of outer-sphere complexes with enzyme-bound Mn^{2+} has been proposed[41] in the case of enolase.

Aconitase (citrate hydrolyase) is one of a number of lyases which are activated by the addition of Fe^{II} and a reducing agent and it had been suggested that the role of the metal involves the formation of an enzyme–iron(II)–substrate bridge complex. Indirect evidence had previously been obtained for the catalytically inactive aconitase–manganese(II)–substrate bridge complexes by proton relaxation studies on water, and it had been shown that Fe^{II} and Mn^{II} compete for two tight metal-binding sites on the enzyme. Villafranca and Mildvan[42] have recently confirmed the existence of metal-bridged complexes by n.m.r. studies on the protons of the substrate citrate and the inhibitor *trans*-aconitate using both the manganese(II)- and the iron(II)-enzymes.

The oxidation of NADH by Fe^{III} is a complex reaction that can be divided

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[36] D. H. Buisson and H. Sigel, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1025.
[37] D. S. Sigman, G. M. Wahl, and D. J. Creighton, *Biochemistry*, 1972, **11**, 2236.
[38] G. H. Reed, H. Diefenbach, and M. Cohn, *J. Biol. Chem.*, 1972, **247**, 3066.
[39] G. H. Reed and M. Cohn, *J. Biol. Chem.*, 1972, **247**, 3073.
[40] G. L. Cottam, A. S. Mildvan, J. R. Hunsley, and C. H. Suelter, *J. Biol. Chem.*, 1972, **247**, 3802.
[41] T. Nowak, A. S. Mildvan, and G. L. Kenyon, *Biochemistry*, 1973, **12**, 1690.
[42] J. J. Villafranca and A. S. Mildvan, *J. Biol. Chem.*, 1972, **247**, 3454.

into four main steps, *viz.* the formation of the reactive complex, the one-electron oxidation of NADH by the metal, the dissociation of the resulting complex, and, finally, the reaction between the oxidation products of the NADH. The mechanism of the first stage in this process has recently been investigated by the stopped-flow method and it has been shown[43] that the formation of the reactive bis-complex $[Fe(NADH)_2]^{3+}$ involves the intermediate $[Fe(NADH)]^{3+}$:

$$Fe^{3+} + NADH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(NADH)]^{3+} \tag{2}$$

$$[Fe(NADH)]^{3+} + NADH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Fe(NADH)_2]^{3+} \tag{3}$$

The rate constants at 25 °C are: $k_2 = (5.0 \pm 0.2) \times 10^3\ l\ mol^{-1}\ s^{-1}$, $k_{-2} = 0.6 \pm 0.1\ s^{-1}$, $k_3 = (1.30 \pm 0.05) \times 10^3\ l\ mol^{-1}\ s^{-1}$, $k_{-3} = 0.03 \pm 0.01\ s^{-1}$, and it is apparent that the low dissociation rate of $[Fe(NADH)_2]^{3+}$ is responsible for the enhanced stability of the bis-complex relative to the mono-complex.

Although the spectral properties of catalytically essential, chromophoric metal ions in metallo-enzymes are thought to reflect the nature of the metal co-ordination sphere, the precise definition of the co-ordination geometry of metals at the active sites of metallo-enzymes has proved to be very difficult. In a recent note[44] it is suggested that the Faraday effect might provide a way of gaining additional information on such problems. The magnetic circular dichroism (m.c.d.) spectra of cobalt complexes and enzymatically active cobalt proteins have been examined and it is concluded that they are particularly helpful in recognizing overall geometry of co-ordination. It appears that the overall geometry of the metal at the active sites of Co-carboxypeptidase and Co-thermolysin is tetrahedral, and is not altered significantly by addition of inhibitors. On the other hand, the m.c.d. spectra of Co-alkaline phosphatase and the alkaline form of Co-carbonic anhydrase are quite similar to, but not identical with, that of $[Co(Me_6tren)Br_2]$, a complex in which the cobalt(II) is known to be five-co-ordinate. Furthermore, the addition of acetazolamide, an inhibitor for the latter enzyme, has the remarkable effect of transforming the m.c.d. spectrum of Co-carbonic anhydrase into one closely resembling tetrahedral geometry. (A similar result has been obtained[45] with anionic inhibitors but the latter authors interpret the high-pH m.c.d. spectrum of the free Co^{II} enzyme in terms of a trigonally distorted tetrahedral geometry.) The change of the m.c.d. spectrum of Co-alkaline phosphatase on forming a complex with phosphate is marked, but the resultant spectrum does not resemble those of any of the models studied. M.c.d. spectra of Co^{II} enzyme derivatives resembling those of octahedral model compounds had not been encountered when the note was written. The same

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[43] M. Gutman and M. Eisenbach, *Biochemistry*, 1973, **12**, 2314.

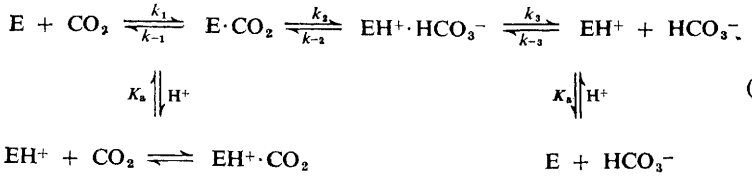
[44] T. A. Kaden, B. Holmquist, and B. L. Vallee, *Biochem. Biophys. Res. Comm.*, 1972, **46**, 1654.

[45] J. E. Coleman and R. V. Coleman, *J. Biol. Chem.*, 1972, **247**, 4718.

group has also reported[46] the use of e.s.r. spectroscopy to investigate the geometry of the metal co-ordination in cobalt(II)-enzymes.

Prince and Woolley[47] have reviewed the chemistry of the zinc-containing enzyme carbonic anhydrase with special reference to the part played by the metal. They point out that none of the results published to date shows beyond all doubt that the pK_a of *ca.* 7, which is a recurrent feature of carbonic anhydrase chemistry, is associated with the ionization of a zinc-bound water molecule (although it is difficult to offer an alternative explanation and the existence of this zinc aquo-complex seems to the authors to be a necessary condition for the activity of the enzyme).

Khalifah and Edsall[48] suggest that reaction (4) represents the simplest realistic mechanism capable of reproducing all the observed pH-dependent



$$\begin{tikzcd}
E + CO_2 \arrow[r, shift left, "k_1"] \arrow[d, shift left, "H^+"] & E{\cdot}CO_2 \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & EH^+{\cdot}HCO_3^- \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] & EH^+ + HCO_3^- \arrow[l, shift left, "k_{-3}"] \arrow[d, shift left, "H^+"] \\
EH^+ + CO_2 \arrow[u, shift left, "K_a"] \arrow[r, shift left] & EH^+{\cdot}CO_2 \arrow[l, shift left] & & E + HCO_3^- \arrow[u, shift left, "K_a"]
\end{tikzcd}$$

(4)

kinetics of this enzyme. (It has, in fact, been assumed in mechanistic discussions involving carbonic anhydrase for several years.) The crux of the model is that the hydration reaction rate is proportional to [E], the concentration of the high-pH form of the enzyme, and that the dehydration reaction rate is proportional to [EH^+], the concentration of the low-pH form of the enzyme. A crucial assumption of this mechanism is that the equilibrium between E and EH^+ (which is defined by the pK_a of *ca.* 7) is attained very rapidly ('essentially instantaneously'), thereby maintaining the relative concentrations of the two forms of the enzyme at the equilibrium value appropriate for a given pH. Koenig and Brown have now pointed out[49] that this assumption cannot hold since it requires a second-order rate constant for the conversion of E into EH^+ in considerable excess of the diffusion-controlled limit. They present evidence which shows that only the high-pH form of the enzyme is active, both for the hydration and the dehydration reactions. In addition, they suggest that at high pH there is an H_2O ligand on the metal (not OH^-, as is often argued) and that the substrate for the dehydration reaction is the neutral H_2CO_3 molecule. They suggest that at high substrate concentration H_2CO_3 reaches the active site by collision with the enzyme molecule and subsequent surface diffusion to the active site, whereas at lower substrate concentrations (corresponding to $[HCO_3^-] < 10^{-3}$ M) the generation of

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[46] F. S. Kennedy, H. A. O. Hill, T. A. Kaden, and B. L. Vallee, *Biochem. Biophys. Res. Comm.*, 1972, **48**, 1533.

[47] R. H. Prince and P. R. Woolley, *Angew. Chem. Internat. Edn.*, 1972, **11**, 408.

[48] R. G. Khalifah and J. T. Edsall, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 172.

[49] S. H. Koenig and R. D. Brown, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 2422.

H_2CO_3 near the enzyme by the recombination reaction (5) can supply an adequate flux of substrate to the active site.

$$H^+ + HCO_3^- \longrightarrow H_2CO_3 \qquad (5)$$

The kinetics of the binding of anions and sulphonamides to carbonic anhydrase have been measured[50] by the stopped-flow technique. The results are consistent with a mechanism involving a pH-dependent equilibrium between two co-ordination forms of the enzyme in which anions selectively combine with the low-pH form of the enzyme whereas sulphonamides combine with the high-pH form. The effect of pH on the anion affinity correlates with the pH dependence of the spectral change associated with the cobalt(II) form of the enzyme. Further evidence on the similarity of the conformations at the active sites of the zinc and cobalt(II) forms of carbonic anhydrase has been provided[51] by spin-labelling. A nitroxide-substituted sulphonamide was used as the spin label and its e.s.r. spectrum was found to be almost identical in the two forms of the enzyme–inhibitor complex.

^1H and ^{19}F n.m.r. spectroscopy has been used[52] to investigate the interaction between various carboxylate inhibitors and Co^{II} carbonic anhydrase. Analysis of the temperature dependence of the transverse relaxation time T_2 has yielded the rate constants for formation and dissociation of the complexes, and values in the region of 2×10^8 l mol^{-1} s^{-1} and 10^5 s^{-1}, respectively, have been obtained (Table 4). Anion association is thus two to three orders of magnitude faster than the corresponding process in hexa-aquocobalt(II).

Table 4 *Estimated association and dissociation rate constants*[a] *for carboxylate complexes of cobalt*(II) *carbonic anhydrase C* (25 °C)

Ligand	k_{form}/l mol^{-1} s^{-1}	k_{diss}/s^{-1}
Formate	3.9×10^8	6.0×10^4
Monofluoroacetate	2.2×10^8	2.0×10^5
Difluoroacetate	1.9×10^8	1.0×10^5
Trifluoroacetate	2.0×10^8	1.5×10^5

[a] From ref. 52.

Two model studies have been reported by Prince and Woolley which have a bearing on the role of the zinc in carbonic anhydrase. A macrocycle (4) has been synthesized[53] which, when co-ordinated to zinc, produces a complex which also contains one water molecule in the inner co-ordination sphere; this water molecule has a pK_a of *ca.* 8—a value considerably closer to that postulated for carbonic anhydrase (*ca.* 7) than is the value for hexa-aquozinc

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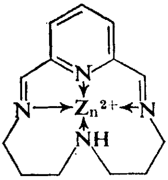
[50] P. W. Taylor and A. S. V. Burgen, *Biochemistry*, 1971, **10**, 3859.
[51] P. Mushak and J. E. Coleman, *J. Biol. Chem.*, 1972, **247**, 373.
[52] P. W. Taylor, J. Feeney, and A. S. V. Burgen, *Biochemistry*, 1971, **10**, 3866.
[53] R. H. Prince and P. R. Woolley, *Nature Phys. Sci.*, 1972, **240**, 117.



(4)

(*ca.* 10.0). The hydration of acetaldehyde has been studied[54] as a 'typical' reaction involving nucleophilic attack upon the carbonyl group. It is catalysed by zinc ions and the catalysis is enhanced by the presence of acetate and hydroxide ions. The significance of these observations is discussed in terms of possible mechanisms for the action of carbonic anhydrase.

The visible and near-i.r. spectral properties of the enzymatically active cobalt(II) carboxypeptidase have been examined and it is concluded[55] that the co-ordination geometry of the metal atom at the active site is a distorted tetrahedron (in agreement with the m.c.d. results[44]). Consideration of the magnetic susceptibility of this enzyme, on the other hand, suggests[56] that the metal has a five-co-ordinate geometry whereas that in the corresponding nickel enzyme, which is also active, is octahedral. It is difficult[56] to reconcile this result with the entatic state concept[2] of catalytic activity.

The effect of edta on alkaline phosphatase from *E. coli* and on the cobalt(II) and copper(II) derivatives of the protein has been studied[27] by the measurement of enzyme activity and by e.s.r. spectroscopy. From dialysis experiments on an edta-contaminated apoenzyme, it was found that the edta binds to the metal-free protein. Furthermore, in the complete absence of edta only two Zn^{2+} or Co^{2+} ions per enzyme molecule were required for full enzyme activity and it is suggested[27] that reports in the literature that more than two metal (ons are necessary (four is the number commonly quoted) may be explained by varying levels of edta contamination in the enzyme and apoenzyme preparations. The ligand edta also affects the e.s.r. spectrum of copper alkaline phosphatase, thus accounting for the two types of signal reported previously and their different behaviour towards phosphate.

From e.s.r. studies on copper(II)–alkaline phosphatase it is concluded[57] that the two metal ions at the active site have at least three equivalent nitrogen ligands, probably histidyl side-chains. A preliminary report[58] on ^{31}P n.m.r. relaxation rates for the ternary complex of the manganese(II) enzyme with phosphate indicates that the activation energy E_a for phosphate exchange is 8.0 kcal mol^{-1}. In addition, the lifetime of this ternary complex is much

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[54] R. H. Prince and P. R. Woolley, *J.C.S. Dalton*, 1972, 1548.
[55] S. A. Latt and B. L. Vallee, *Biochemistry*, 1971, **10**, 4263.
[56] R. C. Rosenberg, C. A. Root, R. H. Wang, M. Cerdonio, and H. B. Gray, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 161.
[57] J. E. Taylor and J. E. Coleman, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 859.
[58] R. S. Zukin, D. P. Hollis, and G. A. Gray, *Biochem. Biophys. Res. Comm.*, 1973, **53**, 238.

shorter than the enzyme turnover time, a fact consistent with the participation of the complex in the enzymatic mechanism.

^{35}Cl N.m.r. has been used[59] to study the active-site zinc ions of horse liver alcohol dehydrogenase. The Cl^- probe interaction with the metal is completely removed by the binding of two molecules of reduced coenzyme per molecule. The fact that 1,10-phenanthroline has no effect on the Cl^- linewidth but is an effective competitor with coenzyme for the Zn^{2+} ions suggests to the authors[59] that the zinc is octahedrally co-ordinated in the enzyme. A model for this enzyme has been proposed[60] which involves the zinc-catalysed reduction of 1,10-phenanthroline-2-carboxaldehyde by *N*-propyl-1,4-dihydronicotinamide. Another zinc-enzyme model, involving transesterification between the two ligands of a metal-bridged ternary complex, has been reported[61] and the fact that bivalent metal ions (especially Zn^{2+}) greatly enhance the rate of pyruvate aldolization has been used as further evidence[62] for the proposal that class II (metallo-) aldolase reactions involve the co-ordination of metal ions to the carbonyl oxygen of the substrate. Further work on the mechanism of the formation and dissociation of peptide complexes of copper(II) has been reported.[63]

4 Reactions involving Metals in Porphyrins and Related Ring Systems

Antonini and Brunori[64] have published a further critical summary of the contributions in the haemoglobin field over the past few years. They have also measured the kinetics of the binding of oxygen and carbon monoxide to *Gastrophilus* haemoglobin[65] and of oxygen to mixtures of oxy- and carbon monoxide haemoglobin,[66] and for the reaction between oxygen and haemoglobin bound to haptoglobin.[67] Gibson and co-workers have reported[68] the kinetics for the binding of CO to shark and fish haemoglobins and Schmelzer *et al.*[69] have used flash photolysis to follow the reaction of CO with human haemoglobin. The n.m.r. bromide-probe technique has been used[70] to

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[59] R. L. Ward and J. A. Happe, *Biochem. Biophys. Res. Comm.*, 1971, **45**, 1444.

[60] D. J. Creighton and D. S. Sigman, *J. Amer. Chem. Soc.*, 1971, **93**, 6315.

[61] D. S. Sigman and C. T. Jorgensen, *J. Amer. Chem. Soc.*, 1972, **94**, 1724.

[62] A. A. Gallo and H. Z. Sable, *Biochim. Biophys. Acta*, 1973, **302**, 443.

[63] *E.g.* A. Zuberbühler and T. A. Kaden, *Helv. Chim. Acta*, 1972, **55**, 623; G. R. Dukes and D. W. Margerum, *Inorg. Chem.*, 1972, **11**, 2953.

[64] E. Antonini and M. Brunori, 'Hemoglobin and Myoglobin in the Reactions with Ligands', North-Holland, Amsterdam, 1971.

[65] C. E. Phelps, E. Antonini, M. Brunori, and G. Kellett, *Biochem. J.*, 1972, **129**, 891.

[66] M. Brunori and E. Antonini, *J. Biol. Chem.*, 1972, **247**, 4305.

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[68] M. E. Anderson, J. S. Olson, Q. H. Gibson, and F. G. Carey, *J. Biol. Chem.*, 1973, **248**, 331.

[69] U. Schmelzer, R. Steiner, A. Mayer, T. Nedetzka, and H. Fasold, *European J. Biochem.*, 1972, **25**, 491.

[70] T. R. Collins, Z. Starčuk, A. H. Burr, and E. J. Wells, *J. Amer. Chem. Soc.*, 1973, **95**, 1649.

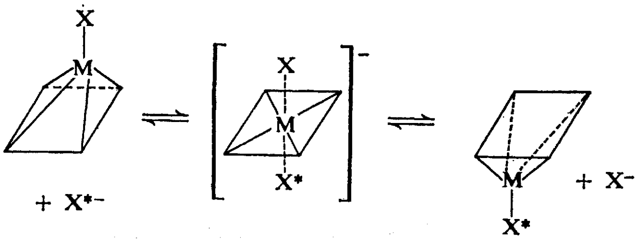
measure the rates of formation and dissociation of the complex with methaemoglobin, and the apparent contradiction between the kinetic and thermodynamic results for the binding of small molecules to methaemoglobin has been rationalized[71] by the suggestion that the ligand-binding mechanism contains a minimum of two reaction steps.

In model studies for complex biological systems, it is evidently desirable to obtain data on reactions which have an exact analogy in the protein system. In deoxy-myoglobin and -haemoglobin the active site involves a five-co-ordinate high-spin iron(II) protoporphyrin IX (pp IX) system and, until recently, no suitable model had been reported for this. Collman and Reed[72] have outlined the synthesis of unsubstituted iron *meso*-tetraphenylporphyrin (tpp) and the conversion of this isolated complex into a series of Fe^{II} derivatives, including a five-co-ordinate high-spin complex containing 2-methylimidazole, which appears to be just such a model. In addition, Stynes and James have measured[73] the kinetics of the reaction of CO with six-co-ordinate $[Fe(pp\ IX)(pip)_2]$ and $[Fe(tpp)(pip)_2]$ (where pip is piperidine) in toluene and have shown that the mechanism involves the dissociation of one piperidine molecule to give a five-co-ordinate (piperidine)Fe(porphyrin) complex as an intermediate. They suggest that the protoporphyrin IX system also provides a good model for the iron active site in deoxy-myoglobin and -haemoglobin.

Structural and magnetic data have revealed that the high-spin forms of iron porphyrins suffer significant displacements of the iron atom out of the porphyrin plane. These displacements, which should be larger for the ferrous (*ca.* 0.75 Å) than for the ferric ion (*ca.* 0.4—0.5 Å), reflect the inability of the tetrapyrrole 'hole' to accommodate these fairly large high-spin ions (this being the reason that five-co-ordinate geometry is common among the high-spin complexes). On adding a sixth ligand, the spin multiplicity of the ground state decreases, generally yielding diamagnetic Fe^{II} and spin-doublet Fe^{III} species whose smaller ionic radii are more easily accommodated within the porphyrin plane. The conversion of iron(II) from an out-of-plane, high-spin into an in-plane, diamagnetic, six-co-ordinate species upon oxygenation is typical of the haem proteins, and the kinetics of the movement of the iron atom relative to the porphyrin plane are evidently of considerable significance to a full mechanistic description of the action of these biological macromolecules. La Mar has given a preliminary report[74] of the porphyrin 'inversion' for the high-spin complexes of tetra-*p*-tolylporphyrin, *p*-methyl-tpp–FeCl, and octaethylporphyrin, where the 'inversion' is induced by facile halogen exchange [reaction (6)] and measured by n.m.r. line-broadening.

Solvent exchange rates have been measured, by n.m.r. spectroscopy, for two further high-spin iron(III) porphyrins[75] and a manganese(III) porphyrin[76]

[71] M. H. Klapper and H. Uchida, *J. Biol. Chem.*, 1971, **246**, 6849.
[72] J. P. Collman and C. A. Reed, *J. Amer. Chem. Soc.*, 1973, **95**, 2048.
[73] D. V. Stynes and B. R. James, *J.C.S. Chem. Comm.*, 1973, 325.
[74] G. N. La Mar, *J. Amer. Chem. Soc.*, 1973, **95**, 1662.
[75] J. Hodgkinson and R. B. Jordan, *J. Amer. Chem. Soc.*, 1973, **95**, 763.
[76] L. Rusnak and R. B. Jordan, *Inorg. Chem.*, 1972, **11**, 196.



(6)

in DMF and in methanol; in all cases the solvent is significantly more labile in the porphyrin complex than on the bare metal ion.

The frequent presence of an imidazole-co-ordinated residue in an axial position, coupled with the suggestions that metal–imidazole bond rupture might play an important role in biological processes of coenzyme B_{12} and the cytochrome *c* system, indicates that a detailed characterization of the structure and dynamics of the imidazole–metal bond in such porphyrin complexes could have significant biological implications. La Mar and Walker[77] present some preliminary data on the exchange of *N*-methylimidazole (*N*MIm) on the bis-adduct of *N*MIm with [Fe(tpp)Cl] in $CDCl_3$, and Kolski and Plane[78] describe temperature-jump studies on the reaction between imidazole and the iron(III) derivative of ethylenediamine-substituted protoporphyrin IX in water.

The kinetics have been reported[79] for the reaction of amine complexes of cobalt(II) protoporphyrin IX dimethyl ester with oxygen in toluene to give products believed to be peroxo-bridged complexes. The reaction is first-order in cobalt and oxygen and goes from first- to zero-order in amine (L) with increasing amine concentration, the rate law being consistent with a rate-determining step which involves a unimolecular distortion of a 1 : 1 cobalt–oxygen complex. Anomalously high rates for L = imidazole or benzimidazole are tentatively explained in terms of hydrogen-bonding effects involving the acidic proton on the imidazole ring. Similarities with haemoglobin and myoglobin are discussed. The rates of substitution at the metal centre in cobalt(III)–tetra-(*N*-methyltetrapyridyl)porphin are so high that the stopped-flow and temperature-jump techniques had to be used[80] to follow the reaction with thiocyanate.

A general deformation mechanism has been proposed[81] which rationalizes the kinetic data that have been obtained for the incorporation of metals into porphyrins and the acid-catalysed solvolysis of metal porphyrins. In addition, the idea of porphyrin deformation by metal ions, protons, or *N*-alkyl groups, leading to subsequent reactions on the opposite side of the porphyrin plane,

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[77] G. N. La Mar and F. A. Walker, *J. Amer. Chem. Soc.*, 1972, **94**, 8607.

[78] G. B. Kolski and R. A. Plane, *J. Amer. Chem. Soc.*, 1972, **94**, 3740.

[79] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, 1973, **95**, 1142.

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[81] R. Khosropour and P. Hambright, *J.C.S. Chem. Comm.*, 1972, 13.

predicts S_E2 character for the second-order kinetics observed for the replacement of one metal ion co-ordinated in a porphyrin molecule by another. The kinetics have been reported for the incorporation of copper into various porphyrins.[82, 83]

The kinetics of the catalase-like activity of cobalt(III)-haematoporphyrin IX ($Co^{III}HP$) has been studied and the following reaction scheme proposed:[84]

$$H_2O_2 \rightleftharpoons H^+ + OOH^- \qquad \text{(fast)}$$

$$Co^{III}HP + OOH^- \rightleftharpoons Co^{III}HP(OOH^-)$$

$$Co^{III}HP(OOH^-) + H_2O_2 \rightleftharpoons Co^{III}HP(OOH^-)H_2O_2$$

$$Co^{III}HP(OOH^-)H_2O_2 \longrightarrow Co^{III}HP + H_2O + OH^- + O_2$$

Ligands such as NH_3, alaninate, and adeninate are competitive inhibitors[85] of the catalase-like activity, whereas others, including adenosine and ATP, have no effect on the reaction. The decomposition of H_2O_2 is also catalysed by the iron(III)[86] and cobalt(II)[87] complexes of 4,4′,4″,4‴-tetrasulphophthalocyanine.

Kinetic and equilibrium data for the binding of azide, imidazole, and pyridine to horse heart ferricytochrome *c* are consistent[88] with a model in which the ligands bind to the iron by displacing the co-ordinated methionine-80. Analogous data on the binding of carbon monoxide to seven different examples of cytochrome *c′* (which differ from other *c*-type cytochromes in existing predominantly in the high-spin form at neutral pH values) indicate[89] that the mechanism is complex in all cases, with five equilibria controlling the process. The interaction of CO with cytochrome P-450 is affected by camphor, the rate constants for the formation of the carbon monoxide adduct in the absence and presence of camphor being[90] 5.1×10^6 and 3.8×10^4 l mol^{-1} s^{-1}, respectively. Recent data on the reduction of cytochrome *c* have been used[91] to illustrate the application of the known principles of electron-transfer reactions of metal complexes in solution to biological redox processes. The kinetics of reduction of cytochrome *c* by chromium(II) in the presence of various anions have been interpreted[92] in terms of an electron-transfer pathway involving adjacent attack on the iron(III) centre. The reduction is

[82] R. S. Das, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1263.

[83] N. Johnson, R. Khosropour, and P. Hambright, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1063; J. James and P. Hambright, *Inorg. Chem.*, 1973, **12**, 474.

[84] P. Waldmeier and H. Sigel, *Inorg. Chem.*, 1972, **11**, 2174.

[85] P. Waldmeier and H. Sigel, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1741.

[86] P. Waldmeier and H. Sigel, *Inorg. Chim. Acta*, 1971, **5**, 659.

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[89] M. A. Cusanovich and Q. H. Gibson, *J. Biol. Chem.*, 1973, **248**, 822.

[90] J. A. Peterson and B. W. Griffin, *Arch. Biochem. Biophys.*, 1972, **151**, 427.

[91] N. Sutin, *Chem. Brit.*, 1972, **8**, 148.

[92] J. K. Yandell, D. P. Fay, and N. Sutin, *J. Amer. Chem. Soc.*, 1973, **95**, 1131.

catalysed by I^-, N_3^-, and SCN^- ions and it is proposed that these reactions (for which the rate constants are quoted) feature a remote electron-transfer pathway (possibly by way of the exposed edge of the porphyrin system). Similar reactivity patterns ($Cl^- < I^- < N_3^- \sim SCN^-$) in this and model systems are consistent with this hypothesis. An analogous two-path mechanism has been proposed[93] for reduction by dithionite.

The binding of ethyl isocyanide to ferroperoxidase has been measured[94] by the stopped-flow method, as have the oxidations of ferrocyanide,[95] sulphite,[96] and nitrite[96] by HRP-I and HRP-II. Bielski[97] has used pulse radiolysis to study the HRP–ascorbic acid–H_2O_2 system and has detected spectral changes which are characteristic of the formation and disappearance of compound II.

Hydroxymethyl hydroperoxide (HMP) is a peroxide substrate and a rapid irreversible inhibitor of HRP. Direct measurement of the rate constant k_1 for the formation of the HMP–HRP complex has in the past been precluded by the presence of H_2O_2 in the preparations of HMP; an indirect method gave $k_1 \simeq 2 \times 10^5\ l\ mol^{-1}\ s^{-1}$. By using catalase to remove the hydrogen peroxide from aqueous solutions of HMP, Marklund[98] has been able to measure k_1 directly by a stopped-flow technique. He obtains the value of $5 \times 10^5\ l\ mol^{-1}\ s^{-1}$, which he compares with the values of 1.5×10^6 and $3.6 \times 10^6\ l\ mol^{-1}\ s^{-1}$ for MeOOH and EtOOH, respectively. The lower value for the HMP probably originates in the repulsion between the non-polar region around the sixth co-ordination position of the haematin Fe (indicated by *X*-ray analysis) and the hydroxy-group of HMP.

Epstein and Schejter[99] have questioned the customary interpretation of the pK_a of ferric HRP at 10.8 as being associated with the deprotonation of an iron-bound water molecule. They have measured the kinetics of the process and suggest that, in fact, a conformational change of the molecule is involved.

Pratt[7] has written a book on the inorganic aspects of vitamin B_{12} and several other reviews of the chemistry of B_{12} and B_{12} models have appeared.[100–103] A common feature of all reactions catalysed by coenzyme B_{12} is the transfer of hydrogen between adjacent carbon atoms of the substrates. Abeles and co-workers have provided further evidence[104, 105] in favour of a

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[94] C. Phelps, E. Antonini, and M. Brunori, *Biochem. J.*, 1972, **128**, 377.
[95] M. L. Cotton and H. B. Dunford, *Canad. J. Chem.*, 1973, **51**, 582.
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[101] R. H. Prince and D. A. Stotter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 321, 341.
[102] C. K. Poon, *Coordination Chem. Rev.*, 1973, **10**, 1.
[103] G. N. Schrauzer, *Pure Appl. Chem.*, 1973, **33**, 545.
[104] T. H. Finlay, J. Valinsky, K. Sato, and R. H. Abeles, *J. Biol. Chem.*, 1972, **247**, 4197.
[105] T. H. Finlay, J. Valinsky, A. S. Mildvan, and R. H. Abeles, *J. Biol. Chem.*, 1973, **248**, 1285.

tentative mechanism that they have proposed[106] for the dioldehydrase-catalysed conversion of 1,2-propanediol into propionaldehyde and of ethylene glycol into acetaldehyde (a reaction which requires a vitamin B_{12} coenzyme). Their experiments establish that dioldehydrase can bring about the homolytic cleavage of the C—Co bond of coenzyme B_{12} and suggest the possibility that radical species may be intermediates in the catalytic reaction. Support for their proposal has come from work on closely related enzymes,[107, 108] although the advantages of a rival scheme involving heterolysis of the C—Co bond have been restated.[109] The chemical transfer of alkyl groups from alkylcobalamins to mercuric ion has been studied in detail[110] and it has been shown that heterolytic C—Co cleavage occurs during electrophilic attack by mercuric ion, to give alkylmercury and aquocobalamin as the reaction products. A pulse-radiolysis study of cobalamin reduction has shown[111] that the decay of the hydrated electron and the formation of B_{12r} are concomitant bimolecular processes, with rate constants ranging from $5 \times 10^{10}\, l\, mol^{-1}\, s^{-1}$ at pH 6.1 to $3 \times 10^{10}\, l\, mol^{-1}\, s^{-1}$ at pH 11.1. The importance of Co^{III} π-complexes in reactions involving vitamin B_{12} has been suggested.[112]

Kinetic measurements have been reported[113] for a series of reactions of bis(dioximato)cobalt(II) complexes with organic halides; the evidence suggests that a radical mechanism is involved. The influences of electronic and steric factors are discussed and the possible influence of axial ligand replacements in modifying the reactivity of vitamin B_{12r} (for which these complexes serve as model systems) is considered. The oxidation,[114, 115] reductive dealkylation,[116] and axial ligation[117, 118] of cobaloximes have been studied kinetically, and it has been suggested[119] that the large range of self-exchange rates observed in cobalt macrocyclics (a factor of 10^{10}) cannot be related to 'spin effects'; it is more likely to be a reflection of ligand reorganizational barriers.

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[116] G. N. Schrauzer, J. A. Seck, R. J. Holland, T. M. Beckham, E. M. Rubin, and J. W. Sibert, *Bioinorg. Chem.*, 1973, **2**, 93.
[117] K. L. Brown and R. G. Kallen, *J. Amer. Chem. Soc.*, 1972, **94**, 1894.
[118] K. L. Brown, D. Chernoff, D. J. Keljo, and R. G. Kallen, *J. Amer. Chem. Soc.*, 1972, **94**, 6697.
[119] D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *J.C.S. Chem. Comm.*, 1972. 495,

5 Redox Reactions involving Metals in other Biological and Model Systems

Dunham *et al.*[120] have recently summarized their spectroscopic and magnetic susceptibility results on spinach and other two-iron ferredoxins; they show how the results allow a precise definition of the active centre and provide a stringent set of criteria against which any further structural information may be tested. The c.d. and absorption spectra of spinach ferredoxin and another two-iron iron–sulphur protein, adrenodoxin, suggest[121] that the reduced forms contain a high-spin ferrous ion in a distorted tetrahedral environment. The reaction between adrenodoxin and excess 1,10-phenanthroline apparently[122] follows zero-order kinetics under aerobic conditions but first-order kinetics under anaerobic conditions; the activation energies are 3.3 and 12.6 kcal mol^{-1}, respectively. A reaction sequence is proposed.[122]

Further work has been reported[123, 124] with Fe–Mo models for nitrogenase, and a molecular mechanism has been proposed[125] for the action of molybdenum in enzymes. In all reactions catalysed by Mo enzymes, the product and substrate differ by two electrons and two protons (or some multiple thereof). The co-ordination chemistry of Mo suggests that there is a distinct relationship between acid–base and redox properties of Mo complexes, and that a coupled electron–proton transfer (to or from substrate) may be mediated by Mo in enzymes. Each of the molybdenum enzymes (nitrogenase, nitrate reductase, xanthine oxidase, aldehyde oxidase, and sulphite oxidase) is discussed[125] and it is shown that a simple molecular mechanism embodying coupled proton–electron transfer can explain many key experimental observations.

E.s.r. studies at liquid-helium temperatures[126] have given new information relating to the structure and mechanism of action of xanthine oxidase, and further studies[127] have been made on the 'rapid' and 'slow' changes in intensity of the two molybdenum(v) signals during anaerobic reduction of the enzyme. The structure and function of ferritin, an iron storage protein which seems to have close links with xanthine oxidase, have been reviewed.[128]

A recent suggestion that e.s.r. spectroscopy may be unable to detect certain copper(II) centres in such enzymes as laccase and caeruloplasmin because they exist in the form of spin-paired cupric dimeric units has led

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[120] W. R. Dunham, G. Palmer, R. H. Sands, and A. J. Bearden, *Biochim. Biophys. Acta*, 1971, **253**, 373.

[121] W. A. Eaton, G. Palmer, J. A. Fee, T. Kimura, and W. Lovenberg, *Proc. Nat. Acad. Sci. U.S.A.*, 1971, **68**, 3015.

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[123] G. N. Schrauzer, P. A. Doemeny, R. H. Frazier, and G. W. Kiefer, *J. Amer. Chem. Soc.*, 1972, **94**, 7378.

[124] E. E. van Tamelen, J. A. Gladysz, and J. S. Miller, *J. Amer. Chem. Soc.*, 1973, **95**, 1347.

[125] E. I. Stiefel, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 988.

[126] D. J. Lowe, R. M. Lynden-Bell, and R. C. Bray, *Biochem. J.*, 1972, **130**, 239.

[127] J. C. Swann and R. C. Bray, *European J. Biochem.*, 1972, **26**, 407.

[128] R. R. Crichton, *Angew. Chem. Internat. Edn.*, 1973, **12**, 57.

Byers and Williams[129] to consider the properties which might be associated with such units. They conclude that, in principle at least, it is clearly possible to distinguish copper (II) dimers from copper(I) systems by the temperature dependence of their proton n.m.r. spectra provided the interaction between the paramagnetic ions is not too strong.

The stopped-flow technique has been used[130] to study the anaerobic reduction of fungal laccase B by hydroquinone, ascorbate, and ferrocyanide, for which a model is formulated, and the reduction of caeruloplasmin by the hydrated electron has been followed by pulse radiolysis.[131] The latter technique has also been used[132] to study the inhibition of another copper-containing enzyme, superoxide dismutase, by cyanide ions. Comparison of the rates and activation parameters for the reduction by chromous ion of 'blue' copper in laccase, stellacyanin, and spinach and French-bean plastocyanins indicates[133] that reduction of the Cu(614) site in laccase may occur by intramolecular electron transfer from one of the Cu(330) sites. The value of 17.4 kcal mol^{-1} for the activation enthalpy associated with the reduction of cytochrome *c* by the same species is consistent[133] with a mechanism in which major conformational changes in the protein accompany electron transfer.

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[129] W. Byers and R. J. P. Williams, *J.C.S. Dalton*, 1973, 555.

[130] L. E. Andréasson, B. G. Malmström, C. Strömberg, and T. Vänngård, *European J. Biochem.*, 1973, **34**, 434.

[131] M. Faraggi and I. Pecht, *J. Biol. Chem.*, 1973, **248**, 3146.

[132] G. Rotilio, R. C. Bray, and E. M. Fielden, *Biochim. Biophys. Acta*, 1972, **268**, 605.

[133] J. W. Dawson, H. B. Gray, R. A. Holwerd, and E. W. Westhead, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 30.

Part IV

ORGANOMETALLIC COMPOUNDS

By
R. D. W. KEMMITT
M. A. R. SMITH

1

Substitution

BY R. D. W. KEMMITT AND M. A. R. SMITH

Substitution of nickel, palladium, and platinum complexes forms part of a recent review on the kinetics of reactions of these compounds.[1] A review up to 1971 on the chemistry of Co^I cyanides contains references relevant to Sections 2 [Mixed-ligand Carbonyls: displacement of CO], 3, and 4 of this chapter.*

1 Exchange Reactions

The specific rates of ^{13}CO exchange with the equatorial and axial CO ligands in $[HMn(CO)_5]$ are $6.7 \pm 1.1 \times 10^{-6}\ s^{-1}$ and $19 \pm 4.8 \times 10^{-6}\ s^{-1}$, respectively.[2] The ratio of equatorial and axial rate constants is in the range 0.25—0.5 and in accordance with an earlier suggestion[3] this points to hydride migration to give an acyl intermediate in the exchange process, *i.e.*

$$[HMn(CO)_5] + {}^{13}CO \longrightarrow [(HCO)Mn(CO)_4({}^{13}CO)]$$
$$[(HCO)Mn(CO)_4({}^{13}CO)] \longrightarrow [HMn(CO)_4({}^{13}CO)] + CO$$

The corresponding ratio in the exchange of ^{13}CO with $[Mn(CO)_5Br]$ is 1.35, indicating a dissociative mechanism.[4] Both results appear to preclude intramolecular equatorial–axial CO exchange.

cis-$[Ru(CO)_4(SiCl_3)_2]$ undergoes stereospecific (equatorial) carbonyl exchange with ^{13}CO. The reaction is first-order overall ($\Delta H^{\ddagger} = 115.0 \pm 4.3\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = 12.9 \pm 1.3\ J\ mol^{-1}\ K^{-1}$) and is postulated to proceed *via* a five-co-ordinate intermediate as in Scheme 1. *trans*-$[Ru(CO)_4(SiCl_3)_2]$, as well as *cis*-$[Ru(CO)_4(GeCl_3)_2]$, also undergoes exchange to give the *cis*-disubstituted product, thereby suggesting the common five-co-ordinate intermediate in Scheme 1.[5]

The preparation of ^{56}Mn-labelled $[IMn(CO)_5]$ by neutron irradiation is of obvious potential use in the study of exchange reactions.[6] The rate of exchange

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* See ref. 49 in Section 4.

[1] A. Peloso, *Coordination Chem. Rev.*, 1973, **10**, 123.

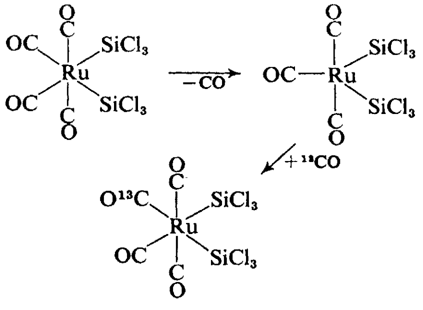
[2] A. Berry and T. L. Brown, *J. Organometallic Chem.*, 1971, **33**, C67.

[3] K. Noak and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101.

[4] A. Berry and T. L. Brown, *Inorg. Chem.*, 1972, **11**, 1165.

[5] R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 272.

[6] S. C. Srinivasan and D. R. Wiles, *Chem. Comm.*, 1971, 1633.



Scheme 1

of triphenylphosphine in $[(h^5\text{-}C_5H_5)Mn(CO_2Me)(NO)(PPh_3)]$ is the same as the rate of racemization of the (+)- and (−)-forms of the complex. Dissociation of phosphine is therefore proposed as the rate-determining step in the racemization.[7]

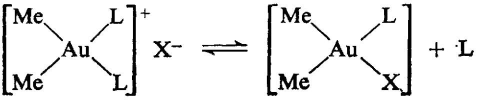
Kinetic parameters for the exchange of phosphorus bases in $[MeCo(dmgH)_2L]$ [$(dmgH)_2$ = dimethylglyoximato] are $\Delta H^{\ddagger} = 96.5 \pm 11.6$ kJ mol^{-1}, $\Delta S^{\ddagger} = 34.5 \pm 4$ J mol^{-1} K^{-1} [L = $P(OMe)_3$], and $\Delta H^{\ddagger} = 86.0 \pm 6.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = 23.6 \pm 1.3$ J mol^{-1} K^{-1} (L = PPh_3).[8]

Rapid phosphine exchange at ambient temperature is postulated in $[Me_2Ni(PMe_2Ph)_3]$ and $[Me(PhO)Ni(PMe_2Ph)_2]$.[9] The surmise[10] that broadening of hydridic resonances in *trans*-$[PtHX(PR_3)_2]$ (X = NCO or NCS) complexes is due to phosphine exchange has been predicated in a recent communication by Pidcock.[11] Examination of the half-widths of the hydride signal at 268 K in both the S- and N-bonded forms of *trans*-$[PtH(NCS)(PEt_3)_2]$ shows that even in the presence of an excess of phosphine exchange is negligible. Furthermore, the hydridic resonances of the N-bonded form are still significantly broader than those of the S-bonded form, an observation readily ascribed to interaction with the ^{14}N quadrupole.[11]

Ligand-exchange rates in the species $[L_4Ag]^+X^-$, L_3AgX, $[L_3Ag]^+X^-$, L_2AgX, and $[L_2Ag]^+X^-$ (L = tri-*p*-tolylphosphine or triethyl phosphite) are independent of L but dependent on the co-ordinating ability of X. This probably reflects S_N1 and S_N2 mechanisms in the respective cases of poor and good counterions.[12] In the series $[Me_2AuL_2]^+X^-$ (L = Me_3P, Me_2PPh, or $MePPh_2$), ^1H n.m.r. measurements indicate that phosphine exchange is facilitated by increasing phenyl substitution. Slow phosphine exchange in $[Me_2Au(Ph_3P)_2]ClO_4$ (*i.e.* with a poorly co-ordinating counterion) even at

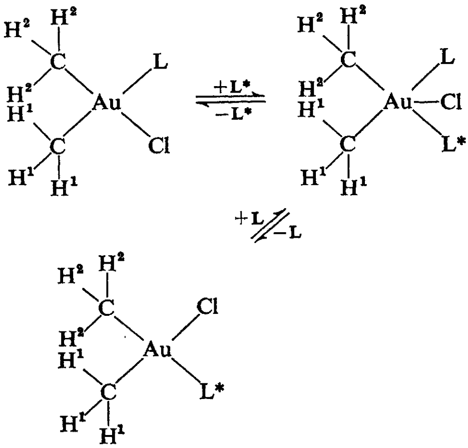
[7] H. Brunner and H.-D. Schindler, *Z. Naturforsch.*, 1971, **26b**, 1220.
[8] T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Amer. Chem. Soc.*, 1972, **94**, 384.
[9] E. A. Jeffery, *Austral. J. Chem.*, 1973, **26**, 219.
[10] M. W. Adlard and G. Socrates, *J.C.S. Chem. Comm.*, 1972, 17.
[11] A. Pidcock, *J.C.S. Chem. Comm.*, 1973, 249.
[12] E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, 1972, **94**, 6386.

313 K indicates that the exchange mechanism probably proceeds *via* nucleophilic attack of the anion on gold, thereby displacing the equilibrium



to the right.[13]

The intermolecular exchange of the nitrogenous base L in $[\mathrm{Ru(CO)(Pr^{i}\text{-}tpp)L}]$ [$\mathrm{Pr^{i}}$-tpp = tetrakis-(*p*-isopropylphenyl)porphinato dianion; L = 4-t-butylpyridine, 2-methylpyridine, 3,5-dimethylpyrazole, 4,5-dimethylpyridazine, or 3,6-dimethylpyridazine] proceeds *via* a dissociative mechanism (independent of L). Intramolecular exchange is also found and is 20—85 times faster than the intermolecular process.[14] $[\mathrm{Me_2AuCl(py)}]$ exhibits an exchange process which causes the methyl signals to coalesce on raising the temperature or adding pyridine. The reaction is in fact found to be first-order in pyridine and an associative mechanism based on the exchange of pairs of protons in 2-methylallylpalladium(II) complexes is proposed (Scheme 2).[15]



Scheme 2

The equilibrium constants at 295 ± 1 K for the anion-exchange process

$$[\mathrm{MeHgOCOMe}] + [\mathrm{PhHgSPh}] \rightleftharpoons [\mathrm{MeHgSPh}] + [\mathrm{PhHgOCOMe}]$$

estimated from $^{199}\mathrm{Hg}$–$^{1}\mathrm{H}$ coupling constants are 0.52 (pyridine), 0.43 (dimethyl sulphoxide), and 0.16 (chloroform).[16]

[13] C. F. Shaw, J. W. Lundeen, and R. S. Tobias, *J. Organometallic Chem.*, 1973, **51**, 365.
[14] S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometallic Chem.*, 1972, **39**, 179.
[15] H. Hagnauer, G. C. Stocco, and R. S. Tobias, *J. Organometallic Chem.*, 1972, **46**, 179.
[16] R. J. Kline and L. F. Sytsma, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1.

2 Substitution in Carbonyls: Carbon Monoxide Replacement

Simple Carbonyls.—With regard to simple mononuclear carbonyls, interest has centred once more around photochemical reactions. Earlier reports that photolysis of $[Cr(CO)_6]$ in argon matrix at 20 K[17] or hydrocarbon glasses at 77 K[18] or flash photolysis in cyclohexane at ambient temperature[19] all lead initially to the formation of C_{4v} $[Cr(CO)_5]$ are in some doubt. The chief discrepancy is in the position of maximum absorption of the product(s) in the visible spectrum (542 nm in argon and 483 and 485 nm in the respective hydrocarbon media). A current paper, in dealing with the photolysis of $[Cr(CO)_6]$ in methane at 20 K, suggests that the products formed in hydrocarbons are $[Cr(CO)_5S]$, where S is the hydrocarbon solvent.[20] However, $[Cr(CO)_5]$ is still proposed as the initially formed species in a re-examination of the flash photolysis of $[Cr(CO)_6]$ in extensively purified cyclohexane.[21] λ_{max} for $[Cr(CO)_5]$ is reported as 503 nm and a second species having $\lambda_{max} = 445$ nm is found to have a longer lifetime. The second species was not identified but was postulated to arise from reaction with solvent impurities, a conclusion which could be applied to the species earlier labelled as D_{3h} $[Cr(CO)_5]$. Under an atmosphere of CO, $[Cr(CO)_5]$ recombines to form the hexacarbonyl with a rate constant of $3 \pm 1 \times 10^6$ l mol^{-1} s^{-1}.[21] Substitution of CO in $[M(CO)_6]$ (M = Cr, Mo, or W) by thiazolidine-2-thione under u.v. irradiation has been shown to follow a dissociative course by determining quantum yields and studying initial rate dependence.[22] In comparison, the rate law for the reaction

$$[M(CO)_6] + 3MeCN \longrightarrow [M(CO)_3(MeCN)_3] + 3CO$$

(M = Cr, Mo, or W) is found to contain an additional associative term. The results suggest that MeCN is as good a nucleophile as PPh_3 and $AsPh_3$ and that when M = W the associative path is the dominant one.[23]

Di- and Tri-nuclear Carbonyls.—Substitution reactions of $[Ru_3(CO)_{12}]$ with Group Vb donors follow the rate law: $k_{obs} = k_1 + k_2[L]$. For L = $AsPh_3$ or PPh_3, k_2 is quite small, and kinetic parameters for the first-order process ($\Delta H_1^{\ddagger} = 133 \pm 1$ kJ mol^{-1}, $\Delta S_1^{\ddagger} = 85.3 \pm 2.5$ J mol^{-1} K^{-1}) are in good agreement with those for ^{14}CO exchange with the complex. The corresponding parameters for the bimolecular process, which in contrast to earlier work does proceed at an appreciable rate (probably by nucleophilic attack at Ru), are given in Table 1.[24]

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[17] M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939.

[18] M. J. Boylan, P. S. Braterman, and A. Fullarton, *J. Organometallic Chem.*, 1971, **31**, C29.

[19] J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1971, **29**, 269.

[20] M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Organometallic Chem.*, 1972, **34**, C34.

[21] J. M. Kelly, H. Hermann, and E. Koerner von Gustorf, *J.C.S. Chem. Comm.*, 1973, 105.

[22] D. DeFilippo, F. Devillanova, C. Preti, E. F. Trogu, and P. Viglino, *Inorg. Chim. Acta*, 1972, **6**, 23.

[23] K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3759.

[24] A. J. Poë and M. V. Twigg, *J. Organometallic Chem.*, 1973, **50**, C39.

Table 1 *Rate data for the bimolecular substitution of* $[Ru_3(CO)_{12}]$ *in decalin* (*from ref.* 24)

Ligand	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S_2^{\ddagger}$/J mol^{-1} K^{-1}	$10^4\, k_2$/l mol^{-1} s^{-1} *at* 323 K
$AsPh_3$	~55	~−160	~4
PPh_3	64.6±0.6	−101±2	12
PPh_3[a]	64.5±1.2	−101±4	14
$P(OPh)_3$	60.1±1.0	−113±3	16
$P(OCH_2)_3CEt$	57.7±1.9	−101±6	160
$P(OEt)_3$	59.6±0.4	−94±1	190
PBu^n_3	50.2±3.1	−115±10	520

[a] Reaction in 1,4-dioxan.

The observed rate of formation of $[HCo(CO)_4]$ in the reaction of dihydrogen with $[Co_2(CO)_8]$ in n-heptane is a result of two competing mechanisms A and B.

A:
$$[Co_2(CO)_8] \xrightleftharpoons[\text{fast } K_D^{(1)}]{} [Co_2(CO)_7] + CO \qquad (1)$$

$$[Co_2(CO)_7] + H_2 \xrightleftharpoons[\text{slow } k_1]{\text{fast}} [H_2Co_2(CO)_7] \qquad (2)$$

$$[H_2Co_2(CO)_7] \xrightleftharpoons[\text{fast}]{\text{slow } k_2} [HCo(CO)_4] + [HCo(CO)_3] \qquad (3)$$

$$[HCo(CO)_3] + CO \xrightleftharpoons[\text{fast}]{K_D^{(2)}} [HCo(CO)_4] \qquad (4)$$

B:
$$[Co_2(CO)_8] + H_2 \xrightarrow[\text{slow}]{k_1'} 2[HCo(CO)_4] \qquad (5)$$

Thus, $k_{obs} = k_1 K_D^{(1)}[CO]^{-1} + k_1'$. In accordance with these kinetics, the reaction is independent of CO at high p_{CO} whereas at low p_{CO} inhibition by CO is observed. The overall equilibrium constant, *i.e.* that in

$$[Co_2(CO)_8] + H_2 \rightleftharpoons 2[HCo(CO)_4]$$

was measured and also derived by kinetic analysis of the above mechanism. Data are summarized in Table 2.[25]

Table 2 *Equilibrium constants for the reaction* $[Co_2(CO)_8] + H_2 \rightleftharpoons 2[HCo(CO)_4]$ *in n-heptane derived by static and kinetic methods* (*from ref.* 25)

Temp./K	$K = \dfrac{[HCo(CO)_4]^2 \times 10^2}{[Co_2(CO)_8][H_2]}$	$K = \dfrac{2k_1K_D^{(1)} \times 10^2}{k_2K_D^{(2)}}$
307	4.6	4.50
317	5.5	5.74
327	6.5	6.49
337	7.6	7.33

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[25] F. Ungvary, *J. Organometallic Chem.*, 1972, **36**, 363.

Two reports[26, 27] have appeared on the reaction of octacarbonyldicobalt with alkynes. In the reaction with oct-1-yne, oct-2-yne, or diphenylacetylene[26] ($R^1C_2R^2$) in toluene k_{obs} was found to fit the rate law

$$k_{\text{obs}} = \frac{k_1[R^1C_2R^2]}{(k_{-1}/k_2)(1 + k_{-2}/k_3)[CO] + [R^1C_2R^2]} \qquad (6)$$

derived by steady-state analysis of the following mechanism at constant p_{CO}:

$$[Co_2(CO)_8] \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [Co_2(CO)_7] + CO$$

$$[Co_2(CO)_7] + R^1C_2R^2 \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} [Co_2(CO)_7(R^1C_2R^2)]$$

$$[Co_2(CO)_7(R^1C_2R^2)] \xrightarrow{k_3} [Co_2(CO)_6(R^1C_2R^2)] + CO$$

Such an analysis is only valid if the rate of production of $[Co_2(CO)_7(R^1C_2R^2)]$ is small, and in fact the kinetics become complex and depart from pseudo-first-order if this condition is not fulfilled, *i.e.* when the concentration of $R^1C_2R^2$ is not greater than that of $[Co_2(CO)_8]$ at constant p_{CO}. Rearranging equation (6) gives

$$\alpha = \frac{k_{-1}}{k_1 k_2}\left(1 + \frac{k_{-2}}{k_3}\right)[CO] \qquad (7)$$

where α is the slope of the plot of k_{obs}^{-1} against $[R^1C_2R^2]^{-1}$ and plots of α against [CO] are, as expected, linear with zero intercept. This provides evidence in favour of the present mechanism over that in a previous paper[28] which postulated production of 'a reactive form of octacarbonyldicobalt' rather than dissociation to $[Co_2(CO)_7]$ and CO. An analogous kinetic analysis of this model would necessitate a positive intercept. A second paper[27] deals with the reaction between $[Co_2(CO)_8]$ and hept-1-yne in n-heptane and proposes the following mechanism to fit the dependence on initial rates:

$$[Co_2(CO)_8] + \text{hept-1-yne} \underset{K}{\overset{\text{fast}}{\rightleftharpoons}} [(\text{heptyne})Co_2(CO)_7] + CO$$

$$[(\text{heptyne})Co_2(CO)_7] \xrightarrow{k} [(\text{heptyne})Co_2(CO)_6] + CO$$

Such a scheme does no more than explain the inverse dependence on [CO]. Moreover, initial rates were determined at equal concentrations of $[Co_2(CO)_8]$ and hept-1-yne, a situation not recommended in the former more thorough study.[26]

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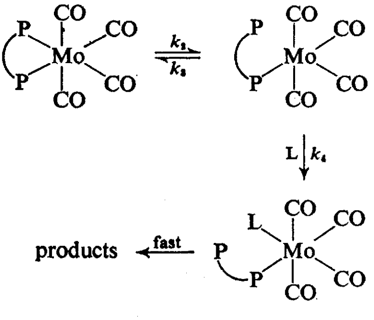
[26] P. C. Ellgen, *Inorg. Chem.*, 1972, **11**, 691.

[27] F. Ungvary and L. Marko, *Chem. Ber.*, 1972, **105**, 2457.

[28] M. R. Tirpak, J. H. Wotiz, and C. A. Hollingsworth, *J. Amer. Chem. Soc.*, 1958, **80**, 4265.

Mixed-ligand Carbonyls.—*Group VI.* The kinetics of the reactions of [(P-en)Mo(CO)$_4$] [(P-en) = ethylenediphosphine, $H_2PC_2H_4PH_2$] with L = $P(OPh)_3$, $P(OEt)_3$, or $\mathrm{PBu^n}_3$ are diagnostic of differing mechanisms in each case.[29] (i) $P(OPh)_3$. A limiting rate at high concentrations of phosphite is accommodated by a pre-equilibrium step involving dechelation of (P-en) (Scheme 3). In addition, the products of the reaction, *cis*-[(P-en){$P(OPh)_3$}-Mo(CO)$_3$] and *cis*-[{$P(OPh)_3$}$_3$Mo(CO)$_3$], and the non-linearity of k_{obs}^{-1} *versus* $[P(OPh)_3]^{-1}$ plots necessitate a further term in the rate expression. This is found to represent competing dissociative loss of CO. (ii) $\mathrm{PBu}^{\mathrm{n}}_3$. Plots of k_{obs} against $[\mathrm{PBu}^{\mathrm{n}}_3]$ are linear with a positive intercept on the ordinate. By virtue of the increased nucleophilicity of $\mathrm{PBu}^{\mathrm{n}}_3$ over $P(OPh)_3$ the predominant bimolecular term is deemed not to be the appropriate limiting term which could be deduced from the previous mechanism having $k_3 \gg k_4[\mathrm{L}]$. $\Delta S^{\ddagger}$ for the reaction (-50.4 J mol^{-1} K^{-1}) supports the postulate that the mechanism is truly bimolecular. (iii) $P(OEt)_3$. Initial rate dependence on $[P(OEt)_3]$ leads to a similar mechanism to that involving $P(OPh)_3$ but without the necessity of a dissociative step. The rate data for $P(OEt)_3$ are compared with those for other *cis*-[L_2Mo(CO)$_4$] complexes. The chelation reaction



Scheme 3

$$[(\mathrm{LL})\mathrm{M(CO)_5}] \longrightarrow [(\mathrm{LL})\mathrm{M(CO)_4}] + \mathrm{CO}$$

(M = Cr, Mo, or W; LL = $Me_2PC_2H_4PMe_2$, $Ph_2PCH_2PPh_2$, $Ph_2PC_2H_4PPh_2$, $Ph_2PC_3H_6PPh_2$, or $Ph_2PC_2H_4AsPh_2$) is found to follow first-order kinetics. A dissociative mechanism is indicated by the similarity in reaction rate between the phosphorus and arsenic bases, by a positive $\Delta S^{\ddagger}$ (+6—71 J mol^{-1} K^{-1}), and by the magnitude of $\Delta H^{\ddagger}$ (132—155 kJ mol^{-1}). Entropy is also deemed responsible for the observation that the smaller the chelate ring the faster the reaction in the series LL = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, or 3).[30]

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[29] G. R. Dobson and A. J. Rettenmaler, *Inorg. Chim. Acta*, 1972, **6**, 507.

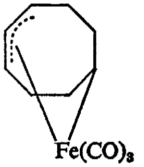
[30] J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J.C.S. Dalton*, 1973, 347.

Group VII. In the photochemical substitution reaction

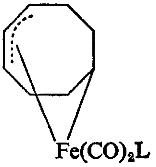
$$[Mn(NO)(CO)_4] + L \xrightarrow{h\nu} [Mn(NO)(CO)_3L] + CO$$

quantum yields are found to be independent of L when L = $AsPh_3$ but dependent on L for L = PPh_3. This is interpreted as indicative of an S_N1 pathway for the weaker nucleophile, whereas for the stronger one S_N1 and S_N2 pathways are involved.[31] $[(h^5\text{-}C_5H_5)Mn(CO)_2]$ and $[(h^5\text{-}C_5H_4Me)Mn(CO)_2]$ have been observed as a result of photolysis of the parent tricarbonyl in methylcyclohexane–Nujol glasses at 80 K.[32]

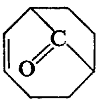
Group VIII. Some insight has been gained into the interesting reaction whereby $[(1,2,3,6\text{-}h^4\text{-}C_8H_{12})Fe(CO)_3]$ (1) reacts with L (L = CO, tertiary phosphines, or phosphites) to give (3) and $[Fe(CO)_2L_3]$.[33] Two reaction paths are apparent from the kinetics. For L = PPh_3 or $P(OPh)_3$ substitution of CO *trans* to the iron–carbon bond takes place *via* a CO dissociative mechanism, limiting pseudo-first-order rate constants from which are independent of the nature of L. If the reaction is performed with stronger nucleophiles (alkylphosphines and alkyl phosphites) the kinetics are given by



(1)



(2)



(3)

$$k_{obs} = k_1 + k_2[L]$$

The value of k_1 is the same for all L and is identical to the limiting rate constants for L = PPh_3 and $P(OPh)_3$. The k_1 path is postulated to arise from production of (2) *via* rate-determining dissociation of CO whereas the k_2 path corresponds to formation of $[FeL_3(CO)_2]$ and the transannular ketone (3).[33] The reaction

$$[(h^5\text{-}Z)Fe(CO)_2I] + P(OR)_3 \longrightarrow [(h^5\text{-}Z)Fe(CO)\{P(OR)_3\}I] + CO$$

(Z = C_5H_5, indenyl, or tetrahydroindenyl; R = Et or Ph), is largely independent of $[P(OR)_3]$ and therefore follows an S_N1 course. However, the reaction rate at 368.2 K in n-octane for the indenyl complex is ~600 times that for the cyclopentadienyl and tetrahydroindenyl complexes. Explanation on steric grounds is readily dismissed on the basis of similar rates for C_5H_5 and C_9H_{11} complexes. The reason is postulated to be facilitation of carbonyl

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[31] D. P. Keeton and F. Basolo, *Inorg. Chim. Acta*, 1972, **6**, 33.
[32] P. S. Braterman and J. D. Black, *J. Organometallic Chem.*, 1972, **39**, C3.
[33] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **52**, C31.

dissociation by the participation of the aromatic ring in the indenyl complex in the bonding in the activated state, thereby lowering its energy.[34] A similar explanation was tendered to account for faster reaction rates and an additional associative path in the reaction of $[(h^5\text{-}C_9H_7)Mo(CO)_3X]$ with phosphorus bases.[35] However, the increase in rate for the iron–indenyl complexes is reflected mainly in an increase in entropy of activation whereas that in the molybdenum analogue is enthalpy-controlled. The carbonyl substitution reaction

$$[Fe_3(CO)_9XY] + L \longrightarrow [Fe_3(CO)_8LXY] + CO$$

[X and Y are chalcogens; L = CO, $AsPh_3$, $P(OPh)_3$, or PBu^n] follows first-, first- plus second-, or second-order kinetics in n-heptane (Table 3). Similar reactions for $[Fe_3(CO)_9X_2]$ are also summarized in Table 3. The rising predominance of second-order kinetics with increasing nucleophilicity of L is expected. However, the decreasing electronegativity of the chalcogens down the list in Table 3 might be expected to inhibit rate-determining nucleophilic attack of L on iron rather than promote it, as is observed. The authors postulate attack of L on the chalcogen to account for this trend.[36] Chelation and disubstitution reactions,

Table 3 *Orders of the reactions of* $[Fe_3(CO)_9X_2]$ *and* $[Fe_3(CO)_9XY]$ *with* L (*from ref.* 36)

	L			
Complex	CO	$AsPh_3$	$P(OPh)_3$	PBu^n_3
$[Fe_3(CO)_9S_2]$	1st	1st	1st	2nd
$[Fe_3(CO)_9SSe]$	1st	1st	1st + 2nd	—
$[Fe_3(CO)_9STe]$	1st	1st	1st + 2nd	—
$[Fe_3(CO)_9Se_2]$	1st	1st	1st + 2nd	—
$[Fe_3(CO)_9SeTe]$	1st + 2nd	1st + 2nd	2nd	—
$[Fe_3(CO)_9Te_2]$	2nd	2nd	2nd	2nd

$$[Fe(CO)(NO)_2L] + \text{diphos} \longrightarrow [Fe(NO)_2(\text{diphos})] + L + CO$$

[L = PPh_3, PBu^n_3, $P(OBu^n)_3$, $P(OPh)_3$, or $AsPh_3$] and

$$[Fe(CO)(NO)_2L] + L \longrightarrow [Fe(NO)_2L_2] + CO$$

[L = PPh_3, PBu^n_3, or $P(OBu^n)_3$] obey second-order rate laws except for L = PPh_3 or PBu^n_3, when an additional dissociative term is found. The dissociative rate constant is the same for both reactions and this mechanistic

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[34] D. J. Jones and R. J. Mawby, *Inorg. Chim. Acta*, 1972, **6**, 157.

[35] A. J. Hart-Davis, C. White, and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 441; C. White and R. J. Mawby, *ibid.*, 1970, **4**, 261.

[36] R. Rossetti, P. L. Stanghellini, O. Gambino, and G. Cetini, *Inorg. Chim. Acta*, 1972, **6**, 205.

path is further corroborated by $\Delta S^{\ddagger} = 17.2 \pm 12.9\ \text{J mol}^{-1}\ \text{K}^{-1}$ (chelation) and $-8.6 \pm 12.9\ \text{J mol}^{-1}\ \text{K}^{-1}$ (disubstitution) for $L = PPh_3$.[37]

In contrast to recent work[24] on the substitution of $[Ru_3(CO)_{12}]$ (see earlier), which demonstrates the important contribution of a bimolecular process to the overall rate, the substitution of $[Ru_3(NO)_2(CO)_{10}]$ with L (PPh_3 or $PMePh_2$) follows purely first-order kinetics. Disubstitution occurs to give $[Ru_3(NO)_2L_2(CO)_8]$ and the stages are separate enough to verify that the same kinetics apply to both stages. In view of the work on $[Ru_3(CO)_{12}]$ the results are somewhat surprising since the presence of the electron-rich NO ligands might have been expected to promote a bimolecular mechanism further.[38]

A theoretical treatment of the electronic effects of h^3-C_3H_5 and h^5-C_5H_5 is in agreement with previous results that $[(h^3\text{-}C_3H_5)Co(CO)_2]$ and $[(h^5\text{-}C_5H_5)Co(CO)_2]$ react with PPh_3 by S_N1 and S_N2 mechanisms respectively.[39]

Pseudo-first-order rate constants measured at 353 K for the reaction

$$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2] + Ph_2C_2 \longrightarrow [Ni_2(Ph_2C_2)(h^5\text{-}C_5H_5)_2] + 2CO$$

are said to approach a limiting value at $[Ph_2C_2] > 5.0 \times 10^{-2}\ \text{mol l}^{-1}$.[40] Such an observation would be consistent with the mechanism

$$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2] \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} [Ni_2(CO)_2(h^5\text{-}C_5H_5)_2]^*$$

$$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2]^* + Ph_2C_2 \xrightarrow{k_2} [Ni_2(Ph_2C_2)(h^5\text{-}C_5H_5)_2] + 2CO$$

leading to the rate law

$$k_{\text{obs}} = \frac{k_1 k_2 [Ph_2C_2]}{k_{-1} + k_2[Ph_2C_2]}$$

$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2]^*$ denotes a 'reactive form' of the starting complex, a hypothesis which has already been shown to be incorrect in the case of the reaction of $[Co_2(CO)_8]$ with alkynes[26, 28] (see earlier). In direct contrast to this, Ellgen reports that even at $[Ph_2C_2] = 0.50\ \text{mol l}^{-1}$ at 353 K in the same reaction in the same solvent a limiting rate was not reached.[41] After pointing out that the alternative reaction paths,

$$4[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2] \longrightarrow 2[Ni_3(CO)_2(h^5\text{-}C_5H_5)_3] + [Ni(CO)_4] + [Ni(h^5\text{-}C_5H_5)_2]$$

and

$$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2] + 2CO \longrightarrow [Ni(CO)_4] + [Ni(h^5\text{-}C_5H_5)_2]$$

as well as the basic substitution reaction are readily feasible under the rather

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[37] G. Cardaci and S. M. Murgia, *Inorg. Chim. Acta*, 1972, **6**, 222.

[38] J. R. Norton and J. P. Collman, *Inorg. Chem.*, 1973, **12**, 476.

[39] D. A. Brown, H. L. Clarke, and N. J. Fitzpatrick, *J. Organometallic Chem.*, 1973, **47**, C11.

[40] P. L. Stanghellini, R. Rossetti, O. Gambino, and G. Cetini, *Inorg. Chem.*, 1971, **10**, 2672.

[41] P. C. Ellgen, *Inorg. Chem.*, 1972, **11**, 2279.

forcing conditions used, the author proposes the rate law

$$k_{\text{obs}} = k_{\text{d}} + k_{\text{r}}[\text{Ph}_2\text{C}_2]$$

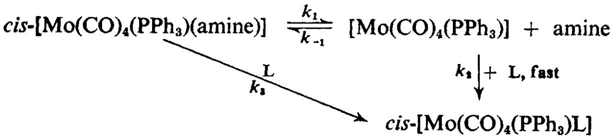
to fit the system. The k_{d} term is the rate constant for the decomposition of $[\text{Ni}_2(\text{CO})_2(h^5\text{-C}_5\text{H}_5)_2]$ in the absence of Ph_2C_2, whereas k_{r} deals with bimolecular attack of the acetylene on nickel. This situation is not markedly different from that found in the reaction between $[\text{Ni}_2(\text{CO})_2(h^5\text{-C}_5\text{H}_5)_2]$ and L (L = CO, PClPh_2, PPh_3, or PBu^{n}_3),[40] *i.e.*

$$[\text{Ni}_2(\text{CO})_2(h^5\text{-C}_5\text{H}_5)_2] + 2\text{L} \longrightarrow [\text{Ni}(h^5\text{-C}_5\text{H}_5)_2] + [\text{Ni}(\text{CO})_2\text{L}_2]$$

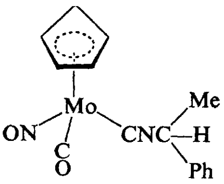
where k_{obs} is found to depend linearly on [L] with no sign of a limiting rate. An associative mechanism is further supported by the fact that the reaction rates increase with increasing basicity of L.[40]

3 Substitution in Carbonyls: Replacement of other Ligands

Substitution of the amine in *cis*-$[\text{Mo}(\text{CO})_4(\text{PPh}_3)(\text{amine})]$ by L [L = PPh_3, AsPh_3, SbPh_3, PBu^{n}_3, $\text{P}(\text{OCH}_2)_3\text{CEt}$, or $\text{P}(\text{C}_6\text{H}_{11})_3$; amine = $\text{NHC}_5\text{H}_{10}$ or NC_5H_5] proceeds *via* the mechanism shown in Scheme 4, and according to the rate law $k_{\text{obs}} = k_1 + k_3[\text{L}]$. The value of k_1 is always independent of the nature (or concentration) of L and is found to equal the rate constant in the first-order thermal dissociation of $[\text{Mo}(\text{CO})_4(\text{PPh}_3)(\text{amine})]$. An associative k_3 term is found only at high concentrations of the strong nucleophiles PBu^{n}_3 and $\text{P}(\text{OCH}_2)_3\text{CEt}$. Competition studies for the co-ordinatively unsaturated intermediate $[\text{Mo}(\text{CO})_4(\text{PPh}_3)]$ show what is only a slight preference for small nucleophiles. The substitution equilibrium, however, is very sensitive to the steric nature of L.[42] Nucleophilic attack on (4) proceeds with inversion of configuration about molybdenum.[43]



Scheme 4



(4)

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[42] C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, 1973, **12**, 1286.
[43] H. Brunner and M. Lappus, *Angew. Chem. Internat. Edn.*, 1972, **11**, 923.

Reactions of R_4NX with $[(\text{arene})M(CO)_3]$ (M = Cr, Mo, or W; X = F, Cl, Br, I, OH, SCN, N_3, or OEt) lead rapidly to products of general formula $[R_4N]_3[(CO)_3MX_3M(CO)_3]$. Promotion of this type of ionic reaction may explain why these complexes serve as catalysts in Friedel–Crafts reactions.[44]

Solvent appears to facilitate the substitution of Cl^- in the photolysis of $[(h^5\text{-}C_5H_5)Fe(CO)_2Cl]$ at 400 nm in DMSO or pyridine.[45]

4 Formation of Carbonyls

The suitability as models for biological protein systems of protoporphyrin IX (ppIX) and tetraphenylporphyrin (tpp) complexes, $[\text{Fe(ppIX)(piperidine)}_2]$ and $[\text{Fe(tpp)(piperidine)}_2]$, has been tested by examining their reactions with CO. Elucidation of the mechanism,

$$\begin{tikzcd}
{[(\text{pip})_2\text{Fe(porphyrin)}]} \arrow[r, shift right, "-\text{pip}\ k_1"'] & {[(\text{pip})\text{Fe(porphyrin)}]} \arrow[l, shift right, "+\text{pip}\ k_{-1}"'] \arrow[d, shift right, "+\text{CO},\ k_2"'] \\
& {[(\text{pip})\text{Fe(porphyrin)CO}]} \arrow[u, shift right, "-\text{CO},\ k_{-2}"']
\end{tikzcd}$$

from the kinetics shows that the examination is vindicated on two counts. Firstly, the importance of a five-co-ordinate intermediate imitates the active site in deoxy-myoglobin and -haemoglobin and secondly the k_{-2} value for the protoporphyrin IX complex is very close to the corresponding parameter in CO dissociation reactions of haemoglobin and myoglobin.[46] Although a five-co-ordinate intermediate arises from the kinetics of a similar reaction between *trans*-$[\text{Fe}^{\text{II}}(\text{dpgH})_2L_2]$ (dpgH = diphenylglyoximato-anion; L = pyridines, piperidine, imidazole, nicotine, or PPh_3) and CO, the corresponding term to k_{-2} above compares poorly with that in the reaction of the protein.[47]

The reaction

$$[Co(CN)_5H]^{3-} + 2CO + OH^- \longrightarrow [Co(CN)_3(CO)_2]^{2-} + 2CN^- + H_2O$$

has been shown by CO uptake and spectrophotometric methods to follow the rate law

$$-d[Co(CN)_5H^{3-}]/dt = k[Co(CN)_5H^{3-}][OH^-]$$

Comparison of k with that in other similar systems leads to the mechanism[48]

$$[Co(CN)_5H]^{3-} + OH^- \rightleftharpoons [Co(CN)_5]^{4-} + H_2O$$

$$[Co(CN)_5]^{4-} \longrightarrow [Co(CN)_4]^{3-} + CN^-$$

$$[Co(CN)_4]^{3-} + 2CO \longrightarrow [Co(CN)_3(CO)_2]^{2-} + CN^-$$

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[44] J. F. White and M. F. Farona, *J. Organometallic Chem.*, 1972, **37**, 119.

[45] L. H. Ali, A. Cox, and T. J. Kemp, *J.C.S. Dalton*, 1973, 1475.

[46] D. V. Stynes and B. R. James, *J.C.S. Chem. Comm.*, 1973, 325.

[47] L. Vaska and T. Yamaji, *J. Amer. Chem. Soc.*, 1971, **93**, 6673.

[48] G. Guastalla, J. Halpern, and M. Pribanic, *J. Amer. Chem. Soc.*, 1972, **94**, 1575.

This reaction and similar reactions, mostly up to 1971, some of relevance to earlier sections in this chapter, have recently been reviewed.[49] The equilibrium

$$[Rh(CO)_2X]_2 + 2CO \rightleftharpoons 2[Rh(CO)_3X]$$

lies increasingly to the right at elevated CO pressures in the series X = Cl, Br, or I and in more polar solvents. Increased temperature has the reverse effect.[50]

The solid-state reaction between $[Pd_2Cl_4L_2]$ (L = thiophane, dimethyl sulphoxide, diethyl sulphoxide, or diethyl sulphide) and CO proceeds only when the CO is moistened by methanol. Preliminary cleavage of the dimer bridge by methanol followed by insertion of CO is therefore proposed. Pseudo-first-order rate constants indicate the *trans*-effect series: thiophane > DESO > DMSO > Et_2S.[51]

5 Cyclopentadienyls

The paucity of reports on (h^5-C_5H_5) as a leaving group has continued in spite of evidence that chromocene, manganocene, and nickelocene are quite labile. Exchange of Li(h^1-C_5D_5) or [Ni(h^5-C_5D_5)$_2$] with [M(h^5-C_5H_5)$_2$] (M = V, Cr, Mn, Fe, Co, or Ni) appears to follow second-order kinetics.[52] The reaction of [(h^3-C_3H_5)M(h^5-C_5H_5)] (M = Ni or Pd) with $P(OR)_3$ (R = Et or Ph),

$$[(h^3\text{-}C_3H_5)M(h^5\text{-}C_5H_5)] + 4P(OR)_3 \longrightarrow [M\{P(OR)_3\}_4] + C_8H_{10}$$

shows third-order kinetics for M = Ni, R = Et, and second-order kinetics for M = Pd, R = Ph. The proposed mechanism,

$$[(h^3\text{-}C_3H_5)M(h^5\text{-}C_5H_5)] + P(OR)_3 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \underset{(5)}{[(h^3\text{-}C_3H_5)M(h^5\text{-}C_5H_5)\{P(OR)_3\}]}$$

$$(5) + P(OR)_3 \xrightarrow{k_2} (6) \longrightarrow \text{product after several fast stages}$$

on steady-state treatment of [(5)] yields the rate law

$$\text{Rate} = \frac{k_1k_2[(h^3\text{-}C_3H_5)M(h^5\text{-}C_5H_5)][P(OR)_3]^2}{k_{-1} + k_2[P(OR)_3]}$$

The observed kinetics are therefore the two limiting forms, *i.e.* when $k_{-1} \gg k_2[P(OR)_3]$ or *vice versa.*[53]

6 Phosphine and Phosphite Compounds

The equilibrium constants in chloroform at 300 K for formation of the

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[49] J. Halpern, G. Guastalla, and J. Bercaw, *Coordination Chem. Rev.*, 1972, **8**, 167.

[50] D. E. Morris and H. B. Tinker, *J. Organometallic Chem.*, 1973, **49**, C53.

[51] E. A. Andronov, Yu. N. Kukushkin, and V. G. Churakov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1312.

[52] M. E. Switzer and M. F. Rettig, *J.C.S. Chem. Comm.*, 1972, 687.

[53] V. Harder and H. Werner, *Helv. Chim. Acta*, 1973, **56**, 549.

dinuclear $Re^I—N{\equiv}N—Re^V$ complexes,

$$[Re(PMe_2Ph)_4(N_2)Cl] + [Re(O)XCl_2(PPh_3)_2] \rightleftharpoons [(PMe_2Ph)_4ClRe—N{\equiv}N—Re(O)XCl_2(PPh_3)] + PPh_3$$

are 0.28 ± 0.03 (X = Cl) and $4 \pm 2 \times 10^{-3}$ (X = OMe), which is deemed to illustrate the sensitivity of the $Re^I(N_2)$ complex to the Lewis acidity of the Re^V complex.[54]

The equilibrium constants for the reaction

$$ML_3 + C_2H_4 \rightleftharpoons [(C_2H_4)ML_2] + L$$

[M = Ni, Pd, or Pt; L = PPh_3, P(*p*-tol)$_3$, or P(*m*-tol)$_3$] are given in Table 4.

Table 4 *Equilibrium data for the equilibrium* $ML_3 + C_2H_4 \underset{K}{\rightleftharpoons} (C_2H_4)ML_2 + L$ *in benzene at* 298 K (*from ref.* 55)

ML_3	K
$[Ni(PPh_3)_3]$	300 ± 40
$[Pt\{P(p\text{-}C_6H_4Me)_3\}_3]$	0.21 ± 0.002
$[Pt(PPh_3)_3]$	0.122 ± 0.003
$[Pt\{P(m\text{-}C_6H_4Me)_3\}_3]$	0.07 ± 0.02
$[Pd\{P(p\text{-}C_6H_4Me)_3\}_3]$	0.016 ± 0.002
$[Pd(PPh_3)_3]$	0.013 ± 0.002
$[Pd\{P(m\text{-}C_6H_4Me)_3\}_3]$	0.004 ± 0.001

Changes in K with the metal are postulated to reflect mainly changes with the metal–olefin bond strength whereas changes with the phosphine are said to reflect interplay between varying steric and electronic effects. In addition, no dissociation of ML_3 or $[ML_2(C_2H_4)]$ in benzene was observed.[55] This last is in disagreement with earlier reports which quote K values for these equilibria but which are largely assumed in order to fit observed kinetics (*e.g.* ref. 56). However, the kinetic behaviour of substitution reactions of PtL_3 complexes has recently received a much more satisfactory explanation than that given in previous reports based on a dissociative mechanism.[57]

The model system

$$[Pt(PPh_3)_3] + MeC_2Ph \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [Pt(PPh_3)_2(MeC_2Ph)] + PPh_3 \qquad (8)$$

follows both associative [as shown by equation (8)] and dissociative [(9) and (10)] pathways,

$$[Pt(PPh_3)_3] \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} [Pt(PPh_3)_2] + PPh_3 \qquad (9)$$

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[54] D. J. Darensbourg, *Inorg. Chim. Acta*, 1972, **6**, 527.

[55] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.

[56] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer Chem. Soc.*, 1968, **90**, 4491.

[57] J. Halpern and T. A. Weil, *J.C.S. Chem. Comm.*, 1973, 631; and references therein.

$$[\mathrm{Pt(PPh_3)_2}] + \mathrm{MeC_2Ph} \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} [\mathrm{Pt(PPh_3)_2(MeC_2Ph)}] \qquad (10)$$

which lead, when the equilibrium lies far to the right and under steady-state conditions for $[\mathrm{Pt(PPh_3)_2}]$, to the rate law

$$\text{Rate} = [\mathrm{Pt(PPh_3)_3}][\mathrm{MeC_2Ph}]\left(k_1 + \frac{k_2k_3}{k_{-2}[\mathrm{PPh_3}] + k_3[\mathrm{MeC_2Ph}]}\right)$$

which is followed over a considerable concentration range for both forward and reverse reactions. It is interesting to note that the forward reaction proceeds predominantly by the dissociative and the back reaction by the associative path.[57] The kinetics of the reaction between $[\mathrm{Ni\{P(OPh)_3\}_4}]$ and maleic anhydride (man),

$$[\mathrm{Ni\{P(OPh)_3\}_4}] + \mathrm{man} \longrightarrow [\mathrm{Ni\{P(OPh)_3\}_2(man)}] + 2\mathrm{P(OPh)_3}$$

in methyl methacrylate or styrene depend on rate-determining dissociation of the starting complex. Furthermore, the intermediate $[\mathrm{Ni\{P(OPh)_3\}_3}]$ and man react to generate free radicals capable of initiating copolymerization of the solvent or of the maleic anhydride, albeit of low efficiency.[58]

The nature of silver(I) phosphine or phosphite complexes in dichloromethane at <200 K has been thoroughly investigated by ^{31}P n.m.r. spectroscopy. In solutions of four equivalents of L (L = tri-*p*-tolylphosphine or triethyl phosphite) to one of AgX, $[\mathrm{L_4Ag}]^+\mathrm{X}^-$ predominates for all counter-ions except the halides and CN^-. In the latter cases the equilibrium

$$[\mathrm{L_4Ag}]^+\mathrm{X}^- \rightleftharpoons \mathrm{L_3AgX} + \mathrm{L}$$

lies to the right (Table 5). Conductimetric and n.m.r. measurements on 3L–AgX and 2L–AgX solutions show that for poorly co-ordinating anions $[\mathrm{L}_n\mathrm{Ag}]^+\mathrm{X}^-$ (n = 2 or 3) is formed, whereas in the case of such ions as Cl^- or CN^- $\mathrm{L}_n\mathrm{AgX}$ is found.[12] An account of ligand exchange in these systems above 200 K is included in Section 1 of this chapter.

Table 5 *Equilibrium data for* $\mathrm{L_4AgX} \rightleftharpoons \mathrm{L_3AgX} + \mathrm{L}$ *in dichloromethane (from ref.* 12)

Anion X	*Ligand*	K/mol l^{-1}	*Temp.*/K
F	$\mathrm{P(C_7H_7)_3}$	~0.7	173
Cl	$\mathrm{P(OEt)_3}$	0.03	173
Cl	$\mathrm{P(C_7H_7)_3}$	0.3	187
Br	$\mathrm{P(OEt)_3}$	0.04	173
Br	$\mathrm{P(C_7H_7)_3}$	0.7	187
I	$\mathrm{P(OEt)_3}$	0.7	173
I	$\mathrm{P(C_7H_7)_3}$	$>10^4$	173
CN	$\mathrm{P(OEt)_3}$	$>10^4$	173
CN	$\mathrm{P(C_7H_7)_3}$	$>10^4$	173

[58] C. H Bamford and E. O. Hughes, *J.C.S. Faraday I*, 1972, 1474.

7 Metal–Metal Bond Cleavage

Work during the current period has centred around elucidation of the nature of the intermediates formed during substitution reactions of dimeric metal carbonyl complexes. There are some ambiguities.

There appeared to be some evidence to suggest that the reactive intermediates in some reactions are due to a metal-migration process (involving metal–metal bond heterolysis and nucleophilic attack of the reduced metal atom on the carbon of a CO ligand on the oxidized metal) and not simply to reversible ligand dissociation {as recently demonstrated in the reaction between alkyne and $[Co_2(CO)_8]$}.[26] Kinetic and equilibrium characteristics of substitution and, in some cases, thermal decomposition reactions of $[MnRe(CO)_{10}]$, $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$, $[Re_2(CO)_9(PPh_3)]$, and $[Ru(CO)_4SiMe_3]_2$ point to such a process.[59] However, later publications indicate that metal–metal bond homolysis may be occurring in all of these examples[59–61] except $[Re_2(CO)_{10}]$ and $[Re_2(CO)_9(PPh_3)]$. Rates of reaction between $[M(CO)_4L]_2$ and L [M = Mn, L = PPh_3 or $P(OPh)_3$; M = Re, L = PPh_3] are independent of [L] and half-order in [complex], thereby indicating reversible homolytic scission of the metal–metal bond as the first stage in an otherwise dissociative process.[61] In conjunction with these results, the e.s.r. spectrum of $\cdot Mn(CO)_5$ produced by the photolysis of $[Mn_2(CO)_{10}]$ at 3500 Å (350 nm) in THF has recently been reported.[62] In addition there is evidence from the products formed on u.v. irradiation of $[Re_2(CO)_{10}]$ in CCl_4 and in benzene containing benzyl halide that Re—Re bond homolysis occurs.[63]

The dependence of substitution rates on metal–metal bond strengths emerges from good correlations between the activation enthalpy of reaction of $[M_2(CO)_{10}]$ (M = Mn, Tc, or Re), $[MnRe(CO)_{10}]$, and $[Mn(CO)_4L]_2$ [L = PPh_3 or $P(OPh)_3$] with oxygen, with corresponding force constants for the metal–metal bond vibration and with $h\nu$ for the $\sigma \rightarrow \sigma^*$ transition, which involves orbitals from metal–metal interaction.[60]

8 Olefin and Acetylene Compounds

Since 1971 several studies involving olefins or acetylenes as leaving groups have appeared. Consequently this section is included in this chapter for the first time. The displacement of *cis*-cyclo-octene from $[(h^5\text{-}C_5H_5)Mn(CO)(CS)(C_8H_{14})]$ by PPh_3 proceeds at a rate that is independent of $[PPh_3]$, which together with a value of $\Delta S^{\ddagger}$ of 85.0 ± 11.6 J mol^{-1} K^{-1} indicates a likely S_N1 mechanism.[64] Loss of $CH_2{=}CHX$ from five-co-ordinate $[Fe(CO)_4(CH_2{=}CHX)]$ (X = OEt, Bu, Ph, CO_2Me, or CN) on reaction with CO also

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[59] D. DeWit, J. P. Fawcett, A. J. Poë, and M. V. Twigg, *Coordination Chem. Rev.*, 1972, **8**, 81.

[60] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1973, 267.

[61] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **51**, C17.

[62] S. A. Hallock and A. Wojcicki, *J. Organometallic Chem.*, 1973, **54**, C27.

[63] M. Wrighton and D. Bredesen, *J. Organometallic Chem.*, 1973, **50**, C35.

[64] I. S. Butler and A. E. Fenster, *Inorg. Chim. Acta*, 1973, **7**, 79.

involves rate-determining dissociation of the substrate but in a pre-equilibrium:

$$[(\mathrm{CH_2{=}CHX})\mathrm{Fe(CO)_4}] \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [\mathrm{Fe(CO)_4}] + \mathrm{CH_2{=}CHX}$$

$$[\mathrm{Fe(CO)_4}] + \mathrm{CO} \xrightarrow{k_2} [\mathrm{Fe(CO)_5}]$$

Steady-state treatment of $[\mathrm{Fe(CO)_4}]$ yields

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{CO}]}{k_{-1}[\mathrm{CH_2CHX}] + k_2[\mathrm{CO}]}$$

and, as predicted, plots of k_{obs}^{-1} *versus* [olefin] at constant [CO] are linear and k_1^{-1} was obtained from the intercept. The effect of the substituent X on k_1, the rate constant for loss of olefin, may be seen in Table 6, and in this context a plot of $\log k_1$ *versus* the Hammett value σ_{p} is linear.[65] Displacement of C_2H_4 from $[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$ is postulated to take place in a number of stages in which loss of olefin is always rate determining:

$$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2] \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [(h^5\text{-}C_5H_5)Rh(C_2H_4)] + C_2H_4$$

$$[(h^5\text{-}C_5H_5)Rh(C_2H_4)] + L \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} [(h^5\text{-}C_5H_5)Rh(C_2H_4)L]$$

$$[(h^5\text{-}C_5H_5)Rh(C_2H_4)L] \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} [(h^5\text{-}C_5H_5)RhL] + C_2H_4$$

$$[(h^5\text{-}C_5H_5)RhL] + L \underset{k_4}{\overset{k_{-4}}{\rightleftharpoons}} [(h^5\text{-}C_5H_5)RhL_2]$$

The observed rate of C_2H_4 evolution is controlled by the relative values of k_1 and k_3, which are in turn governed by whether L (see Table 6) stabilizes or destabilizes the intermediate $[(h^5\text{-}C_5H_5)Rh(C_2H_4)L]$. L may therefore influence the observed rate even though the reaction is dissociative. Values obtained are summarized in Table 6.[66]

The acetylene-exchange reaction

$$\mathrm{YC_6H_4C{\equiv}CH} + [(\mathrm{PPh_3})_2\mathrm{Pt(XC_6H_4C{\equiv}CH)}] \longrightarrow$$
$$\mathrm{XC_6H_4C{\equiv}CH} + [(\mathrm{PPh_3})_2\mathrm{Pt(YC_6H_4C{\equiv}CH)}]$$

initially appeared to follow an analogous mechanistic path to that of $[(\mathrm{CH_2CHX})\mathrm{Fe(CO)_4}]$ above, with the incoming acetylene taking the place of CO in the rate law. The appropriate linear relationships do, in fact, hold. However, microscopic reversibility requirements are not met by this scheme, *i.e.* k_{-1}/k_2 for X = H, Y = *p*-MeO is not equal to k_2/k_{-1} for X = *p*-MeO, Y = H, and so on throughout all pairs of X and Y studied (H, *p*-NO_2, and *p*-MeO). In order to account for this discrepancy an alternative mechanism

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[65] G. Cardaci and V. Narciso, *J.C.S. Dalton*, 1972, 2289.

[66] R. Cramer, *J. Amer. Chem. Soc.*, 1972, **94**, 5681.

Table 6 *Rate constants* (k_1) *for olefin displacement by* L

Ref.	*Substrate*	L	*Solvent*	$10^4k_1/s^{-1}$	*Temp.*/K
64	$[(h^5\text{-}C_5H_5)Mn(CO)(CS)(C_8H_{14})]$	PPh_3	Methylcyclohexane	0.95	323
65	$[(CH_2CHPh)Fe(CO)_4]$	CO	Toluene	1.6	323
65	$[(CH_2CHOEt)Fe(CO)_4]$	CO	Toluene	3.9	318
65	$[(CH_2CHBu)Fe(CO)_4]$	CO	Toluene	1.3	323
65	$[(CH_2CHCN)Fe(CO)_4]$	CO	Toluene	0.009	318
65	$[(CH_2CHCO_2Me)Fe(CO)_4]$	CO	Toluene	0.06	318
66[a]	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	PPh_3	Diphenyl ether	1.73	391
66	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	$Ph_2PC_2H_4PPh_2$	Diphenyl ether	2.80	391
66	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	4-Ph-C_5H_5N	Diphenyl ether	2.45	391
66	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	Bipyridyl	Diphenyl ether	1.90	391
66	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	*p*-MeC_6H_4CN	Diphenyl ether	2.15	391
66	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	$PhCH_2CH{=}CH_2$	Diphenyl ether	1.70	391
66	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	Diethyl fumarate	Diphenyl ether	2.93	391
66	$[(h^5\text{-}C_5H_5)Rh(C_2H_4)_2]$	1,5-cod	Diphenyl ether	3.45	391

[a] Ref. 66; rate constant may apply to dissociation of the first and/or second ethylene ligand. The limits are $k_1 \rightarrow 2k_1$.

was proposed (ac and ac′ are the respective acetylenes),

$$\begin{tikzcd}
 & & {[L_2Pt(ac)_2]} \arrow[r, "k'_x"] & {[L_2Pt(ac)]} \\
{[L_2Pt(ac)]} \arrow[r, "k_1"] & {[L_2Pt(ac)]} \arrow[ur, "k_x", "ac"'] \arrow[dr, "k_y"', "ac'"] & & \\
 & & {[L_2Pt(ac)(ac')]} \arrow[r, "k'_y"] & {[L_2Pt(ac')]}
\end{tikzcd}$$

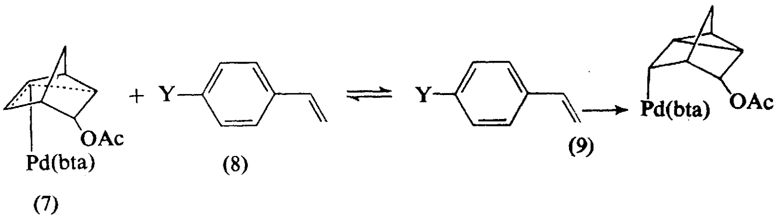
where $[L_2Pt(ac)]$ after the k_1 step has undergone a rate-determining stereochemical change and k_x, k_y, k'_x, and k'_y are all fast. This leads to the same form of rate law as that from the pre-equilibrium scheme and also accommodates two intermediates of the type $[L_2Pt(ac)(ac')]$, removing the necessity for the microscopic reversibility requirements above.[67] It is worth noting that values of k_1 here, and in those examples where it is postulated to arise from dissociation of olefin, are of the same order (Table 6).

In contrast to the predominantly dissociative mechanisms described above, the reaction

$$\textit{trans}(\mathrm{N})\text{-}[\mathrm{PtCl}(\textsc{l}\text{-prolinato})(\text{olefin})] + \text{olefin}' \longrightarrow \textit{trans}(\mathrm{N})\text{-}[\mathrm{PtCl}(\textsc{l}\text{-prolinato})(\text{olefin}')] + \text{olefin}$$

(olefin = 2-methylbut-2-ene or *trans*-but-2-ene; olefin′ = 2,3-dimethylbut-2-ene, 2-methylbut-2-ene, *trans*-but-2-ene, or styrene) is said to proceed according to an associative pathway. Values for $\Delta S^{\ddagger}$ [$\Delta S^{\ddagger} = -190$ J mol^{-1} K^{-1} (olefin = 2-methylbut-2-ene) and -168 J mol^{-1} K^{-1} (olefin = *trans*-but-2-ene)] are in agreement with this.[68]

Increased exothermicity of reaction as the π-donor ability of the substituent Y increases in the equilibrium shown in Scheme 5 (bta = benzoyltrifluoroacetonate) is regarded as symptomatic of predominant olefin-$\pi \rightarrow$ metal-d-orbital σ-bonding in determining the thermodynamic stability of the metal–olefin bond in (9).[69] However, the long-held theory that the metal-d-orbital$\rightarrow$ olefin-π^*-orbital model predominates has also received some recent support.[70]



Scheme 5

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[67] C. D. Cook and K. Y. Wan, *Inorg. Chem.*, 1971, **10**, 2696.
[68] K. Konya, J. Fujita, H. Kido, and K. Saito, *Bull. Chem. Soc. Japan*, 1972, **45**, 2161.
[69] E. M. Ban, R. P. Hughes, and J. Powell, *J.C.S. Chem. Comm.*, 1973, 591.
[70] F. R. Hartley, *Chem. Rev.*, 1973, **73**, 163.

9 Miscellaneous Reactions

Equilibrium constants for the reaction

$$[(PhCH_2)_4M] + py \rightleftharpoons [(PhCH_2)_4M(py)]$$

in chlorobenzene are 12.6 ± 0.6 (M = Zr) and 460 ± 30 (M = Hf) at 313 K.[71]

The reaction between OH^- and *cis*- and *trans*-$[Fe(CNMe)_4(CN)_2]$ to give Fe^{2+} and free ligands proceeds *via* S_N2 attack of OH^- on iron.[72]

A number of papers have been concerned with substitution reactions of Vitamin B_{12} model compounds. Kinetics of the substitution of the alkylaquo-1,3-bis(acetyl monoximeimino)propanato-cobalt ions (MH_2O) by L are consistent with formation of an intermediate MH_2O,L only when L contains an aromatic group.[73] S_N1 substitution reactions of the axial aquo-ligand in methyl aquo-cobaloxime by thiols,[74] primary amines, and 4-substituted pyridines[75] have been described.

Prompted by earlier results[76] which indicated that the rate law for substitution of Cl^- in square-planar *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = phenyl, *p*-tolyl, or mesityl) complexes included an associative as well as the normal dissociative path only in the case of substitution by strong biphilic ligands (*e.g.* CN^-, $SeCN^-$), Ricevuto *et al.* have re-examined the reaction with weakly nucleophilic pyridine in methanol:

$$trans\text{-}[Pt(PEt_3)_2(R)Cl] + py \rightleftharpoons trans\text{-}[Pt(PEt_3)_2(R)(py)]^+ + Cl^-$$

The reaction is anomalous (i) in obeying the rate law $k_{obs} = k_1 + k_2[py]$ and (ii) in having k_1 different from the constant value found in the reaction with other nucleophiles.[77] Careful analysis shows that k_{obs} is determined by competition for the intermediate *trans*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ by Cl^- and py:

$$trans\text{-}[Pt(PEt_3)_2(R)Cl] + MeOH \underset{k_1}{\overset{k_2}{\rightleftharpoons}} trans\text{-}[Pt(PEt_3)_2(R)(MeOH)]^+ + Cl^-$$

$$trans\text{-}[Pt(PEt_3)_2(R)(MeOH)]^+ + py \underset{k_3}{\overset{k_4}{\rightleftharpoons}} trans\text{-}[Pt(PEt_3)_2(R)(py)]^+ + MeOH$$

At constant [py] and $[Cl^-]$ this leads to the rate law

$$k_{obs} = \frac{k_1[py] + k_4k_2/k_3[Cl^-]}{k_2/k_3[Cl^-] + [py]} \tag{11}$$

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[71] J. J. Felten and W. P. Anderson, *J. Organometallic Chem.*, 1972, **36**, 87.

[72] G. Condorelli, L. Giallongo, A. Giuffrida, and G. Romeo, *Inorg. Chim. Acta*, 1973, **7**, 7.

[73] G. Tauzher, R. Dreos, G. Costa, and M. Green, *J.C.S. Chem. Comm.*, 1973, 413.

[74] K. L. Brown and R. G. Kallen, *J. Amer. Chem. Soc.*, 1972, **94**, 1894.

[75] K. L. Brown, D. Chernoff, D. J. Keljo, and R. G. Kallen, *J. Amer. Chem. Soc.*, 1972, **94**, 6697.

[76] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1969, **8**, 2207; 1970, **9**, 1525.

[77] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.

from which all rate constants can be evaluated, either directly or by subsidiary experiment in the case of k_3. The value of k_1 (for each R) agrees well with values of the rate constant for the dissociative path in the reaction with strong nucleophiles. This is readily understood, since in the latter cases $k_2 = k_4 = 0$ (the reaction is irreversible) and equation (11) reduces to $k_{obs} = k_1$. Good agreement is also obtained between the measured overall equilibrium constant and that from $K = k_1k_3/k_2k_4$. The reactions represented by k_1, k_3, and k_4 are inhibited with increasing bulk of R, whereas that represented by k_2 is little affected, probably as a result of the small size of Cl^-.[78]

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[78] V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1972, 1857.

2

Metal–Alkyl, –Aryl, and –Allyl Bond Formation and Cleavage

BY R. D. W. KEMMITT AND M. A. R. SMITH

1 General

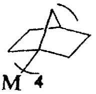
Sufficient evidence exists to suggest that the instability of transition-metal–carbon σ-bonds is not a consequence of a weak metal–carbon bond but is caused by the possibility of decomposition by pathways having low activation energy.[1] Pathways readily available for the cleavage of metal–carbon bonds include

$$\beta\text{-elimination; } M{-}CH_2CH_2R \rightarrow MH + CH_2{=}CH_2R$$

$$\text{reductive elimination; } M{-}(CH_2R)_2 \rightarrow M + RCH_2CH_2R$$

$$\text{dinuclear elimination; } 2M{-}CH_2R \rightarrow 2M + RCH_2CH_2R$$

The suppression of these pathways can result in the isolation of a number of metal–carbon compounds. Since the last volume of these Specialist Periodical Reports a number of transition-metal bicyclo[2,2,1]hept-1-yls (1) have been isolated which are clearly inert to β-elimination, since this would generate a double bond at a bridgehead.[2] Recently it has been suggested that where *d–d* excited states of the appropriate symmetry exist, bond-weakening distortions are vibronically facilitated and metal–carbon bond homolysis becomes more likely.[3] However, there are a number of exceptions to this theory and the idea has been questioned.[4]



(1) M = Fe, Zr, Hf, V, Cr, Mn, Fe, or Co

2 Group IV

Titanium.—There is evidence to suggest that whereas thermal decomposition of $MeTiCl_3$ in non-co-ordinating solvents does not involve free radicals, in co-

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[1] P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657.
[2] B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 1972, **94**, 2512.
[3] D. M. P. Mingos, *J.C.S. Chem. Comm.*, 1972, 165.
[4] P. S. Braterman, *J.C.S. Chem. Comm.*, 1972, 761.

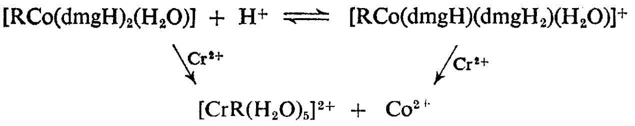
ordinating solvents a free-radical mechanism predominates. Further studies now indicate, however, that thermal decomposition in co-ordinating solvents does not always involve radicals.[5] Thus with diethyl ether as solvent, free radicals are not formed, and hydrogen abstraction occurs from co-ordinated solvent. Methyl-group exchange occurs on addition of a toluene solution of $Al_2(CH_3)_6$ to $Ti(CD_3)_4$ in hexane–diethyl ether (10 : 1) mixture.[6] Decomposition of the mixture yields CD_4, CD_3H, and CDH_3 and it is suggested that these arise from intramolecular hydrogen abstraction in $Ti(CH_3)_n(CD_3)_{4-n}$ ($n \leqslant 4$). However, the hydrogen could originate from co-ordinated diethyl ether, especially since exchange is shown to occur *via* ether-solvated compounds.

3 Group VI

Chromium.—Organic radicals R$^\cdot$ are known to react with $[Cr(H_2O)_6]^{2+}$ to form organo-chromium(III) complexes $[CrR(H_2O)_5]^{2+}$. The specific rates of reaction of a number of organic radicals with $[Cr(H_2O)_6]^{2+}$ have now been measured by a pulse-radiolytic technique. The order of reactivity of the radicals towards $[Cr(H_2O)_6]^{2+}$ decreases in the order $\dot{C}H_2CO_2H > \dot{C}H_2OH > Me\dot{C}HOH > Me_2\dot{C}OH > Me\dot{C}HOEt$. Since this is the order of spin density of the unpaired electron on the α-carbon atom it is concluded that the specific rates of reaction can be correlated with the unpaired electron density on the reactive carbon atom.[7] Organocobaloximes also react with $[Cr(H_2O)_6]^{2+}$ essentially quantitatively according to the equation

$$[RCo(dmgH)_2(H_2O)] + [Cr(H_2O)_6]^{2+} + 2H^+ + 4H_2O \longrightarrow [Co(H_2O)_6]^{2+} + [CrR(H_2O)_5]^{2+} + 2dmgH_2$$

Reactions have been studied for R = Et, Pr^n, CH_2Ph, CH_2CMe_3, Pr^i, and 2-octyl. The reactions follow a second-order rate expression, the kinetics being consistent with the mechanism shown in Scheme 1.



$$\begin{tikzcd}[RCo(dmgH)_2(H_2O)] + H^+ \arrow[rr, shift left, harpoon] \arrow[dr, "Cr^{2+}"] & & {[RCo(dmgH)(dmgH_2)(H_2O)]^+} \arrow[ll, shift left, harpoon] \arrow[dl, "Cr^{2+}"'] \\ & {[CrR(H_2O)_5]^{2+} + Co^{2+}} & \end{tikzcd}$$

Scheme 1

Of four possible processes considered it was suggested that the reactions proceed either by a concerted transfer of a carbanion from cobalt to chromium accompanied by electron transfer from chromium to cobalt or alternatively by an S_H2 mechanism involving bimolecular homolytic substitution at saturated

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[5] J. D. McCowan, *Canad. J. Chem.*, 1973, **51**, 1083.

[6] A. S. Khachaturov, L. S. Bresler, and I. Ya. Poddubnyi, *J. Organometallic Chem.*, 1972, **42**, C18.

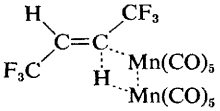
[7] H. Cohen and D. Meyerstein, *J.C.S. Chem. Comm.*, 1972, 320.

carbon. Further, since there is a marked decrease in rate with substitution at the α carbon there is probably inversion of configuration at the carbon centre.[8] Studies on chromium(III) alkyls of the type $RCrCl_2(THF)_3$ (R = Me, Et, Pr^n, or Bu^i; THF = tetrahydrofuran) reveal that on pyrolysis the complexes yield more alkane than alkene. Further, since no evidence for chromium hydride intermediates could be found these decompositions could involve radicals even though β-elimination is possible. The alkyls decrease in stability with increase in chain length.[9]

4 Group VII

Manganese.—Cleavage of the carbon–manganese bond in *trans*-$[CF_3CH{=}CCF_3Mn(CO)_5]$ by $[HMn(CO)_5]$ or bromine occurs with retention of configuration to give *trans*-$[CF_3CH{=}CHCF_3]$ or *trans*-$[CF_3CH{=}CBrCF_3]$, respectively.[10]

These reactions may proceed *via* a four-centre transition state, *e.g.* (2), or involve addition to the double bond followed by elimination. However, cleavage of *trans*-$[(HO_2C)CH{=}C(CO_2H)Mn(CO)_5]$ with bromine occurs with complete inversion of configuration.



(2)

5 Group VIII

Iron.—Epoxides react rapidly with Na^+ $[Fe(CO)_2(h^5\text{-}C_5H_5)]^-$ in tetrahydrofuran solution to give the alkoxides (3), which on treatment with either fluoroboric or hexafluorophosphoric acids yield the cationic alkene complex (5). The alkene in (5) may be easily displaced from the iron by treatment with sodium iodide in acetone. This conversion of epoxide into alkene occurs with complete retention of configuration, *e.g.* *cis*-but-2-ene oxide gives *cis*-but-2-ene. This result therefore supports a mechanism involving S_N2 opening of the epoxide by the carbonylate anions followed by a concerted process involving *trans*-migration of the iron group and loss of water from the protonated alcohol (4).[11]

Cobalt.—The kinetics and mechanisms of reactions involving cobalt–carbon bond cleavage and formation have been discussed in review articles on vitamin B_{12} and cobaloxime model complexes.[12, 13] Interest in these systems

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[8] J. H. Espenson and J. S. Shveima, *J. Amer. Chem. Soc.*, 1973, **95**, 4468.

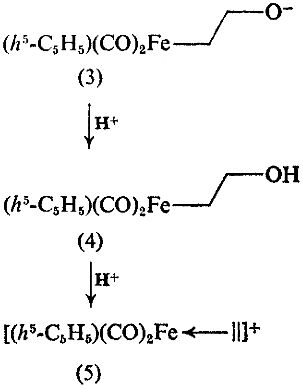
[9] K. Nishimura, H. Kuribayashi, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1972, **37**, 317.

[10] B. L. Booth and R. G. Hargreaves, *J. Organometallic Chem.*, 1971, **33**, 365.

[11] W. P. Giering, M. Rosenblum, and J. Tancrede, *J. Amer. Chem. Soc.*, 1972, **94**, 7170.

[12] J. Lewis, R. H. Prince, and D. A. Stotter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 341.

[13] D. Dodd and M. D. Johnson, *Organometallic Chem. Rev.*, 1973, **52**, 1.



(3) (4) (5)

has been further stimulated since it was realized that the biological conversion of mercury into methylmercury derivatives has led to a very significant danger to the environment. Kinetic measurements on the reactions of organocobaloximes with mercury(II) perchlorate in aqueous perchloric acid solution,

$$[RCo(dmgH)_2(H_2O)] + Hg^{2+} \longrightarrow RHg^+ + [Co(dmgH)_2(H_2O)]^+$$

are consistent with the second-order rate law

$$-d[RCo(dmgH)(H_2O)]/dt = k[Hg^{2+}][RCo(dmgH)_2(H_2O)]$$

where R = alkyl, benzyl, or aryl. The rates of reaction decrease in the order $k_{MeCo} > k_{EtCo} > k_{Pr^iCo}$, consistent with an S_E2 mechanism. The reactivities of the arylcobalt complexes are considerably higher than those of the alkyl compound and there is rate enhancement when electron-donating substituents are present in the aromatic ring.[14] Reactions with thallium(III) follow a similar kinetic pattern.[14] Bis(di-oximato)cobalt(II) complexes $[Co(dH)_2L]$ (dH_2 = dimethylglyoxime or 1,2-cyclohexanedione dioxime; L = neutral amine or phosphine ligand) react with benzyl halides in solution to form stable organocobalt complexes *via* a free-radical mechanism. The rate-determining step is

$$[Co(dH)_2L] + RX \longrightarrow [XCo(dH)_2L] + R^\cdot$$

For the compounds $[Co(dH)_2L]$ reacting with benzyl bromide in benzene solution the activation parameters are $\Delta H^{\ddagger} = 10.1\ \text{kcal mol}^{-1}$ and $\Delta S^{\ddagger} = -32\ \text{cal deg}^{-1}\ \text{mol}^{-1}$ ($L = PPh_3$); $\Delta H^{\ddagger} = 9.9\ \text{kcal mol}^{-1}$ and $\Delta S^{\ddagger} = -29\ \text{cal deg}^{-1}\ \text{mol}^{-1}$ (L = pyridine).[15] Solvent effects on the reactions are small but the axial ligand has a large effect on the rate, an electron-donating ligand enhancing the oxidation of cobalt(II) to cobalt(III). However, ligands such as tricyclohexylphosphine and piperidine enhance the

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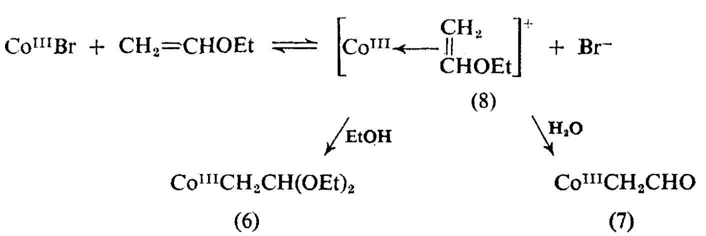
[14] P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, 1973, **95**, 3166.

[15] J. Halpern and P. F. Phelan, *J. Amer. Chem. Soc.*, 1972, **94**, 1881.

rate of reaction to a much smaller degree than would be expected considering the basicities of these ligands, and in these instances steric rather than electronic factors dominate. In agreement with the mechanisms the reactivity sequence of the halides is RI > RBr > RCl.

In contrast to such cobalt(I) complexes as $[Co(dmgH)_2(PR_3)]^-$ the complexes $[Co(CN)_2(CO)(PPh_3)_2]^-$ and $[Co(CN)_2(CO)(PEt_3)_2]^-$ exhibit only weak nucleophilic activity towards organic halides. The presence of the carbonyl ligand presumably stabilizes the cobalt(I) complex against oxidation.[16]

The formation of the acetal and aldehyde complexes (6) and (7) respectively from ethyl vinyl ether and bromo(pyridine)cobaloxime in the presence of triethylamine and ethanol is consistent with the formation of an intermediate π-complex (8) as shown in Scheme 2. Similar reactions are observed with cobalamins and these reactions provide further evidence for cobalt(III) π-complexes in coenzyme-B_{12}-dependent rearrangements.[17]



Scheme 2

One-electron oxidation of some alkylcobalt(III) complexes $[RCo(dmgH)_2L]$ greatly increases nucleophilic attack at the α-carbon, resulting in cleavage of the metal–carbon bond.[18a] Oxidative cleavage of benzylaquobis(dimethylglyoximato)cobalt(III) with excess $[IrCl_6]^{2-}$ in dilute aqueous $HClO_4$ proceeds rapidly according to the equation

$$[Co(dH)_2(H_2O)(CH_2Ph)] + 2[IrCl_6]^{2-} + 2H_2O \longrightarrow$$
$$[Co(dH)_2(H_2O)_2]^+ + 2[IrCl_6]^{3-} + PhCH_2OH + H^+$$

Preliminary kinetic evidence and assumption of the usual role of a one-electron outer-sphere oxidant for $[IrCl_6]^{2-}$ together with other evidence can be accommodated by the mechanism[18b]

$$[Co(dH)_2(H_2O)R] + [IrCl_6]^{2-} \xrightarrow[\text{determining}]{\text{rate}} [Co(dH)_2(H_2O)R]^+ + [IrCl_6]^{3-}$$

followed by

$$[Co(dH)_2(H_2O)R]^+ + 2H_2O \longrightarrow$$
$$[Co(dH)_2(H_2O)_2]^+ + ROH + [IrCl_6]^{3-} + H^+$$

[16] J. Bercaw, G. Guastalla, and J. Halpern, *Chem. Comm.*, 1971, 1594.

[17] R. B. Silverman and D. Dolphin, *J. Amer. Chem. Soc.*, 1973, **95**, 1686.

[18] (*a*) S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J.C.S. Chem. Comm.*, 1972, 685; (*b*) P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, 1972, **74**, 659.

Alternatively a stepwise free-radical sequence could operate:

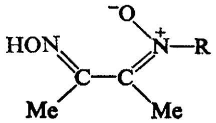
$$[Co(dH)_2(H_2O)R]^+ + H_2O \longrightarrow [Co(dH)_2(H_2O)_2]^+ + R^\bullet$$

$$R^\bullet + [IrCl_6]^{2-} + H_2O \longrightarrow ROH + [IrCl_6]^{3-} + H^+$$

When the cobalt complex is initially in excess the stoicheiometry of the reaction changes to

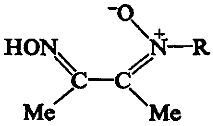
$$[Co(dH)_2(H_2O)R] + [IrCl_6]^{2-} + H^+ \longrightarrow$$

$$[IrCl_6]^{3-} + H_2O + Co^{2+} + dH_2 +$$



In addition, a small amount (1—2%) of bibenzyl can be isolated. In the absence of excess $[IrCl_6]^{2-}$, $[Co(dH)_2(H_2O)R]^+$ probably decomposes according to the equation

$$[Co(dH)_2(H_2O)R]^+ + H^+ \longrightarrow Co^{2+} + dH_2 + H_2O +$$



Alternatively, since some bibenzyl is formed, a stepwise mechanism involving formation of a benzyl radical could occur. In view of these findings it is possible that certain vitamin-B_{12}-dependent reactions could involve such oxidative dealkylation reactions.[18b]

The photolysis and thermolysis of alkylcobaloximes $[Co(CHR^1CHR^2R^3)(dmgH)_2(py)]$ in the absence of oxygen are reported to proceed *via* β-elimination to yield $R^1HC{=}CR^2R^3$ plus $[HCo(dmgH)_2(py)]$.[19]

Rhodium.—Dimethyl acetylenedicarboxylate undergoes a *cis*-insertion[20] rather than a *trans*-insertion[21] into the rhodium–hydrogen bond of $[RhH(CO)(PPh_3)_3]$. Thus cleavage of the rhodium–carbon bond in the resulting alkenyl complex $[Rh\{C(CO_2Me){=}CH(CO_2Me)\}(CO)(PPh_3)_2]$ with hydrogen chloride, which gives dimethyl fumarate, may go with inversion of configuration at carbon.[21] However, cleavage of the rhodium–carbon bond with methyl iodide proceeds predominantly with retention of configuration. This latter reaction, which involves oxidative addition of methyl iodide to rhodium(I), provides a convenient stereospecific synthesis of trisubstituted alkenes.[20]

Palladium.—The results of studies on certain palladium–carbon bond-fission reactions are consistent with a mechanism involving a hydride shift to form a

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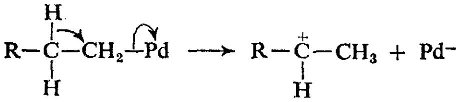
[19] K. N. V. Duong, A. Ahond, C. Merienne, and A. Gaudemer, *J. Organometallic Chem.*, 1973, **55**, 375.

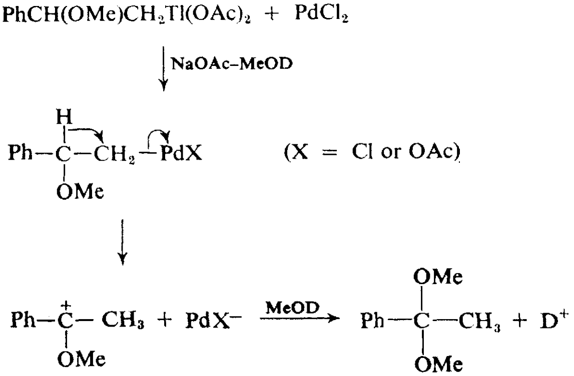
[20] J. Schwartz, D. W. Hart, and J. L. Holden, *J. Amer. Chem. Soc.*, 1972, **94**, 9269.

[21] B. L. Booth and A. D. Lloyd, *J. Organometallic Chem.*, 1972, **35**, 195.



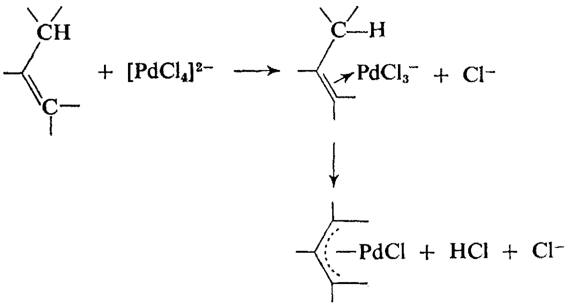
Scheme 3

carbonium ion intermediate (Scheme 3). There is evidence for a similar process in the reaction of alkoxythallates of styrene with $PdCl_2$ in methanol, which gives acetophenone or its alkyl acetal *via* a thallium–palladium transmetallation. Thus when the reaction is carried out in MeOD there is no deuterium incorporation in the acetal, and the mechanism is therefore consistent with Scheme 4.[22]



Scheme 4

The mechanism of formation of *h*³-allyl-palladium systems can involve co-ordination of an alkene to the palladium followed by proton elimination from the allylic carbon atom (Scheme 5). Reactions with alkenes containing



Scheme 5

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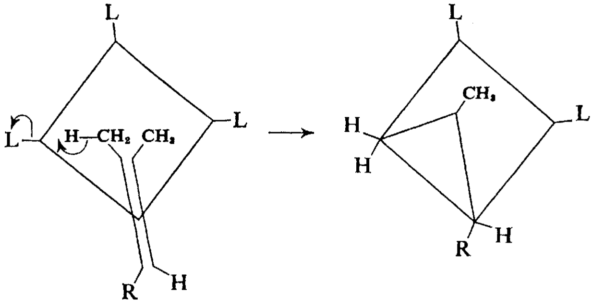
[22] S. Uemura, K. Zushi, M. Okano, and K. Ichikawa, *J.C.S. Chem. Comm.*, 1972, 234.

bulky substituents on the terminal carbon atoms can lead to formation of h^3-allyl complexes, with these substituting in the less stable *anti*-configuration. The mechanism of this reaction (Scheme 6) involves twisting of the co-ordinated alkene followed by loss of a *cis*-ligand and attack of palladium on the methyl group, which leaves a bulky substituent in an *anti*-position. Twisting in the alternative direction would increase steric crowding between the substituted R and the *cis*-ligand. Ligands such as triphenylphosphine and dimethyl sulphoxide can catalyse *anti–syn* rearrangements by the π–σ–π mechanism. However, the reluctance of bulky groups when in the less stable *anti*-position to undergo *anti*→ *syn* rearrangement may be correlated either with steric hindrance between the group R in the σ-bonded intermediate and the ligand which effects the rearrangement or with the substituent on the central carbon in the h^3-allyl ligand.[23]



Scheme 6

Electrodialysis studies of the system $[Pd^{36}Cl(h^3\text{-}^{14}C_4H_7)]_2$ plus triphenylphosphine reveal the presence predominantly of Cl^- and $[Pd(C_4H_7)(PPh_3)_2]^+$ ions at low concentrations and temperatures, whereas at higher concentrations and temperatures the formation of $C_4H_7^-$ and $[PdCl(PPh_3)_3]^+$ is observed. Kinetic studies on the reaction of excess triphenylphosphine with the allyl complex have been interpreted in terms of ML_2 and ML_3 intermediates [$M = PdCl(h^3\text{-}C_4H_7)$, $L = PPh_3$] which yield ML, L, and ions.[24]

Palladium(II) chloride reacts with the diene isomers of hexa-2,4-diene stereospecifically to give a pair of epimeric diastereomers as outlined in Scheme 7. Treatment of these allyl compounds with excess of a co-ordinating ligand such as dimethyl sulphoxide, triphenylphosphine, or lithium bromide leads to the initial dienes stereospecifically *via* conversion into a σ-complex followed by a β-elimination.[25] The two diastereomers (9) and (10) epimerize in

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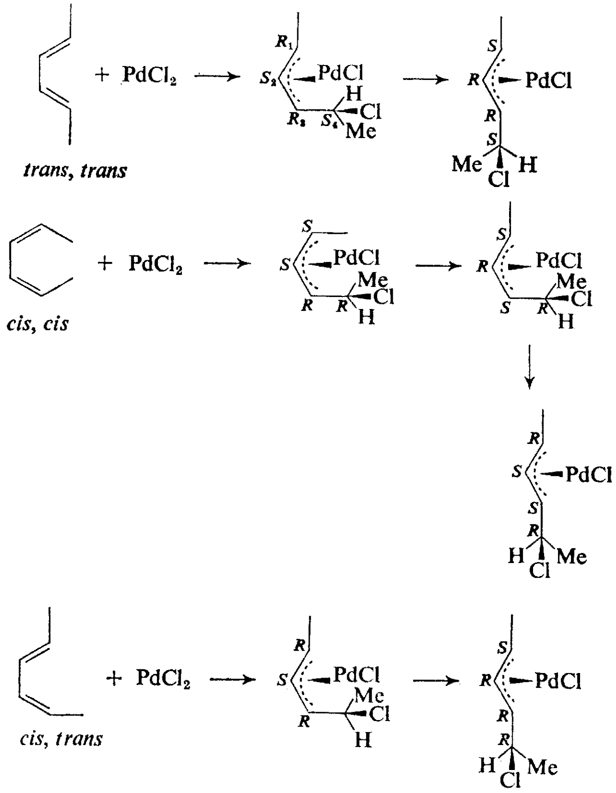
[23] J. Lucas, J. E. Ramakers-Blom, T. G. Hewitt, and J. J. De Boer, *J. Organometallic Chem.*, 1972, **46**, 167.

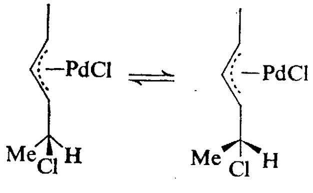
[24] V. N. Sokolov, G. M. Khvostic, I. Ya. Poddubnyi, and G. P. Kondratenkov, *J. Organometallic Chem.*, 1973, **54**, 361.

[25] J. Lucas, P. W. N. M. Van Leeuwen, H. C. Volger, and A. P. Kouwenhoven, *J. Organometallic Chem.*, 1973, **47**, 153.



Scheme 7

solution at room temperature, racemization occurring at the chloro-substituted carbon. For the diastereomers epimerizing in $CDCl_3$ solution, the first-order rate constant is $7.45 \times 10^{-4}\ s^{-1}$ at 35.5 °C and the activation energy is 22 ± 0.5 kcal mol^{-1}. Solvent effects are small but rates increase with increasing polarity of solvent. The small influence of added hydrogen chloride on the rate constant is considered to be due to cancellation of common-ion and salt effects. The complexes (9) and (10) also undergo stereospecific methanolysis,



(9) (10)

and the ease of this process as compared with the solvolysis of 2-chlorobut-1-ene is consistent with the formation of a metal-stabilized carbonium ion. N.m.r. data are consistent with direct attack on the ligands with inversion of configuration.[25]

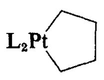
Following the study of the formation of $[PdCl_2(h^3\text{-}C_3H_5)]^-$ from $[PdCl_4]^{2-}$ and allyl alcohol in acidic aqueous solutions a kinetic study of the reaction between $[PdCl_4]^{2-}$ and allyl ether as well as allyl alcohol, which both yield $[PdCl_2(h^3\text{-}C_3H_5)]^-$, has now been reported. For allyl ether the rate law has the form

$$k_{\text{obs}} = k\frac{[(CH_2{=}CHCH_2)_2O]}{[H^+][Cl^-]^2}$$

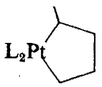
and a mechanism which involves rate-determining attack of co-ordinated hydroxide on a co-ordinated double bond of the allyl ether is proposed.[26]

Platinum.—The thermal decomposition of di-n-butylbis(triphenylphosphine)-platinum(II) in methylene chloride to n-butane, but-1-ene, and a platinum(0) complex follows first-order kinetics. The mechanism of reaction is suggested to take place by an intramolecular process involving initial dissociation of a triphenylphosphine ligand to give a three-co-ordinate intermediate, β-elimination of hydrogen to give a four-co-ordinate butene–hydride intermediate, and several rapid additions of the platinum–hydrogen bond to the co-ordinated butene, followed by reductive elimination of n-butane from a butyl hydride intermediate. A vacant co-ordination site on the platinum is a prerequisite for thermal decomposition under the conditions used and the rate-determining step is dissociation of a triphenylphosphine ligand. However, in the presence of 1 mole of added triphenylphosphine, reductive elimination becomes rate-determining.[27]

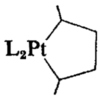
In contrast to the acyclic platinum(II) alkyls $[PtEt_2(PPh_3)_2]$ and $[PtBu^n_2(PPh_3)_2]$, the platinocycles (11), (12), (13), and (14) are thermally more stable.



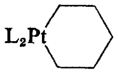
(11)



(12)



(13)



(14)

L = PPh_3

Rates of decomposition are first-order in platinocycle up to 60% decomposition and the products of decomposition suggest a mechanism (Scheme 8)

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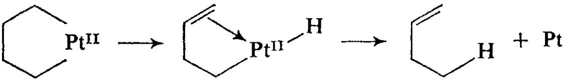
[26] R. Pietropaolo, F. Faraone, S. Sergi, and D. Pietropaolo, *J. Organometallic Chem.*, 1972, **42**, 177.

[27] G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5258.



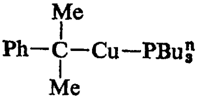
Scheme 8

similar to that suggested for the decomposition of [PtBu$^n_2$(PPh$_3$)$_2$]. However, the detailed mechanisms of decomposition of the two types of complex must differ since, whereas addition of triphenylphosphine to solutions of the n-butyl complex inhibits its thermal decomposition, addition of triphenylphosphine to solutions of (11) increases the rate of decomposition of this complex.[28]

Cleavage of an alkyl group from complexes of the type *cis*-[PtR$_2$(PR$_3$)$_2$] (R = Me, Et, Me, Me$_3$SiCH$_2$, or PhCH$_2$) by the radicals Bu^{t}O· or PhS· has been shown to take place by a bimolecular homolytic substitution (S_H2) at the platinum. This is the first example of a radical substitution at a transition-metal centre.[29]

6 Group I

Copper and Silver.—Although the decomposition of [Cu(Bu^n)(Bu$^n_3$P)] takes place by a predominantly non-radical pathway to give alkene and a copper(I) hydride intermediate, the thermal decomposition of neophyl(tri-n-butylphosphine)copper(I) (15) in ether solution between 30 and 125 °C occurs mainly by a free-radical mechanism, presumably because a β-hydride elimination mechanism is not possible here. The resulting neophyl radicals take part in competing 1,2-phenyl migration and coupling and hydrogen-abstraction reactions. The corresponding silver(I) complex undergoes thermolysis *via* a similar pathway.[30] The oxidation of alkyl radicals by copper(II) involves the formation of an intermediate copper(III) species RCu^{III} followed by reductive elimination of acetic acid from a copper(III) hydride acetate to form copper(I) acetate plus R—H or alkylated solvent formed by attack of R$^+$ on solvent.[31] The products of this reaction also result from the oxidation of lead tetra-alkyls by copper(II) acetate, and a similar mechanism may operate.[32]



$$\mathrm{Ph{-}C(Me)_2{-}Cu{-}PBu^n_3}$$

(15)

The reduction of copper(II) acetate, trifluoromethanesulphonate, and chloride by tetraethyl-lead in acetic acid solutions is suggested to take place *via* a metastable ethylcopper(II) intermediate which undergoes rapid homolysis.[33]

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[28] J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1973, **95**, 4451.

[29] D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 350.

[30] G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 1972, **94**, 232.

[31] C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 843, 856.

[32] N. A. Clinton and J. K. Kochi, *J. Organometallic Chem.*, 1972, **42**, 229.

[33] N. A. Clinton and J. K. Kochi, *J. Organometallic Chem.*, 1972, **42**, 241.

7 Actinides

Uranium.—Uranium alkyls of the type $[U(Bu^n)(h^5\text{-}C_5H_5)_3]$ are thermally stable and appear to resist β-elimination and probably decompose by a free-radical pathway. Decomposition of $[U(Bu^n)(h^5\text{-}C_5H_5)_3]$ in $[^2H_8]$toluene produces butane with only about 5% incorporation of deuterium, suggesting that hydrogen abstraction occurs principally within a solvent cage from the cyclopentadienyl rings.[34]

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[34] T. J. Marks and A. M. Seyam, *J. Amer. Chem. Soc.*, 1972, **94**, 6545.

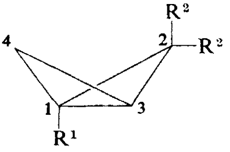
3

Homogeneous Catalysis

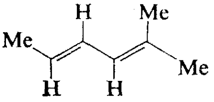
BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Isomerization

Strained Carbocyclic Systems.—There is now a considerable amount of information on the catalysis of the isomerization of bicyclo[1,1,0]butane derivatives, for example (1), by transition-metal complexes, and reading in this field would be usefully preceded by reference to the appropriate section in Volume 2 of this series. In summary, isomerization products have been detected which result from many combinations of bond cleavage in (1) by the use of both different catalysts and ring substituents. An attempt can be made to generalize by stating that, as extremes, Ag^I catalysts lead, for example when $R^1 = R^2 = Me$, to (2) and (3) by C-1—C-3 and C-1—C-2 cleavage whereas Rh^I catalysis results in (4) and (5) by cleavage of C-1—C-3 and/or C-2—C-3.[1] Departures from the general rule as well as intermediate cases exist, but this will serve as a useful starting point. Current interest has turned increasingly to elucidation of the intermediates involved in these reactions, especially in the case of Rh^I catalysis, and these reports will be examined first.



(1)



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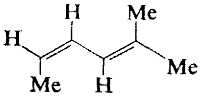

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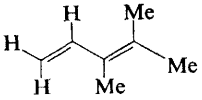

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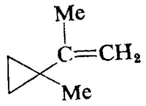

(5)

In the case of Rh^I catalysis, it is generally agreed that the reactive intermediate has a formal carbenoid structure[1] (see tricycloheptane isomerization later). In the presence of $[Rh(nor)Cl]_2$, (1; $R^1 = R^2 = H$; or $R^1 = Me$,

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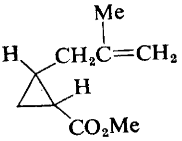
[1] P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 7733.

R^2 = H) undergoes C-1—C-3 and C-2—C-3 cleavage but to give ultimately dimeric products.[2] In the presence of methyl methacrylate and $[Rh(nor)Cl]_2$ (1; R^1 = Me, R^2 = H) gives (6)[2] whereas (7), (8), and (9) result from the isomerization of (1; R^1 = Me, R^2 = Ph) in the presence of $[Rh(CO)_2Cl]_2$.[3,4] All these products evince the occurrence of a carbene as intermediate. This is generally held to be represented by the resonance hybrids (10) and (11).[2,3,5] A recent suggestion proposes that the relative π-donor abilities of the metal affect the populations of the contributors to the overall resonance picture of the carbenoid intermediate, thereby altering the subsequent course of the isomerization as, for example, in the course of Ag^I and Rh^I catalysis.[6] In addition, there is evidence to suggest that in order to form both (4) and (5) *via* (10) and (11) cleavage of side and centre bonds is stepwise, with initial side-bond (C-2—C-3) cleavage by the catalyst.[1,5]



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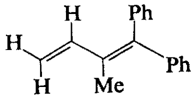
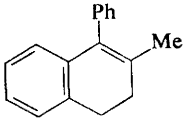
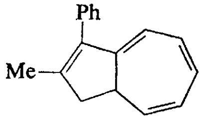


(7)



(8)



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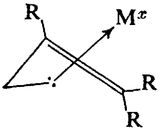
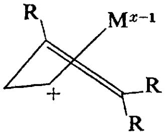


(10)



(11)

The catalytic effect of many different complexes of fourteen metals on the isomerization of (1; R^1 = R^2 = Me) leads mainly to the 'normal' products (4) and (5). However, $[CuC_6F_5]_4$ by a combination of C-1—C-2, C-2—C-3, and C-1—C-3 cleavage gives (2), (3), and (5).[7] The effect of ring substituents on the reaction may be seen by comparison with the products of the same reaction of (1; R^1 = Me, R^2 = Ph) when C-2—C-3 cleavage does not occur and only the phenyl analogues of (2) and (3) are formed.[4] Catalysis by $AgBF_4$ follows the same course as that by the copper tetramer.[4,7] In comparison with these results $Zn(BF_4)_2$, ZnI_2, $Cu(BF_4)_2,6H_2O$, $HgBr_2$, and $SnCl_2$ promote conversion of (1; R^1 = R^2 = Me) only into (5).[7] The use of methanol rather than chloroform in the silver(I)-catalysed reaction of (1; R^1 = R^2 = Me; R^1 = Me, R^2 = Ph; or the 3-methyl analogue of the latter) results in a

[2] P. G. Gassman and R. R. Reitz, *J. Organometallic Chem.*, 1973, **52**, C51.

[3] P. G. Gassman, *Angew. Chem. Internat. Edn.*, 1972, **11**, 323.

[4] P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, 1972, **94**, 2877.

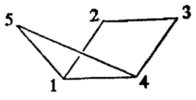
[5] P. G. Gassman and F. J. Williams, *J.C.S. Chem. Comm.*, 1972, 80.

[6] R. Noyori, *Tetrahedron Letters*, 1973, 1691.

[7] P. G. Gassman, G. R. Meyer, and F. J. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 7741.

change from normal C-1—C-3 and C-1—C-2 cleavage to that normally associated with Rh^{I} (C-1—C-3 *plus* C-2—C-3).[8] Also worth recording in this context is the recent discovery that, when performed in methanol, the silver-ion catalysis of hexamethylbicyclobutane reactions is autocatalytic in that catalyst acid is produced as Ag^{+} is complexed by methanol. This result necessitates cancellation of silver-ion catalysis of the skeletal isomerization pathway.[9] A similar observation has been made in an examination of tricyclo-[4,1,0,0]heptane in methanol with additional results showing that acid production depends on the type of transition-metal complex used.[10] Bond cleavage in the course of catalysis by silver ion of the isomerization of substituted bicyclobutanes has been shown to be dependent upon the position of the substituents. Substitution at C-2 and C-4 generally favours C-1—C-2 and C-3—C-4 cleavage (double edge) whereas at C-1 and C-3 substitution promotes cleavage of one edge and the centre bond (C-1—C-3).[11,12] The two mechanisms are reconciled with first steps in which Ag^{+} oxidatively inserts into an edge or preferentially cleaves the centre bond to generate an argento-carbonium ion.

The catalytic isomerization of bicyclo[2,1,0] pentane (12) to give cyclopentene (13) in which only the centre bond is formally cleaved is in marked contrast to the rearrangement of the bicyclobutanes above, in which not only are two bonds generally cleaved, but the process is deemed stepwise with initial cleavage of a side bond. Preliminary mechanistic studies indicate that in the presence of [Rh(CO)$_2$Cl]$_2$ a side bond of the cyclobutane fragment is in fact cleaved to give (14) and that an intermediate hydride (15) is involved in which X represents the moiety undergoing hydrogen transfer, perhaps (14). This also accounts for the observation that 1-deuteriocyclopentene undergoes deuterium scrambling when added to this system, but not when treated with the catalyst alone.[13] Recent support for a hydride intermediate has appeared, but initial



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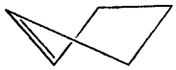

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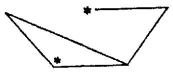

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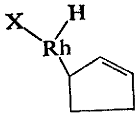

(15)

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[8] P. G. Gassman and T. Nakai, *J. Amer. Chem. Soc.*, 1972, **94**, 5497.

[9] L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Amer. Chem. Soc.*, 1972, **94**, 9222.

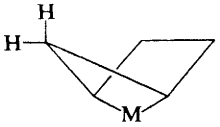
[10] P. G. Gassman and R. R. Reitz, *J. Amer. Chem. Soc.*, 1973, **95**, 3057.

[11] L. A. Paquette, *Angew. Chem. Internat. Edn.*, 1972, **11**, 328.

[12] L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, 1972, **94**, 7780.

[13] P. G. Gassman, T. J. Atkins, and J. T. Lumb, *J. Amer. Chem. Soc.*, 1972, **94**, 7757.

oxidative addition of the catalyst, $[Rh(CO)_2Cl]_2$, across the centre bond to give (16) followed by (17) is emphasized.[14]



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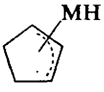


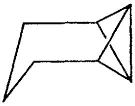
(17)

As in the case of the bicyclobutanes, products of the isomerization of tricyclo[4,1,0,0]heptane (18) vary according to the catalyst. Thus, Table 1 summarizes the range of products (19), (20), and (21) which are found during the course of these reactions.[15] In analogy also with the bicyclobutane system, the products are deemed to arise from stepwise bond cleavage with the intermediacy of a carbenoid complex.[15, 16] Probably the most useful addition in this particular area, however, is evidence from n.m.r. studies for *direct* observation of this type of intermediate. Two groups have synchronously obtained duplicate n.m.r. spectra of an intermediate (22) by use of low temperature[17] or by

Table 1 *Product dependence on catalyst in the isomerization of tricyclo-*[4,1,0,0]*heptane (from ref.* 15 *except where indicated)*

Catalyst	*Product*
ZnI_2	(20), (21)
$HgBr_2$	(20), (21)
$[Rh(CO)_2Cl]_2$	(20)
$[Ir(CO)_3Cl]_2$	(20)
$[h^3\text{-}C_3H_5PdCl]_2$	(20)
$[PdCl_2(PhCN)_2]$[a]	(20)
$[CuC_6F_5]_4$	(20)
$[Rh(CO)PPh_3Cl]_2$	(19), (20)
$[Ru(CO)_3Cl_2]_2$	(19), (20)
PtO_2	(19), (20)
$SnCl_2,2H_2O$	(19)
$AgBF_4$[b]	(21)

[a] Also refs. 16 and 17. [b] Ref. 18.



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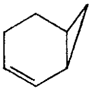

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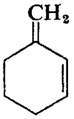

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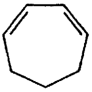

(21)

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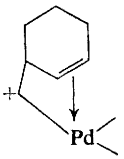
[14] K. B. Wiberg and K. C. Bishop, *Tetrahedron Letters*, 1973, 2727.
[15] P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 1972, **94**, 7748.
[16] W. G. Dauben and A. J. Kielbania, *J. Amer. Chem. Soc.*, 1972, **94**, 3671.
[17] S. Masamune, M. Sakai, and N. Darby, *J.C.S. Chem. Comm.*, 1972, 471.

using large concentrations[16] of the catalyst $[PdCl_2(PhCN)_2]$, although the latter authors prefer a palladium–carbon double bond in (22). It is interesting and perhaps disappointing to note that (22) results from edge- *plus* centre-bond cleavage whereas stepwise cleavage has been advocated above. However, in the low-temperature study[17] (22) is preceded by an unassigned intermediate which is quite stable for relatively long periods at 223 K – perhaps the edge-cleaved complex. Silver(I)-assisted rearrangements of tricycloheptane derivatives are commonly thought to give (21) *via* intermediate argento-carbonium ions. Amongst recent mechanistic studies of these reactions are deuterium isotope[18] and ring-substituent effects.[11,19] Highly stereoselective methyl migration appears to be away from the potential benzylic carbonium ion in the silver(I)-catalysed rearrangement of the tricyclo[3,2,0,0]heptane derivative (23) to give (24). This probably indicates strongly favoured interaction of silver with the phenyl substituent.[20]



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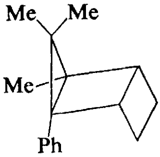

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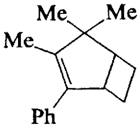
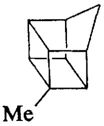


(24)

The rate of isomerization of the homocubane (25) to (26) in the presence of Ag^I approaches a limiting value at high concentrations of (25). This is interpreted as indicative of pre-equilibrium formation of an Ag^+ σ-bonded complex which subsequently rearranges in a slow step, a conclusion also supported by the magnitude and sign of ρ^* derived from the isomerization of other substituted analogues of (25).[21] The substituted bishomocubane (27) (R = Me or CH_2OAc) isomerizes to the cuneane derivatives (28) and (29) in the presence of silver ion. The stereochemistry of the products is not dependent on the nature of R.[22]



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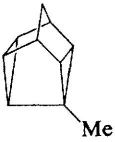

(26)

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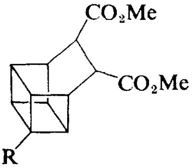
[18] L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, 1972, **94**, 7771.
[19] L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, *J. Amer. Chem. Soc.*, 1972, **94**, 7761.
[20] L. A. Paquette and L. M Leichter, *J. Amer. Chem. Soc.*, 1972, **94**, 3653.
[21] L. A. Paquette and J. S. Ward, *Tetrahedron Letters*, 1972, 4909.
[22] L. A. Paquette, R. S. Beckley, D. Truesdell, and J. Clardy, *Tetrahedron Letters*, 1972, 4913.



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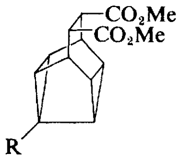

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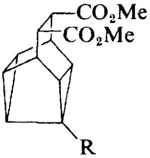
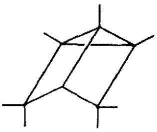


(29)

We have noted above the markedly different products obtained in the catalytic isomerization of bicyclobutanes and tricycloheptanes with Rh^I and Ag^I. It is interesting, then, that the catalytic isomerization of (30) and (31) to give (32) in chloroform is promoted by both $[Rh(CO)_2Cl]_2$ and $AgClO_4$,



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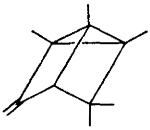

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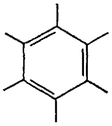
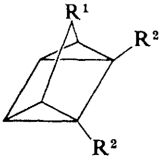


(32)

archetypes in the production of different isomers above.[23] Isomerizations of quadricyclane derivatives (33) commonly give the appropriate norbornadiene (34). However, the $[Rh(CO)_2Cl]_2$-catalysed isomerization of 3-oxaquadricyclane (35) gives the hydroxyfulvene (36).[24] Further investigation of this



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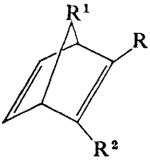

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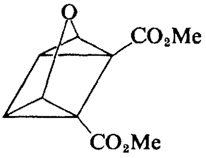

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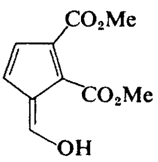

(36)

apparently anomalous system occasioned an examination of the effect of various substituents on the isomerization of (33; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = CO_2Me$; or $R^1 = Pr^c$ or $CH{=}CMe_2$, $R^2 = CO_2Me$), using both $[Rh(CO)_2Cl]_2$ and $[Rh(nor)Cl]_2$. In all cases examined the appropriate norbornadiene was obtained irrespective of R^1. However, an ester substituent

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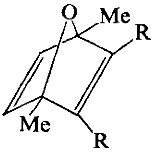
[23] H. Hogeveen and J. Thio, *Tetrahedron Letters*, 1973, 3463.

[24] A. Bruggink and H. Hogeveen, *Tetrahedron Letters*, 1972, 4961.

at R^2 caused a considerable retardation of the rate.[25] Of related interest to the oxaquadricyclane isomerization is the Rh^I- and H^+-catalysed reaction of (37) with methanol to give respectively (38) plus (39) or (39) alone. The intermediacy of (38) in the acid-catalysed reaction is not finally dismissed, however.[26]



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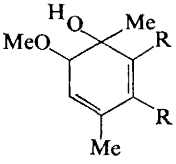

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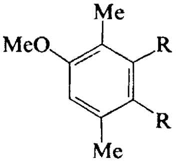
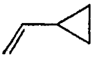


(39)

Derivatives of vinylcyclopropane (40) do not isomerize but do react with $[Fe_2(CO)_9]$ to give the iron–π-allyl heterocycle (41).[27, 28] This may be compared with similar π-allyl products from the reaction of cyclobutanes with Rh^I and Pd^{II} complexes.[29] An interesting comparison with these results is the reaction of $[Rh(C_2H_4)_2(acac)]$ with (42) to give (43), which at elevated temperatures rearranges to (44). Of the two mechanistic pathways proposed for the rearrangement one involves opening of the cyclopropane ring and production of a π-allyl as part of the cyclopentane ring (45).[30] In view of the above results this pathway must be favoured.



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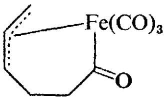

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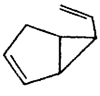

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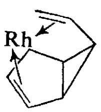

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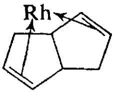

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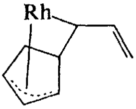
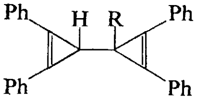


(45)

The bicyclopropenyl compounds (46) (R = Me or OMe) are catalytically isomerized by silver(I) to (47) (R = Me or OMe) and (48) or (49). The different products are rationalized in terms of initial retrocarbene fission and an overall mechanism in which the bridgehead substituent R can dictate the

[25] H. Hogeveen and B. J. Nusse, *Tetrahedron Letters*, 1973, 3667.
[26] H. Hogeveen and T. B. Middelhoop, *Tetrahedron Letters*, 1973, 3671.
[27] R. Aumann, *Angew. Chem. Internat. Edn.*, 1972, **11**, 522.
[28] R. Aumann, *Angew. Chem. Internat. Edn.*, 1973, **12**, 574.
[29] R. Rossi, P. Diversi, and L. Porri, *J. Organometallic Chem.*, 1971, **31**, C40.
[30] V. Aris, J. M. Brown, and B. T. Golding, *J.C.S. Chem. Comm.*, 1972, 1206.

point of ring closure.[31, 32] In addition the thermolytic isomerization of (47; R = Me) gives (50), thus demonstrating that the Dewarbenzene is an intermediate in the thermal isomerization of the bicyclopropenyl (46; R = Me) to give (48) and (50).[31]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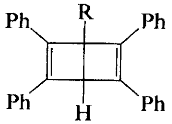
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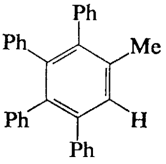
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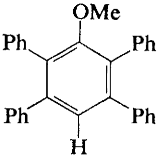
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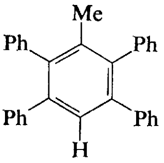
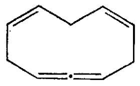
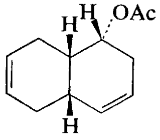
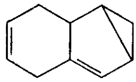

(50)

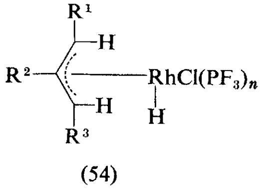
The mercury(II)-catalysed rearrangement of the cyclodeca-1,2,5,8-tetraene (51) in the presence of HOAc gives (52), (53), and an unassigned product. Transannular rearrangement *via* a mercury–carbene intermediate is favoured.[33]


(51)


(52)


(53)

Alkenes.—Deuterium exchange of propene with MeOD homogeneously catalysed by complexes of platinum, rhodium, and nickel can be monitored by microwave spectroscopy. The results show considerable incorporation of deuterium at C-2, a result which cannot be accommodated by the π-allyl–metal hydride mechanism for exchange/isomerization of olefins.[34a] However, the π- or 'h^3'-allyl–metal hydride mechanism for olefin isomerization has received some useful supporting evidence. The compound (54) can be generated


(54)

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[31] R. Weiss and S. Andrae, *Angew. Chem. Internat. Edn.*, 1973, **12**, 150.

[32] R. Weiss and S. Andrae, *Angew. Chem. Internat. Edn.*, 1973, **12**, 152.

[33] R. W. Thies, P. K. Hong, and R. Bushwell, *J.C.S. Chem. Comm.*, 1972, 1091.

[34] (*a*) C. A. Tolman and L. H. Scharpon, *J.C.S. Dalton*, 1973, 584; (*b*) J. F. Nixon and B. Wilkins, *J. Organometallic Chem.*, 1972, **44**, C25.

at 200 K and recognized by its ^{19}F n.m.r. spectrum. On warming $[RhCl(PF_3)_2]_2$ is formed and olefin liberated. In accordance with the requirements of the mechanism one olefin is liberated if the original allyl was symmetric and two (of the appropriate type) if the allyl was asymmetric.[34b] The isomerization of deuterium-substituted 3-ethylpent-1-ene to 3-ethylpent-2-ene, catalysed by $[Fe_3(CO)_{12}]$ is deemed to proceed *via* this type of mechanism.[35] In contrast, the isomerization of pent-1-ene to *cis*- and *trans*-pent-2-ene is advocated to proceed *via* a pentyl intermediate in the case of catalysis by solutions of $[Ni\{P(OEt)_3\}_4]$–CF_3CO_2H,[36] $[OsHCl(CO)(PPh_3)_3]$,[36] or $[RuHCl(PPh_3)_3]$.[37] *cis* : *trans* Ratios in the products are 2.3 (Ni), 6.0 (Os), and 1.5 (Ru). Only in the nickel complex is complex dissociation unnecessary to generate the catalyst. In this case the catalyst is $[HNi\{P(OEt)_3\}_4]^+$. This species also acts as catalyst in the isomerization of but-1-ene to but-2-ene.[38] Reaction rates are proportional to [catalyst] and to $[P(OEt)_3]^{-1}$. Interpretation of these and other reaction characteristics leads to a complex, many-featured mechanism from which we would point out that dissociation of $[HNi\{P(OEt)_3\}_4]^+$ is essential before the main mechanism comes into play, a perhaps surprising result in view of the absence of this step in the isomerization of pent-1-ene.[36]

These and other recent studies of the homogeneous catalysis of the isomerization of alkenes summarized are in Table 2.

Table 2 *Homogeneous catalysis of the isomerization of alkenes*

Catalyst	*Substrate*	*Reference*
$[Fe(CO)_5] + h\nu$	Allylic ethers	39
$[Fe_3(CO)_{12}]$	3-Ethyl[3-^{2}H]pent-1-ene	35
$[RuHCl(PPh_3)_3]^{a,b}$	Pent-1-ene	37
$[RuCl_2(PPh_3)_3]$	1,4-Diarylbutenes	40
$[RuCl_2(PPh_3)_3]$	2-Methyl-1,4-diphenylbutenes	40
$[OsHCl(CO)(PPh_3)_3]^{a,b}$	Pent-1-ene	36
$[HCo(CO)_4]$	[^{2}H$_6$]Propene	41
$[HCoN_2(PPh_3)_3]^{a,b}$	*cis*-Pent-2-ene	42
$[Rh(CO)_2Cl]_2$	Vinyl epoxides	43
$[IrX(CO)(PR_3)_2]$	Heptenes	44
$[HNi\{P(OEt)_3\}_4]^{+\ a,b}$	But-1-ene	38
$[HNi\{P(OEt)_3\}_4]^{+\ a}$	Pent-1-ene	36
$[PdCl_2(PhCN)_2]$	*trans*-[^{2}H$_2$]Ethylene	45
Ag^+	Maleylacetones	46

[a] Kinetic data reported. [b] Precursor to the active catalyst.

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[35] C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, 1973, **95**, 2248.

[36] D. Bingham, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1928.

[37] D. F. Ewing, B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1287.

[38] C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94**, 2994.

[39] A. J. Hubert, A. Georis, R. Warin, and P. Teyssie, *J.C.S. Perkin II*, 1972, 366.

[40] J. Blum and Y. Becker, *J.C.S. Perkin II*, 1972, 982.

[41] P. Taylor and M. Orchin, *J. Amer. Chem. Soc.*, 1971, **93**, 6504.

[42] S. Tyrlik, *J. Organometallic Chem.*, 1972, **39**, 371.

[43] G. Adams, C. Bibby, and R. Prigg, *J.C.S. Chem. Comm.*, 1972, 491.

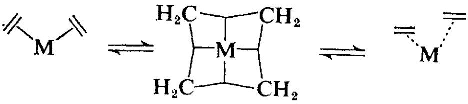
[44] W. Strohmeier and R. Fleischmann, *J. Organometallic Chem.*, 1972, **42**, 163.

[45] B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1204.

[46] R. A. Johnson and S. Saltzer, *J. Amer. Chem. Soc.*, 1972, **94**, 4755.

2 Disproportionation

The metal-catalysed disproportionation of alkenes has been postulated to involve an adsorbed 'cyclobutane' intermediate. However, since cyclobutanes are not products of the reactions and cyclobutanes do not react readily with the catalytic systems the cyclobutane model has been criticized.[47] Instead it has been proposed that the reaction proceeds *via* a reversible rearrangement of two co-ordinated alkenes into a multi-three-centred complex which involves four sp^3-hybridized CH_2 units (Scheme 1). An important feature of this mechanism is that whereas in the bis-alkene complex the two alkene ligands only donate four electrons to the metal, in the tetramethylene complex eight electrons are donated by the organic ligand to the metal. Thus if a bis-alkene complex, *e.g.* $[Mo(alkene)_2(CO)_4]$, is to be transformed into a tetramethylene intermediate two carbonyl ligands must dissociate if the intermediate is to retain a noble-gas structure. Evidence for this point and the proposed mechanism has been obtained.[48] Thus when non-4-ene is treated with $[W(CO)_3(toluene)]$ in heptane at 98 °C in an open system, disproportionation of nonene to octenes plus decenes takes place and both carbon monoxide and toluene are found in the reaction products. However, in a closed system, which would inhibit dissociation of carbon monoxide, no disproportionation of nonene is observed and only isomerization takes place. These results can be interpreted in terms of Scheme 2. Further evidence for these proposals follows from the observation that an excess of nonene also inhibits disproportionation but not isomerization in an open system. In a closed system disproportionation and isomerization are inhibited by an excess of nonene since $[W(alkene)_3(CO)_3]$ is not a catalyst for either reaction.[48] Further evidence for this concerted formation of a tetramethylene complex in disproportionation reactions follows from the observations that the activities of cobalt molybdate catalysts for the disproportionation of propene parallel activities for converting diazomethane into nitrogen and ethylene.[49] Definitive evidence for a metal–carbene intermediate has also been obtained in the disproportionation of electron-rich alkenes (55), which is catalysed by $[RhCl(PPh_3)_3]$ or *trans*-$[RhCl(CO)(PPh_3)_2]$.[50] The active catalysts for the disproportionation of two electron-rich alkenes, C_2X_4 with C_2Y_4, are the carbene complexes $[RhCl(CX_2)(PPh_3)_2]$ and $[RhCl(CY_2)(PPh_3)_2]$, which can be isolated. They can react *via* intermediates



Scheme 1

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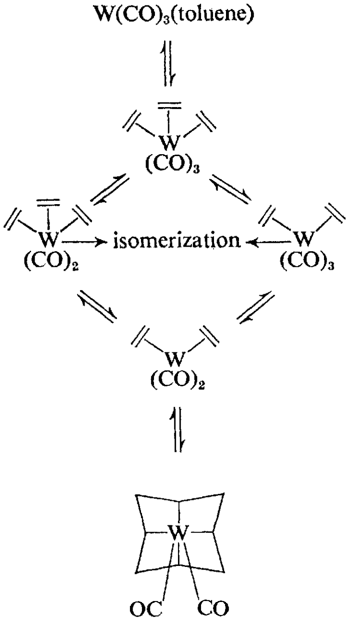
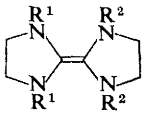
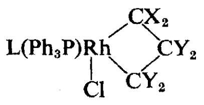
[47] G. S. Lewandos and R. Pettit, *Tetrahedron Letters*, 1971, 789.
[48] G. S. Lewandos and R. Pettit, *J. Amer. Chem. Soc.*, 1971, **93**, 7087.
[49] P. P. O'Neill and J. J. Rooney, *J.C.S. Chem. Comm.*, 1972, 104.
[50] D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 927.



Scheme 2

of the type (56). An alkene-disproportionation catalyst prepared from [$Mo(CO)_6$] and Al_2O_3 is able to effect the transformation of ethylene to propene. The formation of an intermediate methylene complex seems likely.[51]





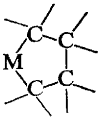
(55) $R^1 = R^2 = Ph$

$R^1 = R^2 = p\text{-}MeC_6H_4$

$R^1 = Ph, R^2 = p\text{-}MeC_6H_4$

(56) $L = PPh_3$ or CO

Metallocyclic intermediates of the type (57) could also be involved in disproportionation reactions. Evidence for the involvement of a metallocycle has



(57)

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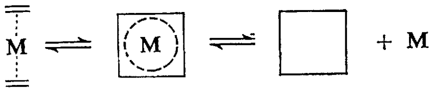
[51] P. P. O'Neill and J. J. Rooney, *J. Amer. Chem. Soc.*, 1972, **94**, 4383.

been obtained from the reactions of 1,4-dilithiobutane and deuterium-substituted derivatives with WCl_6, which yield ethylene.[52]

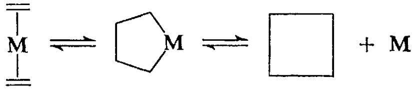
X-Ray photoelectron spectra of a disproportionation catalyst prepared by condensing hexacarbonylmolybdenum on to γ-alumina indicate that the oxidation state of the molybdenum is greater than one and less than six and that the metal is attached to electron-withdrawing sites on the alumina.[53] The disproportionation reaction has been reviewed.[54]

3 Oligomerization

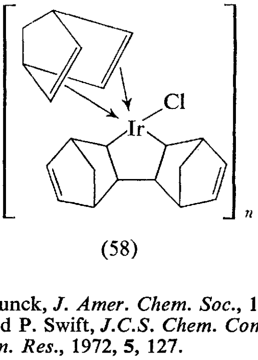
Certain transition metals catalyse the thermally forbidden [2 + 2] cycloaddition reactions to form a cyclobutane ring or the corresponding cycloreversion reaction. One of the proposed mechanisms for this reaction (Scheme 3) involves the metal acting as a template which provides *d*-orbitals of the appropriate symmetry to interact with orbitals of the organic molecules, thereby promoting reaction. An alternative mechanism involves a non-concerted pathway in which a metallocyclopentane intermediate is formed followed by reductive elimination (Scheme 4). Evidence for the latter pathway has been obtained from the reaction of norbornadiene with [IrCl(cyclo-octa-1,5-diene)] which yields the complex (58). Reaction of (58) with an excess of triphenyl-



Scheme 3



Scheme 4



(58)

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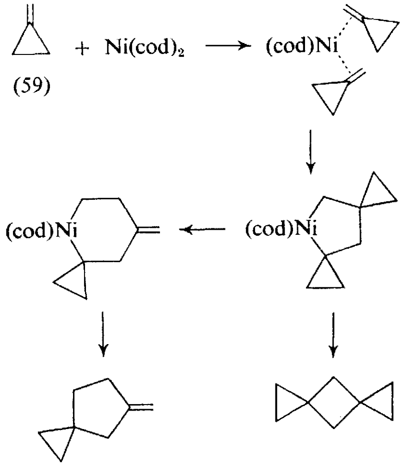
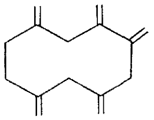
[52] R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, 1972, **94**, 2538.
[53] D. A. Whan, M. Barber, and P. Swift, *J.C.S. Chem. Comm.*, 1972, 198.
[54] N. Calderon, *Accounts Chem. Res.*, 1972, **5**, 127.

phosphine yields the *exo-trans-exo*-dimer of norbornadiene.[55] Metallocyclopentane intermediates are also probably involved in the cyclodimerization of methylenecyclopropane (59) which is catalysed by bis(cyclo-octa-1,5-diene)-nickel (Scheme 5).[56] The nickel(0)-catalysed cyclo-oligomerization of allene leading to 1,2,4,6,9-pentamethylenecyclodecane (60) is also a non-concerted process since a linear allene trimer complex [Ni(C_9H_{12})] can be isolated as a triphenylphosphine adduct (61).[57] A potential barrier controlling the growth reaction to particular oligoallenes can be set up by addition of phosphines to the system,[58] as has been demonstrated previously in the oligomerization of



Scheme 5



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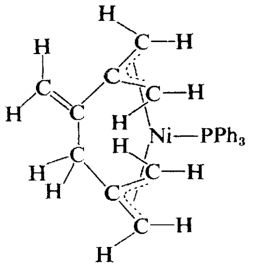

(61)

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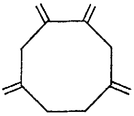
[55] A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 597.

[56] P. Binger, *Angew. Chem. Internat. Edn.*, 1972, **11**, 309.

[57] S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Comm.*, 1971, 863.

[58] S. Otsuka, A. Nakamura, T. Yamagata, and K. Tani, *J. Amer. Chem. Soc.*, 1972, **94**, 1037.

butadiene by nickel catalysts.[59] Thus addition of tertiary alkyl- or arylphosphines to the system produces a mixture of oligoallenes containing (62) as a major product, whereas if a triaryl phosphite is added 1,2,4-trimethylenecyclohexane (63) is obtained regardless of the steric requirements of the phosphite.[58] The oligomerization and co-oligomerization reactions of butadiene have been reviewed.[59] The stereochemistry of the products formed by the nickel(0)-catalysed dimerization and oligomerization of methyl-substituted 1,3-dienes can only be explained by a multistep mechanism. Thus for example the product obtained by the head-to-tail dimerization of *trans*-piperylene has the structure (64) and not (65) as would be expected for a concerted process.[59,60] Treatment of the cyclododecatriene complex [Ni(cdt)(PR$_3$)] with isoprene gives the complex (66) which provides further evidence that the catalytic dimerization of 1,3-dienes proceeds *via* a multistep process.[60]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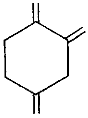
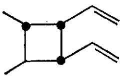

(63)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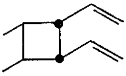
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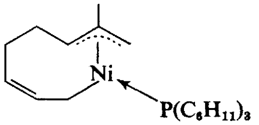

(66)

Dichlorobis(benzonitrile)palladium(II) catalyses the dimerization of ethylene to a mixture of butenes of composition but-1-ene 4%, *cis*-but-2-ene 36%, and *trans*-but-2-ene 60%. Kinetic studies on this reaction show that it is first-order with respect to ethylene. However, the reaction proceeds only after an induction period and there is no immediate change in the rate of reaction on increasing the pressure of ethylene. The palladium complex also catalyses isotopic exchange between C_2H_4 and C_2D_4 and an identical induction period is again observed. A palladium hydride species is presumed to be the active catalyst. This hydride is produced during the induction period by a slow reaction of ethylene with [PdCl$_2$(PhCN)$_2$].[61] The proposed mechanism is illustrated in Scheme 6. The nickel(II) aryl complexes [NiBr(aryl)(PPh$_3$)$_2$], in the presence of boron trifluoride etherate, also catalyse the dimerization of ethylene. A

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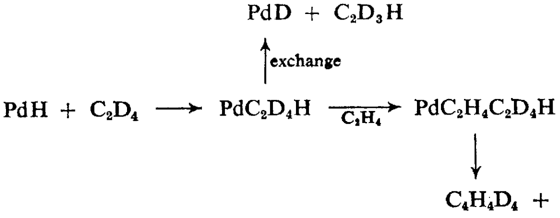
[59] H. Buchholz, P. Heimbach, H.-J. Hey, H. Selbeck, and W. Wiese, *Coordination Chem. Rev.*, 1972, **8**, 129.

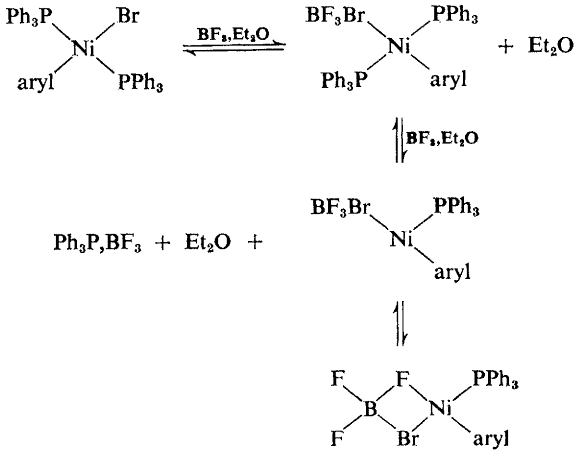
[60] B. Barnett, B. Büssemeier, P. Heimbach, P. W. Jolly, C. Krüger, L. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, 1972, 1457.

[61] T. Kitamura, K. Maruya, Y. Moro-oka, and A. Ozaki, *Bull. Chem. Soc. Japan*, 1972, **45**, 1457.



Scheme 6

nickel hydride species, formed from a nickel complex and ethylene, is again thought to be the active catalyst. The role of the aryl ligands in this system is not clear but rates of dimerization decrease in the order of ligands, *o*-tolyl > naphthyl > mesityl $\gg$ Br. The presence of the boron trifluoride etherate enhances the loss of a triphenylphosphine ligand to give a vacant co-ordination site on the nickel (Scheme 7).[62] The formation of butenes from this reaction could



Scheme 7

either result from the breakdown of a vinyl–ethyl complex (67) or a vinyl–butyl complex (68). An examination of the products formed during the codimerization of ethylene and propene catalysed by this nickel system suggests that the intermediate (67) is involved in the dimerization of ethylene (Scheme 8). However, it has not been possible to detect a nickel–vinyl intermediate.[63] Treatment of triethylalane with $[TiPh_2(h^5\text{-}C_5H_5)_2]$, $[TiCl_2(h^5\text{-}C_5H_5)_2]$, or $[TiCl(h^5\text{-}C_5H_5)_2]$ produces a model alkene-polymerization catalyst, which was

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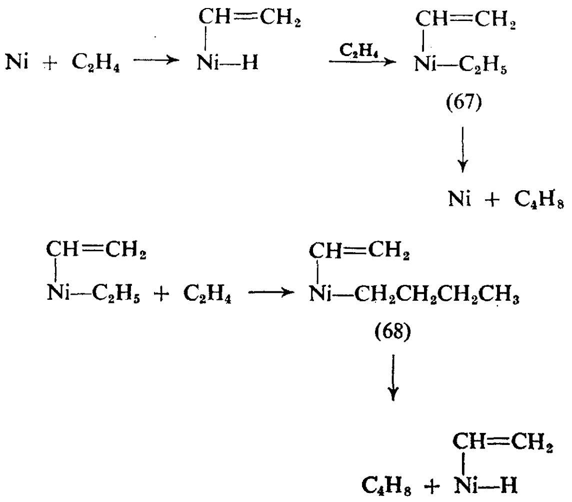
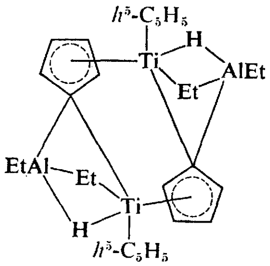
[62] K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Japan*, 1972, **45**, 2255.

[63] K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Japan*, 1973, **46**, 993.



Scheme 8

formulated as $[TiAlEt_2(h^5\text{-}C_5H_5)_2]_2$.[64] However, this catalyst has now been shown to be a hydride complex (69).[65] The kinetics of ethylene polymerization and butadiene polymerization catalysed homogeneously by $[RuClH(PPh_3)_3]$ in *NN*-dimethylacetamide at 50—85 °C have been studied. In the ethylene system the rates are first-order in alkene and first-order in catalyst. Activation parameters are $\Delta H^{\ddagger} = 20\ \text{kcal mol}^{-1}$ and $\Delta S^{\ddagger} = -7.7\ \text{cal K}^{-1}\ \text{mol}^{-1}$. The proposed mechanism involves insertion of ethylene into the ruthenium–hydrogen bond followed by rate-determining interaction of the ethyl complex with further ethylene. The activation parameters apply to the composite term



(69)

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[64] P. Corradini and A. Sirigu, *Inorg. Chem.*, 1967, **6**, 601; G. Natta, G. Mazzanti, P. Corradini, U. Giannini, and S. Cesca, *Atti. Accad. naz. Lincei, Rend., Classe Sci. fis. mat. nat.*, 1959, **26**, 150.

[65] F. N. Tebbe and L. J. Guggenberger, *J.C.S. Chem. Comm.*, 1973, 227.

$K'k'$.[66] In the ethylene dimerization reaction, catalysed by rhodium chlorides

$$\mathrm{RuH} + \mathrm{C_2H_4} \underset{K}{\rightleftharpoons} \mathrm{RuC_2H_5}$$

$$\mathrm{RuC_2H_5} + \mathrm{C_2H_4} \underset{K'}{\rightleftharpoons} \mathrm{Ru(C_2H_5)(C_2H_4)}$$

$$\mathrm{Ru(C_2H_5)(C_2H_4)} \xrightarrow{k'} \mathrm{RuCH_2CH_2C_2H_5}$$

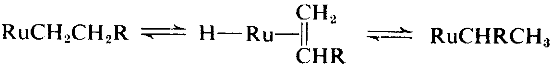
in HCl–ethanol solutions, the activation parameters ($\Delta H^{\ddagger} = 16$ kcal mol^{-1}, $\Delta S^{\ddagger} = -20$ cal K^{-1} mol^{-1}) were related to the insertion reaction:[67]

$$[\mathrm{RhCl_3(C_2H_5)(C_2H_4)}]^- \xrightarrow{k} [\mathrm{RhCl_3CH_2CH_2C_2H_5}]^-$$

However, it is suggested that these parameters correspond to a composite constant kK_e[66] where K_e refers to the pre-equilibrium:

$$[\mathrm{RhCl_3(C_2H_5)}]^- + \mathrm{C_2H_4} \underset{K_e}{\rightleftharpoons} [\mathrm{RhCl_3(C_2H_5)(C_2H_4)}]^-$$

Analysis of the ethylene polymer suggests a high degree of chain branching and this could arise *via* isomerization of an alkyl complex (Scheme 9). The rate of butadiene polymerization is *ca.* 15 times greater than that of ethylene polymerization and the rate of insertion is probably at least 50 times greater.[66] Activation parameters for the butadiene system ($\Delta H^{\ddagger} = 27$ kcal mol^{-1}, $\Delta S^{\ddagger} = 21$ cal K^{-1} mol^{-1}) refer directly to the insertion reaction. The greater activation energy of the butadiene system can be related to the stronger (chelating) co-ordinating power of butadiene. The more favourable entropy of activation in the butadiene system accounts for the greater rate of insertion. This entropy factor could either be related to the breaking of a butadiene chelate ring in the transition state involving insertion or be a consequence of a reduction of solvation of the transition-state complex. However, the exact mechanism of the polymerization of butadiene by this ruthenium system is not clear. The mechanism could involve σ-butenyl intermediates, Ru—$\mathrm{CH_2CH_2}$-$\mathrm{CH{=}CH_2}$ or Ru—$\mathrm{CHMeCH{=}CH_2}$ and proceed in a similar manner to that proposed for ethylene polymerization. Alternatively polymerization could proceed by reaction of butadiene with an h^3-allyl intermediate (Scheme 10).[66] This latter process is generally accepted as an important part of the mechanism of polymerization of butadiene by nickel catalysts.



$$\mathrm{RuCH_2CH_2R} \rightleftharpoons \mathrm{H{-}Ru{-}}\overset{\mathrm{CH_2}}{\underset{\mathrm{CHR}}{\|}} \rightleftharpoons \mathrm{RuCHRCH_3}$$

Scheme 9

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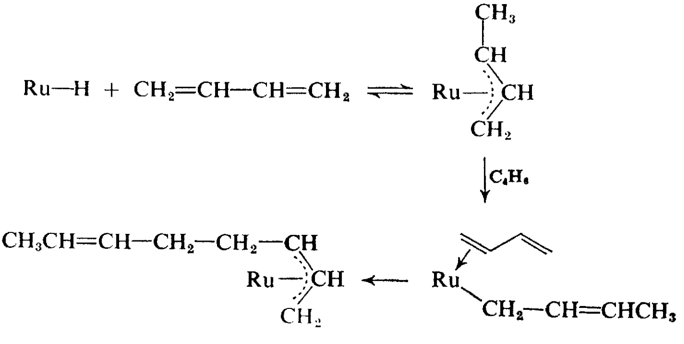
[66] B. R. James and L. D. Markham, *J. Catalysis*, 1972, **27**, 442.

[67] R. Cramer, *J. Amer. Chem. Soc.*, 1965, **87**, 4717.

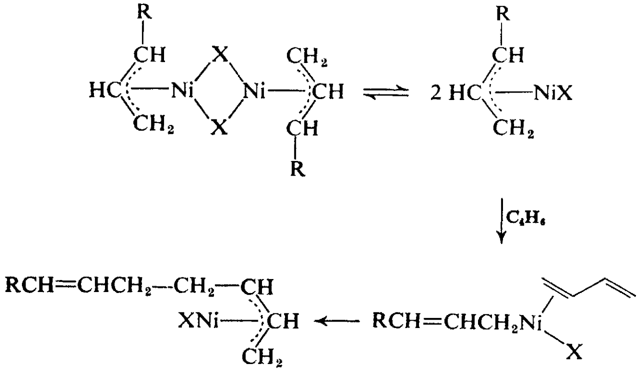


Scheme 10

The polymerization of butadiene by [NiI(h^3-allyl)]$_2$ is first-order with respect to the monomer concentration and follows the rate law[68–70]

$$\text{Rate} = k[\text{Ni}]^{1/2}[\text{C}_4\text{H}_6]$$

The square-root dependence of the rate on the nickel concentration is attributed to the dimer–monomer equilibrium in which the monomer is the active species. Co-ordination of the monomer to the active nickel species causes the h^3-allyl ligand to adopt an h^1-configuration which is followed by 'insertion' of the diene into the nickel–carbon bond (Scheme 11). The polymerization of butadiene catalysed by [NiI(h^3-allyl)]$_2$ proceeds predominantly by a living-polymer mechanism and is influenced by the solvent. Thus the rate of polymerization (and of a chain-transfer reaction) increases in the series benzene <



Scheme 11

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[68] D. Babitskii, B. A. Dolgoplosk, V. A. Kormer, M. I. Lobach, E. I. Tinyakova, and V. A. Yakovlev, *Izvest. Akad. Nauk S.S.S.R.*, 1965, 1478.

[69] J. F. Harrod and L. R. Wallace, *Macromolecules*, 1969, **2**, 449.

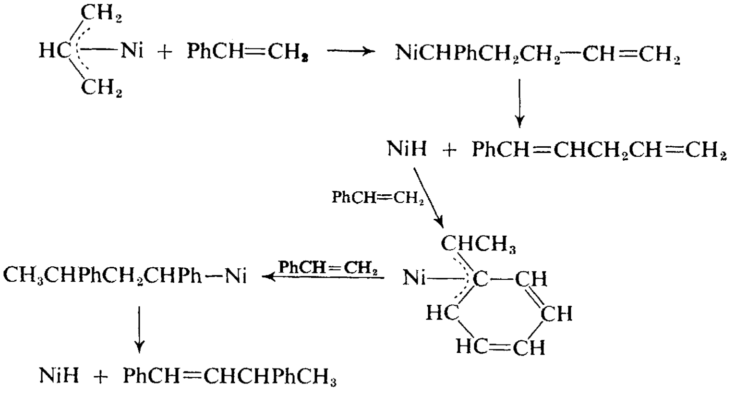
[70] G. Henrici-Olivé, S. Olivé, and E. Schmidt, *J. Organometallic Chem.*, 1972, **39**, 201.

THF < 1,2-dichloroethane. If this order of solvent effect reflects the co-ordinating ability $C_6H_6 > THF > C_2H_4Cl_2$ of these solvents then a solvent such as benzene will compete with the diene for the monomeric nickel species.[70]

The allyl complex $[NiI(h^3\text{-allyl})]_2$ also catalyses the dimerization of styrene at 0 °C stereospecifically to *trans*-1,3-diphenylbut-1-ene. The rate law found for this reaction is[70]

$$-\mathrm{d}[\text{styrene}]/\mathrm{d}t = k[\text{styrene}][\text{Ni}]$$

An induction period is observed in this reaction which decreases with an increase in styrene concentration. This induction period may correspond to the formation of a nickel hydride species which is then followed by insertion steps and β-elimination (Scheme 12). An analogous β-elimination reaction is not observed in butadiene polymerization since in this instance there is no methylene group β to the nickel. The nickel catalyst in the styrene dimerization may be predominantly monomeric since e.s.r. studies indicate the presence of a paramagnetic nickel(II) species. This is consistent with the kinetic studies, which indicate that the rate is proportional to the nickel concentration. Styrene exerts a chain-transfer action on the polymerization of butadiene and there is also some copolymerization.[70]



Scheme 12

This 'insertion' reaction of 1,3-dienes with h^3-allyl complexes has been studied in some detail with palladium complexes (see Chapter 4). Studies with 2-chlorobutadiene reveal the formation of multiple insertion products containing up to 40 carbon atoms. The insertion proceeds *via* an intermediate σ-allyl (Scheme 13). The insertions produce the repeating unit $—[CH_2CH{=}CClCH_2]—$ by a series of 1,4-additions to the diene, 1,2-addition not occurring. The presence of a chlorine substituent both in the reacting h^3-allyl complex and in the h^3-allyl insertion product enhances the rate of insertion.[71]

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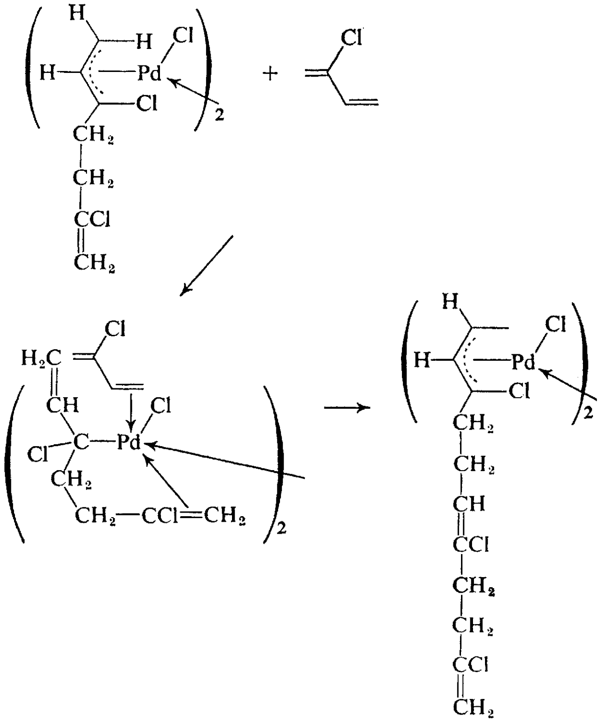
[71] D. J. S. Guthrie and S. M. Nelson, *Coordination Chem. Rev.*, 1972, **8**, 139.

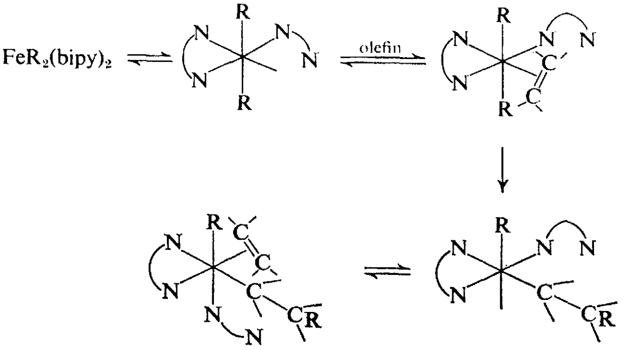


Scheme 13

Acrylonitrile, methacrylonitrile, acrolein, methyl vinyl ketone, methyl acrylate, alkyl methacrylates, and 2-vinylpyridine polymerize in the presence of the complexes [$FeR_2(bipy)_2$] (R = Me, Et, or Pr^n). From a study of the kinetics of these polymerization reactions,[72] together with a study of the decomposition of the iron complexes in the presence of various substituted alkenes,[73] it appears that the polymerization involves a slow initiation process followed by rapid propagation and a unimolecular termination process (Scheme 14). The termination process takes place either by β-elimination from the (C—C)$_n$R–iron group or by transfer of hydrogen from an iron–alkyl bond to this group.[72] Similar catalyst systems involving Schiff bases (70) in place of bipyridyl can be generated by treating [$Fe(acac)_3$] or [$Ni(acac)_2$] with aluminium alkyls in the presence of a Schiff base. The iron complexes catalyse cyclodimerization of butadiene and isopropene whereas the nickel complexes catalyse cyclotrimerization of butadiene. Variations in the Schiff base structure have a profound effect on the rates of reactions. In general rates increase when

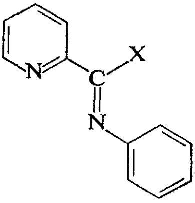
[72] T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Japan*, 1972, **45**, 1111.

[73] T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Japan*, 1972, **45**, 1104.



Scheme 14

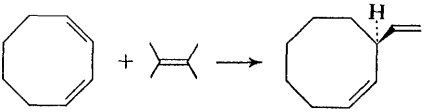
electron density at the anil nitrogen in (70) is increased. This will increase electron density at iron and possibly enhance the interaction of the diolefin with the iron.[74]



(70)

4 Co-addition and Co-oligomerization

There are few asymmetric syntheses which proceed under catalytic conditions. Reactions which have been studied usually involve hydrogenation using optically active catalysts in which chiral centres are formed as a result of C—H bond formation. However, using h^3-allylnickel halide–phosphine–Lewis acid catalyst systems, a procedure has been developed for converting cyclo-octa-1,3-diene and ethylene into 3-vinylcyclo-octene (71) having an optical purity of up to 70%. High optical induction occurs at the lowest possible temperatures and when the phosphines used contain bulky optically active organic groups.[75]



(71)

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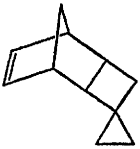
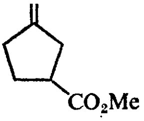
[74] C.-Y. Wu and H. E. Swift, *J. Catalysis*, 1972, **24**, 510.

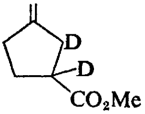
[75] B. Bogdanovic, B. Henc, B. Meister, H. Pauling, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1023.

A catalytic asymmetric cycloaddition reaction between norbornadiene and methylenecyclopropane can also be achieved in the presence of a [Ni(cod)$_2$]-(−)-benzylmethylphenylphosphine catalyst to give the cycloadduct (72) in an optically active form.[76] This reaction may proceed *via* a metallocyclopentane intermediate.[56] The reactions of methylenecyclopropane with [Ni(cod)$_2$]-phosphine systems do not appear to involve cleavage of the three-membered ring.[56, 76] However, the bis(acrylonitrile)nickel-catalysed cycloaddition reaction of methylenecyclopropane with methyl acrylate, which yields 3-methoxycarbonylmethylenecyclopentane (73), does involve C—C bond cleavage.[77] Reaction with the deuterium-substituted compound CHD=CDCO$_2$Me gives the cyclopentane derivative (74). An intermediate of the type (75) may be involved in this reaction.

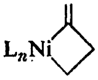

(72)



(73)

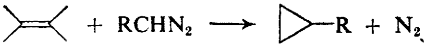


(74)



(75)

The cyclopropanation reaction (Scheme 15) of olefins can be catalysed by several metal species but copper complexes are usually the most efficient.



Scheme 15

Copper(I) triflate, Cu(CF$_3$SO$_3$), is a highly active catalyst for the cyclopropanation of olefins with diazo-compounds. The copper(I) complex is quite soluble in a number of olefins and these solutions react vigorously with ethyl diazoacetate. The addition of catalytic amounts of Cu(CF$_3$SO$_3$) to a solution of ethyl diazoacetate in hex-1-ene or oct-1-ene causes a rapid and quantitative evolution of nitrogen and formation of the ethyl 2-alkylcyclopropanecarboxylates in good yields. The rate of nitrogen evolution can be expressed as

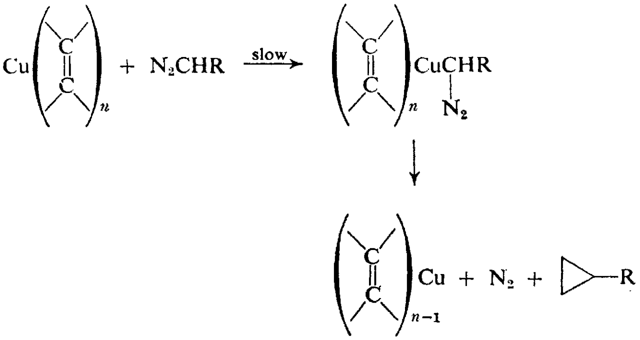
$$\frac{d[N_2]}{dt} = \frac{k[Cu(CF_3SO_3)][N_2CHCO_2Et]}{[\text{hex-1-ene}]}$$

---

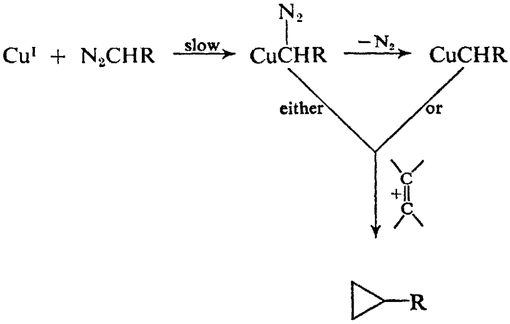
[76] R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, *J. Amer. Chem. Soc.*, 1973, **95**, 1674.

[77] R. Noyoro, Y. Kumagai, I. Umeda, and H. Takaya, *J. Amer. Chem. Soc.*, 1972, **94**, 4018.

Activation parameters are $\Delta H^{\ddagger} = 19.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.90$ cal deg^{-1} mol^{-1}. The retarding effect of hex-1-ene on the rate of reaction suggests that the catalyst is deactivated by multiple co-ordination of the alkene. The behaviour of the copper(I) triflate system is consistent with a mechanism which involves co-ordination of the diazo-compound with an equilibrium mixture of copper(I) olefin complexes followed or accompanied by rapid intramolecular collapse to products (Scheme 16). In this scheme olefin co-ordination dominates selectivity rather than carbene reactivity. Thus the relative activities of hex-1-ene and tetramethylethylene are the same towards CH_2 and $CHCD_2Et$ using $Cu(SO_3F)$ as catalyst. However, in copper acetylacetonate or phosphite, halide, and sulphide systems, selectivity is largely determined by electrophilic attack on the alkene by a transient copper–carbene complex (Scheme 17). With these catalysts olefin co-ordination is not important and hence cyclopropanation of the most highly substituted (nucleophilic) olefin is favoured.[78]



Scheme 16



Scheme 17

Attempts to copolymerize methyl methacrylate and isoprene lead to severe retardation of polymerization. The retardation reaction involves attack of a

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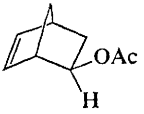
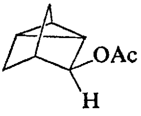
[78] R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 3300.

propagating polymer radical on an unstable nickel(I) species, generating a terminal π-allylic derivative in the polymer chain.[79, 80]

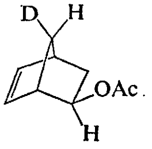
Acetic acid readily adds to norbornadiene in the presence of a strong protonic acid catalyst to form (76) and (77). It has now been shown that



(76)

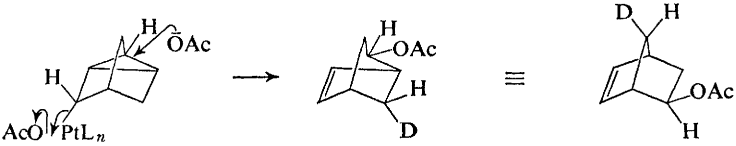


(77)



(78)

$[Pt(PPh_3)_3]$ and to a slightly lesser extent $[Pt(OCOCF_3)_2(PPh_3)_2]$ will catalyse the formation of (76). However, experiments with $MeCO_2D$ have shown that, unlike the acid-catalysed reaction, the metal-catalysed reactions involve a highly stereoselective skeletal rearrangement to *syn*-7-deuterio-*exo*-5-acetoxybicyclo[2,2,1]hept-2-ene (78). This reaction may involve (79) as a transient intermediate which reacts as shown in Scheme 18.[81]



(79)

$+ L_nPt$

Scheme 18

5 Homogeneous Hydrogenation

Although the hydrogenolysis of molecular oxygen catalysed heterogeneously by metal surfaces was one of the first recognized catalytic reactions, the corresponding homogeneous reaction is not so well known. It has now been found that a variety of triphenylphosphine complexes catalyse homogeneously the combination of molecular hydrogen and oxygen to form water (Table 3). Catalysis by the complexes $[PtO(PPh_3)_n]$ and $[IrCl(CO)(PPh_3)_2]$ is first-order in both H_2 and O_2 and about half-order in the complex.[82]

The hydrogenation of organic compounds using homogeneous catalysts has been reviewed.[83]

Manganese.—The hydride *cis*-$[MnH(CO)_4(PPh_3)]$ reduces a variety of organic halogen compounds at room temperature. Competition experiments show that the order of reactivity for halogenomethanes is C—I > C—Br > C—Cl, *i.e.*

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[79] J. Ashworth and C. H. Bamford, *J.C.S. Faraday I*, 1973, **69**, 314.
[80] J. Ashworth and C. H. Bamford, *J.C.S. Faraday I*, 1973, **69**, 302.
[81] E. F. Magoon and L. H. Slaugh, *J. Organometallic Chem.*, 1973, **55**, 409.
[82] L. Vaska and M. E. Tadros, *J. Amer. Chem. Soc.*, 1971, **93**, 7099.
[83] R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, 1973, **73**, 21.

Table 3 *Rates and activation parameters for the combination of molecular hydrogen and oxygen catalysed by metal complexes in toluene at 25 °C (from ref. 82)*

Complex	$k_0 \times 10^6$/l mol^{-1} sec^{-1}[a]	$\Delta H^{\ddagger}$/kcal mol^{-1}
$[PtO(PPh_3)_n]$	13.2	2.8
$[IrCl(CO)(PPh_3)_2]$	9.6	8.8
$[Rh(ClO_4)(CO)(PPh_3)_2]$	6.9	6.1
$[RhCl(CO)(PPh_3)_2]$	5.9	—
$[RuCl_2(PPh_3)_3]$	1.1	—
$[IrBr(CO)(PPh_3)_2]$	0.76[b]	—
fac-$[IrH_3(CO)(PPh_3)_2]$	0.43	—
$[IrH(CO)(PPh_3)_3]$	0.26	—
$[RhCl(PPh_3)_3]$	0.20[c]	—
$[IrH_3(PPh_3)_3]$	0.07[c]	10.0

[a] $d[H_2O]/dt = -d[H_2]/dt = -\frac{2}{3}d[H_2 + O_2]/dt = k_0$. [b] At 65° C. [c] At 45 °C.

reactivities increase with decreasing bond dissociation energy. Although kinetic studies are not conclusive the observations of an induction period, low activation energy, and absence of solvent effects suggest a radical mechanism for these reactions analogous to that postulated for similar reactions of trialkyltin hydrides.[84]

Cobalt.—The pentacyanocobaltate(II) ion catalyses the hydrogenation of conjugated dienes selectively to alkenes. Two types of mechanism have been proposed for these reactions, one involving organocobalt intermediates and the other involving free-radical intermediates. The hydrogenation of activated alkenes such as styrene and cinnamate[85–87] appears to involve radicals but the hydrogenation of phenylbuta-1,3-diene, butadiene, and isoprene involves organocobalt intermediates.[88,89] Butadiene hydrogenation involves intermediate *cis*- and *trans*-σ-but-2-enyl and *syn*-h^3-(1-methylallyl) complexes.

Attempts to induce asymmetric hydrogenation of activated olefins *e.g.* $CH_2{=}C(Ph)CO_2Na$ using a μ-[*S*-(+)-*NN'*-dimethyl-1,2-propanediamine]-bis[tetracyanocobaltate(II)] system give only slightly optically active products.[90] This is a similar result to that obtained with an optically active α-amino-acid–cyanocobaltate system.[91]

The hydrogenation of cyclohexene can be catalysed by $[CoH_3(PPh_3)_3]$. Free triphenylphosphine inhibits hydrogenation, and the first step in the reaction is most probably dissociation of a phosphine ligand. Addition of cyclohexene is

[84] B. L. Booth and B. L. Shaw, *J. Organometallic Chem.*, 1972, **43**, 369.
[85] W. Strohmeier and N. Iglauer, *Z. phys. Chem. (Leipzig)*, 1966, **51**, 50.
[86] L. Simandi and F. Nagy, *Acta Chim. Acad. Sci. Hung.*, 1965, **46**, 137.
[87] J. Halpern and L. Wang, *J. Amer. Chem. Soc.*, 1968, **90**, 6665.
[88] T. Funabiki, M. Mohri, and K. Tarama, *J.C.S. Dalton*, 1973, 1813.
[89] T. Funabiki, M. Matsumoto, and K. Tarama, *Bull. Chem. Soc. Japan*, 1972, **45**, 2723.
[90] Y. Ohgo, K. Kobayashi, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Japan*, 1972, **45**, 933.
[91] Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Japan*, 1970, **43**, 505.

$$[Co(PPh_3)_2] + 1\tfrac{1}{2}H_2 \rightleftharpoons [CoH_3(PPh_3)_2]$$

$$[CoH_3(PPh_3)_2] + PPh_3 \rightleftharpoons [CoH_3(PPh_3)_3]$$

$$[Co(PPh_3)_2] + PPh_3 \rightleftharpoons [Co(PPh_3)_3]$$

$$[CoH_3(PPh_3)_2] + C_6H_{10} \rightleftharpoons [CoH_3(PPh_3)_2C_6H_{10}]$$

Scheme 19

considered to be rate determining (Scheme 19). Since excess of phosphine does not inhibit H_2–D_2 exchange, cyclohexene is activated on a phosphine site.[92a]

Homogeneous hydrogenation of cyclohexene can also be catalysed by $[CoH(CO)_2(PBu^n_3)_2]$.[92b] The rate-determining step is direct reaction of hydrogen with the intermediate cobalt–olefin complex, which may occur *via* instantaneous H—H bond cleavage and C—H bond formation. Activation parameters are $\Delta H^{\neq} = 19.2$ kcal mol^{-1} and $\Delta S^{\neq} = -17.2$ cal deg^{-1} mol^{-1}.

Rhodium and Iridium.—The hydrogenation of olefins catalysed by $[RhCl(PPh_3)_3]$ involves oxidative addition of hydrogen to a rhodium(I) species which is usually thought to be $[RhCl(PPh_3)_3]$ or its dissociation product $[RhCl(PPh_3)_2]$. Kinetic measurements on the addition of hydrogen show that $[RhCl(PPh_3)_2]$ is at least 10^4 times as reactive as $[RhCl(PPh_3)_3]$ or $[Rh_2Cl_2(PPh_3)_4]$. The mechanism of the oxidative addition of hydrogen to $[RhCl(PPh_3)_3]$ is[93]

$$[RhCl(PPh_3)_3] + H_2 \underset{K_1}{\rightleftharpoons} [RhClH_2(PPh_3)_3]$$

$$[RhCl(PPh_3)_3] \underset{K_2}{\rightleftharpoons} [RhCl(PPh_3)_2] + PPh_3$$

$$[RhCl(PPh_3)_2] + H_2 \underset{K_3}{\rightleftharpoons} [RhClH_2(PPh_3)_2]$$

$$[RhClH_2(PPh_3)_2] + PPh_3 \underset{\text{fast}}{\rightleftharpoons} [RhClH_2(PPh_3)_3]$$

From spectral[94] and n.m.r.[95] measurements it is apparent that the equilibrium

$$2[RhCl(PPh_3)_2] \rightleftharpoons [Rh_2Cl_2(PPh_3)_4$$

lies far to the right. However, under the reaction conditions the reaction of hydrogen with $[RhCl(PPh_3)_2]$ is sufficiently fast to preclude the formation of $[Rh_2Cl_2(PPh_3)_4]$, which therefore does not take a significant part in the reaction. It is apparent that despite its low concentration $[RhCl(PPh_3)_2]$ is an important species in hydrogenation reactions, as originally suggested.[96] The dimer

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[92] (*a*) J. L. Hendrikse and J. W. H. Coenen, *J. Catalysis*, 1973, **30**, 72; (*b*) G. F. Ferrari, A. Andreetta, G. F. Pregaglia, and R. Ugo, *J. Organometallic Chem.*, 1972, **43**, 213.

[93] J. Halpern and C. S. Wong, *J.C.S. Chem. Comm.*, 1973, 629.

[94] H. Arai and J. Halpern, *Chem. Comm.*, 1971, 1571.

[95] P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94**, 3240.

[96] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[$Rh_2Cl_2(PPh_3)_4$] reacts with hydrogen to give [$Rh_2H_2Cl_2(PPh_3)_4$] and kinetic studies reveal that the reactivities of the rhodium(I) in [$RhCl(PPh_3)_3$] and [$Rh_2Cl_2(PPh_3)_4$] are very similar.[93] A kinetic study on the hydrogenation of cyclohexene catalysed by [$RhCl(PPh_3)_3$] has led to the suggestion that at high concentration of alkene the dissociation of [$RhCl(PPh_3)_3$(alkene)] is a principal source of triphenylphosphine.[97] It is usually considered that the hydrogenation of [$RhCl(PPh_3)_3$] is reversible.[95, 96] However, this may not be so since there appears to be some discrepancy between the amount of hydrogen absorbed and the amount recoverable in benzene, methylene chloride, or 50% chloroform–ethanol solutions.[98]

Chlorotris(triphenylphosphine)rhodium(I) can also catalyse hydrogen transfer from dioxan to an alkene. The rate-determining step in this reaction is considered to be oxidative addition of C—H bonds of dioxan to the catalyst:[99]

$$[RhCl(C_4H_8O_2)(PPh_3)_2] \longrightarrow [RhClH(C_4H_7O_2)(PPh_3)_2]$$

$$[RhClH(C_4H_7O_2)(PPh_3)_2] \longrightarrow [RhClH_2(C_4H_6O_2)(PPh_3)_2]$$

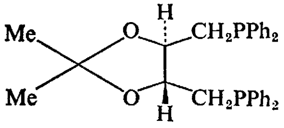
The d^{10} complexes [$M(NO)(PPh_3)_3$] (M = Co, Rh, or Ir) are co-ordinatively saturated. However, dissociation of a phosphine ligand or a conformational change of the type linear $NO^+ \rightarrow$ bent NO^- can provide a vacant co-ordination site. Studies with these complexes show that their ability to act as hydrogenation catalysts varies in the order $Rh > Ir \gg Co$.[100, 101] However, whether there is a change in the bonding of the NO during reaction is not known. The greater reactivity of the rhodium complex can be correlated with its ability to dissociate a phosphine ligand more readily.[101]

The stereochemistry of the addition of hydrogen to an olefinic double bond catalysed by [$RhCl(PPh_3)_3$] has been shown to involve *cis* addition,[102] in agreement with earlier studies.[96, 103, 104]

Recent publications have shown that reasonably efficient catalytic asymmetric reduction of alkenes can be achieved with rhodium complexes containing chiral phosphine or amide ligands. However, catalysts containing phosphine ligands in which the chirality is on the phosphorus have now been described. Such systems give very high yields of optically active α-amino-acids by catalytic asymmetric reduction of α-acrylaminoacrylic acids. Very high optical purities are obtained with the *o*-anisylmethylcyclohexylphosphine-rhodium catalyst and acylphenylalanines. Optimum yields are obtained with catalysts prepared by the addition of two chiral phosphine ligands to complexes of the type [$RhCl(diene)]_2$. The catalysts are probably cationic complexes, [$Rh(diene)L_2]^+$.[105] Catalytic asymmetric reduction of simple ketones

[97] S. Siegel and D. Ohrt, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 15.
[98] G. G. Strathdee and R. M. Given, *J. Catalysis*, 1973, **30**, 30.
[99] T. Nishiguchi, K. Tachi, and K. Fukuzumi, *J. Amer. Chem. Soc.*, 1972, **94**, 8916.
[100] G. Dolcetti, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 705.
[101] W. Strohmeier and R. Endres, *Z. Naturforsch.*, 1972, **27b**, 1415.
[102] Y. Senda, S. Mitsui, H. Sugiyama, and S. Seto, *Bull. Chem. Soc. Japan*, 1972, **45**, 3498.
[103] F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1574.
[104] A. J. Birch and K. A. M. Walker, *Tetrahedron Letters*, 1966, 4939.
[105] W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J.C.S. Chem. Comm.*, 1972, 10.

can also be achieved using similar catalysts.[106] A catalytic system involving a chiral diphosphine, (−)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (80), has been described.[107]



(80)

Although sulphur poisons heterogeneous hydrogenations, rhodium complexes containing sulphur ligands can catalyse hydrogenation reactions. The $[RhCl_3(SEt_2)_3]$-catalysed hydrogenation of maleic acid in *NN*-dimethylacetamide at *ca.* 70 °C and 1 atm pressure involves initial reduction to a rhodium(I) species, followed by rapid co-ordination of alkene and activation of molecular hydrogen. The reduction step involves heterolytic cleavage of hydrogen by $[RhCl_3(SEt_2)_2]$:

$$[RhCl_3(SEt_2)_3] \rightleftharpoons [RhCl_3(SEt_2)_2] + SEt_2$$
$$[RhCl_3(SEt_2)_2] + H_2 \longrightarrow [RhHCl_3(SEt_2)_2]^- + H^+$$

Neither of these reactions is observed in benzene but the polar *NN*-dimethylacetamide assists dissociation of the octahedral complex and heterolysis of the hydrogen. Activation parameters for the reduction are $\Delta H^{\neq} = 12.9$ kcal mol^{-1}, $\Delta S^{\neq} = -21$ cal deg^{-1} mol^{-1}. The small isotope effect observed suggests that cleavage of the H—H bond and formation of the Rh—H bond is a concerted process. Hydrogenation probably proceeds *via* oxidative addition of hydrogen to the species $[RhCl_2(SEt_2)(\text{maleic acid})]^-$. Activation parameters for this process are $\Delta H^{\neq} = 21.5$ kcal mol^{-1} and $\Delta S^{\neq} = -1.0$ cal deg^{-1} mol^{-1}. The almost zero value of the activation entropy is consistent with a neutral molecule–ion reaction.[108]

The dimeric rhodium(II) acetate $[Rh_2(OAc)_4]$ also functions as an efficient catalyst for the hydrogenation of terminal olefins. Kinetic studies on the hydrogenation of dec-1-ene in *NN*-dimethylformamide are consistent with activation of hydrogen occurring at one metal centre of the dimer, and again heterolysis of the hydrogen molecule takes place.[109]

Vaska's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$, can act as a homogeneous hydrogenation catalyst. Further studies now show that there is very little dissociation of the complex during reaction. The induction period observed in dimethylformamide is a consequence of an unidentified radical process and this can be eliminated if small amounts of *p*-methoxyphenol are added. In the presence of base it was thought that a large quantity of the intermediate

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[106] P. Bonvicini, A. Levi, G. Modena, and G. Scorrano, *J.C.S. Chem. Comm.*, 1972, 1188.
[107] H. B. Kagan and T.-P. Dang, *J. Amer. Chem. Soc.*, 1972, **94**, 6429.
[108] B. R. James and F. T. T. Ng, *J.C.S. Dalton*, 1972, 355.
[109] C. Y. Hui, W. K. Teo, and G. L. Rempel, *Inorg. Chem.*, 1973, **12**, 757.

hydride, $[IrH(CO)(PPh_3)_2]$, was formed, but subsequent studies show that this reacts readily with hydrogen and triphenylphosphine present to give $[IrH_3(CO)(PPh_3)_2]$.[110] This iridium(III) hydride can also catalyse hydrogenation, the rate-determining step being direct reaction of alkene with $[IrH_3(CO)(PPh_3)_2]$.[111]

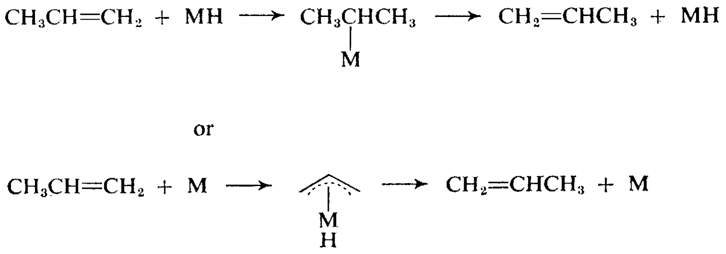
Solutions of the cyclo-octene complex $[IrCl(C_8H_{14})_2]_2$ in *NN*-dimethylacetamide catalyse the hydrogenation of alkenes. Kinetic data are consistent with the mechanism illustrated in Scheme 20.[112]

$$\begin{tikzcd} \text{'IrL}_n\text{'} + \text{olefin} \arrow[r, shift left] & \text{IrL}_m\text{(olefin)} \arrow[l, shift left] \arrow[d, "H_2"] \\ \text{'IrL}_n\text{'} + \text{product} & \text{IrH}_2\text{(olefin)L}_x \arrow[l] \end{tikzcd}$$

Scheme 20

6 Hydrogen Exchange

Some homogeneously transition-metal-catalysed hydrogen (deuterium) exchange reactions are summarized in Table 4. Microwave spectroscopy has extremely high resolution and can be used for precise quantitative analysis. This technique has now been applied to the mechanism of hydrogen–deuterium exchange in propene, catalysed homogeneously by the systems $PtCl_4$–$SnCl_2$–H_2, $[Rh(acac)(C_2H_4)_2]$, or $[Ni\{P(OEt)_3\}_4]$ in MeOD–DCl. The two most common mechanisms for exchange (Scheme 21) involve either a metal hydride addition–elimination sequence or an h^3-allyl intermediate. One feature of the π-allyl mechanism is that no exchange on C-2 can occur. The observation that exchange does occur at C-2, together with other data, suggests that the reaction



Scheme 21

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[110] M. G. Burnett, R. J. Morrison, and C. J. Strugnell, *J.C.S. Dalton*, 1973, 701.
[111] M. G. Burnett and R. J. Morrison, *J.C.S. Dalton*, 1973, 632.
[112] C. Y. Chan and B. R. James, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 135.
[113] C. Masters, *J.C.S. Chem. Comm.*, 1972, 1258.
[114] R. J. Hodges, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 2571.
[115] K. Hirabayashi and I. Yasumori, *J.C.S. Faraday I*, 1973, **69**, 595.

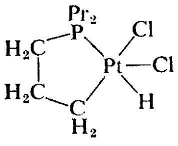
Table 4 *Hydrogen exchange with organic compounds, catalysed by transition-metal compounds*

Catalyst	*Substrate*	*Mechanism*	*Ref.*
$[NiX(aryl)(PPh_3)_2]$ + BF_3,Et_2O	C_2H_4	Nickel σ-ethyl intermediate	62
$[PdX_2(PhCN)_2]$	C_2H_4	Palladium σ-ethyl intermediate	61
$[PtCl_4]^{2-}$–$MeCO_2H$	$RCMe_2CH{=}CH_2$	Oxidative addition at C-5	113
$[PtCl_4]^{2-}$–$MeCO_2H$	Alkanes	Complex involving σ-orbitals of alkane	114
$[PtCl_4]^{2-}$–$MeCO_2H$	Aromatic hydrocarbons	π-Complex	114
$[Pt(SnCl_3)_5]^{3-}$	MeOH	Platinum–hydride intermediate	115

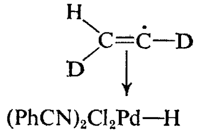
does not take place by the π-allyl mechanism. It is also apparent from these and related studies with but-1-ene that the isomerization of alkenes catalysed by these complexes does not proceed *via* h^3-allyl intermediates in which a C—H bond is broken in the first step.[34a, 116]

Certain halogen-substituted alkanes can undergo hydrogen–deuterium exchange in the presence of $[PtCl_4]^{2-}$–acetic acid catalyst systems. Examination of the photoelectron spectra of these halogen-substituted hydrocarbons shows that H–D exchange occurs in those compounds for which the first ionization energy in the photoelectron spectrum is associated with a molecular orbital involving C—H bonds. However, displacement of the halogen results if the first ionization energy is associated with electrons on the halogen atom.[117]

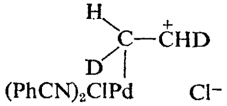
Interactions between metals and *ortho* carbon–hydrogen bonds in arylphosphine or aryl phosphite complexes are now well established. Evidence has now been obtained for hydrogen–deuterium exchange at C-3 of the alkyl group of the complexes $[PtCl_2L]_2$ (L = PPr^n_3 or PBu^n_3). The position of exchange is consistent with formation of a five-membered-ring intermediate (81).[118] H–D Exchange takes place between *trans*-[$^2H_2$]ethylene and solutions of $[CoHN_2(PPh_3)_3]$, $[RuHCl(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, or $[RhH(CO)(PPh_3)_3]$. These exchange reactions are considered to involve ethyl intermediates[119] rather than alkenyl intermediates as suggested for nickel and palladium catalysts (Scheme 22).[61,62] The complex $[PdCl_2(PhCN)_2]$ catalyses the conversion of *trans*- into *cis*-[$^2H_2$]ethylene without isotope redistribution. Radical (82) or carbonium ion (83) intermediates have been proposed for this process.[119]



(81)



(82)



(83)

However, other studies have shown that isotopic exchange between C_2D_4 and C_2H_4 takes place after an induction period during which it is considered that

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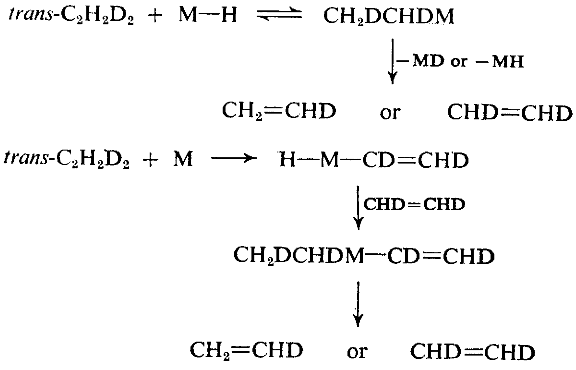
[116] C. A. Tolman, 'Transition Metal Hydrides', ed. E. L. Muetterties, Marcel Dekker, New York, 1971, Ch. 6.
[117] R. J. Hodges, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 2577.
[118] C. Masters, *J.C.S. Chem. Comm.*, 1973, 191.
[119] B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1204.



Scheme 22

the alkene reacts with the catalyst to give an alkenyl–hydride intermediate.[61] H–D Isotopic exchange has been observed to take place between D_2 and $MeCO_2H$, MeOH, EtOH, or morpholine in the presence of Ru^{II}, Os^{II}, Rh^{I}, and Ir^{I} complexes. There is a general decrease in reaction rates with decreasing acidity of the exchangeable hydrogen bonded to N or O. Catalytic activity is also strongly dependent on the nature of the complex.[120] Complete exchange of the aromatic hydrogen atoms between toluene and C_6D_6 can be achieved in the presence of $TaCl_5$, $MoCl_5$, WCl_6, BBr_3, $AlCl_3$, or $SbCl_5$ catalysts.[121]

7 Homogeneous Oxidation

The kinetics of the aqueous oxidation of olefins by palladium(II) chloride have been studied extensively, and at low concentrations of $PdCl_2$ (0.04M) it is generally accepted that the rate equation is given by

$$\frac{-\mathrm{d}[\text{olefin}]}{\mathrm{d}t} = \frac{k_1[\mathrm{PdCl_4^{2-}}][\text{olefin}]}{[\mathrm{Cl^-}]^2[\mathrm{H^+}]}$$

The reaction sequence is given in Scheme 23. Studies at higher concentrations of $PdCl_2$ have led to the suggestion that a higher-order term in Pd^{II} is involved in the rate expression. This has the form $k_2[\mathrm{PdCl_4^{2-}}]^2[\text{olefin}]/[\mathrm{H^+}][\mathrm{Cl^-}]^3$.[122] However, it now appears that $PdCl_2$ does not have this effect.[123] Palladium(II) acetate reacts with hex-1-ene in acetic acid *in vacuo* at 25 °C to give tetra-μ-acetato-bis-(1,2,3-*trihapto*-hexenyl)tripalladium. Some palladium metal is also produced. Hexenyl acetates are formed and hex-1-ene is selectively isomerized

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[120] G. G. Eberhardt, M. E. Tadros, and L. Vaska, *J.C.S. Chem. Comm.*, 1972, 290.

[121] J. L. Garnett, M. A. Long, R. F. W. Vining, and T. Mole, *J.C.S. Chem. Comm.*, 1972, 1172.

[122] I. I. Moiseev, M. M. Vargaftik, S. V. Pestnikov, O. G. Levanda, T. N. Romanova, and Ya. K. Sirkin, *Doklady Akad. Nauk S.S.S.R.*, 1966, **171**, 1365.

[123] P. M. Henry, *J. Amer. Chem. Soc.*, 1972, **94**, 4437.

$$[PdCl_4]^{2-} + C_2H_4 \rightleftharpoons [PdCl_3(C_2H_4)]^- + Cl^-$$

$$[PdCl_3(C_2H_4)] + H_2O \rightleftharpoons [PdCl_2(H_2O)(C_2H_4)] + Cl^-$$

$$[PdCl_2(H_2O)(C_2H_4)] + H_2O \rightleftharpoons [PdCl_2(OH)(C_2H_4)]^- + H_3O^+$$

$$\begin{tikzcd} {[PdCl_2(OH)(C_2H_4)]} \arrow[r, "\text{slow}"] & {>}PdCH_2CH_2OH \arrow[d, "\text{fast}"] \\ & \text{products} \end{tikzcd}$$

Scheme 23

to *cis*-hex-2-ene and *trans*-hex-2-ene. Palladium-catalysed oxidation of hex-1-ene occurs in the presence of oxygen. The oxidation is considered to proceed *via* oxypalladation followed by elimination of PdH(OAc) to give hexan-2-one. Successive addition and re-elimination of PdH(OAc) leads to isomerized esters. Monomeric palladium acetate is considered to be the active catalyst. Catalytic oxidation of hex-2-ene has the characteristics of a free-radical chain reaction.[124] Whereas palladium(II) in acetic acid oxidizes ethylene to vinyl acetate, in the presence of added copper(II) the saturated esters β-chloroethyl acetate and ethylene glycol diacetate are also formed. Studies on the oxidation of cyclohexene by a combination of palladium(II) chloride and copper(II) chloride in acetic acid are consistent with a reaction scheme involving *trans*-aceto-oxy-palladation followed by stepwise movement of the Pd^{II} around the ring by *cis*-palladium(II) hydride eliminations and re-additions.[125] In the presence of iron(III) or other oxidants which oxidize rhodium(I), aqueous acid chloride solutions of $[RhCl_5(H_2O)]^{2-}$ catalyse the oxidation of ethylene to acetaldehyde. A mechanism similar to that proposed for the palladium(II) system is suggested.[126,127] Kinetic studies indicate the presence of both ethylene-dependent and ethylene-independent paths in the rhodium system. The slow step in the ethylene-dependent path is the formation of π-complexes. In the ethylene-independent path the slow step is the formation of tetrachlororhodate(III) complexes (Scheme 24).

Palladium(II) compounds effect the arylation of olefins, *e.g.*

$$C_6H_6 + PhCH{=}CH_2 + Pd^{II} \longrightarrow PhCH{=}CHPh + Pd^0$$

Benzene substituents, although not affecting the overall rate of coupling, do, however, have orientation effects. This has been interpreted in terms of a σ-bonded aryl-palladium complex which is not formed in a rate-determining step of the reaction.[128] However, phenylation of styrene with benzene and

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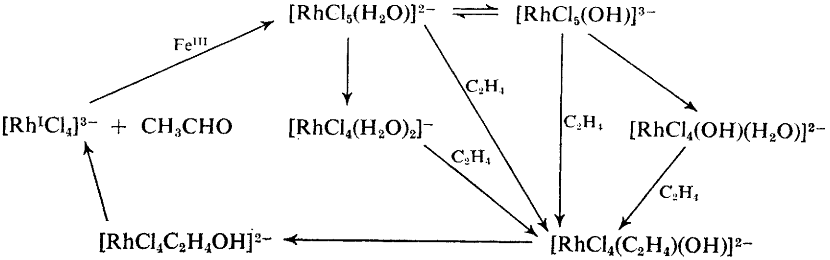
[124] R. G. Brown and J. M. Davidson, *J.C.S. Chem. Comm.*, 1972, 642.

[125] P. M. Henry, *J. Amer. Chem. Soc.*, 1972, **94**, 7305.

[126] B. R. James and M. Kastner, *Canad. J. Chem.*, 1972, **50**, 1698.

[127] B. R. James and M. Kastner, *Canad. J. Chem.*, 1972, **50**, 1708.

[128] Y. Fujiwara, I. Moritani, R. Asano, H. Tanaka, and S. Teranishi, *Tetrahedron*, 1969, **25**, 4815.



Scheme 24

[$^2H_6$]benzene exhibits a significant isotope effect which is taken to indicate that palladium–aryl σ-bond formation is a slow, irreversible step in olefin arylation. Cleavage of the styrene–β-hydrogen bond is also not involved in a rate-determining step.[129] Palladium(II) acetate can also effect the coupling of aromatic compounds and the reaction can be cycled by reoxidizing palladium(0) to palladium(II) with oxygen (Scheme 25).[130] Two-step hydrogen-abstraction

$$\mathrm{Pd^0 + O_2 + C_6H_6 \longrightarrow PhPdOOH}$$

$$\mathrm{PhPdOOH + C_6H_6 \longrightarrow PhPdPh + H_2O_2}$$

$$\mathrm{PhPdPh \xrightarrow{fast} Ph{-}Ph + Pd^0}$$

Scheme 25

reactions, which exhibit primary kinetic isotope effects, are found for this reaction.[130]

The reductions of metal complexes by carbon monoxide may proceed *via* elimination of CO_2 from intermediates of the type MCO_2H. The oxidation of $[Co(CN)_2(CO)(PEt_3)_2]^-$ by $[Fe(CN)_6]^{3-}$ in alkaline aqueous solution is shown to proceed *via* a relatively unstable intermediate, $[(NC)_5Fe^{II}CNCo^{III}(CN)_2(CO_2H)(PEt_3)_2]^{4-}$. The overall reaction proceeds quantitatively according to the equation

$$\mathrm{[Co(CN)_2(CO)(PEt_3)_2]^- + 4[Fe(CN)_6]^{3-} + 4OH^- \longrightarrow}$$
$$\mathrm{[(NC)_5Fe^{II}CNCo^{III}(CN)_2(H_2O)(PEt_3)_2]^{3-} + CO_3^{2-} + 3[Fe(CN)_6]^{4-} + H_2O}$$

The oxidation of CO by $[Fe(CN)_6]^{3-}$,

$$\mathrm{CO + 2[Fe(CN)_6]^{3-} + 4OH^- \longrightarrow CO_3^{2-} + 2[Fe(CN)_6]^{4-} + 2H_2O}$$

can be catalysed by $[Co(CN)_2(CO)(PEt_3)_2]^-$.[131] Similar intermediates may be involved in the reduction of vitamin B_{12} by carbon monoxide.

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[129] R. S. Shue, *J. Amer. Chem. Soc.*, 1971, **93**, 7116.

[130] M. Kashima, H. Yoshimoto, and H. Itatani, *J. Catalysis*, 1973, **29**, 92.

[131] J. E. Bercaw, L. Y. Goh, and J. Halpern, *J. Amer. Chem. Soc.*, 1972, **94**, 6534; *ibid*, 1973, **95**, 988.

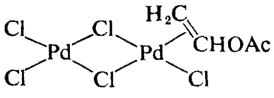
The full paper on the oxidation of triphenylphosphine catalysed by $[Ru(NCS)(NO)(O_2)(PPh_3)_2]$, discussed in Volume 2, p. 314, has now appeared. Hex-1-ene and cyclohexene undergo slight oxidation in the presence of $[Ru(NCS)(NO)(O_2)(PPh_3)_2]$, the catalyst simply initiating a free-radical process.[132]

8 Exchange Reactions

The vinylic and allylic exchange reactions,

$$CH_2{=}CHX \quad \text{or} \quad CH_2{=}CHCH_2X + Y^- \underset{Pd^{II}}{\rightleftharpoons} CH_2{=}CHY \quad \text{or} \quad CH_2{=}CHCH_2Y + X^-$$

are catalysed by palladium(II) (X or Y = OCOR, Cl, OR, NR_2, *etc.*). These reactions are non-oxidative in nature and the rates can be conveniently studied at room temperature. Vinyl exchange can proceed *via* addition of the Pd^{II} and Y followed by elimination of Pd^{II} and X. These reactions have been reviewed.[133] Vinyl ester exchange studies show that in contrast to the *cis* stereochemistry expected by analogy with the Wacker process, acetoxypalladation is a stereochemically pure *trans* process. Further a dimeric π-complex (84) is the reactive species. In the allylic ester exchange reactions the first step involves π-complex formation similar to (84) followed by attack of Y^-. Reactions with allyl propionate and acetate show that the rate is inhibited by allyl propionate owing to π-complex formation:



(84)

$$Li_2[Pd_2Cl_6] + 2 \text{ allyl ester} \rightleftharpoons 2Li[PdCl_3(\text{allyl ester})]$$

Exchange with asymmetrical esters, crotyl propionate and 3-buten-2-yl propionate, shows that two reactions take place. One is exchange with isomerization of crotyl ester to 3-buten-2-ol ester, as expected for the acetoxypalladation mechanism. The other is isomerization without exchange:

$$MeCH{=}CHCH_2OCOEt \underset{HOAc}{\rightleftharpoons} CH_2{=}CHCH(OCOEt)Me$$

In this reaction isomerization occurs *via* a 1,3-acetoxonium intermediate (85), as shown in Scheme 26.

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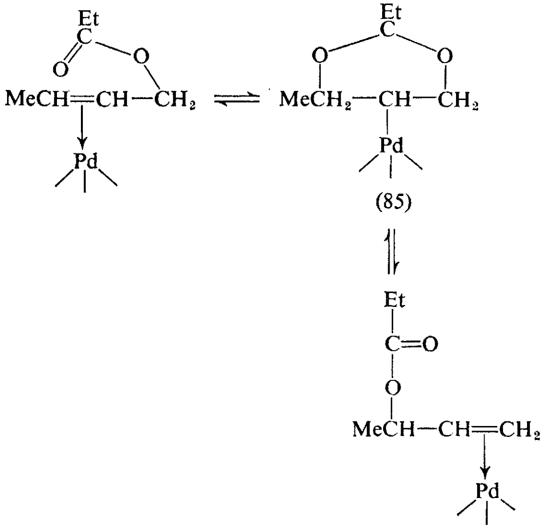
[132] B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, *J.C.S. Dalton*, 1972, 1237.

[133] P. M. Henry, *Accounts Chem. Res.*, 1973, **6**, 16.



Scheme 26

9 Carbonylation and Hydroformylation

Nickel catalysts are known to be effective in the carbonylation of aromatic halides:

$$PhX + CO + H_2O \longrightarrow PhCO_2H + HX$$

A study of this carbonylation reaction catalysed by tetracarbonylnickel in polar aprotic solvents, *e.g.* dimethyl sulphoxide or *NN*-dimethylformamide, in the presence of calcium hydroxide reveals that the reaction can proceed at one atmosphere pressure of carbon monoxide and at 100 °C. The reaction probably involves oxidation–addition of aryl halide to the nickel followed by carbon monoxide insertion. Rates decrease in the order $I > Br > Cl > F$. Chloride ions and bromide ions enhance the reaction and this explains the autocatalytic behaviour observed as these ions are released from the aryl halide during reaction.[134]

The rates of olefin hydrogenation and isomerization by Group VIII metal–phosphine complexes are increased by the presence of hydroperoxides and/or oxygen. A similar rate enhancement is observed in the hydroformylation of alkenes catalysed by $[RhCl(CO)(PPh_3)_2]$. The addition of small amounts of cyclohexenyl hydroperoxide is considered to effect the unusual transformation of $[RhCl(CO)(PPh_3)_2]$ to *cis*-$[RhCl(CO)_2(PPh_3)]$, which appears to be a very active alkene hydroformylation and isomerization catalyst.[135] Asymmetric induction in hydroformylation reactions has been achieved.[136,137]

[134] L. Cassar and M. Foa, *J. Organometallic Chem.*, 1973, **51**, 381.

[135] H. B. Tinker and D. E. Morris, *J. Organometallic Chem.*, 1973, **52**, C55.

[136] M. Tanaka, Y. Watanabe, T. Mitsudo, A. Yamamoto, and Y. Takegami, *Chem. Letters*, 1972, 483.

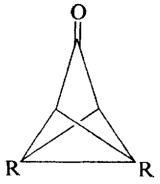
[137] I. Ogata and Y. Ikeda, *Chem. Letters*, 1972, 487.

10 Decarbonylation

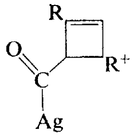
The decarbonylation of acyl halides by Rh^I and Pd^0 systems is well known. $[IrCl(CO)(PPh_3)_2]$ also catalyses selectively and under mild conditions the conversion of aliphatic acid halides possessing β-hydrogens into mixtures of olefins. Aroyl halides, however, are not decarbonylated, owing to the greater stability of aryliridium(III) complexes $[IrCl_2(Ar)(CO)(PPh_3)_2]$. Isolation of intermediates provides further evidence for the proposed reaction mechanisms. The rhodium complexes $[RhCl(CO)_2]_2$, $[RhCl(PPh_3)_3]$, and $[RhCl_3(AsPh_3)_3]$ catalyse the decarbonylation and dehydrohalogenation of acyl halides in the presence of triphenylphosphine to give terminal alkenes.[138] Silver(I) perchlorate effects the decarbonylation of tricyclo[2,1,0,0]pentan-3-one derivatives (86). The rate of decomposition of (86a) follows the rate law

$$-\mathrm{d}[(86a)]/\mathrm{d}t = k[(86a)][AgClO_4]$$

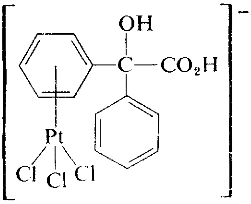
The reactions may proceed *via* a cationic intermediate (87). The reactions provide another source of cyclobutadienes.[139] Heterogeneous Group VIII transition metals deformylate benzilic acid and its derivatives to the corresponding ketones. Solutions of Na_2PtCl_4 in acetic acid have similarly been shown to deformylate benzilic acid, possibly *via* a π-complex (88), to benzophenone. Benzhydrol does not deformylate under these conditions, but does undergo hydrogen–deuterium exchange.[140]



(86) a; R = Me
b; R = Ph



(87)



(88)

11 Hydrosilylation and Hydrogermylation

Both nickel(0)- and nickel(II)-phosphine complexes, *e.g.* $[Ni(C_2H_4)(diphos)]$, $[NiCl_2(diphos)]$, can catalyse hydrosilylation of alkenes. An induction period is observed with the nickel(II) system and it appears that an important step with these catalysts is reduction of nickel(II) to nickel(0). The reduction does not occur below 100 °C. A possible mechanism for the reaction is given in Scheme 27.[141] Asymmetric hydrosilylation of styrene and cyclic dienes with $HSiCl_3$ can

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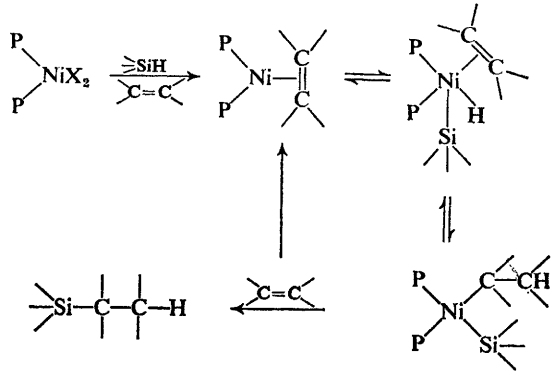
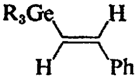
[138] J. Blum, S. Kraus, and Y. Pickholtz, *J. Organometallic Chem.*, 1971, **33**, 227.
[139] H. Ona, M. Sakai, M. Suda, and S. Masamune, *J.C.S. Chem. Comm.*, 1973, 45.
[140] G. E. Calf and J. L. Garnett, *Tetrahedron Letters*, 1973, 511.
[141] Y. Kiso, M. Kumada, K. Maeda, K. Sumitani, and K. Tamao, *J. Organometallic Chem.*, 1973, **50**, 311.



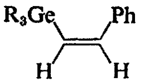
Scheme 27

be achieved using chiral palladium–phosphine complexes.[142] The cationic rhodium complex [Rh{(*R*)-(PhCH$_2$)MePhP}$_2$H$_2$(solvent)$_2$]$^+$ is able to catalyse asymmetric hydrosilylation of ketones.[143]

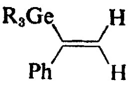
Hydrogermylation of styrene, catalysed by [RhCl(PPh$_3$)$_3$], *cis*-[PtCl$_2$-(PPh$_3$)$_2$], or [PtCl$_6$]$^{2-}$, occurs with retention of stereochemistry at germanium. Mechanisms similar to that suggested for hydrosilylation are proposed.[144] The homogeneously catalysed hydrogermylation of phenylacetylene gives a mixture containing (89), (90), and (91). The *cis*-addition to phenylacetylene occurs with retention of configuration at germanium.[145]



(89)



(90)



(91)

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[142] Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, *J. Amer. Chem. Soc.*, 1972, **94**, 4373.

[143] K. Yamamoto, T. Hayashi, and M. Kumada, *J. Organometallic Chem.*, 1973, **54**, C45.

[144] R. J. P. Corriu and J. J. E. Moreau, *J. Organometallic Chem.*, 1972, **40**, 55.

[145] R. J. P. Corriu and J. J. E. Moreau, *J. Organometallic Chem.*, 1972, **40**, 73.

4

Insertion Reactions

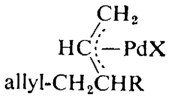
BY R. D. W. KEMMITT AND M. A. R. SMITH

In this chapter a variety of reactions have been gathered together in which a co-ordinating ligand effectively 'inserts' into a metal–ligand σ-bond. The word 'insertion', however, in many of these reactions is misleading since they probably involve migration of the σ-bonded ligand to the co-ordinated ligand.

1 Alkenes and Alkynes

The insertion of alkenes into the platinum–hydrogen bond of systems such as *trans*-$[\mathrm{Pt(H)Cl(PR_3)_2}]$ has been proposed to proceed *via* a five-co-ordinate intermediate in which the hydrogen and alkene are both bound separately to the platinum. However, the importance of cationic intermediates in the insertion of alkenes into the Pt—H bond has been demonstrated.[1,2] Thus the complexes *trans*-$[\mathrm{Pt(H)X(PR_3)_2}]$ readily react with ethylene in the presence of $\mathrm{AgBF_4}$ or $\mathrm{AgPF_6}$ in acetone–methylene chloride solution to give ethyl complexes *via* cationic intermediates, $[\mathrm{PtH(acetone)(PR_3)_2}]^+$.[1] Similarly, insertion reactions are facilitated when the ligand X in the hydrides *trans*-$[\mathrm{Pt(H)X(PR_3)_2}]$ is a good leaving group such as nitrate.[2] Indeed, treatment of *trans*-$[\mathrm{PtH(NO_3)(PEt_3)_2}]$ with ethylene followed by addition of sodium tetraphenylborate gives an intermediate hydride *trans*-$[\mathrm{PtH(C_2H_4)(PEt_3)_2}]\mathrm{BPh_4}$.[2]

1,3-Dienes, $\mathrm{CH_2{=}CRCH{=}CH_2}$, 'insert' into the allylic bonds of the h^3-allyl compounds $[\mathrm{PdX}(h^3\text{-allyl})]$ (X = hfac, acac, or Cl) to give the π-allylic products (1). Structural studies reveal that the 1,3-diene inserts into the most substituted end of an unsymmetrical allyl group and this is in contrast to 1,2-dienes, carbon monoxide, and alkyl isocyanides, which insert into the least substituted end. The rate of insertion is approximately first-order in both complex and diene and the rates of formation of the insertion product (1) decrease in the order: X = hfac$\gg$acac$\approx$Cl; allyl = 2-chloroallyl > allyl > 2-methyl-



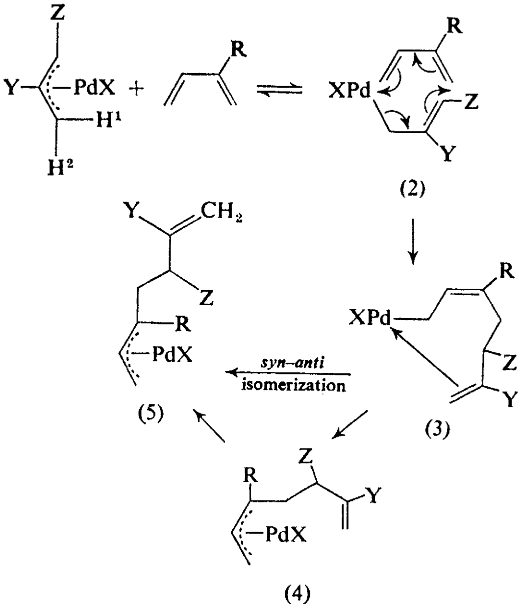
$$\begin{array}{c} \mathrm{CH_2} \\ \mathrm{HC}\text{---}\mathrm{PdX} \\ \text{allyl-}\mathrm{CH_2CHR} \end{array}$$

(1)

[1] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1972, **11**, 1275.

[2] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 1848.

allyl > 2-t-butylallyl; 1,3-diene = butadiene > isoprene > 2,3-dimethylbutadiene > *trans*-pentadiene > *cis*-pentadiene; cyclic 1,3-diene = cyclopentadiene > cyclohexadiene (cyclo-octa-1,3-diene, cycloheptatriene, and cyclo-octatetraene do not insert). The addition of the diene to the allyl complex also effects *syn–anti* proton exchange of the co-ordinated allyl, the rate of this exchange decreasing in the order: X = hfac ≫ acac > Cl; allyl = 2-chloroallyl > allyl > 2-methylallyl > 2-t-butylallyl; 1,3-diene = butadiene ≈ *cis*-pentadiene ≈ *trans*-pentadiene > isoprene > 2,3-dimethylbutadiene ≫ 2,5-dimethylhexa-2,4-diene; cyclic 1,3-dienes = cyclo-octadiene > cyclohexa-diene ≈ cyclopentadiene. The mechanism of the insertion is depicted in Scheme 1. The key steps in this reaction are co-ordination of the 1,3-diene to

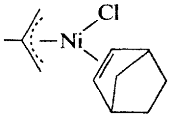


Scheme 1

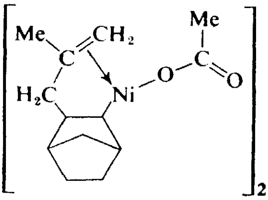
the palladium by the least substituted double bond in a *cis*-planar conformation and formation of a σ-allylic intermediate (2). Carbon–carbon bond formation can now occur *via* an electrocyclic mechanism, which may or may not be concerted, to give (3). The resulting complex (4) can then rearrange *via* a $\pi \rightarrow \sigma \rightarrow \pi$ process induced by the alkenic side-function to give the thermodynamically more stable isomer (5). The rate enhancement by electron-withdrawing ligands such as hfac is probably a consequence of the increased electrophilicity of the palladium, which would increase the stability of both the Pd—C and Pd—olefin bonds in the intermediate (2).[3]

[3] R. P. Hughes and J. Powell, *J. Amer. Chem. Soc.*, 1972, **94**, 7723.

The reaction of norbornene with h^3-methylallylnickel bromide or iodide gives linear polymers of the alkene *via cis*-insertion. Evidence for the stereochemistry of insertion is provided by the reaction of norbornene with h^3-methylallylnickel chloride, which gives the alkene complex (6). Various types of reaction of (6) then result in *cis*-insertion of the norbornene into the nickel–allyl bond. Thus treatment of (6) with sodium acetate gives (7), which is shown by *X*-ray studies to be formed by an *exo-cis*-insertion of the alkene.[4] A similar *cis*-insertion occurs with the corresponding palladium complex.[5]

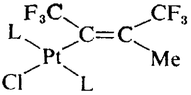


(6)

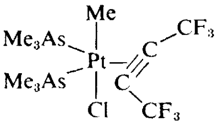


(7)

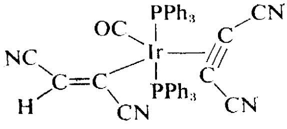
Insertion of an alkyne into a metal–hydrogen or metal–carbon bond is usually thought to occur *via* prior co-ordination of the alkyne into a vacant co-ordination site on the metal. Thus the reaction of hexafluorobut-2-yne with complexes of the type *trans*-[PtClMeL$_2$] (L = tertiary phosphine or arsine) can lead to insertion products, *e.g.* (8), and complexes which may be intermediates in the insertion, *e.g.* (9), can be isolated and characterized.[6–8] Similarly, the reaction of dicyanoacetylene with [IrH(CO)$_2$(PPh$_3$)$_2$] gives (10),[9,10] which is thought to be formed *via* co-ordination of dicyanoacetylene followed by insertion and co-ordination of a second molecule of the acetylene. However, studies on the reaction of dimethyl acetylenedicarboxylate with *trans*-[PtClMe(PMe$_2$Ph)$_2$] (11) in chloroform show that formation of the insertion product (13) does not proceed *via* a simple intramolecular rearrangement of a 1 : 1 adduct (12) but occurs *via* a free-radical mechanism involving (11) and



(8)



(9)



(10)

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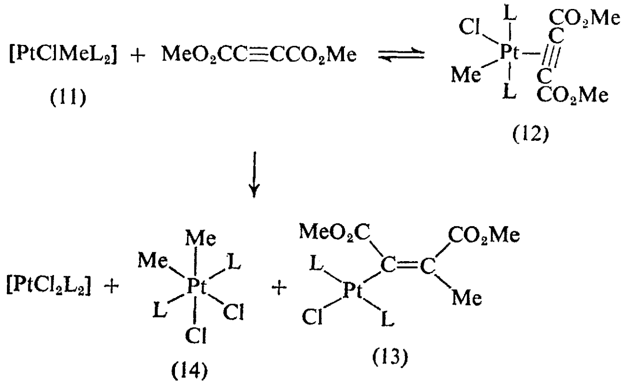
[4] M. C. Gallazzi, T. L. Hanlon, G. Vitulli, and L. Porri, *J. Organometallic Chem.*, 1971, **33**, C45.
[5] M. Zocchi, G. Tieghi, and A. Albinati, *J. Organometallic Chem.*, 1971, **33**, C47.
[6] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1970, **9**, 2670.
[7] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1971, **10**, 18.
[8] B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276.
[9] G. L. McClure and W. H. Baddley, *J. Organometallic Chem.*, 1971, **27**, 155.
[10] R. M. Kirchner and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 1095.



Scheme 2

(12) (Scheme 2).[11] Thus the insertion reaction proceeds on addition of a radical initiator and for a given concentration of initiator the rate of insertion is given by

$$\text{Rate} = k_{\text{ins}}[\text{PtClMeL}_2][\text{PtClMeL}_2(\text{acetylene})]$$

Chloroform solutions of (11) on addition of a radical initiator, *e.g.* $PhCOO_2OCPh$, or on u.v. irradiation in the absence of the acetylene undergo a free-radical reaction to form $[PtCl_2Me_2L_2]$ (14) and $[PtCl_2L_2]$. In the presence of the acetylene the formation of (14) follows the rate law

$$d[\text{PtCl}_2\text{Me}_2\text{L}_2]/dt = k_{1\text{dis}}[\text{PtClMeL}_2] + k_{2\text{dis}}[\text{PtClMeL}_2][\text{PtClMeL}_2(\text{acetylene})]$$

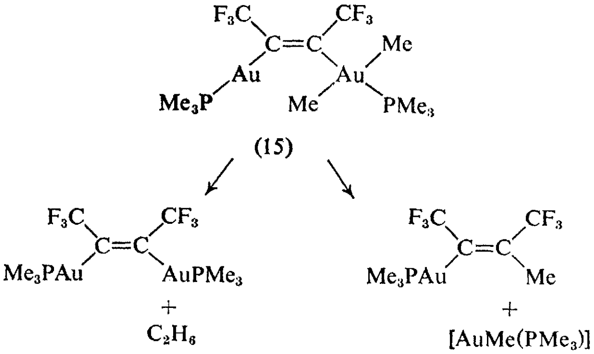
It is suggested that the radical $PtMeL_2^{\bullet}$ plays a key role in the insertion reaction and reacts with (12) according to the equation

$$\text{PtMeL}_2^{\bullet} + [\text{PtClMeL}_2(\text{acetylene})] \longrightarrow \text{PtMeL}_2(\text{acetylene})^{\bullet} + [\text{PtClMeL}_2]$$

followed by formation of the insertion product from the radical.[11] However, since it has recently been shown that the radical $Bu^tO^{\bullet}$ will displace alkyl groups from platinum(II) complexes of the type $[PtMe_2L_2]$,[12] the above reactions could involve Pt—Me homolysis rather than Pt—Cl homolysis. It is apparent that insertion of an electrophilic alkyne into a metal–carbon bond need not proceed by simple rearrangement of a five-co-ordinate intermediate.

The reaction of hexafluorobut-2-yne with $[AuMe(PMe_3)]$ involves methyl transfer and formation of a C_4F_6-bridged complex (15) which can break down as depicted in Scheme 3.[13]

[11] T. G. Appleton, M. H. Chisholm, and H. C. Clark, *J. Amer. Chem. Soc.*, 1972, **94**, 8912.
[12] D. J. Cardin, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 350.
[13] J. A. J. Jarvis, A. Johnson, and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1973, 373.



Scheme 3

2 Other Carbon Compounds

Carbon Monoxide.—The mechanism of the alkyl–acyl insertion reaction usually involves a reversible migration of the alkyl group followed by reaction with a ligand L to form a co-ordinatively saturated product [equation (1)].

$$\mathrm{Na^+[FeR(CO)_4]^-} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{Na^+[Fe(COR)(CO)_3]^-} \xrightarrow[k_2]{\mathrm{L}} \mathrm{Na^+[Fe(COR)(CO)_3L]^-} \qquad (1)$$

Reactions of this type can exhibit rate laws having first, second, or intermediate order, the actual rate law being dependent on the ligand L and the relative rate constants k_{-1} and k_2. Using tertiary phosphines and the complex $\mathrm{Na^+}$ $\mathrm{[Fe(nonyl)(CO)_4]^-}$, the reaction in equation (1) obeys the second-order rate law of equation (2).[14] In such alkyl–acyl transformation reactions polar solvents can often act as transient ligands and affect the rate by increasing k_2.

$$-\mathrm{d[Na^+FeR(CO)_4{}^-]}/\mathrm{d}t = Kk_2\mathrm{[L][Na^+FeR(CO)_4{}^-]} \qquad (2)$$
$$K = k_1/k_{-1}$$

However, it has been found that addition of a few per cent of *N*-methylpyrrolidone or hexamethylphosphoramide to $\mathrm{Na^+}$ $\mathrm{[Fe(nonyl)(CO)_4]^-}$ in THF strongly inhibits the rate. The rate of reaction is also found to be very dependent on the nature of the cation (Table 1).

Table 1 *Effect of cation on the rate of nonyl group migration at* 25 °C *in THF*

Complex	$Kk_2/\mathrm{l\ mol^{-1}\ s^{-1}}$
$\mathrm{Li^+[Fe(nonyl)(CO)_4]^-}$	0.24
$\mathrm{Na^+[Fe(nonyl)(CO)_4]^-}$	0.065
$\mathrm{(Ph_3P)_2N^+[Fe(nonyl)(CO)_4]^-}$	$<1.5\times10^{-4}$
$\mathrm{[Na^+(dicyclohexyl\text{-}18\text{-}crown\text{-}6)][Fe(nonyl)(CO)_4]^-}$	$<7\times10^{-4}$

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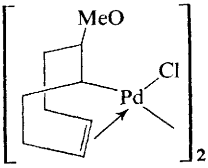
[14] J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, 1972, **94**, 5905.

It is apparent from these studies that migration of the alkyl group to an adjacent terminal carbonyl is facilitated by small polarizing cations which are associated with the carbonyl oxygen and help stabilize the extra negative charge which develops during the migration. The ability of such solvents as *N*-methylpyrrolidone to solvate the ion pair and form solvent-separated ions would then explain the inhibiting effect of these solvents.[14] Oxidation of a number of alkylmetal carbonyl complexes by ceric ion induces carbonyl insertion reactions[15] (Scheme 4). Oxidatively induced carbonyl insertion is also found to take place on treating alkyl complexes of the type $[FeR^1(CO)_2(h^5\text{-}C_5H_5)]$ with copper(II) chloride in alcohols [equation (3)].[16] In this iron system it is found that there is retention of configuration at the migrating carbon centre. The observation that oxidation induces carbonyl insertion has been interpreted in terms of increased electrophilicity of the carbon of the reacting carbonyl group.[15,16] The ability of metal cations to accelerate carbonyl insertion in the anions $[FeR(CO)_4]^-$ may be due to a similar effect.[16] Alkyl migration to a co-ordinated carbonyl ligand occurs with retention of configuration at the migrating carbon centre. Studies on the carbonylation of palladium–carbon σ-bonded complexes of the type (16) show that these reactions also proceed with retention of configuration.[17] It has further been

$$\begin{tikzcd}
{[RCH_2M(CO)_n]} \arrow[r, shift left, "\text{slow}"] \arrow[d, shift left, "-e^-"] & {[RCH_2COM(CO)_{n-1}]} \arrow[l, shift left] & \\
{[RCH_2M(CO)_n]^+} \arrow[r, shift left, "\text{fast}"] \arrow[u, shift left] & {[RCH_2COM(CO)_{n-1}]^+} \arrow[l, shift left] \arrow[d, "\text{MeOH}"] & \\
& RCH_2CO_2Me + H^+ & \\
& & + [M(CO)_{n-1}]
\end{tikzcd}$$

Scheme 4

$$[FeR^1(CO)_2(h^5\text{-}C_5H_5)] + CuCl_2 \xrightarrow{R^2OH} CuCl + R^1CO_2R^2 \qquad (3)$$



(16)

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[15] S. N. Anderson, C. W. Fong, and M. D. Johnson, *J.C.S. Chem. Comm.*, 1973, 163.
[16] K. M. Nicholas and M. Rosenblum, *J. Amer. Chem. Soc.*, 1973, **95**, 4449.
[17] L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, 1972, **94**, 485.

shown that the photochemical decarbonylation of [Fe(COMe)(CO)(PPh$_3$)(h^5-C$_5$H$_3$-1-Me-3-Ph)] proceeds with high stereospecificity at iron.[18] Since the photochemical decarbonylation of [Fe(^{13}COMe)(CO)$_2$(h^5-C$_5$H$_5$)] results in the elimination of a terminal carbonyl,[19] the methyl migration must occur stereospecifically. Decarbonylation of [Fe(COCHMePh)(CO)$_2$(h^5-C$_5$H$_5$)] with [RhCl(PPh$_3$)$_3$] similarly proceeds with configuration retention at the optically active carbon.[20]

These decarbonylation reactions proceed *via* a co-ordinately unsaturated intermediate, and it has been shown that silver-ion abstraction of chloride from the complexes [PtCl(COR)(PPh$_3$)$_2$] in acetone leads to the alkyl complexes [PtR(CO)(PPh$_3$)$_2$]$^+$.[21] In methyl cyanide solution, however, no decarbonylation occurs, and the solvated species [Pt(COR)(MeCN)(PPh$_3$)$_2$]$^+$ is produced. Kinetic studies show that [Mo(COMe)(CO)$_2$(PPh$_2$Pr^i)(h^5-C$_5$H$_5$)] decarbonylates twice as fast as [Mo(COMe)(CO)$_2$(PPh$_3$)(h^5-C$_5$H$_5$)]. These and other effects are not consistent with electronic effects, which would be expected to increase metal–carbonyl back-bonding and retard carbon monoxide loss. It therefore appears that steric effects dominate and that bulky phosphines enhance carbon monoxide loss to give a co-ordinately unsaturated intermediate.[22]

Carbenes.—The chromium carbene [Cr{C(OMe)Ph}(CO)$_5$] reacts with the hydrides R$_3$MH (M = Si, Ge, or Sn) in the presence of pyridine in hexane solution to give [Cr(CO)$_5$(py)] and *cis*-[Cr(CO)$_4$(py)$_2$]. The displaced carbene inserts into the M—H bond of the hydrides to give the compounds R$_3$MCH(OMe)Ph.[23] The rate law for the process is

$$\begin{aligned}-\mathrm{d}[\mathrm{Cr\{C(OMe)Ph\}(CO)_5}]/\mathrm{d}t = {} & k_1[\mathrm{Cr\{C(OMe)Ph\}(CO)_5}] \\ & + k_2[\mathrm{Cr\{C(OMe)Ph\}(CO)_5}][\mathrm{R_3MH}] \\ & + k_3[\mathrm{Cr\{C(OMe)Ph\}(CO)_5}][\mathrm{py}]\end{aligned}$$

and some of the kinetic parameters are reported in Table 2. The proposed

Table 2 *Kinetic results for the reaction of* [Cr{C(OMe)Ph}(CO)$_5$] *with* R$_3$MH *in hexane in the presence of pyridine*

R$_3$MH	$k_{\mathrm{obs}} \times 10^5$/ s^{-1}	$k_2 \times 10^5$/ l mol^{-1} s^{-1}	$\Delta H_1^{\ddagger}$/ kJ mol^{-1}	$T\Delta S_1^{\ddagger}$/ kJ mol^{-1}	$\Delta H_2^{\ddagger}$/ kJ mol^{-1}	$T\Delta S_2^{\ddagger}$/ kJ mol^{-1}
Et$_3$SiH	4.4	11	61	−39	77	−20
Ph$_3$GeH	6.7	111	61	−39	81	−11
Ph$_3$SnH	213	7170	61[a]	−39[a]	41	−38

[a] Assumed values.

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[18] T. G. Attig, P. Reich-Rohrwig, and A. Wojcicki, *J. Organometallic Chem.*, 1973, **51**, C21.

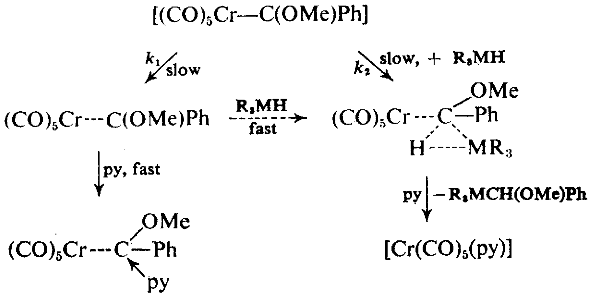
[19] J. J. Alexander, personal communication quoted in ref. 18.

[20] J. J. Alexander and A. Wojcicki, *Inorg. Chem.*, 1973, **12**, 74.

[21] M. Kubota, R. K. Rothrock, and J. Geibel, *J.C.S. Dalton*, 1973, 1267.

[22] K. W. Barnett, T. G. Pollman, and T. W. Solomon, *J. Organometallic Chem.*, 1972, **36**, C23.

[23] J. A. Connor, J. P. Day, and R. M. Turner, *J.C.S. Chem. Comm.*, 1973, 578.

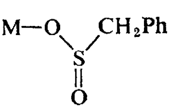


Scheme 5

mechanism is given in Scheme 5. The activation parameters for the slow first-order (k_1) step are consistent with an activated complex in which the chromium–carbene bond is stretched but not broken. The subsequent increased electrophilicity of the α-carbon allows this carbon to react in a fast step with a nucleophilic species such as pyridine or R_3MH to give the products. The activation parameters for the second-order (k_2) step, which under the experimental conditions is the major reaction pathway, are consistent with direct attack of the hydride on the carbene complex. The pyridine can then assist in the displacement of the insertion product from the chromium. The reactions involving tin hydrides do not appear to involve free radicals.[23]

3 Sulphur Dioxide

I.r. and n.m.r. spectroscopy, electrical conductivities, and chemical evidence suggest that the insertion of sulphur dioxide into transition-metal–alkyl and –aryl bonds in complexes of the type $[FeR(CO)_2(h^5\text{-}C_5H_5)]$, $[MoR(CO)_3(h^5\text{-}C_5H_5)]$, $[MnR(CO)_5]$, and $[ReR(CO)_5]$ involves the formation of intermediates which almost certainly have O-bonded sulphinate structures of the type (17) rather than S-bonded alkoxysulphenate structures of the type (18).



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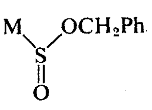

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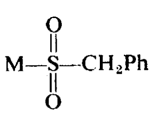

(19)

The O-bonded sulphinates isomerize slowly to the corresponding S-bonded sulphinates, *e.g.* (19), which are the final products of insertion, but attempts to isolate the intermediates have not been successful since on removal of the last traces of SO_2 rapid linkage isomerization to the *S*-sulphinates occurs. This isomerization may be analogous to the conversion of $[(NH_3)_5Co(ONO)]^{2+}$ into $[(NH_3)_5Co(NO_2)]^{2+}$.[24]

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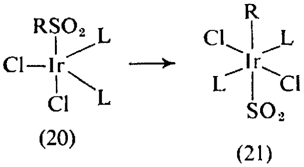
[24] S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Inorg. Chem.*, 1973, **12**, 717.

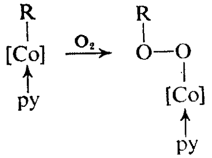
Studies on the reaction of sulphur dioxide with *threo*-[Fe(h^5-C_5H_5)-($CHDCHDCMe_3$)$(CO)_2$] show that insertion proceeds with inversion of configuration at the α-carbon.[25] However, no conclusion concerning retention or inversion of configuration at carbon can be obtained from the reaction of sulphur dioxide with [Fe(h^5-C_5H_5)(CHMePh)$(CO)_2$].[26]

Elimination of sulphur dioxide from an S-bonded sulphinate complex is a process related to sulphur dioxide insertion. Kinetic studies on the rearrangement of the five-co-ordinate sulphinato-complexes (20) to the sulphur dioxide complexes (21) show that if the organic group R contains electron-withdrawing substituents the rate of migration of R from sulphur to iridium is enhanced.[27] These results contrast with studies on the decarbonylation of acyl-iridium complexes in which it is found that migration of R to iridium is inhibited if R contains electron-withdrawing substituents.[28]


(20) (21)

4 Miscellaneous Compounds

Oxygen.—The insertion of oxygen into cobalt–carbon bonds of two optically active alkyl(pyridine)cobaloximes to give 1 : 1 dioxy-adducts (22) has been reported to proceed with retention of configuration of the carbon centre.[29,30] However, other studies suggest that the thermal and photochemical insertions occur with complete loss of configuration, so that a mechanism involving generation of an alkyl radical could occur at some point in the insertion.[31] Interestingly, if R can form a stable free radical or if X is a weak base, the reaction is facilitated, and a five-co-ordinate intermediate, *e.g.* [RCo$(dmgH)_2$], is suggested.[32]


(22)

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[25] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1971, **93**, 1529.

[26] J. J. Alexander and A. Wojcicki, *Inorg. Chim. Acta*, 1971, **5**, 655.

[27] M. Kubota and B. M. Loeffler, *Inorg. Chem.*, 1972, **11**, 469.

[28] M. Kubota, D. N. Blake, and S. A. Smith, *Inorg. Chem.*, 1971, **10**, 1430.

[29] C. Fontaine, K. N. V. Duong, C. Merienne, A. Guademer, and C. Giannotti, *J. Organometallic Chem.*, 1972, **38**, 167.

[30] C. Giannotti, C. Fontaine, and A. Gaudemer, *J. Organometallic Chem.*, 1972, **39**, 381.

[31] F. R. Jensen and R. C. Kiskis, *J. Organometallic Chem.*, 1973, **49**, C46.

[32] C. Giannotti and B. Septe, *J. Organometallic Chem.*, 1973, **52**, C36.

Tin(II) Halides.—The kinetics of the reaction of tin(II) chloride with $[Fe(h^5-C_5H_5)(CO)\{P(OPh)_3\}]_2$ indicate that insertion of the tin into the iron–iron bond is a two-stage process involving the formation of an intermediate in which the iron–iron bond is broken but the carbonyl bridges remain. The activation entropy for the reaction is -0.6 cal mol^{-1} deg^{-1} and the very small entropy change is consistent with the form of the proposed intermediate.[33] This reaction is in contrast to that of tin(II) halides with $[Fe(h^5-C_5H_5)(CO)_2]_2$, in which the first step of the reaction is reversible carbonyl bridge cleavage, and $\Delta S^{\ddagger} = +45.5$ cal mol^{-1} deg^{-1}.[34]

Metals.—Monosubstituted cyclopropanes can displace ethylene from $[PtCl_2(C_2H_4)]_2$ to give the metal-inserted complexes (23). The relative reactivities of the cyclopropanes vary in the order R = $n-C_6H_{13} > PhCH_2 > Ph >$ $o-O_2NC_6H_4$. The cyclopropanes with R = CN, COMe, or CO_2Me do not react. This reactivity sequence suggests that the platinum(II) complex acts as an electrophile in the reaction and that electron-donating substituents on the cyclopropane ring enhance reaction. The stereochemical course of these reactions with $[RhCl(CO)_2]_2$ depends on the balance between the energy necessary for C—C bond fission and the energy regained in forming metal–carbon bonds.[35,36]

(23)

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[33] P. F. Barrett and W. J. Jacobs, *Canad. J. Chem.*, 1972, **50**, 972.
[34] P. F. Barrett and K. K. W. Sun, *Canad. J. Chem.*, 1970, **48**, 3300.
[35] F. J. McQuillin and K. G. Powell, *J.C.S. Dalton*, 1972, 2123.
[36] F. J. McQuillin and K. G. Powell, *J.C.S. Dalton*, 1972, 2129.

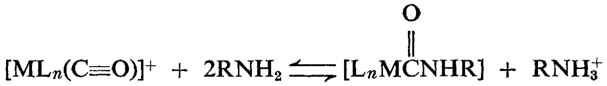
5

Reactions of Co-ordinated Ligands

BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Carbonyls, Nitrosyls, and Azides

Carbonyls.—Primary and secondary amines react with a range of cationic metal carbonyl complexes[1] to give carbonyl compounds according to the equation



$$[ML_n(C{\equiv}O)]^+ + 2RNH_2 \rightleftharpoons [L_nM\overset{\overset{\displaystyle O}{\|}}{C}NHR] + RNH_3^+$$

Kinetic studies[2] on the reactions of primary aliphatic amines with manganese and rhenium complexes of the type *trans*-$[M(CO)_4L_2]^+$ (L = tertiary phosphine ligand) show that the reaction

$$trans\text{-}[M(CO)_4L_2]^+ + 2RNH_2 \rightleftharpoons trans\text{-}[M(CONHR)(CO)_3L_2] + RNH_3^+$$

follows the rate law

$$\text{rate} = k_3[M(CO)_4L_2^+][RNH_2]^2$$

The most probable mechanism for this reaction is considered to be a base-catalysed nucleophilic attack of the amine at the carbon atom of the carbonyl group. This mechanism is similar to that proposed for the reactions of amines with organic esters to form amides. It is also related to the suggested mechanism for the formation of aminocarbene complexes from amines and (methoxycarbene)pentacarbonylchromium complexes. The reactions are faster for the complexes of rhenium than for those of manganese and the rates decrease in the order of ligands $L = PMePh_2 > PPhMe_2 > PPh_3$. Both steric factors and the presence of electron-releasing groups attached to the phosphorus appear to determine the order.[2] Indeed studies on the equilibrium

$$[Mn(CO)_3(h^6\text{-arene})]^+ + 2RNH_2 \rightleftharpoons [Mn(CONHR)(CO)_2(h^6\text{-arene})] + RNH_3^+$$

show that electron-donating substituents in the arene drive this equilibrium to the left.[3]

[1] R. J. Angelici, *Accounts Chem. Res.*, 1972, **5**, 335.

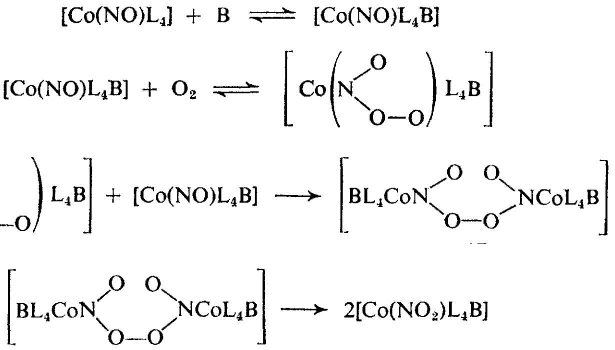
[2] R. J. Angelici and R. W. Brink, *Inorg. Chem.*, 1973, **12**, 1067.

[3] R. J. Angelici and L. J. Blacik, *Inorg. Chem.*, 1972, **11**, 1754.

Nitrosyls.—Oxygen reacts with $[Os(NO)(CO)_2(PPh_3)_2]^+$ in the presence of an isocyanide to give $[Os(NO_2)(CO)(CNR)_2(PPh_3)_2]^+$.[4] Kinetic studies on the related reaction

$$[Co(NO)L_4] + B + \tfrac{1}{2}O_2 \longrightarrow [Co(NO_2)L_4B]$$

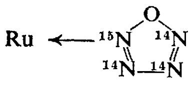
[L_4 = the quadridentate dianions *NN'*-ethylenebis-(1-acetonylethylideneiminato), *NN'*-ethylenebis(benzoylisopropylideneiminato), or *NN'*-ethylenebis(salicylideneiminato); B = nitrogen or phosphorus base] are consistent with the reactions illustrated in Scheme 1. The rate-determining step is considered to be electrophilic attack by oxygen on the nitrosyl oxygen. Thus the rates of reaction increase with increasing basicity of the ligand B.[5] The reaction of *trans*-$[RuCl(NO)(das)_2]Cl_2$ [das = *o*-phenylenebis(dimethylarsine)] with azide proceeds according to the equation



Scheme 1

$$[RuCl(NO)(das)_2]^+ + 2N_3^- \longrightarrow [Ru(N_3)Cl(das)_2] + N_2 + N_2O$$

An examination of the products obtained using ^{15}N-labelled nitrosyl complex strongly suggests the formation of a cyclic transition state (1) since approximately equal amounts of $^{14}N^{14}NO$ and $^{14}N^{15}NO$ are formed.[6] The formation of (1) could be regarded as a [2 + 3] cycloaddition reaction and in this instance be regarded to involve nucleophilic attack by azide at the nitrogen of the nitrosyl ligand.



(1)

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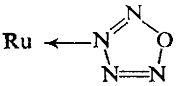
[4] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 119.

[5] S. G. Clarkson and F. Basolo, *J.C.S. Chem. Comm.*, 1972, 670.

[6] P. G. Douglas and R. D. Feltham, *J. Amer. Chem. Soc.*, 1972, **94**, 5254.

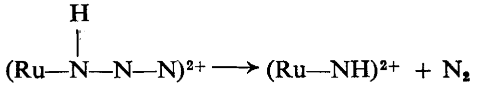
Azides.—The reaction between *trans*-$[\mathrm{Ru(N_3)Cl(das)_2}]$ and $\mathrm{NO^+PF_6^-}$ leads to the nitrogen complex *trans*-$[\mathrm{RuCl(N_2)(das)_2}]^+\ \mathrm{PF_6^-}$, and, as above, it is possible that this reaction also proceeds *via* a cyclic intermediate (2).[6]



(2)

Treatment of *trans*-$[\mathrm{Ru(N_3)Cl(das)_2}]$ with $\mathrm{NO^+\,SbF_6^-}$ also yields the dinitrogen complex, possibly *via* a nitrous oxide, $\mathrm{N_2O}$, complex. The reaction of the azide with HCl gives the dinitrogen complex, and is consistent with initial protonation of the azide:

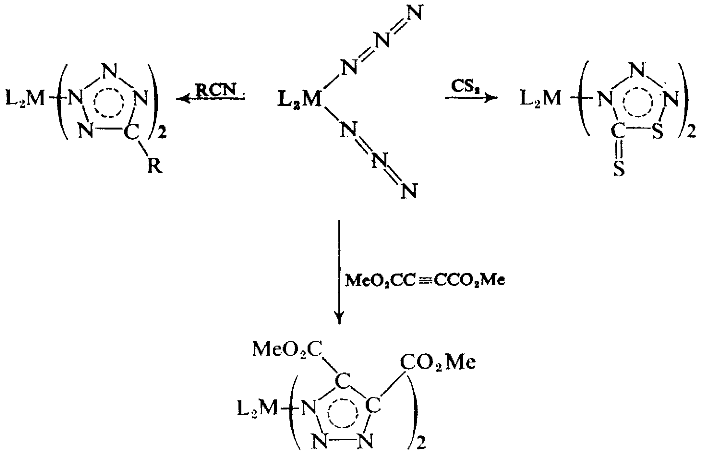
$$(\mathrm{Ru{-}N{-}N{-}N})^+ + \mathrm{H}^+ \longrightarrow (\mathrm{Ru{-}N{-}N{-}N{-}H})^{2+} \longrightarrow (\mathrm{Ru{-}N{-}N})^{2+} + \mathrm{NH}$$



$$(\mathrm{Ru{-}N{-}N{-}N})^+ + \mathrm{H}^+ \longrightarrow (\mathrm{Ru{-}\overset{\overset{H}{|}}{N}{-}N{-}N})^{2+} \longrightarrow (\mathrm{Ru{-}NH})^{2+} + \mathrm{N_2}$$

trans-$[\mathrm{RuCl(NH_3)(das)_2}]^+$ is the other product of this reaction.[6]

The azide ligands in the complexes $[\mathrm{M(N_3)_2L_2}]$ (M = Pd or Pt; L = tertiary phosphine) can act as 1,3-dipoles and form a number of [2 + 3] cycloaddition products with organic nitriles, isocyanides, thiocyanates, isothiocyanates, carbon disulphide, and dimethyl acetylenedicarboxylate.[7] Some of the reactions are summarized in Scheme 2. The rate of reaction of *cis*-$[\mathrm{Pt(N_3)_2L_2}]$ with *para*-substituted benzonitriles $\mathrm{RC_6H_4CN}$ increases in the



Scheme 2

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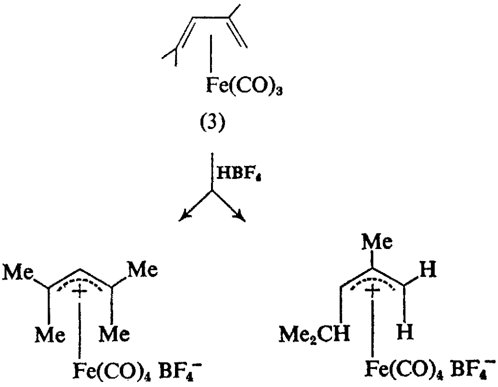
[7] P. Kreutzer, Ch. Weis, H. Boehme, T. Kemmerick, W. Beck, C. Spencer, and R. Mason, *Z. Naturforsch.*, 1972, **27b**, 745.

order R = Me < H < Cl < CO_2Et < NO_2 and L = PPh_3 < PPh_2Bu^n < $PPhBu^n_2$ < PBu^n_3. It therefore appears that cycloaddition is facilitated by electron-deficient nitriles and by the presence of basic phosphines which should enhance electron density at the co-ordinated azide. Activation parameters for the reaction of *cis*-$[Pt(N_3)_2(PR_3)_2]$ with benzonitrile ($\Delta H^{\ddagger} \approx 15$ kcal mol^{-1} and $\Delta S^{\ddagger} \approx 35$ cal mol^{-1} deg^{-1}) are similar to those found for 1,3-dipolar cycloadditions of organic molecules, so there are obviously analogies between these systems.[7]

2 Alkenes and Alkynes

Linear Alkenes and Alkynes.—Protonation of the tricarbonyliron complex of 2,4-dimethylpenta-1,3-diene (3) might be expected to occur at C-1 to give eventually the cationic complex (4) since there is no bulky substituent at C-2 or bulky *anti*-substituent to interfere with carbonyl ligands on the iron.[8,9] However, these steric requirements do not seem to be dominant since protonation of (3) occurs at C-4 to give (5) rather than (4).[10] Further, if the geometry of the tricarbonyl cation is closely related to that of the parent diene complex then it has been suggested that during the disproportionation reaction the entering carbonyl ligand will take up an axial position, which is *syn* to C-2 of the allyl ligand. It then follows that systems which possess a substituent at this position should form the tetracarbonyl more slowly than those which have an *anti*-1-substituent. In agreement with this proposal, the reaction which yields cation (5) is slower than the reaction of (6) with fluoroboric acid, which gives (7).[10] On dissolving either of the cations (4) or (5) in trifluoroacetic acid a mixture of the two cations is slowly obtained. No deuterium incorporation is



(4) (5)

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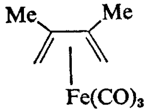
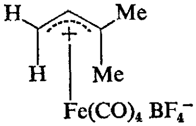
[8] A. N. Nesmeyanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Schembelov, *J. Organometallic Chem.*, 1968, **14**, 395.

[9] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.

[10] D. H. Gibson and R. L. Vonnahme, *J. Amer. Chem. Soc.*, 1972, **94**, 5090.

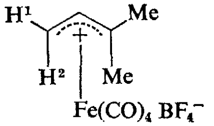


(6)

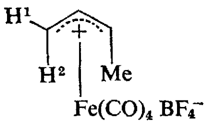


(7)

observed in CF_3CO_2D and the exchange reaction is also observed in non-protic solvents, *e.g.* CH_2Cl_2. These interconversions are therefore 1,4-sigmatropic rearrangements which involve hydrogen migrations in carbonium ions. Orbital symmetry considerations show that this process is not allowed to proceed suprafacially.[11] The mechanism of these reactions may be related to that of the isomerization of allyl alcohols catalysed by pentacarbonyliron,[12] or hydrogen migrations in cycloheptatriene–metal carbonyl complexes (see the section on dienes). The cations (8) and (9) slowly incorporate deuterium when



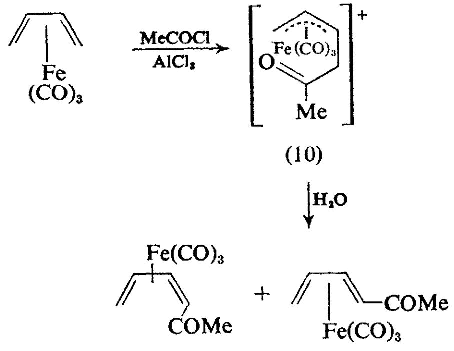
(8)



(9)

dissolved in CF_3CO_2D at the *anti*-methyl substituents and at H^1 and H^2. No spectral evidence for metal hydride or olefin complexes can be obtained, and a process involving exchange between *anti*-methyl and CF_3CO_2D followed by 1,4-hydrogen(deuterium) migration is favoured since deuterium exchange is faster at the methyl group than at H^1 or H^2.[11]

Friedel–Crafts acylation of (butadiene)tricarbonyliron gives *cis*- and *trans*-(dienone)tricarbonyliron complexes *via* an isolable ionic intermediate (10), as shown in Scheme 3.[13] Although (butadiene)tricarbonyliron is 3800 times as



Scheme 3

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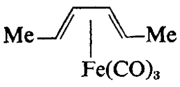
[11] D. H. Gibson and R. L. Vonnahme, *J.C.S. Chem. Comm.*, 1972, 1021.

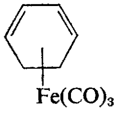
[12] F. G. Cowherd and J. L. Von Rosenberg, *J. Amer. Chem. Soc.*, 1969, **91**, 2157.

[13] E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1969, 1124; A. D. U. Hardy and G. A. Sim, *J.C.S. Dalton*, 1972, 2305.

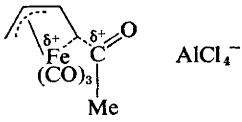
reactive as benzene, substitution at the terminal carbon atoms of the butadiene greatly reduces its reactivity. Thus the compounds (11) and (12) do not yield acyl complexes under the usual conditions of reaction.[14] These reactions are interpreted in terms of a transition state (13) for electrophilic attack in which there is very little positive charge at the allyl carbon atoms.



(11)

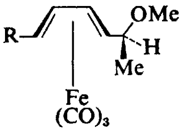


(12)



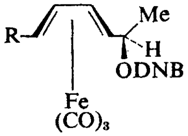
(13)

Reduction of *trans,trans*-(dienone)tricarbonyliron complexes with sodium borohydride gives *ψ-endo*-alcohols stereospecifically.[15] The dinitrobenzoates of the diastereomeric complexes (14) and (15) undergo S_N1 solvolysis, the leaving group departing *exo* from the iron.[15]



ψ-exo
(14)

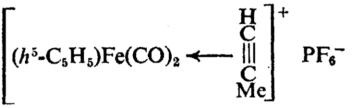
R = Me or Ph



ψ-endo
(15)

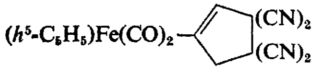
Protonation of the allenyl complex (16) with HPF_6 at −20 °C gives the cationic acetylene complex (17), and this observation, together with product stereochemistry, strongly suggests that the [2 + 3] cycloaddition reactions of (16) with tetracyanoethylene and toluene-*p*-sulphonyl isocyanate, which generate (18) and (19), respectively, proceed *via* an acetylene dipolar ion (20) rather than an allene (21).[16] However, protonation of the related butynyl complex (22) generates stereospecifically a cationic allene complex (23), which on

$[(h^5\text{-}C_5H_5)Fe(CO)_2(CH{=}C{=}CH_2)]$
(16)



$$\left[(h^5\text{-}C_5H_5)Fe(CO)_2 \longleftarrow \begin{array}{c}H\\ C\\ |||\\ C\\ Me\end{array}\right]^+ PF_6^-$$

(17)



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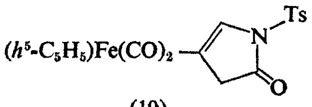

(19)

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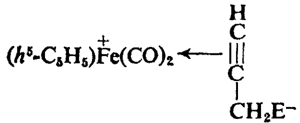
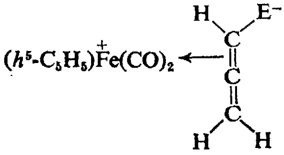
[14] R. E. Graf and C. P. Lillya, *J. Amer. Chem. Soc.*, 1972, **94**, 8282.
[15] D. E. Kuhn and C. P. Lillya, *J. Amer. Chem. Soc.*, 1972, **94**, 1682.
[16] S. Raghu and M. Rosenblum, *J. Amer. Chem. Soc.*, 1973, **95**, 3060.



$(h^5\text{-}C_5H_5)\overset{+}{Fe}(CO)_2 \leftarrow HC\equiv C\text{-}CH_2E^-$

(20)

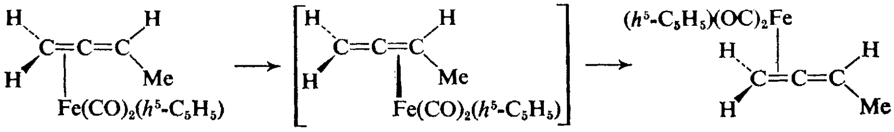


(21)

E = $(CN)_2C{=}C(CN)_2$ or toluene-*p*-sulphonyl isocyanate

$[(h^5\text{-}C_5H_5)Fe(CO)_2(CH_2C\equiv CCH_3)]$

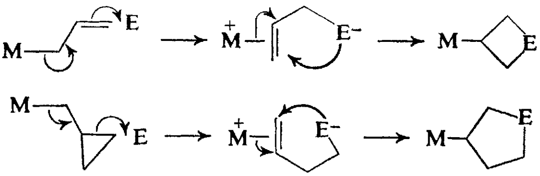
(22)



(23) (24)

warming is converted into an equilibrium mixture containing (23) and (24). This isomerization follows first-order kinetics. The high stereospecificity of the protonation is consistent with a *trans*-periplanar participation of the organic group concerted with protonation. The isomerization of (23) to (24) may occur *via* a process analogous to that proposed for the fluxional behaviour of $[Fe(h^2\text{-}CMe_2{=}C{=}CMe_2)(CO)_4]$.[16]

The reactions of (h^1-allyl)iron and of cyclopropylmethyliron complexes with SO_2 and electrophilic olefins give cycloaddition products.[17] The mechanisms of these reactions are considered to involve dipolar intermediates as illustrated in Scheme 4. These reactions have now been extended to cycloalkenyliron complexes, and it is found that toluene-*p*-sulphonyl isocyanate adds to the cyclopentenyl and cyclohexenyl complexes (25) and (26) to give the adducts (27) and (28), in which cycloaddition occurs *trans* to the bulky organometallic group.[18] Similarly the cyclopentadiene complex (29) gives



Scheme 4

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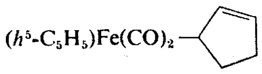
[17] W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **93**, 5299; S. S. Su and A. Wojcicki, *J. Organometallic Chem.*, 1971, **31**, C34.

[18] Y. S. Lo and J. C. Sheehan, *J. Amer. Chem. Soc.*, 1972, **94**, 8251.

(30). The cycloalkenyls (25) and (26) can be obtained by proton abstraction from the cationic cyclopentene (31) and cyclohexene (32) complexes, respectively. However, attempted deprotonation of the corresponding cycloheptene complex by triethylamine was unsuccessful. Molecular models of the cycloheptene complex reveal that in the preferred conformation of the ring, in which the iron group is *exo* to the ring, there are no allylic protons *trans* to the iron group. However, in the cyclopentene and cyclohexene complexes there are *trans*-allylic protons present and it therefore appears that deprotonation of these complexes occurs with a high degree of stereospecificity.[18]



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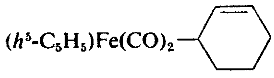
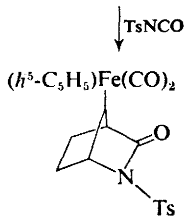
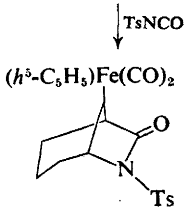


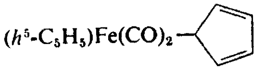
(26)



(27)



(28)



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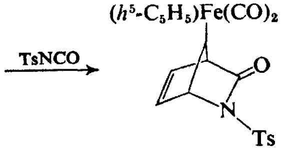
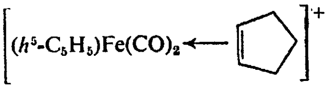
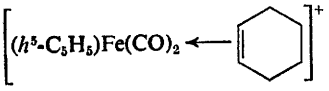


(30)

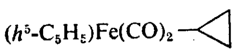


(31)

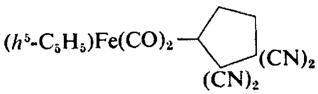


(32)

Ring expansion of the σ-bonded cyclopropane ring complex (33) to give (34) occurs upon treatment of (33) with tetracyanoethylene. A similar adduct (35) arises on reaction of (33) with SO_2.[19] These products can arise through collapse of the dipolar intermediate (36) formed on addition of an electrophile to (33),



(33)



(34)

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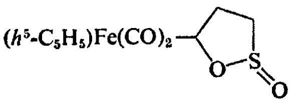
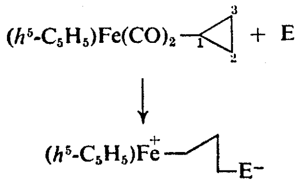
[19] A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, 1972, **94**, 4354.

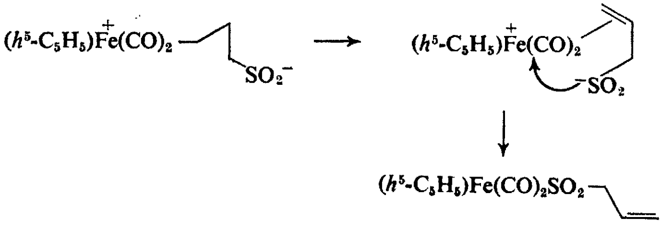


(35)



(36)

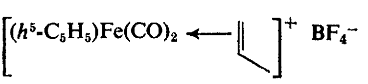
the iron assisting electrophilic cleavage of the bond between C-1 and C-2. In addition to (35) a small amount of the iron allyl sulphone complex (37) can be isolated from the reaction of (33) with SO_2. A competitive hydrogen-migration reaction of the dipolar intermediate can explain the formation of this product (see Scheme 5).



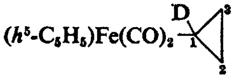
(37)

Scheme 5

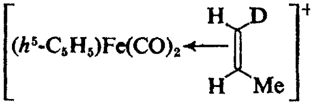
The reaction of (33) with fluoroboric acid gives the propene complex (38). Studies on the 1-deuterio-derivative (39), which yields exclusively the cation (40), show that cleavage of C-1—C-2 takes place and not C-2—C-3. Formation of



(38)



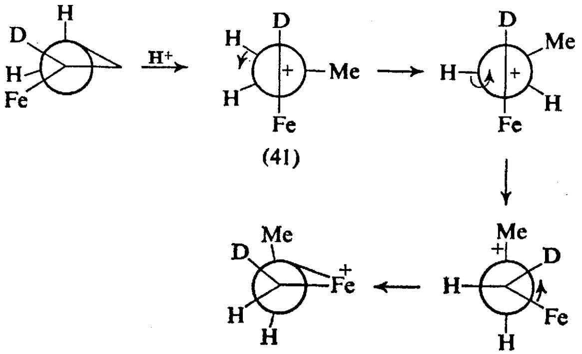
(39)



(40)

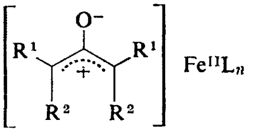
(40) can be rationalized in terms of a cationic metal carbene complex (41) followed by the rearrangements outlined in Scheme 6. The alternative cleavage involving C-2—C-3 cannot be assisted by the iron since the C—C and Fe—C bonds are orthogonal and a concerted process would be excluded.[19]

Although the cycloaddition of allyl anions to olefins ($[_{\pi}4_{s} + {}_{\pi}2_{s}]$ process) is thermally allowed, cycloaddition between allyl cations and olefins



Scheme 6

($[{}_{\pi}2_s + {}_{\pi}2_s]$ process) is thermally forbidden. However, treatment of the oxoallyl-iron(II) intermediates (42) with aryl-substituted olefins, *e.g.* styrene, gives the adducts (43) stereospecifically and with retention of configuration.[20, 21]

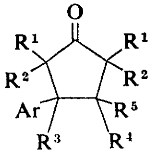


$R^1 = Me, R^2 = H$

$R^1 = Me_2CH, R^2 = H$

$R^1 = R^2 = Me$

(42)



(43)

Cyclic Alkenes.—Electrophilic substitution reactions of organic ligands co-ordinated to a metal can occur by initial attack of the electrophile at either the metal or the organic ligand. In most examples the choice made by the electrophile is not known but recent studies on the protonation of (cyclohexa-1,3-diene)(h^5-cyclopentadienyl)rhodium(I) and its iridium analogue show that the metal directs the entering electrophile *endo* to the co-ordinated ligand.[22] Addition of HSO_3F to solutions of the compounds $[Cr(arene)(CO)_3]$ results in transfer of the acidic hydrogen to the chromium.[23] At low temperatures n.m.r. signals of the protonated and unprotonated forms can be detected. Hydrogen exchange between these forms occurs *via* a mechanism in which fluorosulphate anion abstracts hydrogen from the protonated form in a slow step and donates it to another $[Cr(arene)(CO)_3]$ molecule in a fast step.

The cationic arene complexes $[Mn(C_6H_{6-n}Me_n)(CO)_3]^+$ react with cyanide

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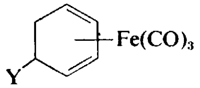
[20] R. Noyori, K. Yokoyama, and Y. Hayakawa, *J. Amer. Chem. Soc.*, 1973, **95**, 2722.

[21] R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutumi, *J. Amer. Chem. Soc.*, 1972, **94**, 7202.

[22] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1972, 2084.

[23] C. P. Lillya and R. A. Sahatjian, *Inorg. Chem.*, 1972, **11**, 889.

ion to give *exo*-cyanocyclohexadienyl complexes[$Mn(C_6H_{6-n}Me_nCN)(CO)_3$]. The cyanide ion preferentially attacks an unsubstituted carbon atom, and it appears that the addition is in part kinetically controlled since the mesitylene complex rearranges in chloroform to yield an isomer in which cyanide is attached to a methyl-substituted carbon atom.[24] The addition of nucleophiles such as CN^-, OR^-, H^-, acac$^-$ *etc.* to cationic metal–dienyl complexes is a well-known reaction. However, these reactions may also be thought of in terms of electrophilic attack by the cationic dienyl complex. Such considerations have led to the discovery that the cation $[Fe(C_6H_7)(CO)_3]^+$ will react as an electrophile with a variety of aromatic molecules to give complexes of type (44).[25] These systems provide a very easy method for determining the reactivity of a variety of organic substrates with electrophiles (see Table 1).



Y = indolyl, methylindolyl, pyrrolyl, furyl, thionyl, imidazolyl, or ferrocenyl

(44)

Table 1 *The reaction of* $[Fe(C_6H_7)(CO)_3][BF_4]$ *with aromatic substrates in acetonitrile at* 20 °C (*from ref.* 25)

Substrate	*Relative rate*
2-Methylindole	35×10^5
N-Methylindole	30×10^5
Indole	5×10^5
Pyrrole	5×10^5
Furan	3×10^3
Thiophen	1

In contrast to its reaction with $[Fe(C_6H_7)(CO)_3][BF_4]$, acetonitrile displaces the tropylium ligand from the complexes $[M(C_7H_7)(CO)_3][BF_4]$ (M = Cr, Mo, or W) according to the equation

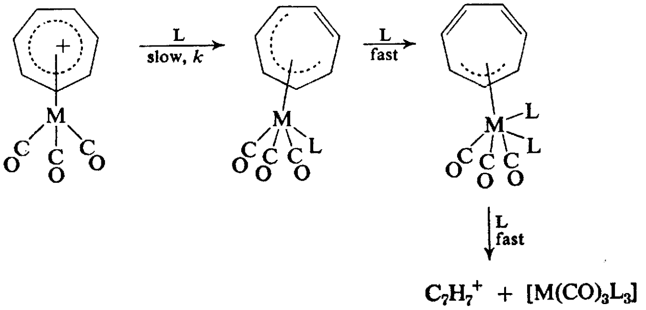
$$[M(C_7H_7)(CO)_3][BF_4] + 3MeCN \longrightarrow cis\text{-}[M(MeCN)_3(CO)_3] + (C_7H_7)BF_4$$

Activation parameters for the reaction, which involves S_N2 displacement of $C_7H_7^+$, are given in Table 2. A mechanism in which the bonding of the $C_7H_7^+$ group changes from an h^7- through to an h^5-, then to an h^3-C_7H_7 system as MeCN ligands become co-ordinated to the metal is favoured for the reaction (Scheme 7). Studies with other nitriles show that the reaction rate decreases in

[24] P. J. C. Walker and R. J. Mawby, *J.C.S. Dalton*, 1973, 622.
[25] L. A. P. Kane-Maguire and C. A. Mansfield, *J.C.S. Chem. Comm.*, 1973, 540.

Table 2 *Activation parameters for the reaction of the complexes* $[M(C_7H_7)(CO)_3][BF_4]$ *with* MeCN (*from ref.* 26)

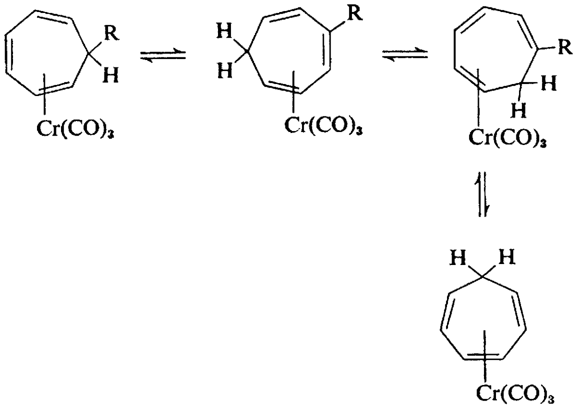
M	$k_{obs}(\times 10^4)/s^{-1}$ at 50.5 °C	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}
Cr	0.065	24.2	−10
Mo	5.50	10.5	−40
W	1.84	15.0	−30



Scheme 7

the order EtCN > MeCN > PhCN, which is the same order as is observed for the reaction of nitriles with $[Mo(CO)_6]$.[26]

Cycloheptatriene and its derivatives readily undergo thermal [1,5] hydrogen migrations which are unimolecular and first-order in the cycloheptatriene complexes. Further studies show that the overall process involves a series of sequential [1,5] hydrogen migrations (Scheme 8).[27] The transition state is formulated as (45) rather than a discrete metal-hydride intermediate (46).



Scheme 8

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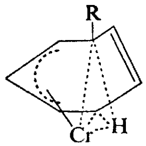
[26] K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1973, 1683.

[27] M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *J.C.S. Perkin II*, 1972, 1141.



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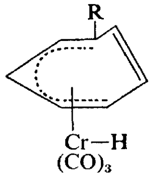
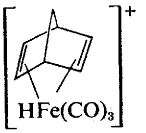
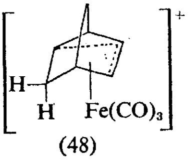


(46)

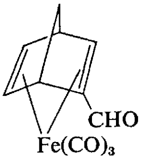
Protonation of (norbornadiene)tricarbonyliron takes place at iron to give the hydride (47). Formation of a homoallylic intermediate (48) is not observed.[28] However, it has now been found that the co-ordinated norbornadiene does undergo electrophilic substitution at carbon on treatment with dichloromethyl ether and titanium tetrachloride followed by hydrolysis to give (49). A homoallylic intermediate (50) is presumably involved.[29]



(47)



(48)



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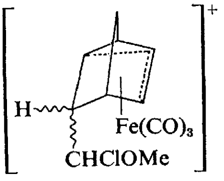

(50)

Although protonation of acyclic dienone tricarbonyliron complexes occurs at oxygen, protonation of the tropone complex (51) in trifluoroacetic acid takes place at a co-ordinated double bond (C-2) stereospecifically at the *exo*-side of the ring. In sulphuric acid, though, protonation is non-stereoselective and probably occurs from either the *endo*- or the *exo*-side.[30] In D_2SO_4, but not in CF_3CO_2D the protons at C-7 and C-2 undergo hydrogen–deuterium exchange and the exchange rate is faster at C-7 than at C-2. Treatment of the cationic species (52) with triethylsilane effects hydride transfer from the *exo*-side of the ring to give (53), which undergoes protonation at oxygen.[30]

Protonation of (cyclo-octa-1,3,5-triene)(h^5-cyclopentadienyl)rhodium in trifluoroacetic acid affords the cation (54), which isomerizes to a mixture of the octadienyl and allyl-olefin complexes (55) and (56), respectively.[31] The com-

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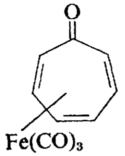
[28] D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, 1967, **89**, 6387.

[29] R. E. Graf and C. P. Lillya, *J.C.S. Chem. Comm.*, 1973, 271.

[30] D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349.

[31] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.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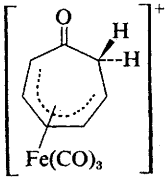
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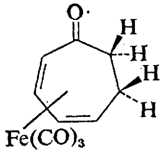
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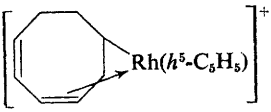
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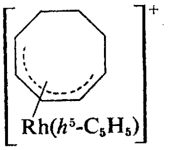

(55)

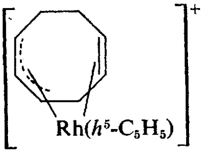

(56)

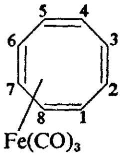
Table 3 *Activation parameters for the reaction* (54)→(55) + (56) (*from ref.* 31)

	Loss of (54)	*Formation of* (55)	*Formation of* (56)
$\Delta H^{\ddagger}$/kcal mol^{-1}:	23.7±2	22.7±2	26.3±1.7
$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}:	3.5±6	−0.5±6	7.6±5

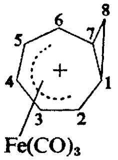
plexes (55) and (56) are formed by first-order processes and the activation parameters for the reactions are given in Table 3. A similar reaction is observed for the corresponding iridium complex but the overall reaction rate is about 1000 times slower. Studies on the iridium complex at low temperature indicate that metal hydrides are intermediates, and that the triene may in part be co-ordinated in a 1,3-manner. The mechanism of the reaction is considered to involve either an intramolecular rearrangement, which gives the dienyl complex from the 1,5-metal hydride and the allyl-olefin complex from the 1,3-metal hydride intermediate, or formation of both products from an intramolecular rearrangement of a 1,3-hydride.

Protonation of (cyclo-octatetraene)tricarbonyliron (57) is known to give (bicyclo[5,1,0]octadienyl)tricarbonyliron (58).[32] Low-temperature (−120 °C) studies have now shown that protonation of (methylcyclo-octatetraene)tricarbonyliron (59), which exists predominantly in the form illustrated, gives initially two monocyclic complexes,(60) and (61).[33] Both these complexes at −62 °C undergo first-order electrocyclic ring-closure reactions to give (62) ($k = 3.5 \times 10^{-4}$ s^{-1}; $\Delta G^{\ddagger} = 15.6$ kcal mol^{-1}) and (63) ($k = 7 \times 10^{-4}$ s^{-1}; $\Delta G^{\ddagger} = 15.3$ kcal mol^{-1}) respectively. The formation of the isomers (60) and (61) provides evidence that the sites of initial protonation of (59) were C-6 and C-7. By analogy these must also be the sites of initial protonation of (57), which gives (64). At −60 °C, (64) undergoes first-order electrocyclic ring closure to give (58) ($k = 3 \times 10^{-4}$ s^{-1}; $\Delta G^{\ddagger} = 15.7$ kcal mol^{-1}). Since it

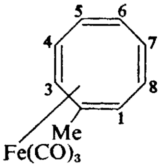
[32] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.
[33] M. Brookhart, E. R. Davis, and D. L. Harris, *J. Amer. Chem. Soc.*, 1972, **94**, 7853.



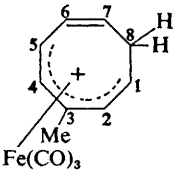
(57)



(58)



(59)



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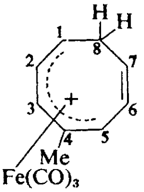
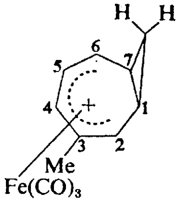
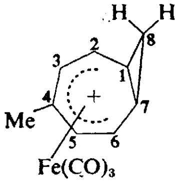


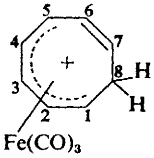
(61)



(62)



(63)



(64)

is known from studies in D_2SO_4 that proton attack occurs *trans* to iron, with the entering deuteron finally occupying the *endo*-methylene position,[32] direct attack of the carbon can be inferred, and thus a metal hydride intermediate is not involved.[33] Since the n.m.r. signals of (64) are sharp at −40 °C the system is not fluxional, and 1,3-oscillations of the iron are not occurring. Such 1,3-shifts must have much higher activation energies than the 1,2-shifts observed in (57). Indeed a 1,2-shift in (64) corresponds to ring closure and formation of (58).[33]

*cis*⁴-Cyclononatetraene (65) is unstable relative to its ring-closed isomers, *cis*-8,9-dihydroindene (66). A tricarbonyliron complex (67) of (65) can be isolated either thermally with $Fe_2(CO)_9$ or photochemically with $Fe(CO)_5$.[34] This complex, in contrast to the parent hydrocarbon, is stable for days at room temperature and undergoes electrocyclic ring closure to (68) at 101 °C with a first-order rate constant of 2.4×10^{-4} s^{-1} and with a free energy of activation of 28.4 kcal mol^{-1}.

Electrophilic molecules, such as tetracyanoethylene or hexafluoroacetone, will also attack cyclic dienes co-ordinated to tricarbonyliron.[35] Thus tetracyanoethylene, hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethyl-

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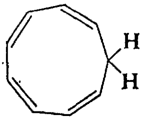
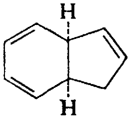
[34] E. J. Reardon and M. Brookhart, *J. Amer. Chem. Soc.*, 1973, **95**, 4311.

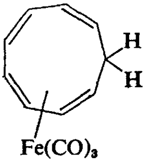
[35] M. Green, S. Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.



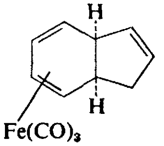
(65)



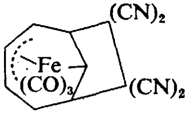
(66)



(67)

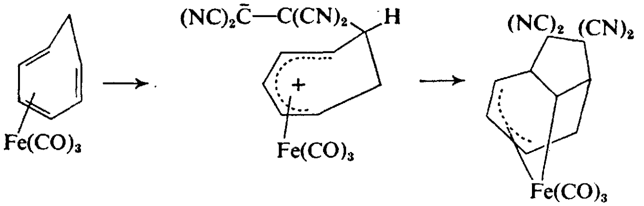


(68)



(69)

ene, and 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene add *exo*-1,3 to (cycloheptatriene)tricarbonyliron to give products which have structures of the type (69).[36] These adducts are thought to be formed *via* transient dipolar species as indicated in Scheme 9. The structures of the organic products formed by



Scheme 9

oxidative degradation of the tetracyanoethylene adducts of (cyclo-octatetraene)tricarbonyliron and (cycloheptatriene)tricarbonyliron also support stepwise cycloaddition reactions of the complexes.[36, 37] In contrast to the reaction with tetracyanoethylene, chlorosulphonyl isocyanate reacts with (cyclooctatetraene)tricarbonyliron to give a 1,4-cycloadduct. This reaction also proceeds stereospecifically from the less hindered surface of the iron complex.[36]

3 Other Ligands

Isocyanides when bonded to a transition metal have a strong tendency to react with amines or alcohols to form carbene complexes. Kinetic studies on the

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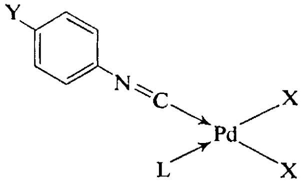
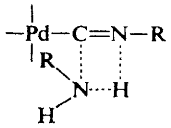
[36] L. A. Paquette, S. V. Ley, M. J. Broadhurst, D. Truesdell, J. Fayos, and J. Clardy, *Tetrahedron Letters*, 1973, 2943.

[37] D. J. Ehntholt and R. C. Kerber, *J. Organometallic Chem.*, 1972, **38**, 139.

reactions of isocyanide complexes of the type (70) with the primary amines p-$ZC_6H_4NH_2$ (Z = MeO, Me, H, Cl, or NO_2) at 30 °C are consistent with a mechanism which involves direct attack of the amine on the isocyanide carbon atom, probably through a concerted path with formation of a four-centre activated complex (71) which does not involve the metal.[38] Support for this mechanism follows from the observation that as the electrophilic nature of the co-ordinated carbon atom is increased the reactivity of the system is increased. Thus the order of reactivity is $O_2NC_6H_4NC \gg C_6H_5NC > MeC_6H_4NC > MeOC_6H_4NC \gg C_6H_{11}NC$. The activation parameters for the reaction of p-toluidine with *cis*-$[PdCl_2(CNPh)(PPh_3)]$ in 1,2-dichloroethane are $\Delta H^{\ddagger} = 9.4\ \text{kcal mol}^{-1}$; $\Delta S^{\ddagger} = -35\ \text{cal mol}^{-1}\ \text{deg}^{-1}$. This large negative value for $\Delta S^{\ddagger}$ is consistent with the rigid structure (71).[38] A similar variation in reactivities is observed in the reactions of ethanol with platinum complexes of the type *cis*-$[PtCl_2(CNR)L]$ (L = PPh_3, $PEtPh_2$, PEt_2Ph, or PEt_3). Thus reaction with ethanol to give an ethoxycarbene complex is fastest when the isocyanide is p-$O_2NC_6H_4NC$ and slowest when the isocyanide is p-$MeOC_6H_4NC$.[39] Variation of the phosphine ligand has little effect on the reaction but it is apparent from studies on reactions of amines with $[PdCl_2(CNBu^t)_2]$, which reacts faster than the corresponding iodide complex, that an electron-withdrawing group on the metal can increase the reactivity of the NC group.[40]

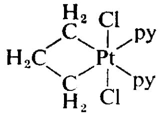


(70) Y = MeO, Me, H, or NO_2;
X = Cl or Br;
L = PPh_3 or $AsPh_3$

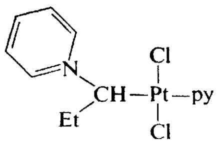


(71)

The octahedral platinum(IV) complex (72) undergoes isomerization in



(72)



(73)

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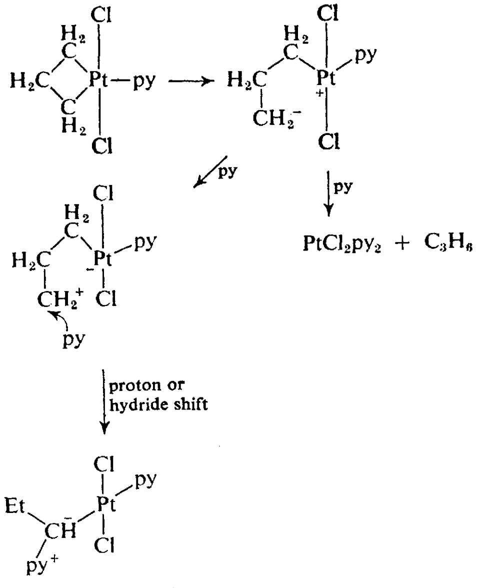
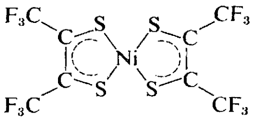
[38] B. Crociani, T. Boschi, M. Nicolini, and U. Belluco, *Inorg. Chem.*, 1972, **11**, 1292.
[39] J. Chatt, R. L. Richards, and G. H. D. Royston, *Inorg. Chim. Acta*, 1972, **6**, 669.
[40] G. A. Larkin, R. P. Scott, and M. G. H. Wallbridge, *J. Organometallic Chem.*, 1972, **37**, C21.

benzene solution to yield the platinum(II) ylide complex (73). The isomerization is first-order in [(72)] and inverse in [pyridine], and a mechanism in which pyridine is lost in a rate-determining step to form a five-co-ordinate intermediate is suggested with an energy of activation of 31.8 ± 2.7 kcal mol^{-1}.[41] Formation of the products may then follow the routes illustrated in Scheme 10.

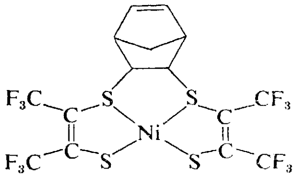


Scheme 10

Norbornadiene reacts with bis-(*cis*-1,2-perfluoromethylethylene-1,2-dithiolato)nickel (74) to give the 1,8-cycloaddition adduct (75). This oxidative cycloaddition reaction obeys second-order kinetics. In cyclohexane as solvent



(74)



(75)

$\Delta H^{\ddagger} \approx 8.6$ kcal mol^{-1} and $\Delta S^{\ddagger} \approx -29.5$ cal K^{-1} mol^{-1}. In 1,1,1-trichloroethane as solvent $\Delta H^{\ddagger} \approx 7.8$ kcal mol^{-1} and $\Delta S^{\ddagger} \approx -37.5$ cal K^{-1} mol^{-1}. The value of the activation entropy for the reaction is typical for a combination reaction and the observed rate enhancement in polar solvents is

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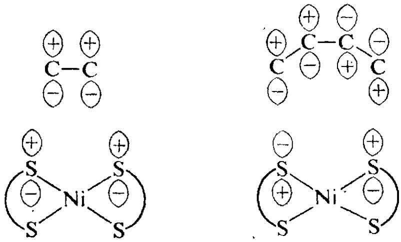
[41] R. D. Gillard and M. F. Pilbrow, *J.C.S. Dalton*, 1973, 102.

consistent with some charge separation in the transition state. Conjugated dienes, *e.g.* 2,3-dimethylbutadiene, also add to (74), the nickel complex adding 1,4 to the diene, but these reactions are too fast for kinetic studies.

Since the reactions with conjugated dienes, unlike those with unconjugated dienes, are thermally reversible it is suggested that the reactions with conjugated dienes are orbitally allowed. The pathways proposed for the reactions are depicted in Scheme 11. It can be seen that the ethylene–nickel dithiet interaction cannot lead to the ground-state adduct and the reaction must either be non-concerted or involve a higher energy state of the nickel complex. In contrast, the pathway for conjugated dienes is orbitally allowed.[42]



Scheme 11

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[42] J. R. Baker, A. Hermann, and R. M. Wing, *J. Amer. Chem. Soc.*, 1971, **93**, 6486.

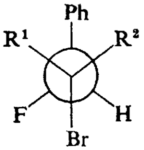
6

Oxidative Addition and Reductive Elimination

BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Introduction

Studies on oxidative-addition reactions of alkyl halides to square-planar iridium(I) complexes and other low-valent metal centres have shown that the reactions may either be regarded as S_N2 processes in which the metal centre acts as a nucleophile or else involve a concerted, three-centre addition. However, it has now been found that the oxidative-addition reaction of many alkyl halides to *trans*-$[IrCl(CO)(PMe_3)_2]$ can also proceed *via* a free-radical pathway. The studies show that the rates of reaction are greatly enhanced if small quantities of oxygen or a radical initiator, *e.g.* benzoyl peroxide, are present and that reaction rates are retarded by traces of radical scavengers, *e.g.* duroquinone or hydroquinone. Studies with the halides (1) show that the reaction proceeds with loss of stereochemistry at carbon. It is also found that the reaction rate decreases in the sequence (1) > 1-bromo-2-phenylethane ≈ *trans*-1-bromo-2-fluorocyclohexane ≈ *cis*-1-bromo-2-fluorocyclohexane > bromocyclohexane, *i.e.* the presence of electron-withdrawing substituents in the alkyl halide enhances the rate of reaction. The suggested mechanism of the reactions is outlined in Scheme 1.[1] It should be noted, however, that methyl iodide reacts



(1)

$R^1 = R^2 = H$
$R^1 = H, R^2 = D$
$R^1 = D, R^2 = H$

$$\begin{aligned}
Ir^{I} + Q^{\cdot} &\longrightarrow Ir^{II}\text{—}Q\\
Ir^{II}\text{—}Q + R\text{—}Br &\longrightarrow Br\text{—}Ir^{III}\text{—}Q + R^{\cdot}\\
Ir^{I} + R^{\cdot} &\longrightarrow Ir^{II}\text{—}R\\
Ir^{II}\text{—}R + R\text{—}Br &\longrightarrow Br\text{—}Ir^{III}\text{—}R + R^{\cdot}
\end{aligned}$$

Scheme 1

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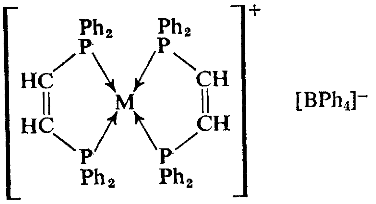
[1] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1972, **94**, 4043.

rapidly with *trans*-[$IrCl(CO)(PMe_3)_2$] even in the presence of radical inhibitors so that an alternative mechanism can operate for this halide and almost certainly for other substrates.[1] Clearly radical pathways may be operative in a number of other oxidative-addition and also reductive-elimination reactions.

Studies on the cobalt(I), rhodium(I), and iridium(I) complexes (2) have revealed the relative reactivity of metal complexes in this triad. The results show an unexpected reactivity order for oxidative addition, *i.e.* Co > Ir > Rh. The kinetic and activation parameters for the addition of molecular hydrogen and oxygen to the complexes (2) are given in Table 1. It appears that the activation enthalpy for oxygenation is proportional to the excitation energy of the $xy \rightarrow x^2-y^2$ electronic transition. Interestingly, [$CoCl(PPh_3)_3$] (which is tetrahedral) is relatively inactive towards oxygen and hydrogen but this is not so for the related rhodium(I) complex, [$RhCl(PPh_3)_3$]. It is therefore apparent that the order of reactivity in a triad depends critically on the structures of the complexes being studied.[2]



(2) M = Co, Rh, or Ir

Table 1 *Second-order constants and activation parameters for the addition of* H_2 *and* O_2 *to the complexes* (2) *in chlorobenzene at* 25 °C (*from ref.* 2)

Gas	M	*k*/ l mol⁻¹ s⁻¹	$\Delta H^{\ddagger}$/ kcal mol⁻¹	$\Delta S^{\ddagger}$/ cal deg⁻¹ mol⁻¹	$\Delta G^{\ddagger}$/ kcal mol⁻¹
O_2	Co	1.7×10^4	3.4	−28	10.3
O_2	Rh	0.12	11.6	−24	18.8
O_2	Ir	0.47	6.5	−38	17.8
H_2	Co	1.2×10^5	3.6	−23	11.0
H_2	Ir	6.7×10^3	5.0	−24	12.2

2 Group VIII Elements

Iron.—The reaction of pentacarbonyliron with iodine is known to yield *cis*-[$FeI_2(CO)_4$]. A study of the kinetics of the thermal reaction has been reported using stopped-flow techniques.[3] The observed overall rate laws are interpreted

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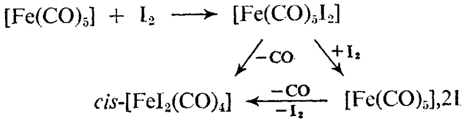
[1] L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 6671.

[3] G. R. Dobson, R. T. Jernigan, and P.-T. Chang, *J. Organometallic Chem.*, 1973, **54**, C33.

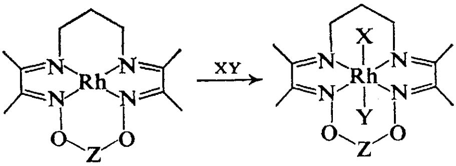


Scheme 2

in terms of the formation of 1 : 1 and 1 : 2 pentacarbonyliron–iodine adducts (Scheme 2). The intermediate $[Fe(CO)_5I_2]$ had been observed previously.[4] It seems possible that this might be a metal donor–acceptor adduct, *e.g.* $[(CO)_5Fe{\rightarrow}I_2]$. The reaction can also follow a photochemical pathway, which probably involves the formation of iodine radicals.[3]

Rhodium.—Sodium cyanide reacts with $[RhCl(CO)_2]_2$ in methanol to form $[RhH(CN)_5]^{3-}$. A transient intermediate, $[Rh(CN)_4]^{3-}$, has now been detected in this reaction. This intermediate decays by oxidatively adding HCN to form $[RhH(CN)_5]^{3-}$. The activation parameters for this oxidative-addition reaction are $\Delta H^{\ddagger} = 1.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -42$ cal deg^{-1} mol^{-1}. This entropy of activation is characteristic of other oxidative-addition reactions and is consistent with a considerable loss of freedom in the transition state, as would be expected for the addition of one molecule to another. For the oxidative addition of methyl iodide to $[Rh(CN)_4]^{3-}$, $\Delta H^{\ddagger} = 8.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18$ cal deg^{-1} mol^{-1}. In comparison with other oxidative-addition reactions of methyl iodide to d^8 complexes this is a relatively small negative value for $\Delta S^{\ddagger}$, and the authors claim that steric effects contribute significantly to values of $\Delta S^{\ddagger}$ in these systems. Thus since $[Rh(CN)_4]^{3-}$ will be smaller than a complex with bulky phosphines, transition states involving $[Rh(CN)_4]^{3-}$ will have a greater effect on the entropy of the solution. Some data have also been obtained on the reaction of methyl iodide with $[Rh(CN)_3(CO)]^{2-}$ and $[Rh(CN)_2(CO)_2]^{1-}$. Some acyl product $[Rh(COMe)(CN)_5]^{3-}$ can result from these reactions, possibly by a Rh^{I}-catalysed interconversion of a Rh^{III} species.[5]

A variety of addenda, *e.g.* iodine, acetyl chloride, benzyl chloride, chloroform, and methylene chloride, oxidatively add to the rhodium(I) complexes (3) to give the rhodium(III) complexes (4). The relative rates of oxidative addition of alkyl halides suggest nucleophilic attack of rhodium(I) at carbon. A one-electron (radical) path does not seem to be operative since the oxidative-



(3) Z = H or BF$_2$ (4)

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[4] M. F. Farona and G. R. Camp, *Inorg. Chim. Acta*, 1969, **3**, 395.
[5] R. A. Jewsbury and J. P. Maher, *J.C.S. Dalton*, 1972, 2089.

addition reaction with 6-bromohexene proceeds without rearrangement.[6] The 6-hexenyl radical is known to close rapidly and irreversibly to a five-membered ring.

Iridium.—The oxidative addition of alkyl halides to *trans*-$[IrCl(CO)(PMe_3)_2]$, which has been shown to be a free-radical process,[1] has been discussed in Section 1. Oxidative addition of methyl iodide to *trans*-$[IrCl(CO)(PPh_3)_2]$ exhibits solvent dependence. A polar transition state has therefore been proposed and the reaction has been compared with the Menschutkin reaction, the quaternization of a tertiary amine.[7] The effects of pressure and solvent on the oxidative addition of methyl iodide and oxygen to *trans*-$[IrCl(CO)(PPh_3)_2]$ have now been studied. A value of *ca.* -17 cm^3 mol^{-1} has been obtained for the volume of activation which can be related to the change in the volume of the reacting molecules when forming the transition state. This value corresponds with values obtained for the Menschutkin reactions and it is concluded that a linear transition state is probably formed, either (5) or (6).[8]

$$\underset{(5)}{\mathrm{Ir{-}{-}{-}Me{-}{-}{-}I}} \qquad \underset{(6)}{\mathrm{Ir{-}{-}{-}I{-}{-}{-}Me}}$$

Studies with silanes, however, suggest that activation enthalpies in these systems may be largely a consequence of deformation of the square-planar complex as it approaches the transition state. Some evidence for this is provided by the similarity of kinetic parameters of the phosphine and silane reactions:

$$[IrH(CO)(PPh_3)_2] + PPh_3 \rightleftharpoons [IrH(CO)(PPh_3)_3] \qquad (k_{+P}, k_{-P})$$

$$[IrH(CO)(PPh_3)_2] + Me_3SiH \rightleftharpoons [Ir(H_2)(SiMe_3)(CO)(PPh_3)_2] \qquad (k_{+Si}, k_{-Si})$$

$\Delta H^{\ddagger}_{-P} = \Delta H^{\ddagger}_{-Si} \approx 23$ kcal mol^{-1}, $\Delta S^{\ddagger}_{-P} = \Delta S^{\ddagger}_{-Si} \approx 16$ cal deg^{-1} mol^{-1}, $\Delta H^{\ddagger}_{P} - \Delta H^{\ddagger}_{Si} = 0$ kcal mol^{-1}, and $\Delta S^{\ddagger}_{P} - \Delta S^{\ddagger}_{Si} = 13$ cal deg^{-1} mol^{-1}. It would appear that phosphine addition and silane oxidative addition could be mechanistically similar processes.[9]

The rates of reaction of methyl iodide with the complexes *trans*-$[IrCl(CO)L_2]$ increase in the order of ligands L = $P(OPh)_3 < PPh_3 < P(p\text{-tolyl})_3 < PMePh_2 < PEt_3 < PMe_2Ph$. The complex *trans*-$[IrCl(CO)(AsPh_3)_2]$ also reacts more rapidly than *trans*-$[IrCl(CO)(PPh_3)_2]$. These reactions follow second-order kinetics and it is suggested that the variation in rates is consistent with nucleophilic attack by iridium at the carbon of the methyl iodide. However, the rates of reactions of methyl iodide with the complexes *trans*-$[IrX(CO)L_2]$ [L = PPh_3, $AsPh_3$, $P(p\text{-tolyl})_3$, or PMe_2Ph] increase in the order of halide ligands $I < Br < Cl < F$. This is the reverse order from that expected since the more electronegative halogens would be expected to reduce the basicity of the

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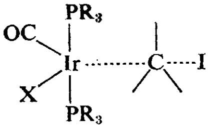
[6] J. P. Collman, D. W. Murphy, and G. Dolcetti, *J. Amer. Chem. Soc.*, 1973, **95**, 2687.

[7] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.

[8] H. Steiger and H. Kelm, *J. Phys. Chem.*, 1973, **77**, 290.

[9] J. F. Harrod, C. A. Smith, and Khin Aye Than, *J. Amer. Chem. Soc.*, 1972, **94**, 8321.

complexes. It is suggested that in the transition state for the reaction (7) the iridium–carbon bond more closely resembles that in the product than in the reactant, *i.e.* in (7) the iridium is effectively Ir^{III}. If the fluoride ligand does not σ-bond as effectively as iodide to the iridium(III) then the Ir^{III}—C bond in the five-co-ordinate transition state will be stronger when X = F than when X = I. The fluoride complex will therefore react more rapidly.[10] Similarly the rates of reaction of methyl iodide with the complexes *trans*-$[IrClL(PPh_3)_2]$ increase in the order of ligands L = $CO < PPh_3 < N_2$.[10]



(7)

In contrast to these reactions with methyl iodide the rates of the reactions of the thiols *p*-YC_6H_4SH with the complexes *trans*-$[IrX(CO)(PPh_3)_2]$ increase in the order of halide ligands X = $Cl < Br < I$.[11] This is the same order as is observed with oxygen and hydrogen oxidatively adding to the iridium. It appears that this order of reactivity is observed in oxidative-addition reactions which proceed *via* a six-co-ordinate transition state.[10] Activation parameters for the reactions with the thiols are given in Table 2. Since these enthalpies of activation are ~8—10 kcal mol^{-1} and the average of the strength S—H bond is ~80 kcal mol^{-1} it seems unlikely that the reactions proceed by initial S—H bond cleavage. A concerted reaction involving the octahedral transition state (8) therefore seems likely. This is also supported by the small kinetic isotope effect observed for the reactions. Consistent with the proposed mechanism,

Table 2 *Activation parameters for the reactions of the thiols p-*YC_6H_4SH *with trans-*$[IrX(CO)(PPh_3)_2]$ *(from ref.* 11)

	X = Cl		X = Br	
Y	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal mol^{-1} deg^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal mol^{-1} deg^{-1}
NO_2	8.4	−30	8.9	−24
Br	9.4	−29	8.7	−28
Cl	9.3	−30	8.2	−30
F	10	−27	9.5	−26
H	7.8	−37	8.6	−31
Me	9.4	−32	9.8	−26
MeO	10	−29	10	−25

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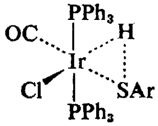
[10] M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, 1973, **7**, 195.

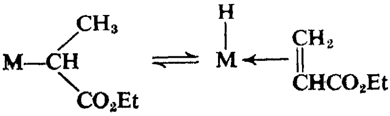
[11] J. R. Gaylor and C. V. Senoff, *Canad. J. Chem.*, 1972, **50**, 1868, 3085.



(8)

rates of reaction increase as the *para*-substituent becomes more electron-withdrawing.[11] Steric factors have also been shown to have a large effect on oxidative addition to complexes of the type *trans*-[IrCl(CO)L$_2$]. Complexes of this type are protonated reversibly by benzoic acid (L = PBu^{t}R$_2$) or hydrochloric acid (L = PBu$^t_2$R). The relative order of the extent of protonation is L = PMe$_2$Ph > PBu^{t}Me$_2$ > PBu^{t}Et$_2$ > PBu^{t}Pr$^n_2$ > PBu$^t_2$Me > PBu$^t_2$Pr^n > PBu$^t_2$Et.[12] Similarly, although *trans*-[IrCl(CO)(PBu^{t}Me$_2$)$_2$] oxidatively adds a variety of molecules, *trans*-[IrCl(CO)(PBu^{t}R$_2$)$_2$] (R = Et, Pr^n, or Bu^n) exhibit a much reduced tendency to undergo oxidative addition.[13]

Palladium.—In contrast to iridium(I) complexes there have been few studies on the stereochemistry of addition of alkyl halides to palladium(0) complexes. The addition of optically active ethyl α-bromopropionate to [Pd(CNBu^t)$_2$] gives *trans*-[PdBr(CHMeCO$_2$Et)(CNBu^t)$_2$] and results in loss of stereochemistry at the carbon centre. Since ethyl acrylate and propionate are formed in this reaction, an equilibrium involving the σ–π rearrangement (Scheme 3) could be responsible for the racemization. However, since loss of stereochemistry is also observed on addition of optically active ethyl bromophenylacetate, which bears no β-hydrogen, this mechanism seems unlikely.[14] The reaction could involve free radicals.



Scheme 3

Platinum.—Iodine oxidatively adds to bis(acetylacetonato)platinum(II) both in solution and in the solid state to yield *trans*-[Pt(acac)$_2$I$_2$].[15] The reaction in solution proceeds *via* a 1 : 1 Lewis acid–base adduct (9) which is formed rapidly before oxidative addition takes place. The adduct (9) is probably similar to that formed in the [Fe(CO)$_5$]–I$_2$ reaction.[3] In the reaction of iodine with the platinum complex the formation of the product is catalysed photochemically by the light beam of the spectrometer used to follow the reaction. The kinetic

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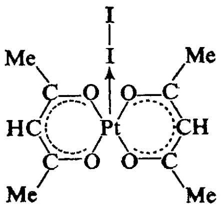
[12] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716.

[13] B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972, 223.

[14] S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *J. Amer. Chem. Soc.*, 1973, **95**, 3180.

[15] P. M. Cook, L. F. Dahl, D. Hopgood, and R. A. Jenkins, *J.C.S. Dalton*, 1973, 294.



(9)

data obtained are consistent with the chain mechanism illustrated in Scheme 4.[16]

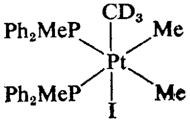
$$\mathrm{I_2} + h\nu \longrightarrow 2\mathrm{I^\bullet}$$
$$\mathrm{I^\bullet} + [\mathrm{Pt^{II}(acac)_2}],\mathrm{I_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Pt^{IV}(acac)_2I_2}] + \mathrm{I^\bullet}$$
$$2\mathrm{I^\bullet} \longrightarrow \mathrm{I_2}$$

Scheme 4

The platinum(IV) complex $[PtIMe_3(PMe_2Ph)_2]$ undergoes a reductive-elimination reaction on pyrolysis:[17]

$$[\mathrm{PtIMe_3(PMe_2Ph)_2}] \longrightarrow [\mathrm{PtIMe(PMe_2Ph)_2}] + \mathrm{C_2H_6}$$

Studies on complexes of the type (10) reveal that no C_2D_6 is formed on pyrolysis, and strongly suggest that the reductive elimination is an intramolecular process.[18] It is also apparent from studies on (10) and related complexes that CH_3 groups are eliminated more readily than CD_3 groups and that groups *trans* to phosphorus are eliminated more readily than the group *trans* to iodine.



(10)

A kinetic study on the elimination of ethane from $[PtIMe_3(PMe_2Ph)_2]$ in 1,4-dioxan over the temperature range 60—90 °C shows that the reaction follows first-order kinetics. Activation parameters are $\Delta H^{\ddagger} = 129\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^{\ddagger} = 87\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Since the activation energy is lower than $\bar{E}$(Pt—Me) for $[PtIMe_3(PMe_2Ph)_2]$, which has a value of $144\ \mathrm{kJ\ mol^{-1}}$, and is also lower than that of $D(Pt—CH_3)$ for $[PtMe_3(h^5\text{-}C_5H_5)]$, which has a value of $163\ \mathrm{kJ\ mol^{-1}}$,[19] reductive elimination from $[PtIMe_3(PMe_2Ph)_2]$ is probably a concerted process.[18]

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[16] D. Hopgood and R. A. Jenkins, *J. Amer. Chem. Soc.*, 1973, **95**, 4461.

[17] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801, 2964, 2969.

[18] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Organometallic Chem.*, 1973, **49**, C61.

[19] K. W. Egger, *J. Organometallic Chem.*, 1970, **24**, 501.

The reaction of *cis*-[$PtCl_2(PMe_2Ph)_2$] with (+)-Me(1-naphthyl)PhSiH in the presence of triethylamine gives (+)-[PtCl{SiMe(1-$C_{10}H_7$)Ph}($(PMe_2Ph)_2$)].[20, 21] If this reaction proceeds *via* initial oxidative addition of the silane to the Pt^{II} complex then it would appear that this oxidative-addition reaction proceeds with retention of configuration at silicon. Cleavage of the Pt—Si bond with $LiAlH_4$ also proceeds with retention of configuration at silicon. However, the analogous reaction with (+)-Et(1-$C_{10}H_7$)PhGeH gives the corresponding Pt—Ge-bonded complex, which on treatment with $LiAlH_4$ produces the racemic germane.[20] The germane is known to racemize when heated alone and it is not clear at what stage in the reaction that stereochemistry is lost. Cleavage of the Pt—Si bond in *trans*-(+)-[PtCl(*SiR_3)($(PMe_2Ph)_2$)] [R_3Si^* = MePh(1-naphthyl)Si] by $LiAlH_4$, PhSH, or Et_3SiH and of that in (−)-[PtH(*SiR_3)($(PPh_3)_2$)] by $LiAlH_4$, PhCOCl, PhC≡CH, or PhSH occurs with retention of configuration at silicon.[22] Again, if these reactions proceed *via* initial oxidative addition of the reactant to the platinum(II) complex then the reductive-elimination reaction proceeds stereospecifically.

3 Oxidative Addition: Other Elements

Molybdenum.—An oxidative-elimination reaction takes place when the complexes [$Mo(CO)_4$(5-X-phen)] (X = H, Me, Cl, or NO_2) are treated with mercuric chloride in acetone. The products are [MoCl(HgCl)$(CO)_3$(5-X-phen)]. Kinetic studies, using stopped-flow techniques, indicate that the reactions proceed *via* initial formation of adducts of stoicheiometry [$Mo(CO)_4$(5-X-phen)],$HgCl_2$ and [$Mo(CO)_4$(5-X-phen)],2$HgCl_2$.[23] These adducts are of the metal donor–metal acceptor type which were first characterized for some d^8 iron(0) and cobalt(I) complexes.[24–26] Consistent with this formulation, the rate of initial attack of $HgCl_2$ on the molybdenum complexes increases as the substituent X becomes more electron-releasing. Donor–acceptor complex formation is also apparent in the reactions of iodine with the d^8 compounds [$Fe(CO)_5$][3] and [$Pt(acac)_2$].[16]

Gold.—Methyl iodide readily oxidatively adds to the anionic complex $Li^+[AuMe_2(PPh_3)]^-$ to yield [$AuMe_3(PPh_3)$]. Alkyl iodides add to the three-co-ordinate complexes to give predominantly *trans*-products, *trans*-[$AuMe_2R(PPh_3)$], although some *cis*-product can be isolated when the R group is not too bulky. Rates of reaction of alkyl halides RX decrease in the order X = I > Br > Cl and R = Me > Et > Bu^n.[27] The reaction between [$AuMe(PPh_3)$] and

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[20] C. Eaborn, P. N. Kapoor, D. J. Tune, C. L. Turpin, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **34**, 153.

[21] C. Eaborn, P. B. Hitchcock, D. J. Tune, and D. R. M. Walton, *J. Organometallic Chem.*, 1973, **54**, C1

[22] C. Eaborn, D. J. Tune, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1972, 1223.

[23] R. T. Jernigan and G. R. Dobson, *Inorg. Chem.*, 1972, **11**, 81.

[24] D. J. Cook, J. L. Dawes, and R. D. W. Kemmitt, *J. Chem. Soc. (A)*, 1967, 1547.

[25] D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *J. Chem. Soc. (A)*, 1968, 1067.

[26] I. W. Nowell and D. R. Russell, *J. Chem. Soc. (A)*, 1972, 2393, 2396.

[27] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1973, **51**, C39.

methyl iodide at 25 °C affords ethane and $[AuI(PPh_3)]$. Examination of the n.m.r. spectrum of the solution reveals the formation of a gold(III) alkyl complex, $[AuMe_3(PPh_3)]$, but none of the expected oxidative-addition product, $[AuIMe_2(PPh_3)]$, can be detected. However, on mixing $[AuIMe_2(PPh_3)]$ with $[AuMe(PPh_3)]$ the alkyl $[AuMe_3(PPh_3)]$ is readily formed together with $[AuI(PPh_3)]$. These reactions are consistent with the catalytic mechanism for reaction of methyl iodide with $[AuMe(PPh_3)]$ shown in Scheme 5. Support

$$[AuMe(PPh_3)] + MeI \longrightarrow [AuIMe_2(PPh_3)]$$
$$[AuIMe_2(PPh_3)] + [AuMe(PPh_3)] \xrightarrow{\text{fast}} [AuMe_3(PPh_3)] + [AuI(PPh_3)]$$
$$[AuMe_3(PPh_3)] \longrightarrow Me{-}Me + [AuMe(PPh_3)]$$

Scheme 5

for the mechanism follows from the reaction of $[AuEt(PPh_3)]$ with methyl iodide, which yields n-butane preferentially.[28] Oxidative addition of iodine to $[Au(CN)_2]^-$ gives *trans*-$[Au(CN)_2I_2]^-$. Kinetic studies suggest that the reaction proceeds in a single step involving concerted *trans*-addition. The reaction is markedly catalysed by iodide ion.[29]

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[28] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1972, **40**, C81.

[29] M. H. Ford-Smith, J. J. Habeeb, and J. H. Rawsthorne, *J.C.S. Dalton*, 1972, 2116.

7

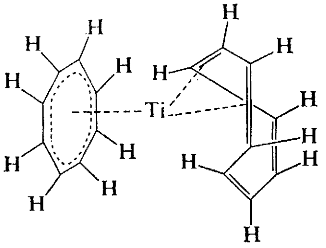
Isomerization; Intramolecular Processes

BY R. D. W. KEMMITT AND M. A. R. SMITH

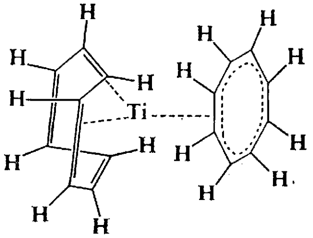
With the advent and perfection of increasingly sophisticated n.m.r. techniques, the number of reports and amount of information on fluxional molecules has increased substantially. This is nowhere more evident than in the field of ^{13}C n.m.r. spectroscopy.

1 Groups IV and V

The variable-temperature behaviour of the ^1H n.m.r. spectrum of $[Ti^{III}(C_8H_8)_2]$ is thought to result from a fluxional process involving a redox conversion (1)⇌(2) having $\Delta G^{\ddagger}_{(336)} = 71.9 \pm 0.9$ kJ mol^{-1}.[1] $[Hf(C_5H_5)_4]$ contains two *monohapto*- and two *pentahapto*-C_5H_5 groups analogous to $[Ti(C_5H_5)_4]$.[2] Intramolecular scrambling of carbonyl groups at 298 K is presumed to account for the appearance of only one (h^5-C_5H_5) resonance in the ^1H n.m.r. spectrum of $[(h^5\text{-}C_5H_5)_2V_2(CO)_5]$, which, in addition, contains grossly unsymmetrical carbonyl bridges.[3]



(1)



(2)

2 Group VI

Chromium.—The acetylene ligand in $[(h^5\text{-}C_5H_5)Cr(NO)(CO)(C_2H_2)]$ adopts a preferred conformation at low temperatures (< 223 K). Above ambient temperature, rotation about the metal–alkyne bond takes place and the two low-temperature ^1H n.m.r. signals coalesce. The free activation energy (51.6—

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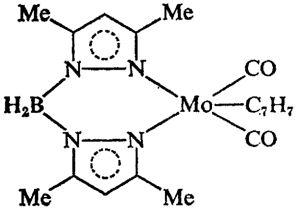
[1] J. Schwartz and J. E. Sadler, *J.C.S. Chem. Comm.*, 1973, 172.

[2] V. I. Kulishov, E. M. Brainina, N. G. Bokiy, and Yu. T. Struchkov, *J. Organometallic Chem.*, 1972, **36**, 333.

[3] F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Amer. Chem. Soc.*, 1973, **95**, 951.

70.2 kJ mol^{-1}) and coalescence temperatures are dependent on the solvent.[4] Information about preferred conformations of the five-membered ditertiary arsine ring in $[(Me_2AsCR^1R^2CR^3R^4AsMe_2)Cr(CO)_4]$ (R^1, R^2 = F or H; R^3, R^4 = F, H, $SiMe_3$, $SiCl_3$, Cl, or CN) may be gained from ^1H and ^{19}F n.m.r. measurements but no kinetic evidence concerning conformational interchange is available.[5] The *cis–trans* isomerization equilibrium of the carbene complex $[Cr(CO)_4(PR_3)\{C(OMe)(Me)\}]$ is first-order in each isomer. The reaction was followed by ^1H n.m.r., and rate constants are independent of added CO or phosphine; furthermore, addition of PR^2_3 to an equilibration involving PR^1_3 results in no incorporation of PR^2_3 in the equilibrium products. These characteristics suggest that a dissociative mechanism is unlikely and, in fact, the authors postulate an intramolecular path to isomerization.[6]

Molybdenum and Tungsten.—*Fluxional, Rotational, and Conformational Molecules.* $[(h^5\text{-}C_5H_5)Mo(CO)_3\text{—}Mo(CO)_2(CNR)(h^5\text{-}C_5H_5)]$ is fluxional. In the low-temperature limit *cis*- and *trans*-forms are detected, whilst bridge–terminal interconversion of nitrile and carbonyl groups is observed in the high-temperature limit.[7] There have been a number of reports on (pyrazolyl)-borato $\{R_nB(pz)^-_{4-n}\}$ complexes of molybdenum. N.m.r. measurements on $[\{B(pz)_4\}Mo(CO)_2(h^5\text{-}C_5H_5)]$,[8] $[\{HB(pz)_3\}Mo(CO)_2(h^5\text{-}C_5H_5)]$,[9] and $[\{Et_2B(pz)_2\}Mo(CO)_2(h^5\text{-}C_5H_5)]$[9] indicate two low-temperature forms due to different conformations of the six-membered bidentate $R_nB(pz)_{4-n}$ chelate. The denticity of $B(pz)^-_4$ in $[\{B(pz)_4\}Mo(CO)_2(h^5\text{-}C_5H_5)]$ in the solid state has been demonstrated by *X*-ray analysis.[8] $[\{H_2B(3,5\text{-}Me_2pz)_2\}Mo(CO)_2(h^3\text{-}C_7H_7)]$ (3) also contains bidentate borate ligand in the solid state[10] and this appears to continue in solution.[11] Although the fluxional nature of (h^3-C_7H_7) together with the conformational flexibility of the MoN_4B ring make the behaviour of the low-temperature n.m.r. spectrum somewhat complex, the Mo–H interaction noted in the solid state[10] probably permits only (4) and (5). The situa-



(3)

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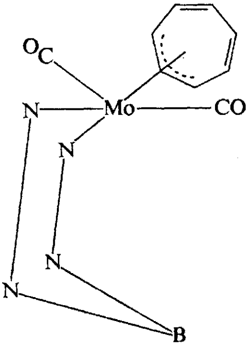
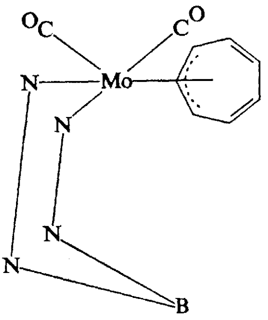
[4] M. Herberhold, H. Alt, and C. G. Kreiter, *J. Organometallic Chem.*, 1972, **42**, 413.
[5] W. R. Cullen, L. D. Hall, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 1972, **94**, 5702.
[6] E. O. Fischer, H. Fischer, and H. Werner, *Angew. Chem. Internat. Edn.*, 1972, **11**, 644.
[7] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 1972, **94**, 6193.
[8] J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **37**, 127.
[9] F. A. Cotton, J. L. Calderon, and A. Shaver, *J. Organometallic Chem.*, 1972, **38**, 105.
[10] F. A. Cotton, J. L. Calderon, M. Jeremic, and A. Shaver, *J.C.S. Chem. Comm.*, 1972, 777.

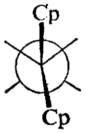


(4)

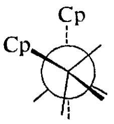


(5)

tion is not clear in the case of [{$Et_2B(pz)_2$}$Mo(CO)_2$(h^3-C_7H_7)].[11] In contrast to these results, $RB(pz)_3$ in [{$RB(pz)_3$}$Mo(CO)_2$(h^3-allyl)] (R = H or pz) is said to be terdentate, and it exhibits fluxional behaviour by virtue of internal rotation about the B—Mo axis.[12] A similar process was, however, recognized for bidentate $H_2B(3,5\text{-}Me_2pz)_2$ above.[11] The *gauche*-rotamer (7), as well as the normal *trans*-form (6), is observed in the i.r. spectrum in polar solvents.



(6)



(7)

Exchange between the two forms is fast on the n.m.r. time-scale at normal temperatures but low-temperature studies in acetone enable both forms to be 'seen' and give $\Delta H^\circ = 1.89 \pm 0.64$ kJ mol^{-1} and $\Delta S^\circ = 14.5 \pm 2.6$ J mol^{-1} K^{-1} for the *gauche→trans* rearrangement.[13] [(h^5-C_5H_5)$_2$MoH{σ-*trans*-$C(CF_3){=}CH(CF_3)$}] exists in two isomeric forms by virtue of restricted rotation about the σ-alkenyl—Mo bond.[14] The stereochemical non-rigidity of the eight-co-ordinate compounds [$H_4M(PR_3)_4$] (M = Mo or W) has been further investigated for a series of phosphines (see Volume 2 of this series), but no kinetic data have been forthcoming.[15] However, the rigid forms of the tungsten complexes persist at higher temperatures than do those of their molybdenum analogues.[16]

[11] F. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **42**, 419.

[12] P. Meakin, S. Trofimenko, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1972, **94**, 5677.

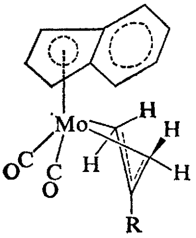
[13] R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 1973, **7**, 153.

[14] A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1972, **94**, 1886.

[15] P. Meakin, L. J. Guggenberger, W. G. Peat, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 1467.

[16] B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J.C.S. Chem. Comm.*, 1972, 34.

Examples of 'flip' and 'σ–π' rearrangement processes of co-ordinated allyl have appeared in this section. The former is apparent in an extensive investigation into the effects of allyl substituents on the configuration of the allyl in [(h^5-C_5H_5)(h^3-allyl)Mo(CO)$_2$] and [(h^5-indenyl)(h^3-allyl)Mo(CO)$_2$] and some tungsten analogues. Anisotropy effects on chemical shifts of the allyl protons in the indenyl complexes allow conclusive identification of (8) and (9).



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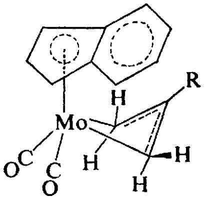


(9)

Equilibrium constants and thermodynamic data are summarized in Table 1. Substitution generally favours the type of conformation shown in (9), although 2-substitution [as in (8) and (9)] specifically favours (8). The presence of a cyclopentadienyl ring rather than an indenyl displaces equilibria in the

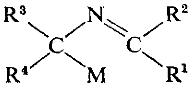
Table 1 *Thermodynamic and equilibrium data for the effect of substituents on the conformation of* h^3*-allyl in* [(h^5-R)M(CO)$_2$(h^3-allyl)] (*from ref.* 17)

M	R[a]	*Substituent*	*Solvent*	ΔH/ kJ mol^{-1}	ΔS/ J mol^{-1} K^{-1}	K_{eq}[b]	*Temp.*/ K
Mo	Cp	2-H	$CHCl_3$	-5.6 ± 0.4	-8.6 ± 1.7	4.27	273
Mo	Cp	2-H	CS_2	-3.0 ± 0.4	-3.0 ± 1.3	2.45	273
W	Cp	2-H	$CHCl_3$	-7.3 ± 0.9	-18.9 ± 3.0	2.65	273
Mo	ind	2-H	$CHCl_3$	-6.0 ± 0.9	-11.6 ± 3.4	3.27	273
Mo	ind	2-H	MeC_6H_{11}	-7.8 ± 1.3	-26.6 ± 3.9	1.30	273
Mo	Cp	2-Me	$CHCl_3$	$+3.4\pm0.9$	-6.5 ± 3.9	0.114	273
Mo	Cp	2-Me	CS_2	$+6.8\pm0.9$	$+2.6\pm3.0$	0.072	273
Mo	ind	2-Me	C_6H_6	—	—	$\lesssim 0.01$	278
W	Cp	2-Me	$CDCl_3$	—	—	~ 0.01	273
Mo	Cp	2-Br	$CHCl_3$	$+4.3\pm0.9$	$+0.9\pm2.6$	0.170	273
Mo	Cp	2-Br	CS_2	$+4.7\pm0.4$	$+5.2\pm2.6$	0.227	273
Mo	ind	2-Br	C_6H_6	—	—	0.02	278
Mo	Cp	2-Cl	C_6H_6	—	—	0.14	278
Mo	ind	2-Cl	C_6H_6	—	—	0.01	278
Mo	Cp	1-Me	CS_2	—	—	7.0	263
Mo	ind	1-Me	CS_2	—	—	3.6	273
Mo	Cp	1,1-Me_2	$CDCl_3$	—	—	>100	273
Mo	ind	1,1-Me_2	$CDCl_3$	—	—	>100	273
Mo	Cp	1,3-Me_2	$CDCl_3$	—	—	17.5	273
Mo	Cp	1,1,2-Me_3	CS_2	—	—	14.1	268
Mo	ind	1,1,2-Me_3	CS_2	—	—	$\lesssim 50$	268

[a] Cp = cyclopentadienyl; ind = indenyl. [b] K_{eq} = [(9)]/[(8)].

R

direction of (9). Investigation of the magnetic anisotropy from the benzene ring suggests that the indenyl ligand rotates freely but has a preferred configuration with the benzene ring over the allyl ligand. Other conformations are possible, however, in the presence of steric hindrance produced by *anti*-substitution in (8).[17] The fluxional behaviour of the aza-allyl group in $[(h^5\text{-}C_5H_5)M(CO)_2(R^1R^2CNCR^1R^2)]$ (M = Mo or W; $R^1 = R^2 =$ *p*-tolyl or *p*-$CF_3C_6H_4$; R^1 = *p*-tolyl, R^2 = *p*-$MeOC_6H_4$; R^1 = *p*-tolyl, $R^2 = C_6H_5$) is of the 'σ–π' type. In fact two averaging processes are observed in the course of variable-temperature n.m.r. investigations. Detachment of the C=N π-system and rotation about the C—N single bond, causing equivalence of R^3 and R^4, occurs first (10) and is followed by an interchange of σ- and π-bonds, (11) and (12), at higher temperature. Activation parameters derived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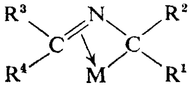
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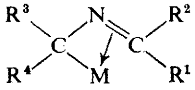
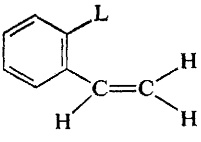
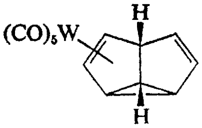

(12)

from the ^{19}F n.m.r. spectra of the complex having $R^1 = R^2 =$ *p*-$CF_3C_6H_4$, $E_a = 50.0 \pm 5.2$ kJ mol^{-1}, $\log_{10}A = 10.8 \pm 1.0$ (M = Mo); $E_a = 29.3 \pm 2.2$ kJ mol^{-1}, $\log_{10}A = 7.2 \pm 0.4$ (M = W), agree well with those from related π-allyl systems.[18] I.r. spectra of complexes $[M(CO)_4R]$ (M = Mo or W) of R (13) which contain R co-ordinated by the Group V donor atom and the olefinic double bond reveal two isomers. It is suggested that these differ in the orientation of their double bonds. Interconversion between the two appears to be fast on the n.m.r. time-scale, even at 183 K.[19] The barrier height for the Cope rearrangement of semibullvalene is raised by formation of a pentacarbonyltungsten complex. The low-temperature n.m.r. spectrum is that of the static structure, whereas the high-temperature spectrum agrees with (14)⇌(15), with the approximate $\Delta G^{\ddagger} = 51.5 \pm 4.3$ kJ mol^{-1} (at 273 K).[20]


(13) L = PPh_2, $AsPh_2$, or $AsMe_2$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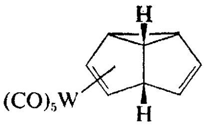
(15)

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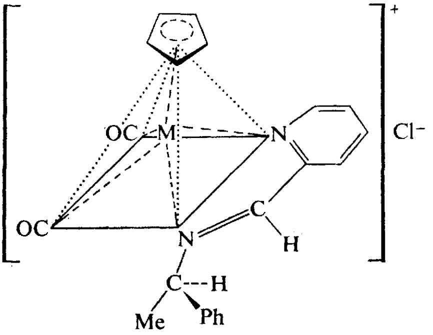
[17] J. W. Faller, C.-C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organometallic Chem.*, 1973, **52**, 361.

[18] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 1535.

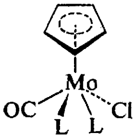
[19] M. A. Bennett and I. B. Tomkins, *J. Organometallic Chem.*, 1973, **51**, 289.

[20] R. M. Moriarty, C.-L. Yeh, and E.-L. Yeh, *J. Amer. Chem. Soc.*, 1972, **94**, 9229.

Optical and Geometrical Isomerization. The reaction of $[(h^5\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo or W) with an optically active Schiff base gives a mixture of diastereoisomers of (16). The five-co-ordinate asymmetry of Mo and W is an innovative development. Diastereoisomers can be separated on the basis of differing solubilities after conversion into the PF_6^- salts.[21] Variable-temperature ^1H n.m.r. spectra of [17; L = $PMePh_2$, PMe_2Ph, $P(OMe)Ph_2$, or $P(OMe)_2Ph$] and $[(h^5\text{-}C_5H_5)W(CO)(PMePh_2)_2Cl]$ are best explained on the basis of *cis*⇌*trans* and/or *cis*⇌*cis* isomerizations (depending on L).[22] The spontaneous isomerization of *trans*-$[Mo(CO)_2(diphos)_2]$ to the *cis*-isomer is inhibited by CO, thereby suggesting a dissociative mechanism.[23]



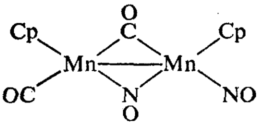
(16)



(17)

3 Group VII

$[(h^5\text{-}C_5H_5)Mn(CO)(NO)]_2$ is similar to $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$[27] and $[(h^5\text{-}C_5H_5)\text{-}Mo(CO)_3\text{—}Mo(CO)_2(CNR)(h^5\text{-}C_5H_5)]$[7] in that all undergo bridge–terminal ligand interchange. Low-temperature ^1H n.m.r. spectra of the manganese complex are consistent with a mixture of *cis*- (18) and *trans*- (19) isomers which undergo bridge–terminal exchange giving (20) (E_a = 59.5 ± 2.6 kJ mol^{-1}) and (21) (E_a = 58.0 ± 2.6 kJ mol^{-1}) as the temperature is raised. However, since in the high-temperature limit only one $(h^5\text{-}C_5H_5)$ ^1H n.m.r. signal is observed, *cis*⇌*trans* equilibration also occurs. Unlike the iron system, this cannot come about by bridge–terminal exchange alone and consequently an



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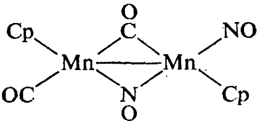

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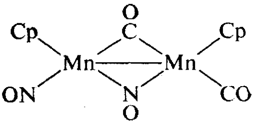
[21] H. Brunner and W. A. Herrmann, *Angew. Chem. Internat. Edn.*, 1972, **11**, 418.

[22] G. Wright and R. J. Mawby, *J. Organometallic Chem.*, 1973, **51**, 281.

[23] L. K. Holden, A. H. Mawby, D. C. Smith, and R. Whyman, *J. Organometallic Chem.*, 1973, **55**, 343.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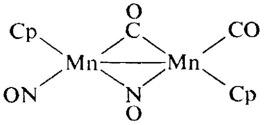
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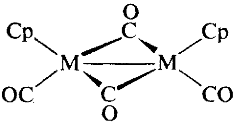
additional configurational inversion mechanism is necessary (E_a = 82.0 ± 10.3 kJ mol^{-1}).[24]

The rigid forms of the normally fluxional complexes [ReH_3(diphos)$_2$], [ReH_3(diars)$_2$], [ReH_3(diphos)(PPh_3)$_2$], [ReH_3(diars)(PPh_3)$_2$],[25] and [ReH_5($PEtPh_2$)$_3$] and [ReH_5($AsEtPh_2$)$_3$][26] have been observed in the slow-exchange-limit n.m.r. spectra. Moreover, the pentahydrides reveal three distinct fluxional processes between 138 and 303 K.

4 Group VIII: Iron Triad

Iron.—*Fluxional, Rotational, and Conformational Molecules. General.* [(h^5-C_5H_5)M(CO)$_2$]$_2$ (M = Fe or Ru) undergoes interconversion between *cis*- (22) and *trans*- (23) bridged forms by virtue of bridge–terminal interchange *via* non-bridged (24) and (25).[27] Only one non-bridged intermediate was detected but otherwise identical conclusions were drawn from a ^{13}C n.m.r. study of the same compound (M = Fe). ^{13}C n.m.r. spectra were obtained by Fourier-transform methods using [Cr(acac)$_3$] to reduce T_1 relaxation times.[28] Reduction of T_1 has also been achieved by solvent (toluene) viscosity effects in the low-temperature ^{13}C n.m.r. of the carbonyl groups in [Fe($Me_2PC_2H_4PMe_2$)(CO)$_3$]. A triplet indicates rapid intramolecular exchange even down to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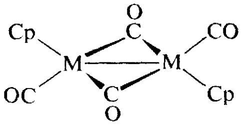
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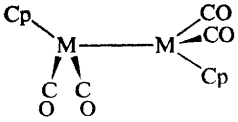
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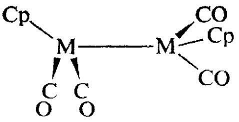
(25)

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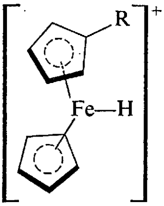
[24] T. J. Marks and J. S. Kristoff, *J. Organometallic Chem.*, 1972, **42**, C91.
[25] A. P. Ginsberg and M. E. Tully, *J. Amer. Chem. Soc.*, 1973, **95**, 4749.
[26] A. P. Ginsberg, S. C. Abrahams, and P. B. Jamieson, *J. Amer. Chem. Soc.*, 1973, **95**, 4751.
[27] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 1972, **11**, 671.
[28] O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, 1972, **94**, 2550.

193 K.[29] Compounds of the type [H_2ML_4] (M = Fe or Ru; L = phosphorus bases) are stereochemically non-rigid. They are largely *cis* in solution but several exist as equilibrium mixtures of *cis*- and *trans*-forms. Rearrangements proceed *via* a 'tetrahedral jump' mechanism, the barriers to which are larger for ruthenium than for iron.[30] The species [(h^5-C_5H_5)Fe(CO)$_2$($SiCl_2Me$)] exists as a mixture of isomers by virtue of rotation about the Fe—Si bond, as is confirmed by measurements of the enthalpy (3.4 kJ mol^{-1}) and entropy (6.0 J K^{-1} mol^{-1}) differences.[31]

Cyclopentadienyl complexes. ^{13}C n.m.r. studies of [(h^5-C_5H_5)(h^1-C_5H_5)Fe(CO)$_2$] confirm previous postulates that the fluxional behaviour of the *monohapto*-ring arises from a series of 1,2-shifts of the Fe—C σ-bond. The activation parameters found, $E_a = 46.1 \pm 2.1$ kJ mol^{-1}, $\log_{10}A = 12.6 \pm 0.5$, are considered more accurate than those derived from earlier ^{1}H n.m.r. work.[32] Solid-state ^{1}H n.m.r. spectra of the same compound indicate that at *ca.* 120 K the *pentahapto*-ring is reorientating and that between ambient temperature and the melting point the *monohapto*-ring also becomes mobile.[33] The interesting concept of ring-tilt has been demonstrated in a series of substituted ferrocenes. Protonation of iron by BF_3,H_2O gives a ferrocenium ion (26) containing tilted *pentahapto*-cyclopentadienyl rings which prevent the normal state of free rotation.[34]



(26)

Large-ring complexes. A crystal-structure determination shows that the complex of bicyclo[6,2,0]deca-1,3,5-triene and [$Fe_2(CO)_6$] has the structure (27). This is the probable ground-state configuration of the complex. Changes in the ^{1}H n.m.r. spectra below 203 K show that in solution the complex is fluxional[35] {possibly by a comparable process to that in [(cyclo-octatetraene)$Fe_2(CO)_6$]}, thereby outdating earlier reports[36] in which the minimum temperature necessary

[29] M. Akhtar, P. D. Ellis, A. G. MacDiarmid, and J. D. Odom, *Inorg. Chem.*, 1972, **11**, 2917.

[30] P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 75.

[31] J. Dalton, *Inorg. Chem.*, 1972, **11**, 915.

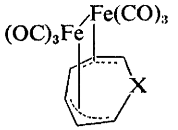
[32] D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organometallic Chem.*, 1972, **42**, 159.

[33] A. J. Campbell, C. A. Fyfe, R. G. Goel, E. Maslowsky, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1972, **94**, 8387.

[34] T. E. Bitterwolf and A. C. Ling, *J. Organometallic Chem.*, 1972, **40**, 197.

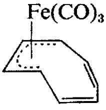
[35] F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometallic Chem.*, 1973, **50**, 227.

[36] F. A. Cotton and G. Deganello, *J. Organometallic Chem.*, 1972, **38**, 147; *J. Amer. Chem. Soc.*, 1972, **94**, 2142.



(27) $X = \begin{array}{c} \mathrm{CH{-}CH_2} \\ | \quad\;\; | \\ \mathrm{CH{-}CH_2} \end{array}$

to slow the exchange process down was not reached. Wide-line n.m.r. spectra of crystalline $[(C_8H_8)Fe(CO)_3]$ (28),[37] $[(C_8H_8)Fe_2(CO)_5]$,[37] $[(C_8H_8)_2Fe]$,[38] and $[(C_8H_8)Fe_2(CO)_6]$ (29)[37] reveal fluxional behaviour in all but the latter complex. In this case no motion is detected in the temperature range 77—430 K. The activation energy (E_a) for rearrangement in solid $[(C_8H_8)Fe(CO)_3]$ and $[(C_8H_8)_2Fe]$ is 35.7 ± 1.7 kJ mol^{-1} and 11.2 ± 0.4 kJ mol^{-1}, respectively. Whereas the accepted rearrangement mechanism involving rotation *via* 1,2 shifts is likely in the former case,[37] a process which has to overcome considerably less hindrance is envisaged in the latter. Small oscillations of the cyclo-octatetraene ring are proposed.[38] The ^{13}C n.m.r. spectra of $[(C_8H_8)Fe(CO)_3]$ in solution not only confirm the fluxional nature of the h^4-C_8H_8 ring but also reveal that the carbonyl groups are themselves subject to an averaging process at temperatures greater than 153 K.[39] Barriers to rearrangement of benzo- (30) and naptho-cyclo-octatetraenetricarbonyliron (31) are 78 and 133 kJ mol^{-1}, respectively. In comparison with that in the unsubstituted cyclo-octatetraene complex (31 kJ mol^{-1}), these values suggest that the rearrangement proceeds *via* energy-demanding quinoidal intermediates, for example (30) → (32) → (33).[40]



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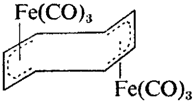
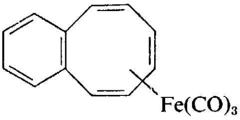


(29)

PF_3 *complexes.* It is likely that $[HFe(PF_3)_4]^-$ and $[M(PF_3)_5]$ (M = Fe, Ru, or Os) are stereochemically non-rigid. All phosphines are equivalent on the



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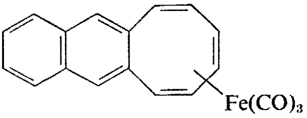

(31)

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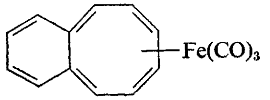
[37] A. J. Campbell, C. A. Fyfe, and E. Maslowsky, *J. Amer. Chem. Soc.*, 1972, **94**, 2690.

[38] A. Chierico and E. R. Mognaschi, *J.C.S. Faraday II*, 1973, **69**, 433.

[39] G. Rigatti, G. Baccalon, A. Ceccon, and G. Giacometti, *J.C.S. Chem. Comm.*, 1972, 1165.

[40] H. W. Whitlock and H. Stucki, *J. Amer. Chem. Soc.*, 1972, **94**, 8594.



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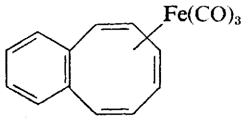
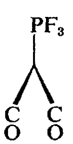


(33)

n.m.r. time-scale even down to 113 K, unlike those in [HM(PF_3)$_4$] and [HML$_4$] [M = Co, Rh, or Ir; L = P(OEt)$_3$, L$_2$ = diphos], where rigid structures are 'frozen out' at low temperatures (see later). The authors do not consider it likely that, in view of the results for the Co, Rh, and Ir complexes, this equivalence could arise from rigid forms {C_{4v} in the case of [HFe(PF_3)$_4$]$^-$} at high temperatures. Rather, the exchange process, probably having a barrier of <21.5 kJ mol^{-1}, has not been arrested on the n.m.r. time-scale even at 113 K.[41] The ^{1}H, ^{19}F, and ^{31}P n.m.r. spectra also indicate rapid rearrangement in [H_2Fe(PF_3)$_4$] at 360 K, but Mössbauer data are interpreted as indicative of rigid forms of [H_2Fe(PF_3)$_4$], K_2[Fe(PF_3)$_4$], and K[HFe(PF_3)$_4$] at 203 K.[42] [(cyclohexa-1,3-diene)Fe(PF_3)(CO)$_2$] is fluxional at room temperature. Cooling to 153 K reveals two isomers, schematically represented as (34) and (35) (the lower positions represent basal and the upper position apical sites in a square pyramid). ΔH for the equilibrium is 3.2 kJ mol^{-1}.[43] ^{19}F n.m.r. spectroscopy shows that [(C_6H_8)Fe(PF_3)$_2$(CO)] exists solely as the isomer (36) at low temperatures. Measurements on the i.r. time-scale show that at room temperature isomer (37) contributes to the overall intramolecular process. Changes



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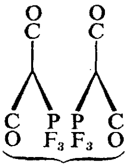

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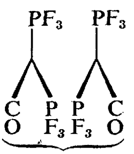

(36)

(37)

in the n.m.r. at intermediate temperatures, therefore, may be attributed to changing isomer populations.[43] The ^{19}F n.m.r. spectrum of [(tmm)Fe(CO)$_2$(PF_3)] (tmm = trimethylenemethane) shows a sharp doublet down to 163 K. Proton spectra, however, resolve into a readily interpretable first-order pattern. These data indicate the presence of the static conformer (38) in the low-temperature limit. Hindered rotation about the Fe—C bond probably poses the barrier to exchange of conformations. Similar explanations are likely in the case of the di- and tri-phosphine-substituted complexes.[44]

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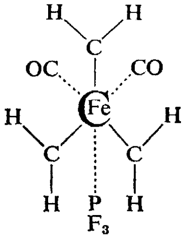
[41] P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1972, **94**, 5271.

[42] T. Kruck and R. Kobelt, *Chem. Ber.*, 1972, **105**, 3772.

[43] J. D. Warren, M. A. Busch, and R. J. Clark, *Inorg. Chem.*, 1972, **11**, 452.

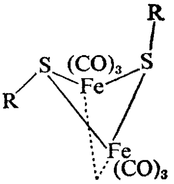
[44] R. J. Clark, M. R. Abraham, and M. A. Busch, *J. Organometallic Chem.*, 1972, **35**, C33.



(38)

A general trend worth noting in this section is the progressively lower temperatures needed to slow down rearrangement processes as the number of phosphines increases.

Geometrical and Optical Isomerization. $[H_2Fe\{PPh(OEt)_2\}_4]$ exists as a temperature-dependent equilibrium of two isomers. Above 273 K one isomer having a distorted *cis*-octahedral configuration was found, whereas this and an additional isomer, having a structure based on a distorted FeP_4 tetrahedron, were detected between 173 and 273 K. The kinetic parameters $\Delta H^{\neq} = 13.4 \pm 0.7$ kJ mol^{-1} and $\Delta S^{\neq} = 67.1 \pm 4.3$ J mol^{-1} K^{-1} were found for the isomerization equilibrium.[45] The equilibrium between *anti*- and *syn*-isomers (39) and (40) has been examined. Equilibrium constants in n-hexane at 313 K are 3.2 (R = Me) and 3.6 (R = Et) for K = [*anti*]/[*syn*], and they reflect destabilization of the *syn*-isomer with increasing size of R. This is postulated to arise from repulsion between the carbonyls and R, rather than mutually between two R groups.[46] The chiral molecule (41) has been resolved into enantiomers. Racemization is much slower than in the case of the analogous butadiene compound. This is attributed to the ease with which the butadiene ligand can decomplex compared with the cyclobutadiene ligand.[47]



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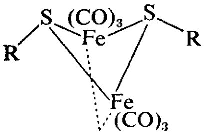

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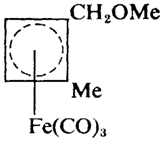

(41)

Ruthenium.—The familiar reorientation mechanism involving 1,2-shifts is proposed to account for experimental and theoretical second moments in wide-line n.m.r. measurements on crystalline $[Ru_3(CO)_4(C_8H_8)_2]$. An energy of activation of 22.1 kJ mol^{-1} was found.[48] The fluxional nature of the cyclo-

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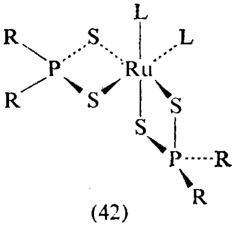
[45] A. Schweizer, D. D. Titus, and H. B. Gray, *J. Amer. Chem. Soc.*, 1973, **95**, 4552.
[46] L. Maresca, F. Greggio, R. Sbrignadello, and G. Bor, *Inorg. Chim. Acta*, 1971, **5**, 667.
[47] R. H. Grubbs and R. A. Grey, *J.C.S. Chem. Comm.*, 1973, 76.
[48] C. E. Cottrell, C. A. Fyfe, and C. V. Senoff, *J. Organometallic Chem.*, 1972, **43**, 203.

octatetraene ring in the solid state is worth contrasting with the absence of such in $[Fe_2(CO)_6(C_8H_8)]$ (29).[37] Compounds in the series $[Ru(PF_3)_x(CO)_{5-x}]$ are stereochemically non-rigid as previously noted for related iron compounds (see earlier).[49] At ambient temperature *cis*-$[Ru(S_2PR_2)_2L_2]$ [R = Me, Et, or Ph; L = PPh_3, $PMePh_2$, PMe_2Ph, or $P(OPh)_3$], exhibit scrambling between R groups by virtue of fast exchange between (42) and its enantiomer. *cis*-$[Ru(S_2PR_2)_2(PMe_2Ph)(CO)]$ undergoes rapid 'flipping' of dithio-groups above 333 K.[50] Unlike their iron analogues, $[HM(PF_3)_4]^-$ (M = Ru or Os) do show low-temperature limiting spectra. This will be discussed in more detail in Section 5.[41]



(42)

Osmium.—The importance of carbonyl cluster compounds of osmium in the field of activation of hydrocarbons has recently been noted.[51] For instance $[Os_3(CO)_{12}]$ reacts with benzene or ethylene to give $[H_2Os_3(C_6H_4)(CO)_9]$ or $[H_2Os_3(C_2H_2)(CO)_9]$, respectively.[52] A crystal-structure determination revealed a vinylidene structure for the C_2H_2 fragment in the latter complex (43).[53] Placement of the hydride protons in (43) is the most likely configuration based on the fluxional behaviour of the molecule. In the high-temperature limit, H_c exchanges with H_d (E_a = 88 kJ mol^{-1}) at a faster rate than H_a with H_b.[52,53] This is envisaged as involving migration of H_b to the Os—Os bond not bridged by hydride, thus allowing H_c–H_d exchange without H_a–H_b exchange. This argument would not pertain to a structure having H_a bridging the same pair of osmium atoms as H_b in (43). The fluxional nature of $[Os_3(C_6H_4)(CO)_7(PMe_2)_2]$ (44) results in an n.m.r. spectrum at room temperature showing equivalence of phosphines, but inequivalence of the methyl groups in each, and an $[AX]_2$ pattern for the C_6H_4 fragments. Cooling results in the emergence of a clear ABXY pattern and broad, but separate, methyl resonances. These observations are interpreted in terms of a mechanism in which, under normal conditions, the C_6H_4 group undergoes rapid rotation relative to the Os_3 triangle with concomitant transfer of carbonyl between osmium atoms ($\Delta G^{\ddagger}_{278}$ = 59.8

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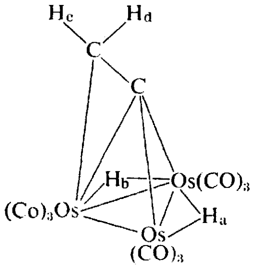
[49] C. A. Udovich and R. J. Clark, *J. Organometallic Chem.*, 1972, **36**, 355.

[50] D. J. Cole-Hamilton, P. W. Armit, and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 917.

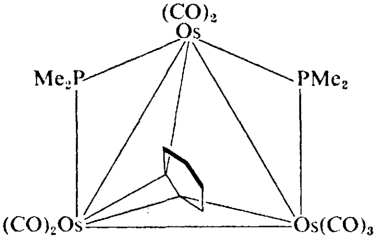
[51] C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J.C.S. Chem. Comm.*, 1972, 87.

[52] A. J. Deeming and M. Underhill, *J. Organometallic Chem.*, 1972, **42**, C60.

[53] A. J. Deeming and M. Underhill, *J.C.S. Chem. Comm.*, 1973, 277.

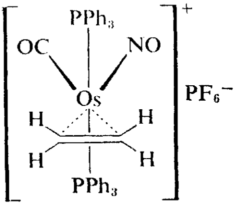


(43)



(44)

kJ mol^{-1}). A similar process is envisaged in the case of $[HOs_3(C_6H_4)(CO)_9(PMe_2)]$ ($\Delta G^{\ddagger}_{277}$ = 58.5 kJ mol^{-1}).[54] Direct evidence for both the mode *and* axis of olefin rotation has appeared for the first time. In the low-temperature limit achieved (183 K) both ^{13}C and ^{1}H n.m.r. spectra of $[Os(CO)(NO)(C_2H_4)(PPh_3)_2]PF_6$ (45) show that each end of the olefin is in a different chemical



(45)

environment. Subsequent warming results in coalescence ($\Delta G^{\ddagger}_{208}$ = 40.9 kJ mol^{-1}) of both types of spectra. This could only come about by rotation with the metal–olefin bond as axis and not with the C—C bond as such.[55] A similar situation is likely in the case of the acetylene complexes $[Os(CO)(NO)AL_2]PF_6$ [L = PPh_3, A = C_2H_2, C_2Ph_2, C_2PhH, or $C_2(CO_2Me)_2$; and L = $P(C_6H_{11})_3$, A = C_2H_2), although only a preliminary report has appeared. It is apparent, however, that bulky groups on A and L slow down the rate of site exchange.[56] Temperature-dependent *cis*$\rightleftharpoons$*trans* isomerization of $[Os(CO)_4(SiMe_3)_2]$ and $[Os(CO)_4(SnMe_3)_2]$ probably proceeds *via* an intramolecular process, although the detailed mechanism must await further investigations.[57]

5 Group VIII: Cobalt Triad

General.—Reference has been made in earlier sections to stereochemical non-rigidity in $[HM(PF_3)_4]^-$ and $[M(PF_3)_5]$ (M = Fe, Ru, or Os) systems.[41] The same report deals with $[HM(PF_3)_4]$ (M = Co, Rh, or Ir), $[HRh\{P(OEt)_3\}_4]$,

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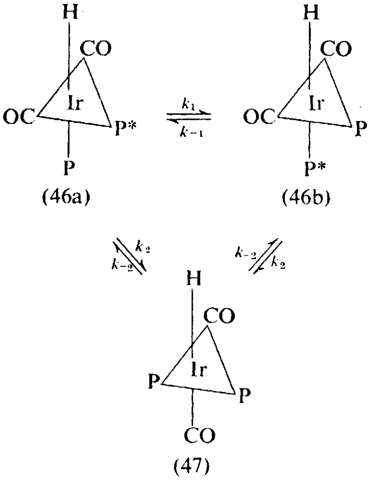
[54] A. J. Deeming, R. S. Nyholm, and M. Underhill, *J.C.S. Chem. Comm.*, 1972, 224.

[55] B. F. G. Johnson and J. A. Segal, *J.C.S. Chem. Comm.*, 1972, 1312.

[56] J. Ashley-Smith, B. F. G. Johnson, and J. A. Segal, *J. Organometallic Chem.*, 1973, **49**, C38.

[57] R. K. Pomeray and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 274.

and $[HIr(CO)_2(PR_3)_2]$ (R = Ph or *p*-tolyl) and will be dealt with fully here. Complexes of the type $[HM(PF_3)_4]$ (M = Ru, Os, Co, Rh, or Ir) and $[HRh\{P(OEt)_3\}_4]$ exhibit intramolecular rearrangement processes at normal temperatures such that all phosphines appear equivalent on the n.m.r. time-scale. Low-temperature studies indicate that static forms have a sub-structure of pseudo-tetrahedral idealized C_{3v} geometry. The rearrangement process is not of the Berry type since the ground state is not trigonal-bipyramidal. In order to account for phosphine equivalence a new mechanism was proposed involving rapid hydrogen transfer between faces of the tetrahedron of phosphines *via* its edges with concomitant M—P bending to enlarge the appropriate edge. The process is termed 'tetrahedral tunnelling' by the authors. Variable-temperature n.m.r. spectra of $[HIr(CO)_2\{P(p\text{-tol})_3\}_2]$ are interpreted in terms of the equilibria shown in Scheme 1. The intramolecular process in (46) has



Scheme 1

$\Delta G^{\ddagger}$ = 36.1 kJ mol^{-1} at 183 K whereas the interconversion of isomers (46) and (47) has $\Delta G^{\ddagger}$ = 47.2 kJ mol^{-1} at 223 K. The compound (46) rearranges more rapidly than (46) and (47) interconvert.[41]

Cobalt.—*Fluxional, Rotational, and Conformational Molecules.* A modification of the tetrahedral tunnelling or jump mechanism mentioned above arises from the fluxional behaviour of the series $[XCo\{P(OR)_3\}_4]$: X = H[41, 58] (non-rigid at 113 K), X = Me[58] (non-rigid at 113 K), X = $\frac{1}{2}$Hg[58] [rigid at (inferred) 113 K], or X = $[\{P(OR)_3\}_4Co]$[58] (rigid at 373 K). Termed the 'tetrahedral edge traverse' mechanism, it accounts for increased barriers as the bulk of X increases, thereby increasing ϕ in (48) from 70.5° up to and beyond 90°. The complex (49; X = H or CO_2Me) is fluxional at 415 K. The rearrangement

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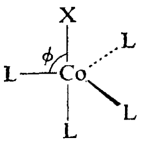
[58] E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, 1973, **95**, 5419.



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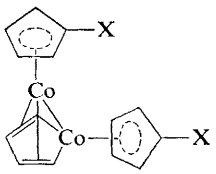

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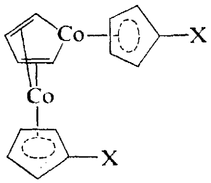
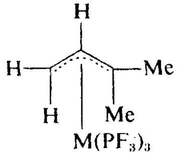


(50)

process proposed is fast exchange between (49) and (50) involving interchange of cobalt atoms with accompanying exchange of metal–carbon σ- and π-bonds; $\Delta H^{\ddagger} = 111 \pm 7.7$ kJ mol^{-1}, $\Delta S^{\ddagger} = 37 \pm 19.5$ J mol^{-1} K^{-1} (X = H) and $\Delta H^{\ddagger} = 104 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 37 \pm 7.7$ J mol^{-1} K^{-1} (X = CO_2Me).[59] At room temperature $[YCCo_3(CO)_7(nor)]$ (Y = Me, Ph, or F) is postulated to undergo a fast isomerization, the components of which have instantaneous structures based on conformations of the norbornadiene ligand relative to the metal cluster.[60] There is no evidence from ^{13}C or ^{1}H n.m.r. spectra that the fluxional processes responsible for ligand equivalence in $[Co(CNBu^t)_5]^+$ or $[CoL_4(MR_3)]^+$ (L = isocyanide) are slowing down at 113 K or 153 K, respectively.[61] Complexes of the type $[Co_4(CO)_{12-n}\{P(OMe)_3\}_n]$ have been briefly mentioned as showing fluxional properties.[62]

Geometrical Isomerization. The 1,1-Dimethyl-h^3-allyl group in $[(h^3\text{-}1,1\text{-}Me_2C_3H_3)M(PF_3)_3]$ (M = Co or Rh) (51) isomerizes to the 1,2-dimethyl isomer on heating to 333 K. The mechanism probably involves a 1,4-hydrogen shift to give (53) with the intermediacy of (52).[63] In the solid state $[Co(diphos)_2Cl]^+$ exists in two isomeric forms which equilibrate immediately upon separate dissolution. A green form is based on a trigonal bipyramid whereas the other, red, isomer is a square pyramid with apical Cl. A dechelation mechanism for the interconversion receives most support.[64] Vapour-phase rearrangement of $[(h^5\text{-}C_5H_5)Co(\pi\text{-carbollyl})]$ generates numerous dicarbollyl isomers. Rearrangement mechanisms are proposed.[65]



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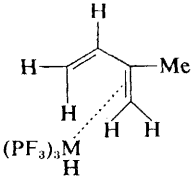

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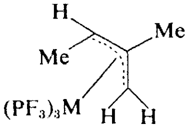

(53)

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[59] M. Rosenblum, B. North, D. Wells, and W. P. Giering, *J. Amer. Chem. Soc.*, 1972, **94**, 1239.

[60] P. A. Elder and B. H. Robinson, *J. Organometallic Chem.*, 1972, **36**, C45.

[61] E. L. Muetterties, *J.C.S. Chem. Comm.*, 1973, 221.

[62] D. Labroue and R. Poilblanc, *Inorg. Chim. Acta*, 1972, **6**, 387.

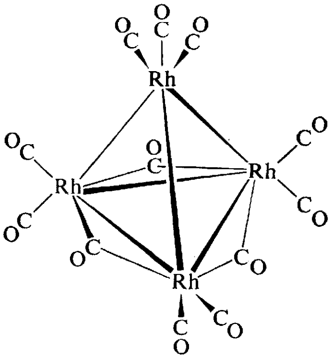
[63] M. A. Cairns, J. F. Nixon, and B. Wilkins, *J.C.S. Chem. Comm.*, 1973, 86.

[64] J. K. Stalik, P. W. R. Corfield, and D. W. Meek, *J. Amer. Chem. Soc.*, 1972, **94**, 6194.

[65] M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1972, **94**, 6679.

Rhodium.—N.m.r. spectroscopy is especially suited to the study of rhodium complexes of fluxional nature, since ^{103}Rh is 100% abundant and has $I = \frac{1}{2}$. Several projects owe their success to this fact.

Several species of stoicheiometry ML_5, *e.g.* $[Fe(PF_3)_5]$[41] and the $[Co(CNBu^t)_5]^+$ cation[61] have already been noted for their highly fluxional nature; in fact to date, the rigid form of such a molecule has not been observed. For the first time, however, there is a report of induced rigidity in an ML_5 cation. In the low-temperature limit, $[Rh\{P(OMe)_3\}_5]^+BPh_4$ shows an excellent A_2B_3X ^{31}P n.m.r. spectrum due to a rigid D_{3h} ML_5 molecule. Warming causes coalescence ($\Delta G^{\ddagger}_{166} = 31.8$ kJ mol^{-1}) to an eventual doublet from coupling to ^{103}Rh, thereby demonstrating that phosphine exchange is intramolecular.[66] ^{13}C n.m.r. spectroscopy provides elegant and unequivocal means of recognizing the fluxional nature of $[Rh_4(CO)_{12}]$ (54)[67] and $[(h^5\text{-}C_5H_5)_2Rh_2(CO)_3]$ (55).[68] In the former there are four different sites for ^{13}C, yet in the high-temperature limit (323 K) one quintet ($J_{RhC} = 17.1$ Hz) is observed, indicating equivalent carbonyls. Reduction in temperature to *ca.* 300 K results in the loss of all fine structure. The fluxional process involved, therefore, is rapid intramolecular scrambling of carbonyl groups, probably *via* the accepted bridge–terminal interchange mechanism.[67] The ^{13}C n.m.r. spectrum of $[(h^5\text{-}C_5H_5)_2Rh_2(CO)_3]$ (55) also shows intramolecular scrambling of carbonyl groups at normal temperatures. The respective high- and low-temperature limiting spectra are: a triplet ($J_{RhC} = 43$ Hz), and a triplet (1) ($J_{RhC} = 45$ Hz) and a doublet (2) ($J_{RhC} = 83$ Hz).[68] The non-rigid form of $[Rh_2(PF_3)_6(ac)]$ (56) (ac = symmetrically or unsymmetrically substituted acetylenes) exhibits equivalence of all six phosphines with respect to R^1 and R^2. In the low-temperature limit the expected inequivalence emerges. The rearrangement process could come about by propeller-like rotation of the PF_3 groups



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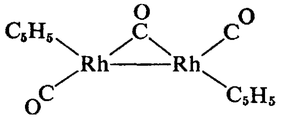

(55)

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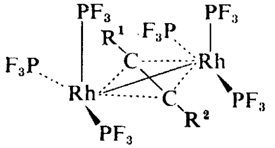
[66] J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, 1973, **95**, 1344.

[67] F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, 1972, **94**, 6191.

[68] J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1973, 79.



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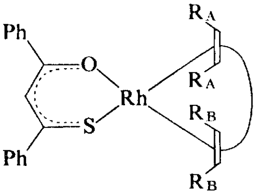
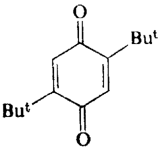


(57)

about the Rh—Rh axis or a concerted rotation of the $[Rh_2(PF_3)_6]$ unit with respect to the acetylene. The barrier to exchange is sensitive to the substituents on the acetylene, ranging from $\Delta G^{\ddagger}_{217} \approx 43$ kJ mol^{-1} (ac = $CF_3C_2CF_3$) to $\Delta G^{\ddagger}_{135} \approx 26$ kJ mol^{-1} (ac = C_4H_9CCH).[69] Evidence for olefin rotation comes from the variable-temperature ^1H n.m.r. spectra of $[L_4Rh(tcne)]$ (L = aryl isocyanides). From the static structure proposed, it would appear that rotation is about the Rh–olefin axis.[70] Intramolecular proton site exchange in [(diolefin)Rh(sdbm)] complexes, schematically represented as (57) (sdbm = 3-mercapto-1,3-diphenylprop-2-en-1-one) results in equivalence of R_A and R_B in the fast-exchange limit. Activation parameters for various olefins are given in Table 2. In the presence of added nucleophiles (*e.g.* DMSO, $AsPh_3$) the process is accelerated and obeys the rate expression: Rate = k_2[complex][L]. A mechanism involving a fluxional five-co-ordinate intermediate is proposed. In the absence of added nucleophile, the rate expression consists of a first- and a second-order term in [complex]. The first-order expression is postulated to arise from a process involving a five-co-ordinate species as above, but with solvent rather than nucleophile participation, whereas the second-order term

Table 2 *Activation parameters for olefin proton site exchange in* [(diolefin)-Rh(sdbm)] (*from ref.* 71)

Diolefin	*Solvent*	E_a/kJ mol^{-1}	log *A*
Norbornadiene	$C_6H_5NO_2$	90.3 ± 3.9	13.5
Norbornadiene	o-$C_6H_4Cl_2$	76.0 ± 2.6	12.2
2,5-Di-t-butyl-*p*-benzoquinone[a]	o-$C_6H_4Cl_2$	70.1 ± 3.9	10.4
Cyclo-octa-1,5-diene[b]	o-$C_6H_4Cl_2$	47.7 ± 2.2	9.1

[a]


. [b] In the presence of $AsPh_3$.

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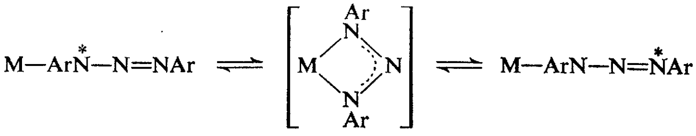
[69] M. A. Bennett, R. N. Johnson, G. B. Robertson, T. W. Turney, and P. O. Whimp, *J. Amer. Chem. Soc.*, 1972, **94**, 6540.

[70] K. Kawakami, T. Kaneshima, and T. Tanaka, *J. Organometallic Chem.*, 1972, **34**, C21.

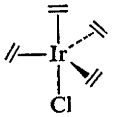
could reflect rearrangement *via* a dimeric species.[71] $[M(MeC_6H_4N{=}N{=}NC_6H_4Me)(PPh_3)_2]$ (M = Rh, Pd, or Pt) and related triazenido-complexes undergo a temperature-dependent exchange process which gives one or two methyl ^1H n.m.r. signals in the fast- or slow-exchange limits. The mechanism in Scheme 2 is proposed.[72] Solutions of the new sulphurdi-imine complex



Scheme 2

$[(C_2H_4)Pt(Bu^tN{=}S{=}NBu^t)Cl_2]$ probably contain N- and S-bonded forms. The N-bonded form undergoes both inter- and intra-molecular di-imine exchange.[73]

Iridium.—The barriers to ethylene rotation in $[Ir(C_2H_4)_4Cl]$ (58) are solvent-dependent. The low-temperature limiting ^1H n.m.r. spectrum for both equatorial and axial olefin ligands was not reached in chloroform at 213 K. In



(58)

toluene, however, the equatorial ethylenes show a well-resolved AA′BB′ pattern at this temperature. Rotation of ethylene in the axial position is not slowed, however, and the picture is further complicated at higher temperatures by intermolecular exchange with free ethylene in the equatorial positions.[74] A series of *X*-ray crystal-structure investigations of fluxional $[(cod)(Ph_{3-n}Me_nP)_2Ir(R)]$ complexes has begun. The first member $[(cod)(Me_2PhP)_2Ir(Me)]$ is a trigonal bipyramid with axial methyl, equatorial phosphines, and cod spanning the remaining sites.[75]

The reaction of $[Ir(CO)_2Cl_2Et]_2$ with L [L = PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OMe)_2Ph$, or $P(OMe)Ph_2$] leads to formation of one isomer (59) of the propionyl complex $[Ir(CO)L_2Cl_2(COEt)]$. This rearranges to a more stable form (60) in a manner which is inhibited by free L. In order to accommodate the kinetics ($k_{obs}^{-1} \propto [L]$), the mechanism in Scheme 3 is proposed. Dissociation of L as the first step is a reasonable consequence of the large *trans* effect of the propionyl ligand.[76]

[71] H. I. Heitner and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 1447.

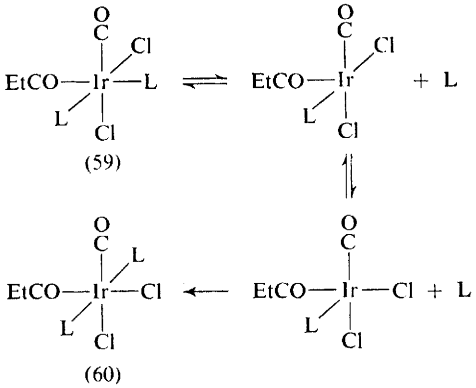
[72] S. D. Robinson and M. F. Uttley, *J.C.S. Chem. Comm.*, 1972, 184.

[73] J. Kuyper, K. Vrieze, and A. Oskam, *J. Organometallic Chem.*, 1972, **46**, C25.

[74] A. L. Onderdelinden and A. van der Ent, *Inorg. Chim. Acta*, 1972, **6**, 420.

[75] M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1972, **11**, 2243.

[76] G. Wright, R. W. Glyde, and R. J. Mawby, *J.C.S. Dalton*, 1973, 220.



(59)

(60)

Scheme 3

6 Group VIII: Nickel Triad

Nickel.—Compounds of the type [(h^5-C_5H_5)Ni(PPh_3)(CH_2R)] are postulated to give rise to variable-temperature n.m.r. effects such as varied ^3J(PNiCH) with R and line broadening (R = $SiMe_3$) by virtue of restricted rotation about the Ni—C bond.[77] It has been pointed out, however, that the n.m.r. behaviour of these compounds could also arise from interconversion between enantiomeric conformations arising from restricted rotation about (and hence chirality of) the phosphorus atom.[78] The process which renders the methyl groups of the acac ligand in [Ni(Et)(acac)(PPh_3)] and [Ni(Me)(acac)(PPh_3)$_2$] equivalent in the rapid-exchange limit is dependent on solvent as well as temperature. Dechelation of acac is considered to be the most likely exchange mechanism.[79]

In the high-temperature limit the ^{19}F n.m.r. spectrum of *trans*-[$NiX_2(PFBu^t_2)_2$] (X = halide) shows an $[AX]_2$ spectrum with $|^1J(PF) - {}^3J(PF)| \approx 2|^2J(PP)_{trans}|$. Reduction in temperature results in the emergence of three such patterns, one of which approximates to a doublet. It is proposed that, in the ground state, the *cis*- and two rotamers of the *trans*-complex are present, the *cis*-complex giving rise to the apparent doublet since $|^1J(PF) - {}^3J(PF)| \gg |^2J(PP)_{cis}.|$[80] We would point out, however, that this is not adequately supported by the corresponding variable-temperature results from the ^1H spectrum, an $[AX_n]_2$ system. In the low-temperature limit an apparently exactly superimposed doublet and singlet are observed. The authors' postulate that the doublet component is due to the *cis*-complex is unlikely, since this would necessitate that $|^3J(PH) - {}^5J(PH)| \gg |^2J(PP)_{cis}|$, when in fact ^3J(PH) in free $PFBu^t_2$ is 13 Hz and $|^2J(PP)_{cis}|$ in these complexes is expected to be

---

[77] J. Thomson, W. Keeney, M. C. Baird, and F. N. Reynolds, *J. Organometallic Chem.*, 1972, **40**, 205.

[78] J. M. Brown and K. Mertis, *J. Organometallic Chem.*, 1973, **47**, C5.

[79] A. Yamamoto, T. Yamamoto, T. Saruyama, and Y. Nakamura, *J. Amer. Chem. Soc.*, 1973, **95**, 4073.

[80] O. Stelzer and E. Unger, *J.C.S. Dalton*, 1973, 1783.

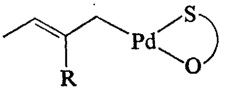
> 13 Hz (' < 90 Hz' in ref. 80). Moreover, it is unlikely that F–H coupling can be ignored. Thermodynamics of the equilibrium

$$\text{NiX}_2\text{L}_2 \text{ (tetrahedral)} \rightleftharpoons \text{NiX}_2\text{L}_2 \text{ (planar)}$$

[X = halide, L = (for example) PR_3, PR_2Ph, or $PRPh_2$ (R = cyclopropyl or cyclohexyl)] are relatively insensitive to the steric nature of the phosphine. Electronic effects are deemed the dominant factor and it is proposed that they are manifested by Ni—P π-bonding.[81]

Palladium.—A number of papers have appeared dealing with the many facets of allyl rearrangement in h^3-allyl complexes of palladium. The criteria for tackling these often complicated systems have already been outlined in this section in Volume 2 of these Reports and need no further mention here. For the sake of convenience the reports will be dealt with in two categories, intramolecular rearrangements and rearrangements promoted by substitution.

Intramolecular Rearrangements. Low-temperature n.m.r. studies of dimeric 2-methylallyl complexes [Pd(h^3-2-Me-allyl)(μ-X)]$_2$ (X = acetate or Cl) indicate several ground-state isomers differing in their relative orientations of the allyl 'arrowhead'. Interconversion of these isomers of the acetate-bridged complex is postulated to take place *via* puckering of the acetate ring rather than allyl rearrangement.[82] This is closely analogous to the situation originally proposed in the unsubstituted allyl complex[83] (see Vol. 2 of these Reports), but this has since been revised (see ref. 91). It appears that interconversion probably takes place *via* partial dissociation of the metal–carboxylate bridge (see later), and of course this would apply equally well to the 2-methylallyl complex. Above ambient temperature the allyl ligand in [(h^3-allyl)Pd(sdbm)] {sdbm = 3-mercapto-1,3-diphenylprop-2-en-1-one – see (57) earlier; allyl may be substituted} undergoes *syn–anti* proton exchange at the carbon atom *cis* to sulphur. The mechanism is probably of the 'π–σ–π' or 'h^3–h^1–h^3' type, the stereospecificity of the exchange being explained in terms of the σ-bonded *cis*-intermediate (61)



(61)

which, perhaps on account of *trans*-influence phenomena, would be expected to be more stable than its *trans*-analogue. At high concentrations *cis–trans* as well as *syn–anti* exchange is needed to account for n.m.r. observations.[84] Exchange processes in [(h^3-crotyl)(amine)PdCl] (h^3-crotyl = h^3-1-methylallyl) are quite complex. Fortunately each appears to occur within separate temperature limits

---

[81] L. Que and L. H. Pignolet, *Inorg. Chem.*, 1973, **12**, 156.

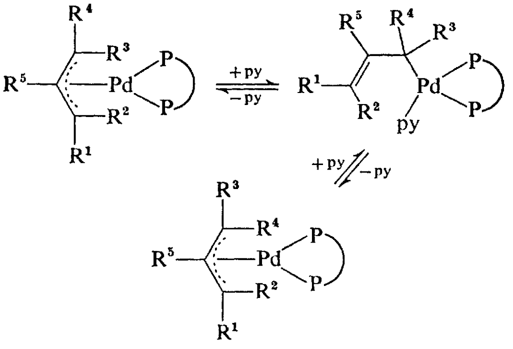
[82] P. W. N. M. Van Leeuwen, J. Lukas, A. P. Praat, and M. Appleman, *J. Organometallic Chem.*, 1972, **38**, 199.

[83] J. Powell, *J. Chem. Soc.* (*A*), 1971, 2233.

[84] S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, 1972, **94**, 6949.

and may be recognized individually. As the temperature increases from the ground-state situation, rotation about the Pd—N bond occurs. Different rotamers exist for complexes having the amine *cis* or *trans* to the allyl 1-position. Above 238 K intermolecular exchange of amine gets under way and it is only above 300 K that *syn–anti* allyl proton-exchange begins. The latter is postulated to proceed by the accepted σ- or h^1-bonded intermediate.[85] The interesting hypothesis[86] that bulky substituents on the 2-position in (h^3-1,2-disubstituted allyl) result in preference for an *anti*-configuration at the 1-position, whereas small 2-substituents favour *syn*, has been investigated in detail by consideration of the series bis-[(h^3-1-benzoyl-2-phenylallyl)PdCl], bis-[(h^3-1-acetyl-2-phenylallyl)-PdCl], bis-[(h^3-1-acetyl-2-methylallyl)PdCl], and bis-[(h^3-1,2-diphenylallyl)-PdCl] and their derivatives with amines. A terminal keto-group in the 1-position was found to be equally essential in attempting to predict stereochemistry. Thus, the percentages of *anti*-isomer in the 1-acetyl-2-R series are 100 (R = Ph), 75 (R = Me), and < 5 (R = H), but that in the pyridine derivative of bis-[(h^3-1,2-diphenylallyl)PdCl] is only 48%.[87] The same general hypothesis[86] predicts that thermodynamic constraints could be placed on rearrangements that result in epimerization of optically active h^3-allyl complexes. This proposal is vindicated by a study of (+)-bis-[(h^3-1-acetyl-2,3-dimethylallyl)PdCl] and some amine derivatives, which, as predicted, isomerize to give *syn*- and *anti*-acetyl epimers, but do not isomerize.[88]

Rearrangements Promoted by Substitution. syn–anti Proton site exchange in [Pd(h^3-allyl)(diphos)]X (X = PF_6 or BF_4; h^3-allyl may be substituted) is accelerated by an added base such as pyridine. The results indicate an S_N2 substitution process as in Scheme 4 and not an allyl rotation as previously proposed.[89] In comparison, *syn–syn* and simultaneous *anti–anti* site exchange



Scheme 4

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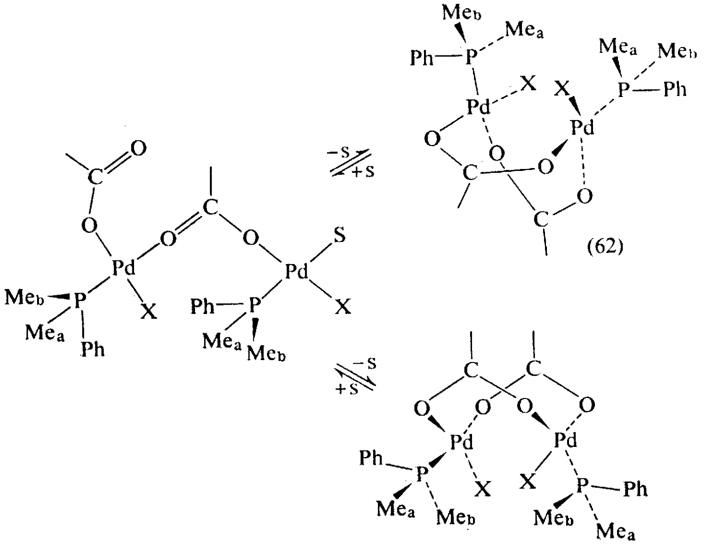
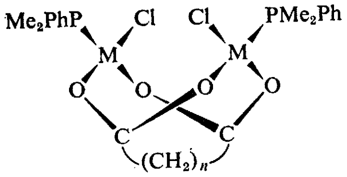
[85] J. W. Faller and M. J. Mattina, *Inorg. Chem.*, 1972, **11**, 1296.
[86] J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, 1971, **93**, 2642.
[87] J. W. Faller, M. T. Tully, and K. J. Laffey, *J. Organometallic Chem.*, 1972, **37**, 193.
[88] J. W. Faller and M. T. Tully, *J. Amer. Chem. Soc.*, 1972, **94**, 2676.
[89] M. Oslinger and J. Powell, *Canad. J. Chem.*, 1973, **51**, 274.

in $[(h^3\text{-}2\text{-RC}_3H_4)Pd(LL)]$ (LL = picolinate or oxinate), which is also accelerated by added base, is best explained by partial substitution of one end of the chelate, although above 300 K *syn–anti* exchange does occur, and this is postulated to go *via* a σ-bonded intermediate probably similar to that in Scheme 4.[90]

The ground state of $[(Me_2PhE)XM(O_2CR)]_2$ (M = Pd or Pt; E = As or P; X = Cl, Br, or I; R = Me, CH_2Cl, CH_2Br, CCl_3, CF_3, CMe_3, or CPh_3) is as in (62). In the high-temperature limit the non-equivalent methyl groups become equivalent by an intramolecular process. A carboxylate ring inversion similar to that proposed to account for allylic exchange[83] is dismissed by virtue of the continued exchange of methyl sites in complexes such as (63) where a carboxylate inversion is prevented. The proposed mechanism involves solvolytic partial dissociation of the carboxylate bridge (Scheme 5), and is further evidenced by the lowering of coalescence temperatures on addition of very weak bridge-splitting ligands, such as MeOH and $MeCO_2H$,



Scheme 5



(63)

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[90] E. Ban, A. Chan, and J. Powell, *J. Organometallic Chem.*, 1972, **34**, 405.

to the chloroform solution.[91] These results occasioned a re-examination of the analogous $[(h^3\text{-}C_3H_5)Pd(acetate)]_2$ system mentioned above,[83] which also showed lowered coalescence temperatures on addition of MeOH or $MeCO_2H$. It is most likely, therefore, that the carboxylate inversion mechanism proposed to account for allylic exchange should be superseded by the present one. Single-temperature studies on ring-substituted styrenes in $[M(styrene)Cl_2]_2$ (M = Pd or Pt) indicate that styrene reorientation is faster for palladium than platinum.[92] In the low-temperature limit, inversion about pyramidal sulphur in $[(RSC_2H_4SR)MX_2]$ (M = Pd or Pt; R = Me, Et, Pr^n, Pr^i, or Bu^n; X = Cl, Br, or I) is arrested and *meso-* and (±)-isomeric forms can be detected in the n.m.r. spectra. The rate of inversion at higher temperatures varies as the *trans*-effect of X and is more rapid for Pd than Pt.[93]

Palladium complexes of the type $[PdX_2L_2]$ (X = halide, L = tertiary phosphine) are commonly isolated as the *trans*-isomer. However, thermodynamics of the *cis*$\rightleftharpoons$*trans* equilibrium (X = Cl, L = PPh_2Me or $PPhMe_2$) deduced as a result of its temperature dependence clearly indicate that, in all but two solvents, the *cis*-isomer is thermodynamically more stable (Table 3). Furthermore, the reaction is always endothermic in the direction of the *trans*-isomer. ΔH therefore favours the *cis*-isomer; ΔS on the other hand favours the *trans*-isomer. However, since ΔH and ΔS are dependent on solvent–complex dipole–dipole interactions, the isomerization generally is solvent-controlled.[94]

Platinum.—The complex of stoicheiometry $[(h^3\text{-allyl})Pt(hfac)]$ exists as the monomer and the dimer (64) in solution at ambient temperature. In the high-temperature limit the ^1H n.m.r. signals of the monomer remain sharp whereas those of the dimer coalesce owing to H^1–H^4 and H^2–H^3 exchange. The process is postulated to proceed *via* the tautomeric mechanism shown in (64).[95] The barriers to olefin rotation in $[PtXYL(C_2H_4)]$ (65; X = Cl, Br, or CF_3CO_2; Y = Cl or Br; L = Group V bases) are said to reflect mainly steric effects of the ligands. The possible exception is electronic in the case of X = CF_3CO_2.[96] Intramolecular rearrangement rates (migration of Pt between double bonds) of the tetramethylallene (tma) complexes $[LPtCl_2(tma)]$ (L = 4-X-pyridine *N*-oxide, RNH_2, $MeCONH_2$, NH_2CONH_2, CD_3CN, CD_3OD, or SPh_2) are found to depend inversely on the basicity of the N donors. Abnormally low rates found in the case of the oxygen ligands are ascribed to their stronger donor properties.[97] The unusual n.m.r. behaviour of (66) is clearly explained in terms of isomerization to the *cis*-form and the resulting effect on intermolecular isoquinoline exchange[98] rather than of the existence of two

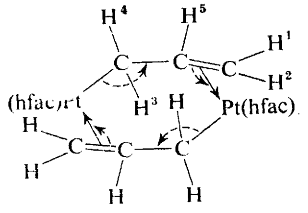
---

[91] J. Powell and T. Jack, *Inorg. Chem.*, 1972, **11**, 1039.
[92] T. Iwao, A. Saika, and T. Kinugasa, *Inorg. Chem.*, 1972, **11**, 3106.
[93] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.
[94] D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, 1973, **12**, 15.
[95] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1973, **55**, C45.
[96] J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1776.
[97] H. E. Wilson and K. Vrieze, *J. Organometallic Chem.*, 1973, **54**, 403.
[98] J. Powell and D. G. Cooper, *J.C.S. Chem. Comm.*, 1973, 486.

Table 3 *Equilibrium thermodynamic data for the reaction cis*-[L_2PdCl_2]$\rightleftharpoons$*trans*-[L_2PdCl_2] *from ref.* 94

	L = $PPhMe_2$			L = PPh_2Me		
Solvent	ΔH^a/kJ mol^{-1}	ΔS^b/J mol^{-1} K^{-1}	ΔG^c/kJ mol^{-1}	ΔH^a/kJ mol^{-1}	ΔS^b/J mol^{-1} K^{-1}	ΔG^c/kJ mol^{-1}
Nitrobenzene	33.1	87.0	6.75	34.8	110.5	1.12
o-Dichlorobenzene	19.3	60.1	1.42	—	—	—
m-Dichlorobenzene	18.9	69.2	−2.19	—	—	−4.51
[$^2H_8$]Toluene	*d*	—	—	*d*	—	—
[$^2H_6$]Benzene	*d*	—	—	*d*	—	—
[$^2H_3$]Nitromethane	18.9	69.6	5.94	24.5	64.1	4.98
[$^2H_6$]Acetone	12.0	34.0	1.68	—	—	—
Tetrachloromethane	24.9	66.0	4.85	27.5	81.2	2.75
1,2-Dichloroethane	—	—	2.66	—	—	1.29
1,1,2-Trichloroethane	*d*	—	—	*d*	—	—
$CDCl_3$	13.3	38.7	1.55	19.7	86.9	−6.70

[a] ±2.2. [b] ±4.3. [c] 305 K. [d] *trans*-Isomer only observed.



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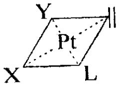

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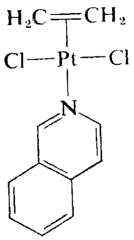

(66)

isoquinoline conformers which undergo solvolysis at different rates, as was previously thought.[99]

7 Gold

Variable-temperature ^1H n.m.r. spectra of $[Au(PPh_3)(RC_5H_4)]$ indicate a rearrangement of a *monohapto*-cyclopentadienyl ring at normal temperatures for R = Me. A doublet structure at low temperatures for the ring protons for R = H is assigned to phosphorus coupling as a result of arrested intermolecular phosphine exchange. No other processes were 'frozen out' on further reduction in temperature. [100] Inversion about sulphur accounts for the variable-temperature ^1H n.m.r. spectra of $[(C_6H_5CH_2)_2SAu^{III}Cl_3]$. At 303 K the methylene protons exhibit an AB pattern which coalesces on raising the temperature to 335 K. In contrast, the inversion process in the gold(I) complex $[(C_6H_5CH_2)_2SAuCl]$ is not completely frozen even at 178 K. This is in agreement with the respective labilities of complexes containing gold in the two oxidation states.[101]

trans-$[Bu^tAuMe_2(PPh_3)]$ spontaneously isomerizes to the *trans*-isobutyl analogue ($k = 1.1 \times 10^{-5}\,s^{-1}$, $\Delta H^{\ddagger} = 125\,kJ\,mol^{-1}$, $\Delta S^{\ddagger} = 69\,J\,mol^{-1}\,K^{-1}$).[102] The hydrido-olefin intermediate proposed to account for the rearrangement is similar to that proposed in the reaction of s-acyl halides with $[IrCl(PPh_3)_3]$ to give straight-chain alkyl derivatives of iridium.[103]

---

[99] L. Spaulding and M. Orchin, *J.C.S. Chem. Comm.*, 1972, 1249.
[100] C. H. Campbell and M. L. H. Green, *J. Chem. Soc.* (*A*), 1971, 3282.
[101] F. Coletta, R. Ettorre, and A. Gambaro, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 667.
[102] A. Tamaki and J. K. Kochi, *J.C.S. Chem. Comm.*, 1973, 423.
[103] M. A. Bennett and R. Charles, *J. Amer. Chem. Soc.*, 1972, **94**, 666.

ERRATA

Vol. 1, 1971

Page 99, last line before Section 5. *For* 'ruthenium' *read* 'rhodium'.

Page 99. In the text, refs. 358 (on its second occurrence), 359, and 360 should read 359, 360, and 361 respectively.

Page 276, fifth line of section headed 'Isomerisation'. *For* 'ruthenium(I)' *read* 'ruthenium(II)'.

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