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ISBN 0 85186 285 3
ISSN 0305-8255
Library of Congress Catalog No. 73-642977

A Specialist Periodical Report

Inorganic Reaction Mechanisms

Volume 4

A Review of the Literature Published between July 1973 and December 1974

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The Chemical Society

Burlington House, London W1V 0BN

ISBN: 0 85186 285 3
ISSN: 0305-8255

Library of Congress Catalog No. 73–642977

Printed in Great Britain by
Adlard & Son Ltd.
Bartholomew Press, Dorking

Foreword

The format, coverage and approach to this fourth volume dealing with Inorganic Reaction Mechanisms are similar to those for the previous volumes of the series. Rather than attempting to refer to all articles in which there is mention of mechanism, we have chosen (with an eye on volume size and cost!) to concentrate on papers in which kinetics and mechanisms in solution form the principal interest. This policy inevitably leads to mention of some papers being cursory with a consequent loss of subtlety. We hope, however, that any resultant oversimplification or misrepresentation is minimal. Review articles cited are those which should be accessible to the great majority of readers.

The period of coverage of the literature is from July 1973 to December 1974. The boundaries at both ends are somewhat vague since not all libraries have issues available at the same time. Care has been taken to ensure that an overlap with Volume 3 is maintained in all areas. Material which is derived from *Chemical Abstracts* rather than from the original source is indicated by inclusion of a *Chem. Abs.* citation in the reference quoted. References to the Russian literature derived from this source quote the page number of the original article whereas those giving the title of the English translation quote the page number of the translation.

As in previous volumes, kinetic data are reported in the form (E_a and $\log A$ or $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) or units (SI or other) used in the original article, although some conversions have been made both in the text and in the tables where comparisons are required.

The Reporters are grateful to many of their colleagues for helpful comments. We are particularly indebted to Professor W. C. E. Higginson and Drs A. G. Sykes, G. Davies, R. J. Cross, and A. G. Lappin for their critical reading of sections of the manuscript.

A. McAULEY

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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
AN	acetonitrile
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_4dien	*NNN"N"*-tetraethyldiethylenetriamine
ete	4,8-dithia-1,11-diazaundecane
gedta	2,2'-ethylenedioxybis(ethyleneiminodiacetate)
glu	glutamate
gly	glycinate
Hb	Haemoglobin
hedta	*N*-(2-hydroxyethyl)ethylenediaminetriacetate
hfac	hexafluoroacetylacetonate
his	histidine
hm	histamine
ida	iminodiacetate
ind	indenyl
mal	malonate
Me_4dien – H	*NNN"N"*-tetramethyldiethylenetriamine minus the nitrogen proton
Me mal	methylmalonate anion
Me_6tren	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
pada	pyridine-2-azo-*p*-dimethylaniline
pdta	propylenediaminetetra-acetate
phen	1,10-phenanthroline
pn	propylenediamine
py	pyridine
salen	*NN'*-bis(salicylaldehydo)ethylenediamine
tar	tartrate
tcne	tetracyanoethylene
tea	triethanolamine
terpy	2,2',2"-terpyridyl
2,3,2-tet	1,4,8,11-tetra-azaundecane
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
K. L. SCOTT

Introduction

BY A. McAULEY AND K. L. SCOTT

The format of this Part of the Report follows closely that of previous volumes. Attempts have been made to cover as comprehensively as possible all the areas involving electron-transfer processes in solution. As in previous Reports, compilations have been made of rate and thermodynamic parameters to allow for ready comparisons of the data.

Several articles have been published dealing with differing areas of the subject together with technical aspects. Developments in instrumentation have been brought up to date,[1] and the range of rapid-reaction techniques now available for investigations of reactions in solution has been reviewed.[2] An empirical approach to ligand effects on the kinetics of substitution and redox reactions[3] has been shown to be applicable to a wide variety of reaction systems and the changes effected on the redox properties of metal ions on ligand co-ordination have been discussed.[4] Especially important in this respect are the stabilization of both cations and anions and back-bonding effects. A short review of inorganic reaction mechanisms has been published[5] and mechanistic assignments have been made using terms in empirical rate laws for both complexation and redox reactions of metal ions in aqueous solution.[6] The importance of hydrogen-ion dependences has also been discussed. Reactions of aquocobalt(III) ions have been described using a phenomenological model for redox reactions.[7]

Metal-ion reduction of both mononuclear[8] and dinuclear[9] carboxylatocobalt(III) complexes have been reviewed. There continues to be substantial interest in this subject and in particular the adjacent-attack mechanism for complexes with simple monocarboxylate ligands now appears to be well understood. The importance of the inner-sphere mechanism in reductions by Eu^{2+} has been amply demonstrated.[10] Gould[11] has also illustrated the usefulness of the comparison of rate data from the reactions of a common oxidant by several reductants. Many workers are currently involved in attempts to measure first-order rates of electron transfer within precursor complexes. In the search for likely systems, the one chosen by Taube[12]

[1] M. H. Davies, B. H. Robinson, and J. R. Keefe, *Ann. Reports* (*A*), 1973, **70**, 123.
[2] 'Investigation of Rates and Mechanisms of Reaction, Part II', ed. G. G. Hammes, Vol. 6 in the series 'Techniques of Chemistry', ed. A. Weissberger, Wiley, New York, 1974.
[3] V. Gutmann and R. Schmid, *Coordination Chem. Rev.*, 1974, **12**, 263.
[4] V. Gutmann, *Structure and Bonding*, 1973, **15**, 141.
[5] A. McAuley, *Ann. Reports* (*A*), 1973, **70**, 487.
[6] G. Davies, *Coordination Chem. Rev.*, 1974, **14**, 287.
[7] I. Bodek and G. Davies, *Coordination Chem. Rev.*, 1974, **14**, 269.
[8] H. Taube, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 964.
[9] A. G. Sykes, *Chem. in Britain*, 1974, **10**, 170.
[10] F. R. F. Fan and E. S. Gould, *Inorg. Chem.*, 1974, **13**, 2639.
[11] F. R. F. Fan and E. S. Gould, *Inorg. Chem.*, 1974, **13**, 2647.
[12] S. S. Isied and H. Taube, *J. Amer. Chem. Soc.*, 1973, **95**, 8198.

appears to be yielding the most promising results. A long-lived intermediate has, however, been identified in a cobalt(III)–iron(II) electron-transfer reaction.[13] The Tl^{I}–Tl^{III} exchange reaction has been shown to be a two-electron transfer without intermediacy of Tl^{II}, and redox potentials have been substantially revised.[14,15]

Redox processes have been described in a review of platinum chemistry with monoammine ligands.[16] Electron-transfer mechanisms involving organometallic intermediates have been discussed.[17] The increasing use of pulse radiolysis has resulted in better characterization of the species produced and the acid–base properties of free radicals in solution have been reviewed.[18] The correlation between redox potentials and pK_a values of the radicals emphasizes the role and importance of acid–base equilibria of these species in electron-transfer reactions. Two volumes on homogeneous catalysis involving metal complexes have been published,[19] in which attempts have been made to systematize the chemistry of reactions of metal ions with small molecules both inorganic (*e.g.* O_2, N_2, CO, *etc.*) and organic (alkenes and alkynes).

The increasing interest in the biological aspects of inorganic mechanisms is reflected in several reviews. Redox reactions of metalloporphyrin complexes have been discussed[20] and the principles of catalysis by metallo-enzymes described with particular reference to proteins interacting with oxygen.[21] Among several interesting papers in an excellent two-volume work edited by Eichhorn is one by Sutin on redox reactions in co-ordination compounds.[22]

[13] R. D. Cannon and J. Gardiner, *Inorg. Chem.*, 1974, **13**, 390.
[14] B. Falcinella, P. D. Felgate, and G. S. Laurence, *J.C.S. Dalton*, 1974, 1367.
[15] H. A. Schwartz, D. Comstock, J. K. Yandell, and R. W. Dodson, *J. Phys. Chem.*, 1974, **78**, 488.
[16] K. P. Beaumont and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **8**, 105.
[17] J. K. Kochi, *Accounts Chem. Res.*, 1974, **7**, 351.
[18] E. Hayon and M. Simic, *Accounts Chem. Res.*, 1974, **7**, 114.
[19] M. M. Taqui-Khan and A. E. Martell, 'Homogeneous Catalysis by Metal Complexes', Vols. I and II, Academic Press, New York, 1974.
[20] J. H. Furhop, *Structure and Bonding*, 1974, **18**, 1.
[21] J. M. Pratt, in 'Techniques and Topics in Bio-inorganic Chemistry', ed. C. A. McAuliffe, Macmillan, London, 1975.
[22] N. Sutin, in 'Inorganic Biochemistry', ed. G. L. Eichhorn, Elsevier, Amsterdam, 1973.

1

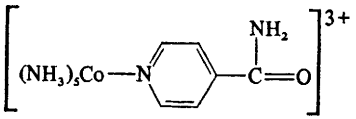
Reactions Between Two Metal Complexes

BY K. L. SCOTT

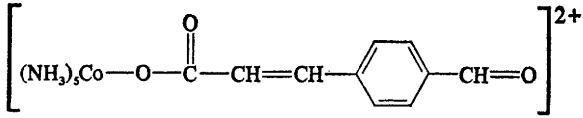
1 Reducing Agents

Chromium(II).—Rate constants and activation parameters for reactions of chromium(II) and of other reductants are given in Table 1 on p. 17.

One of the major interests with Cr^{II} is the determination of the mediating role of organic ligands.[1] The simplest of the inner-sphere mechanisms, designated *adjacent attack*, involves an activated complex in which both metal ions are co-ordinated to a simple ligand, the most common group being carboxylate. Proof that *remote attack* could occur with bifunctional organic ligands was eventually obtained in the reduction of the isonicotinamidopenta-amminecobalt(III) complex (1).[2] The use of complexes with remote carbonyl groups has enabled Gould[3] to add considerably to the list of reactions proceeding by remote attack. Evidence for this mechanism with the *p*-formylcinnamato-complex (2)[3] comes not only from the very high rate and from



(1)



(2)

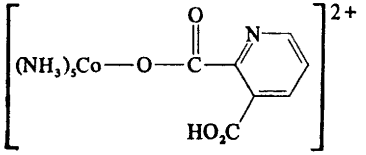
the form of the rate law [equation (1)] but also from the detection of a short-lived

$$-d[Co^{III}]/dt = (k_1 + k_2[H^+])[Co^{III}][Cr^{2+}] \quad (1)$$

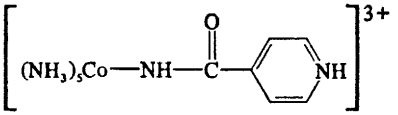
chromium(III) carbonyl complex. Complex (2) is particularly interesting in that mediating action by ten ligand atoms is involved. The intermediate is similar both in its rate of dissociation ($k = 7.6\ s^{-1}$ at 25 °C) and spectrum to the one identified in the Cr^{2+} reduction of the *p*-formylbenzoato-complex.[4] Reduction of the *o*-formyl-

[1] H. Taube, *Ber. Bunsengesellschaft phys. Chem.*, 1972, **76**, 964.
[2] F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 1162.
[3] E. S. Gould, *J. Amer. Chem. Soc.*, 1974, **96**, 2373.
[4] A. Zanella and H. Taube, *J. Amer. Chem. Soc.*, 1972, **94**, 6403.

benzoato-complex[3] displays neither of the criteria for remote attack. Nevertheless the rate is considerably greater than for orthodox adjacent attack and it is tempting to resort to the *adjacent attack with chelation* explanation.[3] The work of Price and Taube[5] shows this not to be valid and the best explanation to be that a pendant group serves to delocalize the reducing electron. Reduction of the 4-benzoylpyridine complex also occurs by fast remote attack.[3] Reactions of the 2,3- [complex (3)], 2,4-, 2,5-, and 2,6-dicarboxylatopyridino-[3] and 2-, 3-, and 4- [complex (4)] carboxamidopyridino[6]-complexes provide interesting comparisons. With the dicarboxylato-complexes[3] a term in $[H^+]^{-1}$ is apparent in addition to the $[H^+]$-independent term



(3)



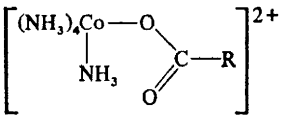
(4)

and a chelated chromium(III) product is found in each case. For the 3- and the 4-carboxamido-complexes[6] second-order rate constants are independent of $[H^+]$ entirely, as expected for adjacent attack, and unstable intermediates are identified as being the same as those formed in the reduction of the nicotinamido- and iso-nicotinamido-complexes.[2] Complexes (1) and (4) are isomers. With the 2-carboxamidopyridino-species only a term in $[H^+]^{-1}$ is observed [rate law (2)],

$$-d[Co^{III}]/dt = k[Co^{III}][Cr^{2+}][H^+]^{-1} \qquad (2)$$

the rate is much greater, and the intermediate is stable. Gould[3] has argued that the rate constants for the $[H^+]^{-1}$-path are too fast in the dicarboxylato-series to represent reaction of the deprotonated (1+)-complex whereas Balahura[6] has assigned the path to reaction of the deprotonated 2-carboxamido-complex. Very similar intermediates were postulated in the respective studies.

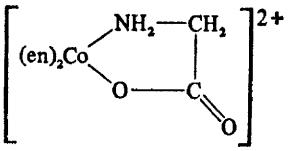
The factors responsible for the enormous variations in rate when bifunctional organic ligands mediate in electron-transfer reactions are by no means understood, but in the case of simple monocarboxylato-ligands the details of the adjacent-attack mechanism seem particularly well worked out. Sykes[7] has reviewed the contribution that dinuclear complexes have played in this. In all simple monocarboxylato-complexes of the type (5) the point of Cr^{2+} attack is the carbonyl oxygen and its accessibility is determined by the size of R. The conformation (5) is more strongly demanded



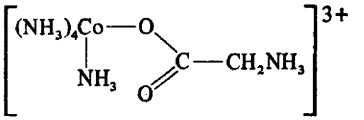
(5)

[5] H. J. Price and H. Taube, *Inorg. Chem.*, 1968, **7**, 1.
[6] R. J. Balahura, *Inorg. Chem.*, 1974, **13**, 1350.
[7] A. G. Sykes, *Chem. in Britain*, 1974, **10**, 170.

as the size of R increases and yet the reverse conformation with the carbonyl group more remote from the cobalt(III) centre is preferred for precursor complex formation.[8] Thus despite the detrimental effect of ethylenediamine ligands, Cr^{2+} reduction of the chelated glycinato-complex (6)[9] is 35 times faster (at 25 °C) than for glycinato-penta-ammine (7)[10] where the 'wrong' conformation is adopted. Gould has established a relationship between second-order rate constants for Cr^{2+}, V^{2+}, and Eu^{2+}

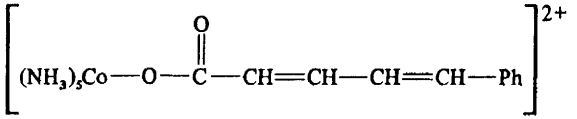


(6)



(7)

reduction and the Taft steric-substituent parameter (E_S).[11,12] Recent work, notably by Balahura, has added support to the ideas of conformational requirements. Nuclear Overhauser effect studies[13] with the complex $[(NH_3)_5CoO_2CH]^{2+}$ showed a 17% enhancement in the integrated intensity of the CH peak on irradiation of the *cis*-NH_3 resonance. A significant proportion at least of the formato-complex must be in the preferred conformation for precursor complex formation. In the crystal structure, the oxygen atom in the complex $[(NH_3)_5CoNH_2COMe]^{3+}$ points between two *cis*-equatorial ammines and the methyl group is directed away.[14] The Cr^{2+} reduction of this complex[15] follows the rate law (2) with the deprotonated form reactive. The rate constant is considerably smaller than with the formamido-complex so that a similar situation to the carboxylato-series obtains which can be rationalized in terms of the same conformational considerations. Cr^{2+} Reduction of the β-styryl-acrylato-complex (8)[3] is retarded by increased $[H^+]$, as protonation of the adjacent



(8)

carbonyl group restricts its availability to Cr^{2+}. As discussed earlier, with a formyl group in the *para*-position, *e.g.* in (2), this same protonation has exactly the reverse effect and promotes the remote rate.

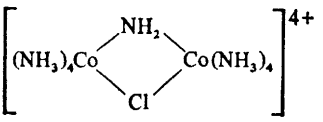
Reductions of the di-μ-hydroxo-μ-benzoato-bis[triamminecobalt(III)] complex and the *o*-chloro-substituted analogue were investigated to see whether any advantage

[8] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.
[9] M. Gilroy, F. A. Sedor, and L. E. Bennett, *J.C.S. Chem. Comm.*, 1972, 181.
[10] R. Holwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, 1972, **11**, 1965.
[11] J. C. Chen and E. S. Gould, *J. Amer. Chem. Soc.*, 1973, **95**, 5539.
[12] F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, 1974, **13**, 2639.
[13] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1973, **12**, 1438.
[14] M. L. Schneider, G. Ferguson, and R. J. Balahura, *Canad. J. Chem.*, 1973, **51**, 2180.
[15] R. J. Balahura and L. Hutley, *Canad. J. Chem.*, 1973, **51**, 3712.

was gained by the introduction of an aromatic ring.[16] The ratios k_{Cr}/k_V were found to be 0.023 and 0.021 respectively and the mechanism therefore is outer-sphere. No obvious enhancement in rate was observed over the analogous formato- and acetato-complexes.[8] The inability of halides in substituted complexes to affect rates either by functioning as sites for inner-sphere attack[16] or by exerting inductive effects,[12] *e.g.* $[(NH_3)_5CoO_2CCH_nF_{3-n}]^{2+}$, is quite remarkable. Unless bonded directly to the metal oxidant, as with $[(NH_3)_5CoCl]^{2+}$, halides appear to be without effect. Major effects are found in complexes containing sulphur. The Cr^{2+} reduction of the mercaptoacetato-complex $[Co(en)_2(SCH_2CO_2)]^+$ has been found previously to proceed at immeasurably fast rate.[17] An *X*-ray study[18] has now revealed that the Co—N bond *trans* to sulphur is 0.04 Å longer than the average *cis*-Co—N bond. Greater rates of reduction with sulphur-containing ligands and greater rates of substitution, with the amazingly labile $[(NH_3)_5CoSO_3]^+$ complex as an extreme example. may find common explanation in this *trans*-bond lengthening.

Correlations of rate-constant data in the form of log–log plots have been used[19] to calculate contributions from outer-sphere paths to reactions proceeding predominantly by inner-sphere mechanisms. Even in the case of Cr^{2+} reduction of the least reactive $[(NH_3)_5CoO_2CR]^{2+}$ complexes, *e.g.* where R = CEt_3, the calculated contribution from an outer-sphere path is only 3% and this confirms the long-held view that essentially quantitative ligand transfer occurs in reactions of this type. The decrease in second-order rate constants with increase in R is more marked with Cr^{2+} than with other reducing agents. In addition to the steric considerations already discussed, the authors[19] suggest that interference of the orbital-overlap process is an additional factor with Cr^{2+}.

Complete reduction of the dinuclear complex (9) by Cr^{2+} proceeds in two stages,[20]



(9)

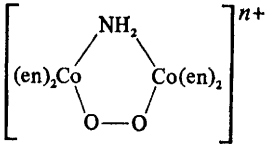
the first of which gives $[Co(NH_3)_5H_2O]^{3+}$ at a rate which is independent of $[H^+]$,

$$-d[(9)]/dt = k[(9)][Cr^{2+}],$$

the μ-bromo-complex behaving in the same way. An outer-sphere mechanism clearly does not operate and the surprising inference is that the μ-chloro-bridge provides a site for inner-sphere electron transfer. It is proposed that chloride ion is bonded to three metal centres in the activated complex and that the successor complex $[(H_2O)_5Cr^{III}ClCo^{III}(NH_3)_5]^{5+}$ rapidly aquates to the observed products. The second stage, corresponding to reduction of $[Co(NH_3)_5H_2O]^{3+}$, obeys rate law (2) in $LiClO_4$

[16] K. Wieghardt and A. G. Sykes, *J.C.S. Dalton*, 1974, 651.
[17] R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, 1970, **92**, 1089.
[18] R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, 1973, **12**, 2690.
[19] F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, 1974, **13**, 2647.
[20] M. R. Hyde and A. G. Sykes, *J.C.S. Dalton*, 1974, 1583.

media with but a single term in agreement with an earlier study;[21] activation parameters have also been reported.[20] A full paper[22] on the reduction of the μ-superoxo-(μ-O_2^-)-complex (10), noted previously,[23] reports the following sequence: (i) outer-sphere reduction of the superoxo-bridge to peroxo-; (ii) inner-sphere reduction of one of the cobalt(III) centres; (iii) two-equivalent reduction of the bridge to hydroxo-; and (iv) reduction of the second cobalt(III). The reduction of the bridge from superoxo- (μ-O_2^-) to peroxo- (μ-O_2^{2-}) at immeasurably fast rate by an outer-sphere mechanism reflects the similarity in the complex geometries. An inner-sphere mechanism for reaction of the μ-peroxo-complex (11) is also to be expected from its known reactions



(10) $n = 4$
(11) $n = 3$

with non-metallic reductants. The product is a novel μ-peroxo mixed dinuclear cobalt(III)–chromium(III) complex. The mechanism of the third reduction involving two equivalents and reduction of the bridge to μ-hydroxo is still not identified. From the kinetic data, two stages both independent of $[Cr^{2+}]$ are observed. The authors suggest that isomerization and possibly decomposition are rate-determining at this point with Cr^{2+} acting as scavenger. However, it seems clear that a mixed dinuclear complex, possibly $[(NH_3)(en)_2Co \cdot OH \cdot Cr(H_2O)_5]^{5+}$, is formed and that reduction of the remaining cobalt(III) is by a slow outer-sphere mechanism.

The classic way of demonstrating a mechanism, *viz.* by product analysis, is not always possible, especially with slow reactions, and the use of linear free-energy relationships is now much in evidence. Sutin[24] has developed an alternative approach to the problem – consideration of the magnitude of the catalytic effect of added anions. This effect is known for the M^{2+} reduction (M = V, Cr, or Fe) of a hard oxidant by the inner-sphere mechanism, and a particularly useful fact comes from the observation that N_3^- is *ca.* 10^5 times more effective than SCN^- in catalysing the rate. The effect of Cl^- and SCN^- on the rates of known outer-sphere reactions are given, using the reductions of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, and $[Co(phen)_3]^{3+}$ by Cr^{II} and V^{II}. At low concentrations of added anion, X^-, the rate law is observed to be

$$-d[Co^{III}]/dt = (k_0 + k_1[X^-])[M^{II}][Co^{III}]$$

The results have been used to demonstrate the mechanism in the reduction of the tetrakis-(4-*N*-methylpyridyl)porphinecobalt(III) complex, $[Co(TMpyP)(H_2O)_2]$.[25]

[21] D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635.
[22] M. R. Hyde and A. G. Sykes, *J.C.S. Dalton*, 1974, 1550.
[23] M. R. Hyde and A. G. Sykes, *J.C.S. Chem. Comm.*, 1972, 1340.
[24] T. J. Przystas and N. Sutin, *J. Amer. Chem. Soc.*, 1973, **95**, 5545.
[25] R. F. Pasternack and N. Sutin, *Inorg. Chem.*, 1974, **13**, 1956.

Observed rate constants are of the form

$$\frac{k_{obs}}{[Cr^{2+}]} = \left(k_0 + \frac{k'_0}{[H^+]}\right) + \left(k_1 + \frac{k'_1}{[H^+]}\right)[L^-] + \left(k_2 + \frac{k'_2}{[H^+]}\right)[L^-]^2$$

and in general show the basic characteristics of a second-order reaction of Cr^{2+} with complex and a term inverse in $[H^+]$. With SCN^- all the terms contribute but with Cl^- the term in $[L^-]^2$ is absent. In perchlorate media only the terms independent of $[L^-]$ are present. Rates of Cr^{2+} reduction by the $[H^+]^{-1}$ path are greater than the rates of substitution of aquo-ligands on the complex and it can be fairly easily concluded that the mechanism is inner-sphere with a transition state of the type $[Co—OH—CrL]^*$. Electron transfer does not occur through the ring. For $[H^+]$-independent terms, rates in the presence of SCN^- and Cl^- are in the ratio of 55:1. This is similar to the ratio of 61:1 found for $[Co(NH_3)_6]^{3+}$ but differs from that for $[Co(phen)_3]^{3+}$ (1.3×10^3). Hence an outer-sphere mechanism and transition state of the kind $[Co(OH_2)—X—Cr]^*$ are indicated. Reduction of an analogous iron(III) complex has been re-investigated and the $[H^+]$-dependence shown to be of the same form as for cobalt(III).

Much interest has been shown in reactions of organocobaloximes since the demonstration of their similarity in some cases to Vitamin B_{12}. Espenson and Shveima[26] report that, in reactions with Cr^{2+}, essentially quantitative transfer of the alkyl group to chromium occurs, together with electron transfer:

$$[RCo(Hdmg)_2H_2O] + Cr^{2+} + 2H^+ \longrightarrow Co^{2+} + [(H_2O)_5CrR]^{2+} + 2H_2dmg$$

The reactions with R = Me, Et, Pr^n, Me_2CH, $PhCH_2$, and Me_3CCH_2 have been studied. Rates are first order in reactants with a dependence on $[H^+]$ which allows specific rates for the neutral and protonated forms of the cobaloxime to be determined. Studies were extended to the corrin complexes themselves with a report[27] on the reductions of methyl-, ethyl-, and aquo-cobalamin:

$$[RCo(corrin)] + Cr^{2+} \longrightarrow [(H_2O)_5CrR]^{2+} + B_{12r}$$

Second-order rate constants are independent of $[H^+]$ in the pH range 0—2.3. The alkylcobalamins are more reactive than the corresponding cobaloximes, and this difference may result from greater strain imposed by the corrin ring substituents. The authors suggest two mechanisms to fit the experimental facts: the very rare bimolecular-homolytic substitution (S_H2) mechanism, or a redox reaction, involving transfer of a carbanion in a concerted process. Either reaction presents conceptual difficulties. The Cr^{2+} reduction of the related $[Co(Hdmg)_2(NH_3)_2]^+$ complex proceeds at a surprisingly high rate[28] according to the rate law (1).

Reduction of the organochromium(III) complexes $[Cr(H_2O)_5(CHI_2)]^{2+}$ (ref. 29) and $[Cr(H_2O)_5(CH_2I)]^{2+}$ (ref. 30) has been studied by a titrimetric method. Stoicheiometries are respectively given by the equations

$$2Cr^{2+} + CrCHI_2^{2+} + H^+ \longrightarrow CrI^{2+} + Cr^{3+} + CrCH_2I^{2+}$$

$$2Cr^{2+} + CrCH_2I^{2+} + 2H^+ \longrightarrow CrI^{2+} + 2Cr^{3+} + CH_4.$$

[26] J. H. Espenson and J. S. Shveima, *J. Amer. Chem. Soc.*, 1973, **95**, 4468.
[27] J. H. Espenson and T. D. Sellers, *J. Amer. Chem. Soc.*, 1974, **96**, 94.
[28] R. H. Prince and M. G. Segal, *Nature*, 1974, **249**, 246.
[29] R. S. Nohr and L. O. Spreer, *J. Amer. Chem. Soc.*, 1974, **96**, 2618.
[30] R. S. Nohr and L. O. Spreer, *Inorg. Chem.*, 1974, **13**, 1239.

The rate in each case is first order in $[Cr^{2+}]$ and $[Cr^{III}]$ and independent of $[H^+]$. With $CrCH_2I^{2+}$ a long-lived intermediate aquates with formation of CH_4 at a rate which identifies it as methylchromium(III):

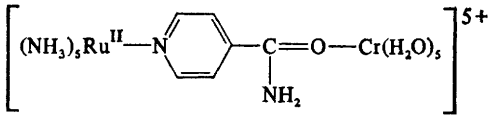
$$2Cr^{2+} + CrCH_2I^{2+} + H^+ \longrightarrow CrCH_3^{2+} + Cr^{3+} + CrI^{2+}$$
$$CrCH_3^{2+} + H^+ \longrightarrow Cr^{3+} + CH_4$$

An inner-sphere mechanism is assigned and, as with the cobaloximes, thereby implicates extraordinary dinuclear complexes.

The rate of reduction of the U^V–Cr^{III} dinuclear complex identified in the Cr^{2+} reduction of U^{VI} has been measured[31]

$$U^V\text{–}Cr^{III} + Cr^{2+} \longrightarrow U^{IV} + 2Cr^{III}$$

and found to increase only slightly with increased $[H^+]$. A much larger medium effect was observed with increased ionic strength. The slow decomposition of the dinuclear complex in the absence of excess Cr^{2+} was also studied. Reaction of Cr^{2+} with the mixed dinuclear complex (12), formed in the Cr^{2+} reduction of isonicotinamido-penta-ammineruthenium(III),[32] has also been studied. The path showing a first-order dependence on $[Cr^{2+}]$ also exhibits an inverse dependence on $[H^+]$ and suggests an inner-sphere mechanism with hydroxo-bridging.



(12)

Reduction of $[Co(NH_3)_6]^{3+}$ by $[Cr(bipy)_3]^{2+}$ and $[Cr(phen)_3]^{2+}$ has been re-investigated.[33] The two-term rate law

$$-d[Cr^{II}]/dt = k_1[Co^{III}][Cr^{II}] + k_2[Cr^{II}]$$

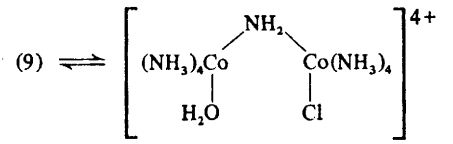
shows that the reaction of $[Cr(bipy)_3]^{2+}$ proceeds by parallel paths, *viz.* the direct outer-sphere reduction of $[Co(NH_3)_6]^{3+}$ (k_1) and dissociation to $[Cr(H_2O)_2(bipy)_2]^{2+}$ (k_2) followed by rapid reaction with $[Co(NH_3)_6]^{3+}$. The *o*-phenanthroline complex behaves in an entirely analogous way with very similar activation parameters. Reduction of $[Co(bn)_3]^{3+}$ by $[Cr(bipy)_3]^{2+}$ is catalysed by γ,γ'-bipyridyl.[34] The effect is interpreted in terms of a fast electron transfer, first to the ligand of a γ,γ'-bipyridyl-chromium(II) complex, and then to cobalt(III). The relationship between activation energy and overall free energy of reaction is found to agree with a newly developed quantum-mechanical theory.

Vanadium(II).—This reducing agent has been widely used to supplement studies involving chromium(II).

Activation parameters have been obtained[35] for the V^{2+} reduction of the complexes $[Co(NH_3)_5F]^{2+}$, $[Co(NH_3)_5Br]^{2+}$, and $[Co(NH_3)_5I]^{2+}$ for comparison with the

[31] A. Ekstrom, *Inorg. Chem.*, 1973, **12**, 2455.
[32] R. W. Craft and R. G. Gaunder, *Inorg. Chem.*, 1974, **13**, 1005.
[33] Y. Narusawa, M. Kimura, and K. Nakano, *Bull. Chem. Soc. Japan*, 1974, **47**, 2017.
[34] J. Ulstrup, *Acta Chem. Scand.*, 1973, **27**, 1067.
[35] M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1973, 2730.

existing data[36,37] for $[Co(NH_3)_5Cl]^{2+}$. Though rate constants show a systematic trend, the activation parameters indicate an inner-sphere substitution-controlled mechanism for the fluoro-complex, whereas the remainder react by an outer-sphere mechanism. Support for this distinction is found in linear free-energy correlations. Sykes and co-authors explain the results in terms of the thermodynamic stability of the precursor complexes. A greater stability for $[(H_2O)_5VFCo(NH_3)_5]^{4+}$ than for analogous complexes can be understood from hard–soft considerations and the inner-sphere mechanism for the redox step is enhanced. With the iodo-complex the rate of reduction is much greater than rates of substitution on V^{2+} and the mechanism, of necessity, is outer-sphere. Reduction of the dinuclear μ-amido-μ-bromo-bis-[tetra-amminecobalt(III)] complex[20] supplements an earlier study with the analogous μ-chloro-complex (9).[36] A first-order dependence of the rate on reactant concentrations is observed under pseudo-first-order conditions (V^{2+} in excess) and no dependence on $[H^+]$. Only a single stage is apparent with no intermediate formation of $[(NH_3)_5CoH_2O]^{3+}$. This fact is sufficient to resolve the question of the identity of the μ-chloro- and μ-bromo-complexes in solution. Hitherto, it had been thought that spontaneous cleavage of the bridge occurred when samples of (9) and the μ-bromo-analogue were dissolved in aqueous solution, and that the equilibrium strongly favoured (13). However, almost a total absence of $[(NH_3)_5CoH_2O]^{3+}$ in the V^{2+} reaction rules out (13) and, contrary to previous belief, the equilibrium must lie well



(13)

to the left. In aqueous solution the complexes therefore retain the bridged structure (9) which *X*-ray crystallography has shown they possess in the solid state. Reduction of the μ-bromo-complex is fast compared with reduction of $[(NH_3)_5CoH_2O]^{3+}$ but comparable to the rate with $[(NH_3)_5CoBr]^{2+}$. Furthermore, activation parameters are very similar and by analogy with the latter it is possible to assign an outer-sphere mechanism.

The rate of V^{2+} reduction (k_V) of a series of 23 penta-amminecobalt(III) complexes containing a variety of organic ligands has been studied[11] for comparison with the known rates for the analogous Cr^{2+} reductions (k_{Cr}). From the results for reduction of five complexes of the type $[Co(NH_3)_5py]^{3+}$ (where the mechanism is undoubtedly outer-sphere) and including the existing data for $[Co(NH_3)_6]^{3+}$ the authors find a linear free-energy relationship, $\log k_V = 1.1 \log k_{Cr} + 1.85$. The remaining complexes react with V^{2+} by the inner-sphere mechanism. However, a rather surprising result presented shows that a linear free-energy relationship exists for these complexes also, $\log k_V = 0.4 \log k_{Cr} + 0.22$. This is the first to be applied to a redox series in which the bridging ligand is varied and suggests that all the reactions

[36] R. S. Taylor, R. N. F. Thorneley, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 856.
[37] K. W. Hicks, D. L. Toppen, and R. G. Linck, *Inorg. Chem.*, 1972, **11**, 310.

proceed by the same mechanism. As the line reaches a ceiling at the expected substitution-controlled upper limit, it is concluded that the V^{2+} reactions are therefore inner-sphere. Complexes in this series, $[Co(NH_3)_5OCOR]^{2+}$, include the formate, acetate, trifluoroacetate, benzoate, and pivalate complexes and rates decrease along the series as the steric hindrance of the group R increases, in just the same way as with Cr^{2+}. With the complexes containing 2,4- and 2,5-pyridinedicarboxylate the V^{2+} reductions (unlike Cr^{2+}) are autocatalytic and the free acids catalyse the outer-sphere V^{2+} reductions of $[Co(NH_3)_6]^{3+}$ and related complexes.

The use of log–log plots does appear to have many benefits. Toppen and Linck[21] first suggested that the ratio k_{Cr}/k_V for reduction of a common oxidant by Cr^{2+} (k_{Cr}) and V^{2+} (k_V) by the outer-sphere mechanism should be constant. Since then the study of many cobalt(III) oxidants has shown this constant to have a value *ca.* 0.020.[8] Chen and Gould's study,[11] gives the following k_{Cr}/k_V values: for the complex containing pyrazole, 0.018; for pyridine, 0.016; for DMF, 0.018; for *NN*-dimethylnicotinamide, 0.021; and for imidazole, 0.017.[19] Such a constant ratio cannot occur if the slope of the log–log plot is as high as 1.1; using all the available data[7,8,11,16,38] from 17 systems gives the relationship $\log k_V = 1.02 \log k_{Cr} + 1.73$. The use of the line rather than the simple k_{Cr}/k_V ratio is to be preferred. This type of diagnostic is extremely useful and can be used to test the early literature. As it happens, a better ratio is obtained in the case of $[Co(NH_3)_6]^{3+}$ from the early literature[38] than from a more recent study[24] at higher ionic strength. Jacks and Bennett[39] quite rightly reasoned that the rate of V^{2+} reduction of $[Ru(NH_3)_6]^{3+}$ could not be slower than the Cr^{2+} rate, as the existing literature implied, since both reactions are outer-sphere. Re-investigation under pseudo-first-order conditions (V^{2+} in excess) showed a first-order dependence on reactant concentrations and independence of $[H^+]$ in the pH range 1—3, but k_V was considerably greater than previously reported. It should be noted, however, that the ratio k_{Cr}/k_V is still four times higher than the well-established ratio for cobalt(III). This may suggest a higher ratio for ruthenium(III) but more likely indicates that the Cr^{2+} rate is lower than reported.

Reductions of the μ-benzoato- and μ-*o*-chlorobenzoato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes[16] follow second-order kinetics and ratios k_{Cr}/k_V confirm an outer-sphere mechanism. The same mechanism is obviously responsible for the immeasurably fast rate of reduction of the μ-superoxo-complex (10) to the μ-peroxo-complex (11).[22] Reduction of the latter is comparable to the rate of isomerization and the complicated kinetics do not provide a clear-cut mechanism.

Iron(II).—A considerable amount of quantitative data has been published on reactions involving reduction by iron(II). Non-bridging ligand effects have been investigated using a series of nitrilotriacetato- and ethylenediamine-*NN'*-diacetato-cobalt(III) complexes,[40] the assumption being that an inner-sphere mechanism operates in the Fe^{2+} reductions through carboxylate bridging. The second-order rate constants vary over eight orders of magnitude, with the complex $[Co(nta)(H_2O)_2]$ by far the most reactive. For Fe^{2+} reduction of this complex, $\Delta H^{\ddagger}$ is considerably smaller than in any of the other reactions reported here or indeed with analogous

[38] A. McAuley, in 'Inorganic Reaction Mechanisms', ed. J. Burgess (Specialist Periodical Reports), The Chemical Society, London, 1974, Vol. 3, p. 17.
[39] C. A. Jacks and L. E. Bennett, *Inorg. Chem.*, 1974, **13**, 2035.
[40] K. Ohashi, *Bull. Chem. Soc. Japan*, 1973, **46**, 1880.

complexes, *e.g.* [Co(edta-OH)(H_2O)]. In the series [Co(nta)(am)]$^-$, the rate constants increase in the order am = glycine < β-alanine < γ-aminobutyric acid, with decreasing ΔH^+. The observation is made that rate constants increase in the same sense as the degree of strain in the amino-acid (am) chelate ring, revealing the beneficial effect of strain in the non-bridging positions in the electron-transfer process. A much lower rate of Fe^{2+} reduction of *cis*-α-[Co(edda)(NH_3)$_2$]$^+$ compared with the diaquo-complex is entirely reflected in the difference in ΔH^+ (5 kcal mol^{-1}).

Further effects of this kind have been investigated[41] by measuring rates of Fe^{2+} reduction of chlorocobalt(III) complexes for comparison with known rate constants. Relative to [$Co(NH_3)_5Cl]^{2+}$, rates for the isomeric ions [$Co(en)_2(NH_3)Cl]^{2+}$ are 1.3×10^{-2} and 4.9×10^{-2} for the *cis*- and *trans*-complexes respectively. Replacement of NH_3 ligands by en causes a decrease in rate and this is more marked in the case of the *cis*-complex where replacement has occurred *trans* to the bridging group.

Kurimura[42] has studied the reduction of [$Co(NH_3)_5X]^{2+}$ complexes (X = F^-, Cl^-, Br^-, I^-, NO_3^-, NCS^-, or N_3^-) by [Fe(edta)]$^{2-}$. The order of reactivity toward [Fe(edta)]$^{2-}$ is in the same sense as with Fe^{2+}, *viz.* X = $F^- > Cl^- > Br^- > I^-$. The reduction of the azido-complex is 5.6×10^4 times faster than that of the thiocyanato-complex and the mechanism is clearly inner-sphere. In addition, the rates for reaction of [$Co(NH_3)_5Cl]^{2+}$ with a series of Fe^{II} reductants increase in the order [Fe(hedta)]$^-$ > [Fe(hdtpa)]$^{2-}$, [Fe(edta)]$^{2-}$ > [Fe(edta)–OH]$^-$ > [Fe(cydta)]$^{2-}$ > [Fe(dtpa)]$^{3-}$. Steric, charge, and stabilization effects are discussed, of which the latter is the most important.

The same series of reductants has been used to compare rates of reduction of the complexes *cis*-[$Co(en)_2(A)Cl]^{2+}$ where A = py or PVP, the polymer poly-4-vinylpyridine.[43] Complexes with degrees of polymerization (*Pn*) of 19 and 98 and degrees of co-ordination (x) = 0.3—0.7 were used. For the series, the rates were fairly well defined by the rate law (3)

$$-d[Co^{III}]/dt = k[Co^{III}][Fe^{II}] \quad (3)$$

With Fe^{2+} as reductant, k is bigger with A = py than with A = PVP. *Pn* appears to be unimportant in this reaction, identical rates being found with *Pn* = 98 and 19 at constant x. For reduction by $[FeZ]^{m-}$ complexes, however, the rate is found to increase with increase in *Pn* and with x. These reactions were studied at pH 5. Also with $[FeZ]^{m-}$ reductants, the rate constant for reaction of the complex with A = PVP is larger than for A = py. This ratio (k_{PVP}/k_{py}) increases with reactant charge,

$$Fe^{2+} < FeSO_4 < [Fe(edta)–OH]^- < [FeZ]^{2-}$$

An inner-sphere mechanism with chloride bridging is assumed in the discussion. The electron-transfer reaction with Fe^{2+} involves two cationic species. Beneficial effects of the polymeric ligand are felt most when reactants are of opposite charge.

The rate constants for Fe^{2+} reduction of the series of complexes [$Co(RNH_2)_5Cl]^{2+}$ and [$Co(RNH_2)_5H_2O]^{3+}$ (R = H, Me, Et, Pr, Bu^n, or Bu^i) in aqueous HNO_3 have been reported.[44] The rate law (3) is obeyed and activation parameters for the series of

[41] Y. Kurimura, K. Ohashi, and S. Ohkubo, *Bull. Chem. Soc. Japan*, 1973, **46**, 3588.
[42] Y. Kurimura, *Bull. Chem. Soc. Japan*, 1973, **46**, 2093.
[43] Y. Kurimura, I. Sekine, E. Tsuchida, and Y. Karino, *Bull. Chem. Soc. Japan*, 1974, **47**, 1823.
[44] R. Mitzner and W. Depkat, *Z. phys. Chem.* (*Leipzig*), 1973, **254**, 196.

chloro-complexes are very similar with $\Delta H^{\ddagger} = 15$—16 kcal mol^{-1} and $\Delta S^{\ddagger} = -10$ to -12.5 cal deg^{-1} mol^{-1}. In the aquo-series $\Delta H^{\ddagger}$ is considerably higher (by 10 kcal mol^{-1}) and $\Delta S^{\ddagger}$ is positive. The one exception is the complex $[Co(Bu^{i}NH_2)_5H_2O]^{3+}$ which has totally different activation parameters. The most obvious explanation would involve distortion in the reactant complex structure.

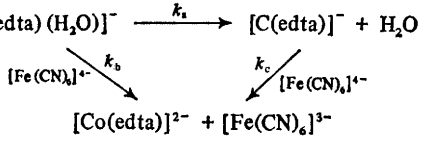
The reduction of the complexes $[Co(NH_3)X]^{2+}$ (X = F^-, Cl^-, or Br^-) by Fe^{II} in DMSO proceeds by an inner-sphere mechanism.[45] A slight increase in second-order rate constants was observed with increased ionic strength and to a lesser extent with increased $[H^+]$. In water the order of reactivity is $X = F^- > Cl^- > Br^-$; in DMSO the order is better described as $X = F^- \gg Cl^- > Br^-$. The comparison of activation parameters is particularly revealing. Those for the chloro- and bromo-complexes in DMSO are different from those for the fluoro-complex. The latter are more similar to activation parameters obtained for the series in aqueous solution, with $\Delta S^{\ddagger}$ both large and negative. To explain a much higher $\Delta H^{\ddagger}$ and a positive $\Delta S^{\ddagger}$ for the chloro- and bromo-complexes in DMSO, the authors suggest a change in co-ordination of the iron(II) in the activated complex to a tetrahedral configuration:

$$[Co(NH_3)_5Cl]^{2+} + [Fe(DMSO)_6]^{2+} \longrightarrow [(NH_3)_5Co-Cl-Fe(DMSO)_3^{4+}]^{+} + 3DMSO$$

Reduction of the ethylenediaminetetra-acetatocobaltate(III) complex by ferrocyanide is thermodynamically unfavourable,

$$[Fe(CN)_6]^{4-} + [Co(edta)]^- \longrightarrow [Fe(CN)_6]^{3-} + [Co(edta)]^{2-} \qquad (4)$$

Nevertheless, the rate constant for the reaction is of great interest and Haim and co-workers have succeeded in measuring it[46] by introducing comparable amounts of ascorbic acid into reactant solutions. This effectively scavenges ferricyanide as it forms and drives reaction (4) to completion. Ascorbic acid reduction of the cobalt(III) complex is negligible at pH 4.5 but becomes more apparent at higher pH. The rate of reaction (4) is however independent of $[H^+]$ and adequately described by the rate law (3). The same technique was applied to determine kinetic parameters for reduction of the analogous complexes $[Co(edta)Cl]^{2-}$ and $[Co(edta)H_2O]^-$. Introduction of the chloro-ligand results in a much greater rate of reduction both by $[Fe(CN)_6]^{4-}$ and by ascorbic acid. At high pH the reaction with ascorbic acid was prohibitively fast and measurements on the main reaction were restricted to pH 4.5. The rate of $[Fe(CN)_6]^{4-}$ reduction of the aquo-complex is comparable to its rate of ring closure and the mechanism shown in the Scheme applies.



Scheme

Independent measurements were made of the rate constant k_a, so enabling rate constants for the two redox reactions to be calculated. Good agreement was obtained

[45] B. A. Matthews and D. W. Watts, *Inorg. Chim. Acta*, 1974, **11**, 127.
[46] L. Rosenhein, D. Speiser, and A. Haim, *Inorg. Chem.*, 1974, **13**, 1571.

with the already determined $[Co(edta)]^-$–$[Fe(CN)_6]^{4-}$ rate constant, k_c. The rate constant k_b is much larger than k_c. The chloro-complex is twice as reactive toward $[Fe(CN)_6]^{4-}$ as the aquo-complex at 25 °C. Results from this study have considerable bearing on the mechanism of reaction (4) in its thermodynamically more favourable sense, *i.e.* in the reverse direction, and are discussed under iron(III) oxidations.

A detailed study[47] has been made of the Fe^{2+} reduction of nitrilotriacetatopentaamminecobalt(III), reported previously[48] to proceed *via* a long-lived dinuclear complex. The dependence on $[Fe^{II}]$ is first order at pH 2.3 but at higher pH the rate becomes independent of $[Fe^{II}]$. In the pH range 1.2—2.2 a plot of $\log\{k_{obs}(1 + [H^+]/K_H[Fe^{II}]^{-1})\}$ against pH is linear and reflects the effect of the equilibrium

$$[(NH_3)_5CoH_2(nta)]^{2+} \rightleftharpoons [(NH_3)_5CoH(nta)]^+ + H^+ \qquad K_H$$

No dependence on the concentration of the glycine buffer mixture was observed. The equilibrium

$$[(NH_3)_5CoH(nta)]^+ + Fe^{2+} \rightleftharpoons [(NH_3)_5Co(nta)Fe^{II}]^{2+} + H^+ \qquad K_{Fe}$$

in which the dinuclear complex becomes the predominant cobalt(III) species in the higher pH and $[Fe^{2+}]$ ranges, accounts for the observed behaviour. Observed rate constants k_{obs} are of the form

$$k_{obs} = k_1K_2[Fe^{II}]/(1 + K_2[Fe^{II}])$$

where Fe^{II} denotes total iron concentration and K_2 is a function of K_{Fe}, K_H, and $[H^+]$. The rate of reaction increases with pH although the linear dependence is lost at pH > 2.2 with a deviation toward lower rates. A further protonation equilibrium is introduced into the rate expression as a result. Plots of k_{obs}^{-1} *vs.* $[Fe^{II}]^{-1}$ yielded a first-order rate constant. Non-reducing metal ions, *e.g.*, the Co^{2+} and Fe^{3+} produced in the reaction, inhibit the rate by complexing with the nta ligand. Stability constants for complexes of this kind and with Ca^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} were determined. The authors argue that the first-order rate constant represents an intramolecular electron-transfer reaction, and likely structures of the precursor complex are discussed.

Interest in the redox reactions of cytochrome *c* continues. Gray *et al.* have reported[49] that reduction by $[Fe(edta)]^{2-}$ shows a first-order dependence on ferricytochrome and reductant concentrations. An outer-sphere mechanism is suggested by the activation parameters which are comparable to outer-sphere reductions of cytochrome *c* and simple redox reactions of iron complexes, *e.g.* $[Fe(CN)_6]^{3-/4-}$ exchange. The rate data suggest reduction of two interconverting forms of the protein, native and high-pH, and this is the first observation of a direct reduction path for the latter. Activation parameters obtained for the outer-sphere Fe^{2+} reductions of polypyridine complexes of Ru^{III} [50] and Fe^{III} [51] suggest an activation process which differs in detail from the Marcus model. In contrast excellent agreement with the theory was found[52] in the reaction of ferrocytochrome *c*, from horse heart and *Candida Krusei*, with $[Co(phen)_3]^{3+}$. The second-order rate law showed no significant dependence on $[H^+]$

[47] R. D. Cannon and J. Gardiner, *Inorg. Chem.*, 1974, **13**, 390.
[48] R. D. Cannon and J. Gardiner, *J. Amer. Chem. Soc.*, 1970, **92**, 3800.
[49] H. L. Hodges, R. A. Holwerda, and H. B. Gray, *J. Amer. Chem. Soc.*, 1974, **96**, 3132.
[50] J. N. Braddock and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 3158.
[51] J. L. Cramer and T. J. Meyer, *Inorg. Chem.*, 1974, **13**, 1250.
[52] J. V. McArdle, H. B. Gray, C. Creutz, and N. Sutin, *J. Amer. Chem. Soc.*, 1974, **96**, 5737.

in the range $6 \leqslant pH \leqslant 9$. Results show the mechanism to be the same as in the protein self-exchange reaction with outer-sphere electron transfer from the exposed heme edge.

Lanthanide(II) Ions.—Europium(II) reduction of a series of 53 penta-ammine-cobalt(III) complexes containing organic ligands has been studied[12] for comparison with rates of reduction by Cr^{2+}. Rates for Eu^{2+} span a range of almost 10^7 and reactivity patterns are similar enough to Cr^{2+} to suggest that the inner-sphere mechanism is important in the redox chemistry of Eu^{2+}. In some cases an $[H^+]$-dependence with Cr^{2+} but not Eu^{2+} was observed, but in no case was an $[H^+]$-dependence found for Eu^{2+} but not for Cr^{2+}. For reduction of complexes containing simple monocarboxylate ligands, $[(NH_3)_5CoO_2CR]^{2+}$ relationships between $\log k_{Eu}$ and Taft's steric-substituent parameter (E_S) and between rate constants for $Eu^{2+}(k_{Eu})$ and $Cr^{2+}(k_{Cr})$ reduction of a common oxidant, $\log k_{Eu} = 0.67 \log k_{Cr} + 0.54$, provide good evidence for the inner-sphere mechanism. Results also suggest that the conformational aspects of adjacent attack discussed for Cr^{2+} are the same for Eu^{2+}.

The rate of Eu^{2+} reduction of U^{VI},

$$U^{VI} + Eu^{II} \longrightarrow U^{V} + Eu^{III}$$

is first order in each reactant and increases slightly with $[H^+]$ in the range 0.05—1.6 mol l^{-1}.[53] The rate is unaffected by the addition of 2×10^{-2} M-Cl^- but is catalysed by similar concentrations of SO_4^{2-}, reflecting the stronger complexing in UO_2SO_4 as opposed to UO_2Cl^+. Activation parameters were found to be very similar to those for Cr^{2+} reduction of the same oxidant, with low $\Delta H^{\neq}$. The lability of Eu^{III} militates against detection of primary products and the inner-sphere mechanism cannot be demonstrated on this basis.

Table 1 *Rate constants and thermodynamic parameters for reduction of metal complexes by chromium*(II), *vanadium*(II), *iron*(II), *and europium*(II). *Second-order rate constants are quoted in* 1 mol^{-1} s^{-1} *at* $T = 25$ °C *unless stated. The units of* $\Delta H^{\neq}$ *and* $\Delta S^{\neq}$ *are* kcal mol^{-1} *and* cal deg^{-1} mol^{-1} *respectively*

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	*Ref.*
Reductant = chromium(II)					
$[(NH_3)_5Co(o\text{-formylbenzoato})]^{2+}$	93	1.2	—	—	3
$[(NH_3)_5Co(p\text{-formylcinnamato})]^{2+}$	2.6×10^2	1.2	—	—	3
$[(NH_3)_5Co(p\text{-formylcinnamato})]^{3+}$	1.8×10^3	1.2	—	—	3[a,b]
$[(NH_3)_5Co(\beta\text{-styrylacrylato})]^{2+}$	*ca.* 1.73	1.2	—	—	3
$[(NH_3)_5Co(\beta\text{-styrylacrylato})]^{3+}$	0.49	1.2	—	—	3[a]
$[(NH_3)_5Co(\text{phenono})]^{2+}$	12.7	1.2	—	—	3[c]
$[(NH_3)_5Co(4\text{-benzoylpyridino})]^{3+}$	4.7×10^4	1.2	—	—	3
$[(NH_3)_5Co(2,3\text{-dicarboxylato-pyridino})]^{2+}$	1.9×10^3	1.2	—	—	3
$[(NH_3)_5Co(2,3\text{-dicarboxylato-pyridino})]^{2+}$	6.7×10^2	1.2	—	—	3[a,d]
$[(NH_3)_5Co(2,4\text{-dicarboxylato-pyridino})]^{2+}$	7.3×10^4	1.2	—	—	3

[a] Acid-dependent pathway. [b] Units are l^2 mol^{-2} s^{-1}. [c] Ligand is 2-carboxy-4′-bromobenzophenone. [d] Units are s^{-1}.

[53] E. Ekstrom and D. A. Johnson, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2557.

Table 1 (*continued*)

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[(NH_3)_5Co(2,4\text{-dicarboxylato-pyridino})]^{2+}$	2.6×10^{4}	1.2	—	—	3[a,d]
$[(NH_3)_5Co(2,5\text{-dicarboxylato-pyridino})]^{2+}$	2.0×10^{3}	1.2	—	—	3
$[(NH_3)_5Co(2,5\text{-dicarboxylato-pyridino})]^{2+}$	1.3×10^{3}	1.2	—	—	3[a,d]
$[(NH_3)_5Co(2,6\text{-dicarboxylato-pyridino})]^{2+}$	1.5×10^{4}	1.2	—	—	3[a,d]
$[(NH_3)_5Co(6\text{-uracilcarboxylato})]^{2+}$	1.01	1.2	—	—	3
$[(NH_3)_5Co(5\text{-uracilcarboxylato})]^{2+}$	1.1×10^{3}	1.2	—	—	3
$[(NH_3)_5Co(2\text{-carboxamido-pyridino})]^{2+}$	1.31×10^{5}	1.0	—	—	6[a]
$[(NH_3)_5Co(3\text{-carboxamido-pyridino})]^{3+}$	1.7×10^{-2}	1.0	—	—	6
$[(NH_3)_5Co(4\text{-carboxamido-pyridino})]^{3+}$	7.8×10^{-2}	1.0	—	—	6
$[(NH_3)_5CoO_2CCH_2F]^{2+}$	0.118	1.0	—	—	12
$[(NH_3)_5CoO_2CCHF_2]^{2+}$	0.113	1.0	—	—	12
$[(NH_3)_5CoO_2CCF_3]^{2+}$	3.9×10^{-2}	1.0	—	—	12
$[(NH_3)_5CoO_2CCHEt_2]^{2+}$	4.7×10^{-2}	1.0	—	—	12
$[(NH_3)_5CoO_2CCHPh_2]^{2+}$	5.8×10^{-2}	1.0	—	—	12
$[(NH_3)_5CoO_2CCHMePh]^{2+}$	5.7×10^{-2}	1.0	—	—	12
$[(NH_3)_5CoO_2C(\text{cyclopentane})]^{2+}$	9.3×10^{-2}	1.0	—	—	12
$[(NH_3)_5CoO_2CCHPr_2]^{2+}$	3.6×10^{-2}	1.0	—	—	12
$[(NH_3)_5CoO_2CCH_2(C_6H_{11})]^{2+}$	0.12	1.0	—	—	12
$[(NH_3)_5Co(o\text{-benzylglycolato})]^{2+}$	0.21	1.0	—	—	12
$[(NH_3)_5Co(\text{oxydiacetato})]^{2+}$	0.22	1.0	—	—	12
$[(NH_3)_5Co(\text{oxydiacetato})]^{2+}$	5.8×10^{-3}	1.0	—	—	12[a,d]
$[(NH_3)_5CoNHCOMe]^{2+}$	5.23×10^{-2}	1.0	14.5	−16	15[a]
$[(NH_3)_3Co\cdot\mu(OH,OH,PhCO_2)\cdot Co(NH_3)_3]^{3+}$	1.5×10^{-3}	1.0	9.46	−40.3	16[e]
$[(NH_3)_3Co\cdot\mu(OH,OH,C_6H_4ClCO_2)\cdot Co(NH_3)_3]^{3+}$	1.6×10^{-3}	1.0	—	—	16
$[(NH_3)_5Co(\text{imidazole})]^{3+}$	3.5×10^{-4}	1.1	—	—	19
$[(NH_3)_4Co\cdot\mu(NH_2,Cl)\cdot Co(NH_3)_4]^{4+}$	11.3	2.0	3.9	−40.6	20
$[(NH_3)_4Co\cdot\mu(NH_2,Br)\cdot Co(NH_3)_4]^{4+}$	2.16×10^{2}	2.0	4.1	−34.2	20
$[(NH_3)_5Co(H_2O)]^{3+}$	2.52	2.0	11.2	−19.3	20[a,d]
$[(en)_2Co\cdot\mu(NH_2,O_2)\cdot Co(en)_2]^{4+}$	$>10^{5}$	2.0	—	—	22
$[(en)_2Co\cdot\mu(NH_2,O_2)\cdot Co(en)_2]^{3+}$	2.1×10^{3}	2.0	7.75	−17.5	22
$[(en)_2Co\cdot\mu(NH_2,O_2H)\cdot Co(en)_2]^{4+}$	16	2.0	5.2	−36	22
$[(NH_3)(en)_2Co\cdot OH\cdot Cr(H_2O)_5]^{5+}$	1.09×10^{-3}	2.0	—	—	22[f]
$[Co(NH_3)_6]^{3+}$	1.0×10^{-3}	1.0	—	—	24
$[Co(NH_3)_6]^{3+}$	1.1×10^{-2}	1.0	—	—	24[b,g]
$[Co(NH_3)_6]^{3+}$	0.73	1.0	—	—	24[b,h]
$[Co(en)_3]^{3+}$	3.4×10^{-4}	1.0	—	—	24
$[Co(en)_3]^{3+}$	1.5×10^{-3}	1.0	—	—	24[b,g]
$[Co(en)_3]^{3+}$	0.32	1.0	—	—	24[b,h]
$[Co(phen)_3]^{3+}$	30	1.0	—	—	24
$[Co(phen)_3]^{3+}$	1.7×10^{2}	1.0	—	—	24[b,g]
$[Co(phen)_3]^{3+}$	2.2×10^{5}	1.0	—	—	24[b,h]
$[Co(TMpyP)(H_2O)_2]$	16	0.5	—	—	25

[e] T = 30 °C. [f] T = 35 °C. [g] Reductant is $CrCl^{+}$. [h] Reductant is $CrNCS^{+}$.

Table 1 (*continued*)

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(TMpyP)(H_2O)OH]^-$	1.3×10^6	0.5	—	—	25[a]
$[Fe(TpyP)(H_2O)_2]$	2.7×10^2	—	—	—	25
$[Fe(TpyP)(H_2O)OH]^-$	8	—	—	—	25[a,d]
$[MeCo(Hdmg)_2H_2O]$	14.5	1.0	—	—	26
$[EtCo(Hdmg)_2H_2O]$	1.3×10^{-2}	1.0	—	—	26
$[PhCH_2Co(Hdmg)_2H_2O]$	5.0	1.0	—	—	26
$[MeCo(Hdmg)(H_2dmg)H_2O]^+$	23	1.0	—	—	26[a]
$[EtCo(Hdmg)(H_2dmg)H_2O]^+$	1.4×10^{-2}	1.0	—	—	26[a]
$[Pr^nCo(Hdmg)(H_2dmg)H_2O]^+$	1.38×10^{-3}	1.0	—	—	26[a]
$[Me_2CHCo(Hdmg)(H_2dmg)H_2O]^+$	1.08×10^{-4}	1.0	—	—	26[a]
$[Me_3CCH_2Co(Hdmg)(H_2dmg)H_2O]^+$	6.1×10^{-5}	1.0	—	—	26[a]
$[PhCH_2Co(Hdmg)(H_2dmg)H_2O]^+$	7.3	1.0	—	—	26[a]
Methylcobalamin	3.6×10^2	*ca.* 1.0	3.8	−34.4	27
Ethylcobalamin	4.4	*ca.* 1.0	11.1	−18.4	27
Aquocobalamin	14.3	*ca.* 1.0	—	—	27
$[Co(Hdmg)_2(NH_3)_2]^+$	40	—	—	—	28
$[Co(Hdmg)(H_2dmg)(NH_3)_2]^{2+}$	7.8×10^2	—	—	—	28[a,b]
$[Cr(H_2O)_5(CHI_2)]^{2+}$	11.2	1.0	6.5	−32	29
$[Cr(H_2O)_5(CH_2I)]^{2+}$	2.9×10^{-2}	1.0	7.7	−39	30
U^{V}–Cr^{III}	5.4×10^2	2.0	3.2	−35.2	31[i]
$[(NH_3)_5RuNC_5H_4CONH_2Cr^{III}(H_2O)_5]^{5+}$	4.74×10^{-4}	1.0	18.1	−13.1	32[j]
$[Co(NH_3)_6]^{3+}$	1.8×10^2	0.11	7.5	−23	33[k]
$[Co(NH_3)_6]^{3+}$	3.1×10^2	0.2	8.2	−20	33[l]
$[Co(bn)_3]^{3+}$	9.8	—	12.8	−11.3	34[k]
$[Co(bn)_3]^{3+}$	2.06×10^2	—	7.8	−36	34[m]
Reductant = *vanadium*(II)					
$[(NH_3)_4Co\cdot\mu(NH_2,Br)\cdot Co(NH_3)_4]^{4+}$	33	2.0	6.7	−29.0	20
$[(NH_3)_5CoF)]^{2+}$	3.95	2.0	11.1	−18.5	35
$[(NH_3)_5CoCl]^{2+}$	10.2	2.0	7.5	−28.8	36
$[(NH_3)_5CoCl]^{2+}$	7.6	1.0	7.4	−29.5	37
$[(NH_3)_5CoBr]^{2+}$	30	2.0	7.2	−27.6	35
$[(NH_3)_5CoI]^{2+}$	1.27×10^2	2.0	7.3	−24.6	35
$[(NH_3)_5Co(imidazole)]^{3+}$	2×10^{-2}	1.0	—	—	11
$[(NH_3)_5Co(pyrazole)]^{3+}$	0.12	1.0	—	—	11
$[(NH_3)_5Co(py)]^{3+}$	0.24	1.0	—	—	11
$[(NH_3)_5Co(DMF)]^{3+}$	0.35	1.0	—	—	11
$[(NH_3)_5Co(NN\text{-dimethylnicotinamide})]^{3+}$	1.38	1.0	—	—	11
$[(NH_3)_5CoO_2CCEt_3]^{2+}$	0.127	1.0	—	—	11
$[(NH_3)_5CoO_2CCMe_3]^{2+}$	0.22	1.0	—	—	11
$[(NH_3)_5CoO_2CCF_3]^{2+}$	0.86	1.0	—	—	11
$[(NH_3)_5CoO_2CPh]^{2+}$	0.59	1.0	—	—	11
$[(NH_3)_5Co(salicylato)]^{2+}$	1.15	1.0	—	—	11
$[(NH_3)_5Co(biphthalato)]^{2+}$	1.2	1.0	—	—	11
$[(NH_3)_5Co(p\text{-nitrobenzoato})]^{2+}$	0.5	1.0	—	—	11
$[(NH_3)_5Co(2\text{-pyridinecarboxylato})]^{3+}$	0.94	1.0	—	—	11

[i] T = 20 °C. [j] Activation parameters determined at I = 0.4 mol l^{-1}. [k] Reductant is $[Cr(bipy)_3]^{2+}$. [l] Reductant is $[Cr(phen)_3]^{2+}$. [m] Reductant is γ,γ'-bipyridylchromium(II) complex.

Table 1 (*contiuued*)

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[(NH_3)_5Co(4\text{-pyridinecarboxylato})]^{3+}$	1.01	1.0	—	—	11
$[(NH_3)_5Co(2,3\text{-pyridinedicarboxylato})]^{3+}$	2.7	1.0	—	—	11
$[(NH_3)_5Co(2,3\text{-pyridinedicarboxylato})]^{2+}$	11.2	1.0	—	—	11
$[(NH_3)_5Co(p\text{-formylbenzoato})]^{2+}$	2.21	4.0	—	—	11
$[(NH_3)_5Co(p\text{-formylbenzoato})]^{3+}$	0.66	4.0	—	—	11[a,b]
$[(NH_3)_5Co(o\text{-formylbenzoato})]^{2+}$	1.24	1.0	—	—	11
$[(NH_3)_5CoO_2CH]^{2+}$	3.5	1.0	—	—	11
$[(NH_3)_5Co(\text{glycolato})]^{2+}$	8.2	1.0	—	—	11
$[(NH_3)_5Co(\text{maleato})]^{2+}$	5.5	1.0	—	—	11
$[(NH_3)_5Co(\text{pyruvato})]^{2+}$	10.5	1.0	—	—	11
$[(NH_3)_5Co(4\text{-benzoylpyridine})]^{3+}$	4.5	1.0	—	—	11
$[(NH_3)_3Co\cdot\mu(OH,OH,\text{-}PhCO_2)\cdot Co(NH_3)_3]^{3+}$	6.74×10^{-2}	1.0	—	—	16[e]
$[(NH_3)_3Co\cdot\mu(OH,OH,\text{-}C_6H_4ClCO_2)\cdot Co(NH_3)_3]^{3+}$	7.9×10^{-2}	1.0	—	—	16
$[(en)_2Co\cdot\mu(NH_2,O_2)\cdot Co(en)_2]^{4+}$	$>2.5\times10^{5}$	2.0	—	—	22
$[(en)_2Co\cdot\mu(NH_2,O_2)\cdot Co(en)_2]^{3+}$	7.7	2.0	—	—	22
$[Co(NH_3)_6]^{3+}$	1×10^{-2}	1.0	—	—	24
$[Co(NH_3)_6]^{3+}$	2.4×10^{-2}	1.0	—	—	24[b,n]
$[Co(NH_3)_6]^{3+}$	24	1.0	—	—	24[b,o]
$[Co(en)_3]^{3+}$	7.2×10^{-4}	1.0	—	—	24
$[Co(en)_3]^{3+}$	1.9×10^{-3}	1.0	—	—	24[b,n]
$[Co(en)_3]^{3+}$	2.4	1.0	—	—	24[b,o]
$[Co(phen)_3]^{3+}$	3.8×10^{3}	1.0	—	—	24
$[Co(phen)_3]^{3+}$	6×10^{3}	1.0	—	—	24[b,n]
$[Co(phen)_3]^{3+}$	6.3×10^{7}	1.0	—	—	24[b,o]
$[Ru(NH_3)_6]^{3+}$	1.26×10^{3}	0.1	0.6	−42	39
Reductant = *iron*(II)					
$[Co(nta)(H_2O)_2]$	1.44	1.0	7.1	−33.9	40
$[Co(nta)(H_2O)(NH_2Et)]$	9.78×10^{-3}	1.0	11.6	−28.8	40
$[Co(nta)(en)]$	4.98×10^{-5}	1.0	15.9	−24.8	40
$[Co(nta)(gly)]^{-}$	4.65×10^{-4}	1.0	13.7	−27.9	40
$[Co(nta)(\beta\text{-ala})]^{-}$	2.51×10^{-3}	1.0	12.3	−29.0	40
$[Co(nta)(\gamma\text{-aminobut})]^{-}$	1.13×10^{-2}	1.0	11.5	−28.7	40
cis-a-$[Co(edda)(H_2O)_2]^{+}$	2.94×10^{-3}	2.45	13.2	−25.8	40
cis-a-$[Co(edda)(NH_3)_2]^{+}$	1.2×10^{-6}	2.45	18.5	−23.5	40
cis-a-$[Co(edda)(en)]^{+}$	1.65×10^{-8}	2.45	24.1	−12.9	40
cis-$[Co(pn)_2(NH_3)Cl]^{2+}$	2.5×10^{-5}	1.0	—	—	41
$[Co(dien)(pn)Cl]^{2+}$	0.8×10^{-5}	1.0	—	—	41
$[Co(dien)(tn)Cl]^{2+}$	1.4×10^{-5}	1.0	—	—	41
cis-$[Co(trien)(NH_3)Cl]^{2+}$	2.5×10^{-6}	1.0	—	—	41
trans-$[Co(en)(NH_3)_2Cl_2]^{+}$	0.36	1.0	—	—	41
trans-$[Co(pn)_2Cl_2]^{+}$	2.6×10^{-2}	1.0	—	—	41
$[Co(NH_3)_5F]^{2+}$	6×10^{3}	0.5	—	—	42[p]
$[Co(NH_3)_5Cl]^{2+}$	4.7×10^{3}	0.5	—	—	42[p]
$[Co(NH_3)_5Br]^{2+}$	3.8×10^{3}	0.5	—	—	42[p]
$[Co(NH_3)_5I]^{2+}$	3.4×10^{3}	0.5	—	—	42[p]
$[Co(NH_3)_5NCS]^{2+}$	0.13	0.5	—	—	42[p]
$[Co(NH_3)_5N_3]^{2+}$	7.3×10^{3}	0.5	—	—	42[p]

[n] Reductant is VCl^{+}. [o] Reductant is $VNCS^{+}$. [p] Reductant is $[Fe(edta)]^{2-}$.

Table 1 (*continued*)

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(NH_3)_5NO]^{2+}$	*ca.* 50	0.5	—	—	42[p]
$[Co(NH_3)_5Cl]^{2+}$	3.5×10^{4}	0.5	—	—	42[q]
$[Co(NH_3)_5Cl]^{2+}$	4.8×10^{3}	0.5	—	—	42[r]
$[Co(NH_3)_5Cl]^{2+}$	4.4×10^{3}	0.5	—	—	42[s]
$[Co(NH_3)_5Cl]^{2+}$	2.9×10^{3}	0.5	—	—	42[t]
$[Co(NH_3)_5Cl]^{2+}$	*ca.* 100	0.5	—	—	42[u]
$[Co(en)_2(py)Cl]^{2+}$	1.1×10^{-3}	0.12	—	—	43[v]
$[Co(en)_2(PVP)Cl]^{2+}$	3.7×10^{-4}	0.12	—	—	43[v]
$[Co(en)_2(py)Cl]^{2+}$	1.3×10^{4}	0.02	—	—	43[r]
$[Co(en)_2(PVP)Cl]^{2+}$	2.8×10^{5}	0.02	—	—	43[r]
$[Co(en)_2(py)Cl]^{2+}$	2.4×10^{4}	0.02	—	—	43[s]
$[Co(en)_2(PVP)Cl]^{2+}$	8.8×10^{4}	0.02	—	—	43[s]
$[Co(en)_2(py)Cl]^{2+}$	1.4×10^{4}	0.02	—	—	43[p]
$[Co(en)_2(PVP)Cl]^{2+}$	2.8×10^{5}	0.02	—	—	43[p]
$[Co(en)_2(py)Cl]^{2+}$	1.2×10^{4}	0.02	—	—	43[t]
$[Co(en)_2(PVP)Cl]^{2+}$	1.9×10^{5}	0.02	—	—	43[t]
$[Co(NH_3)_5Cl]^{2+}$	4.9×10^{-3}	—	16.0	−10.1	44[t]
$[Co(MeNH_2)_5Cl]^{2+}$	2.8×10^{-2}	—	16.0	−11	44[t]
$[Co(EtNH_2)_5Cl]^{2+}$	4.9×10^{-2}	—	15.3	−12.5	44[t]
$[Co(PrNH_2)_5Cl]^{2+}$	5.8×10^{-2}	—	15.7	−10.6	44[t]
$[Co(BuNH_2)_5Cl]^{2+}$	4.5×10^{-2}	—	15.3	−12.5	44[t]
$[Co(Bu^{i}NH_2)_5Cl]^{2+}$	0.117	—	15.1	−10.9	44[t]
$[Co(NH_3)_5H_2O]^{3+}$	6.3×10^{-4}	—	26.7	22.4	44[t]
$[Co(MeNH_2)_5H_2O]^{3+}$	9.7×10^{-3}	—	26	21	44[t]
$[Co(EtNH_2)_5H_2O]^{3+}$	1.42×10^{-2}	—	26.1	21.9	44[t]
$[Co(PrNH_2)_5H_2O]^{3+}$	2.85×10^{-2}	—	25	19.7	44[t]
$[Co(BuNH_2)_5H_2O]^{3+}$	1.65×10^{-2}	—	25.7	21.1	44[t]
$[Co(Bu^{i}NH_2)_5H_2O]^{3+}$	0.141	—	18.3	0.16	44[t]
$[Co(NH_3)_5F]^{2+}$	4.73	0.34	8.8	−26	45[w]
$[Co(NH_3)_5Cl]^{2+}$	9.72×10^{-3}	0.34	21.2	3	45[w]
$[Co(NH_3)_5Br]^{2+}$	2.51×10^{-3}	0.34	21.7	2	45[w]
$[Co(edta)]^{-}$	0.21	0.59	—	—	46[x]
$[Co(edta)H_2O]^{-}$	3.4	0.59	—	—	46[x]
$[Co(edta)Cl]^{2-}$	7.0	0.59	—	—	46[x]
$[Co(NH_3)_5(nta)]$	0.115	1.0	18.7	0	47[a]
Ferricytochrome *c*	2.57×10^{4}	0.1	6.0	−18	49[p]
$[Ru(terpy)_2]^{3+}$	7.23×10^{5}	1.0	−2.8	−41	50
$[Ru(phen)_3]^{3+}$	8.04×10^{5}	1.0	−1.35	−36	50
$[Ru(bipy)_3]^{3+}$	6.41×10^{5}	1.0	−0.3	−33	50
$[Ru(bipy)_2(py)_2]^{3+}$	6.38×10^{5}	1.0	0.3	−31	50
$[Fe(terpy)_2]^{3+}$	8.42	*ca.* 0.3	−0.6	−38	51
$[Fe(bipy)_3]^{3+}$	2.69	*ca.* 0.3	−0.8	−41	51
$[Co(phen)_3]^{3+}$	1.5×10^{3}	0.1	11.3	−6.2	52[y]
$[Co(phen)_3]^{3+}$	2.72×10^{3}	0.1	—	—	52[z]
Reductant = europium(II)					
$[(NH_3)_5CoO_2CH]^{2+}$	15.4	1.0	—	—	12
$[(NH_3)_5CoO_2CCH_3]^{2+}$	2.36	4.0	—	—	12
$[(NH_3)_5CoO_2CCH_2F]^{2+}$	3.8	1.0	—	—	12
$[(NH_3)_5CoO_2CCHF_2]^{2+}$	1.88	1.0	—	—	12

[q] Reductant is $[Fe(hedta)]^{-}$. [r] Reductant is $[Fe(hdtpa)]^{2-}$. [s] Reductant is $[Fe(edta)OH]^{-}$. [t] Reductant is $[Fe(cydta)]^{2-}$. [u] Reductant is $[Fe(dtpa)]^{3-}$. [v] T = 40 °C. [w] In DMSO, T = 25.8 °C. [x] Reductant is $[Fe(CN)_6]^{4-}$. [y] Reductant is horse-heart ferrocytochrome *c*. [z] Reductant is *Candida krusei* ferrocytochrome *c*.

Table 1 (*continued*)

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[(NH_3)_5CoO_2CCF_3]^{2+}$	1.23	1.0	—	—	12
$[(NH_3)_5CoO_2CCCl_3]^{2+}$	0.82	1.0	—	—	12
$[(NH_3)_5CoO_2CEt]^{2+}$	1.19	1.0	—	—	12
$[(NH_3)_5CoO_2CCMe_3]^{2+}$	0.163	1.0	—	—	12
$[(NH_3)_5CoO_2CCEt_3]^{2+}$	0.068	1.0	—	—	12
$[(NH_3)_5CoO_2CCHEt_2]^{2+}$	0.34	1.0	—	—	12
$[(NH_3)_5CoO_2CCHPh_2]^{2+}$	0.5	1.0	—	—	12
$[(NH_3)_5CoO_2CCHMePh]^{2+}$	0.53	1.0	—	—	12
$[(NH_3)_5CoO_2CPh]^{2+}$	0.84	1.0	—	—	12
$[(NH_3)_5CoO_2C$(cyclopentane)$]^{2+}$	0.74	1.0	—	—	12
$[(NH_3)_5CoO_2C$(cyclopropane)$]^{2+}$	1.1	1.0	—	—	12
$[(NH_3)_5CoO_2CCHPr^n_2]^{2+}$	0.29	1.0	—	—	12
$[(NH_3)_5CoO_2CCH_2(C_6H_{11})]^{2+}$	0.8	1.0	—	—	12
$[(NH_3)_5Co$(glycolato)$]^{2+}$	88	1.0	—	—	12
$[(NH_3)_5Co$(lactato)$]^{2+}$	91	1.0	—	—	12
$[(NH_3)_5Co$(*o*-benzylglycolato)$]^{2+}$	11	1.0	—	—	12
$[(NH_3)_5Co$(oxydiacetato)$]^{2+}$	4.9×10^2	1.0	—	—	12
$[(NH_3)_5Co$(pyruvato)$]^{2+}$	1.15×10^3	1.0	—	—	12
$[(NH_3)_5Co$(benzoylformato)$]^{2+}$	3.7×10^4	1.0	—	—	12
$[(NH_3)_5Co$(furoato)$]^{2+}$	3.5	1.0	—	—	12
$[(NH_3)_5Co$(acetoxyacetato)$]^{2+}$	1.43	1.0	—	—	12
$[(NH_3)_5Co$(*S*-benzylthioglycolato)$]^{2+}$	1.84	1.0	—	—	12
$[(NH_3)_5Co$(*Se*-benzylselenoglycolato)$]^{2+}$	1.68	1.0	—	—	12
$[(NH_3)_5Co$(β-benzylmercaptopropionato)$]^{2+}$	1.05	1.0	—	—	12
$[(NH_3)_5Co$(malonato)$]^{2+}$	17	1.0	—	—	12
$[(NH_3)_5Co$(1,1-cyclobutanedicarboxylato)$]^{2+}$	2.2	1.0	—	—	12
$[(NH_3)_5Co$(succinato)$]^{2+}$	2.18	1.0	—	—	12
$[(NH_3)_5Co$(glutarato)$]^{2+}$	1.29	1.0	—	—	12
$[(NH_3)_5Co$(maleato)$]^{2+}$	4.5	1.0	—	—	12
$[(NH_3)_5Co$(*p*-hydroxybenzoato)$]^{2+}$	1.04	1.0	—	—	12
$[(NH_3)_5Co$(salicylato)$]^{2+}$	0.84	1.0	—	—	12
$[(NH_3)_5Co$(*o*-acetylbenzoato)$]^{2+}$	0.99	1.0	—	—	12
$[(NH_3)_5Co$(*o*-thiomethylbenzoato)$]^{2+}$	1.10	1.0	—	—	12
$[(NH_3)_5Co$(*o*-formylbenzoato)$]^{2+}$	1.8	1.0	—	—	12
$[(NH_3)_5Co$(biphthalato)$]^{2+}$	1.6	1.0	—	—	12
$[(NH_3)_5Co$(terephthalato)$]^{2+}$	1.15	1.0	—	—	12
$[(NH_3)_5Co$(*p*-hydroxycinnamato)$]^{2+}$	1.97	1.0	—	—	12
$[(NH_3)_5Co$(*o*-hydroxycinnamato)$]^{2+}$	1.95	1.0	—	—	12
$[(NH_3)_5Co$(furanacrylato)$]^{2+}$	0.84	1.0	—	—	12
$[(NH_3)_5Co$(3-pyridinecarboxylato)$]^{3+}$	1.34	1.0	—	—	12
$[(NH_3)_5Co$(*N*-methyl-2-pyridinecarboxylato)$]^{2+}$	1.06	1.0	—	—	12
$[(NH_3)_5Co$(2,6-pyridinedicarboxylato)$]^{2+}$	3.5×10^3	1.0	—	—	12
$[(NH_3)_5Co$(pyrazinecarboxylato)$]^{2+}$	3.6×10^3	1.0	—	—	12

Table 1 (*continued*)

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[(NH_3)_5CoO_2HCMe]^{3+}$	0.25	4.0	—	—	12[a]
$[(NH_3)_5Co(p\text{-formylbenzoato})]^{2+}$	1.2	4.0	—	—	12
$[(NH_3)_5Co(p\text{-formylbenzoato})]^{3+}$	0.18	4.0	—	—	12[a,b]
$[(NH_3)_5Co(p\text{-formylcinnamato})]^{2+}$	4.2	1.0	—	—	12
$[(NH_3)_5Co(p\text{-formylcinnamato})]^{3+}$	3.0	1.0	—	—	12[a,b]
$[(NH_3)_5Co(\text{mucochlorato})]^{2+}$	80	1.0	—	—	12
$[(NH_3)_5Co(\text{mucochlorato})]^{3+}$	6.1×10^{2}	1.0	—	—	12[a,b]
U^{VI}	1.47×10^{4}	2.0	1.5	34.4	53
UO_2SO_4	3.9×10^{5}	2.0	—	—	53

2 Oxidizing Agents

Cerium(IV).—An attempt has been made[54] to define the mechanism of Ce^{IV} oxidation of Sn^{II} in the presence of halides. The reaction

$$2Ce^{IV} + Sn^{II} \longrightarrow 2Ce^{III} + Sn^{IV}$$

is first-order with respect to reactants and addition of halide ions increases the rate in the order $I^- > Br^- > Cl^-$, *i.e.* in the same sense as the increase in ionic volume. A complicated rate equation was derived and second-order rate constants at constant $[H^+]$ and $[HSO_4^-]$ with variable halide ion concentration $[X^-]$ are given by

$$k = a + b[X^-] + c[X^-]^2 + d[X^-]^3 + \ldots$$

where a, b, c, and d are themselves sums of second-order rate constants. The use of polynomial regression analysis yields a number of values for a, b, and c with some significant results. An elaborate rate law was derived from a probable mechanism in a similar way for the reaction

$$2Ce^{IV} + U^{IV} \longrightarrow 2Ce^{III} + U^{VI}$$

where overall second-order kinetics are obeyed in acidic sulphate media.[55] A decrease in rate was observed as the concentrations of the various S^{VI} species were increased. Though the actual dependence is complicated, the order $SO_4^{2-} > HSO_4^- > H_2SO_4$ was established for the effectiveness of retarding the rate. No significant effect occurs on adding Ce^{III}.

The oxidation of $[Fe(gmi)_3]^{2+}$ [gmi = glyoxalbis(methylimine)] by Ce^{IV} in 4.07M-H_2SO_4 yields ligand-oxidized complexes or iron^{III}.[56] A first stage has been identified kinetically corresponding to the reaction

$$[Fe(gmi)_3]^{2+} + Ce^{IV} \longrightarrow [Fe(gmi)_3]^{3+} + Ce^{III}$$

Disproportionation of the Fe^{III} complex to observed products occurs subsequently and is discussed in Chapter 2.

Iron(III).—Much attention has been given to the reaction between $[Fe(CN)_6]^{3-}$ and the complex $[Co(edta)]^{2-}$. In the original study, Adamson and Gonick[57] established that a mixed dinuclear complex was formed in the reaction

$$[CoY]^{2-} + [Fe(CN)_6]^{3-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [YCo^{III}NCFe^{II}(CN)_5]^{5-} \qquad (5)$$

[54] Y. A. El-Tantawy and A. I. Abu-Shady, *Z. phys. Chem.* (*Frankfurt*), 1974, **88**, 141.
[55] Y. A. El-Tantawy and A. I. Abu-Shady, *Z. phys. Chem.* (*Frankfurt*), 1973, **84**, 225.
[56] H. L. Chum and P. Krumholz, *Inorg. Chem.*, 1974, **13**, 519.
[57] A. W. Adamson and E. Gonick, *Inorg. Chem.*, 1963, **2**, 129.

involving ring-opening, substitution, and inner-sphere electron transfer (Y = edta). Huchital and co-workers have shown that an analogous reaction occurs with the complexes, $[Co(cydta)]^{2-}$ (ref. 58), $[Co(dtpa)]^{3-}$ (ref. 59), and $[Co(pdta)]^{3-}$ (ref. 60). Formation of the dinuclear complex was studied at pH 5 by stopped-flow spectrophotometry and the second-order rate constant, k_5, obtained in each case. With Y = pdta, the rate is the same as with edta, and with Y = dtpa, despite the increased charge, the rate is only slightly less. The magnitude of k_5 is reduced by a factor of 20 with Y = cydta. Use of molecular models shows that whereas the displaced acetate group is free to move away from the cyano-bridge with Y = edta, it is constrained to a position close to the bridge by the cyclohexane ring when Y = cydta. The equilibrium constants K_5 were also determined and the rate constants for the back-reactions were calculated and found to be essentially the same, $10^{-2}k_{-5}/s^{-1}$ = 1.8, 1.4, 1.3, and 1.5 with Y = pdta, edta, cydta, and dtpa respectively.

In the reactions just described, slow disappearance of the dinuclear complex is also observed with eventual formation of mononuclear products,

$$[YCo^{III}NCFe^{II}(CN)_5]^{5-} \longrightarrow [CoY]^- + [Fe(CN)_6]^{4-} \qquad (6)$$

The simplest mechanism, and the one adopted in the papers mentioned, was that of bridge cleavage, *i.e.* successor-complex dissociation. Consequently, the observed first-order rate constants for the disappearance of dinuclear complex were denoted k_6, and at 25 °C $10^3k_6/s^{-1}$ = 22.1, 5.4, and 3.17 for Y = cydta,[58] edta,[58] and pdta[60] respectively.

Subsequently Ogino *et al.*[61] have published similar results with some overlap of the Huchital work. The rate of disappearance of dinuclear complex $[YCo^{III}NCFe^{II}(CN)_5]^{5-}$ follows the order Y = trdta > cydta > edta,pdta ≫ hedta and reasonable agreement was found in the cases where both research groups studied the same system. The reaction of $[Fe(CN)_6]^{3-}$ with Y = hedta is different in that though the dinuclear complex was formed rapidly as usual, the spectrum then remained unchanged for several hours and only a lower limit could be placed on its rate of disappearance. An explanation for this was offered in terms of the quinquedentate nature of the hedta ligand where the *N*-hydroxyethyl group has only weak co-ordinating power. In fact, the whole order of reactivities parallels the tendency of the ligands to take the sexidentate structure. The mechanism for the breakdown of dinuclear complex is seen therefore in terms of S_N2 considerations.

The rates of dinuclear-complex disappearance are low compared with other rates, *e.g.* ring closure of $[Co(edta)H_2O]^-$, and consequently whether $[CoY]^-$ is a primary product was not established. In the meantime Haim *et al.*[46] have published their results on the breakdown of the edta dinuclear complex. The study was extended to pH 10 where the quinquedentate species (if it existed) would be in the hydroxy-form and slow to ring-close. No evidence for a subsequent slow reaction and no change in the rate was observed, thereby ruling out quinquedentate cobalt(III) as an intermediate. Haim has argued from a knowledge of the oxidation potentials, K_5, and the supposed k_6 that the corresponding back reaction k_{-6} would have to proceed at an

[58] D. H. Huchital and R. J. Hodges, *Inorg. Chem.*, 1973, **12**, 998.
[59] D. H. Huchital and R. J. Hodges, *Inorg. Chem.*, 1973, **12**, 1004.
[60] D. H. Huchital and F. C. Maenpa, *J. Coordination Chem.*, 1973, **2**, 277.
[61] H. Ogino, M. Takahashi, and N. Tanaka, *Bull. Chem. Soc. Japan*, 1974, **47**, 1426.

impossibly fast rate for substitution on cobalt(III). Indeed the two products in (6) have been made to react by a clever technique, (see p. 15), and the measured rate constant at 25 °C (0.21 l mol^{-1} s^{-1}) is obviously too high to correspond to the reverse reaction in (6). In fact the rate corresponds to the outer-sphere electron-transfer reaction (7),

$$[CoY]^- + [Fe(CN)_6]^{4-} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [CoY]^{2-} + [Fe(CN)_6]^{3-} \qquad (7)$$

with a rate constant k_{-7} in line with Marcus's theory. The dinuclear complex therefore breaks down to mononuclear cobalt(III) and iron(II) by reverting to initial reactants (k_{-5}) followed by outer-sphere electron-transfer (k_{-7}). Reaction (6) therefore has no mechanistic significance and the observed rate constant k_6 is equal to k_{-7}/K_5. To summarize, the preferred mechanism for the thermodynamically favourable [Co(edta)]$^{2-}$ reduction of [Fe(CN)$_6$]$^{3-}$ is inner-sphere. The successor complex [(edta)Co^{III}NCFe^{II}(CN)$_5$]$^{5-}$ is then a 'dead-end' as regards eventual formation of [Co(edta)]$^-$ and [Fe(CN)$_6$]$^{4-}$. Instead the dinuclear complex reverts to reactants and the final products are formed when the outer-sphere mechanism occurs. Fortunately in the vast majority of inner-sphere reactions studied, the mechanism also involves ligand transfer and the possibility of dinuclear complex 'dead-ends' does not arise.

Mixed dinuclear complexes of this type seem to be attracting widespread attention. Higginson and co-workers have reported[62] the first part of a series of studies on reactions of the complex *trans*-[Co(en)$_2$(SO$_3$)(H$_2$O)]$^+$ with [Fe(CN)$_6$]$^{3-,4-}$, [Co(CN)$_6$]$^{3-}$, and [Fe(CN)$_5$NO]$^{2-}$. The reaction[63] of [Co^{II}(his)$_2$] with [Fe(CN)$_6$]$^{3-}$ and the reactions of *trans*-[Co(dmg)$_2$(C$_2$H$_5$)(H$_2$O)] with [M(CN)$_6$]$^{3-}$ (M = Fe, Cr, or Co) and with [Fe(CN)$_6$]$^{4-}$ have also been studied.[64] Quite apart from their novelty, the importance of mixed dinuclear complexes as a class can be recognized from the fact that they participate in every inner-sphere electron-transfer reaction between complexes of different metals. The hope (as yet unrealized) with systems of this kind is that they will eventually begin to yield first-order rate constants for electron transfer.

The reaction of U^{IV} and [Fe(CN)$_6$]$^{3-}$ has been studied in D_2O by a polarographic method.[65] The rate is first order in each reactant, and the dependence on [H$^+$] is of the form

$$k = k_0K/(K + [H^+])$$

A comparison with the known rate for the reaction in water reveals a kinetic isotope effect with the ratio $k_{H_2O}/k_{D_2O} = 2.5$ at 25 °C. Reaction of U^{IV} with Fe^{III} has also been studied in water–propan-2-ol.[66]

A study of the rates of anion-assisted outer-sphere electron-transfer reactions has been discussed in the section on Cr^{2+} reductions, but includes the effects of Cl^-, SCN^-, and N_3^- on the Fe^{III} oxidation of [Co(phen)$_3$]$^{2+}$.[24]

Rate data for oxidants discussed in this section are given in Table 2.

[62] K. L. Scott, R. S. Murray, W. C. E. Higginson, and S.-W. Foong, *J.C.S. Dalton*, 1973, 2335.
[63] S. Bagger and K. Gibson, *Acta Chem. Scand.*, 1973, **27**, 3227.
[64] J. H. Espenson and R. Russell, *Inorg. Chem.*, 1974, **13**, 7.
[65] L. Treindl and L. Adamcikova, *Chem. Zvesti*, 1973, **27**, 433 (*Chem. Abs.*, 1974, **80**, 30 982).
[66] A. G. Rykov, L. M. Frolova, and G. A. Timofeev, *Radiokhimiya*, 1973, **15**, 875 (*Chem. Abs.*, 1974, **80**, 64 271y).

Table 2 *Reactions involving cerium*(IV) *and iron*(III) *as oxidants* (*for units see Table 1*)

Reaction	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$Ce^{IV} + U^{IV}$	3.2×10^3	3.5	—	—	55[a]
$Ce^{IV} + [Fe(gmi)_3]^{2+}$	4×10^3	—	—	—	56[b]
$[Co(edta)]^{2-} + [Fe(CN)_6]^{3-}$	8×10^4	0.66	—	—	58[c]
$[Co(cydta)]^{2-} + [Fe(CN)_6]^{3-}$	3.58×10^4	0.66	1.9	−35	58[c]
$[Co(dtpa)]^{3-} + [Fe(CN)_6]^{3-}$	1.5×10^4	0.66	—	—	59[c,d]
$[Co(pdta)]^{2-} + [Fe(CN)_6]^{3-}$	8×10^4	0.66	—	—	60[c]
$[Co(edta)]^{2-} + [Fe(CN)_6]^{3-}$	4.5	0.66	—	—	46[e]
$U^{IV} + [Fe(CN)_6]^{3-}$	33.9	2.0	6.7	−29	65[f]
$[Co(phen)_3]^{2+} + Fe^{3+}$	1×10^3	1.0	—	—	24[g]
$[Co(phen)_3]^{2+} + Fe^{3+}$	5.3×10^2	1.1	—	—	24[h]
$[Co(phen)_3]^{2+} + Fe^{3+}$	2.0×10^4	1.0	—	—	24[h,i,j]
$[Co(phen)_3]^{2+} + Fe^{3+}$	2×10^7	1.0	—	—	24[g,j,k]
$[Co(phen)_3]^{2+} + Fe^{3+}$	3.4×10^7	1.0	—	—	24[g,j,l]

[a] T = 6 °C, [$NaHSO_4$] = 1.5 mol l^{-1}, [$HClO_4$] = 2.0 mol l^{-1}. [b] [H_2SO_4] = 4.07 mol l^{-1}. [c] Formation of dinuclear Co^{III}–Fe^{II} complex. [d] T = 30 °C. [e] Formation of mononuclear products by outer-sphere mechanism. [f] In D_2O. [g] [H^+] = 0.01 mol l^{-1}. [h] [H^+] = 1.0 mol l^{-1}. [i] Oxidant is $FeCl^{2+}$. [j] Units are l^2 mol^{-2} s^{-1}. [k] Oxidant is $FeNCS^{2+}$. [l] Oxidant is FeN_3^{2+}.

3 Miscellaneous Redox Reactions

Quantitative rate data for reactions discussed in this section are given in Tables 3 and 4. The use of the ion $[Ru(NH_3)_6]^{2+}$ as an outer-sphere reductant is much in evidence. The effect of sodium polystyrene sulphonate and sodium polyethylene on the rate of reduction of the series of complexes $[Co(en)_2(Cl)A]^{2+}$ (A = py, H_2O, or NH_3), $[Co(en)_2Cl_2]^+$, and $[(NH_3)_5CoBr]^{2+}$ has been investigated,[67] for comparison with known effects in inner-sphere reactions. Though acceleration factors were found for both mechanisms, activation parameters reveal that for outer-sphere a lowering of $\Delta H^{\ddagger}$ and for inner-sphere a more favourable $\Delta S^{\ddagger}$ are responsible. With $[Ru(NH_3)_6]^{2+}$ in large excess, the consumption of horse heart ferricytochrome c[68] obeys the rate law

$$-\mathrm{d[cyt}\ c]/\mathrm{d}t = (k_1 + k_2[H^+])[Ru][\mathrm{cyt}\ c]$$

Observed rate constants as high as 293 s^{-1} clearly demonstrate that reduction proceeds by a path that evades the rate-limiting process within the protein that is observed with Cr^{2+} and dithionate. It is suggested that since high rates of reduction are possible by the simple outer-sphere mechanism, the same mechanism may occur under physiological conditions. Reaction of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5H_2O]^{2+}$ with VO^{2+} gives a dark green dinuclear complex;[69] the same complex as is formed in the redox reaction of $[Ru(NH_3)_5Cl]^{2+}$ with V^{3+}, $[(NH_3)_5Ru^{II}OV(H_2O)_n]^{4+}$. The rate law for the redox reaction in excess VO^{2+} is of the form

$$\mathrm{d[RuOV]}/\mathrm{d}t = k[Ru^{III}][V^{III}]$$

with k dependent on $[H^+]^{-2}$ at pH < 2, but with more complex behaviour at higher pH.

[67] S. Kunugi and N. Ise, *Z. phys. Chem.* (*Frankfurt*), 1974, **91**, 174.
[68] R. X. Ewall and L. E. Bennett, *J. Amer. Chem. Soc.*, 1974, **96**, 940.
[69] H. de Smedt, A. Persoons, and L. de Maeyer, *Inorg. Chem.*, 1974, **13**, 90.

Table 3 *Rate constants and activation parameters for reduction by* $[Ru(NH_3)_6]^{2+}$ *(for units see Table 1)*

Oxidant	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Co(en)_2(py)Cl]^{2+}$	9.3×10^{2}	0.2	—	—	67
$[Co(en)_2(H_2O)C]^{2+}$	3.5×10^{2}	0.2	—	—	67
$[Co(en)_2(NH_3)Cl]^{2+}$	36	0.2	—	—	67
trans-$[Co(en)_2Cl_2]^{+}$	4.4×10^{3}	0.2	5.2	−25	67
$[(NH_3)_5CoBr]^{2+}$	5.3×10^{2}	0.2	10.2	−12	67
Ferricytochrome *c*	3.78×10^{4}	0.1	2.86	−28	68
Ferricytochrome *c*	7×10^{7}	0.1	—	—	68[a]
$[Co(NH_3)_6]^{3+}$	2.4×10^{-2}	0.5	—	—	19
$[(NH_3)_5Co(imidazole)]^{3+}$	3.7×10^{-2}	0.5	—	—	19
$[(NH_3)_5Co(pyrazole)]^{3+}$	0.23	0.5	—	—	19
$[(NH_3)_5Co(py)]^{3+}$	0.67	0.5	—	—	19
$[(NH_3)_5Co(NN$-dimethylformamido$)]^{3+}$	1.2	0.5	—	—	19
$[(NH_3)_5Co(NN$-dimethylnicotinamido$)]^{3+}$	3.7	0.5	—	—	19
$[(NH_3)_5CoO_2CH]^{2+}$	9.2×10^{-2}	0.5	—	—	19
$[(NH_3)_5CoO_2CMe]^{2+}$	2.2×10^{-2}	0.5	—	—	19
$[(NH_3)_5CoO_2CCH_2F]^{2+}$	8.7×10^{-2}	0.5	—	—	19
$[(NH_3)_5CoO_2CCF_3]^{2+}$	0.18	0.5	—	—	19
$[(NH_3)_5CoO_2CCCl_3]^{2+}$	0.25	0.5	—	—	19
$[(NH_3)_5CoO_2CCMe_3]^{2+}$	8.7×10^{-3}	0.5	—	—	19
$[(NH_3)_5CoO_2CCEt_3]^{2+}$	7.2×10^{-3}	0.5	—	—	19
$[(NH_3)_5Co(glycolato)]^{2+}$	4.7×10^{-2}	0.5	—	—	19
$[(NH_3)_5Co(lactato)]^{2+}$	4.7×10^{-2}	0.5	—	—	19
$[(NH_3)_5Co(benzoylformato)]^{2+}$	0.31	0.5	—	—	19
$[(NH_3)_5Co(S$-benzylthioglycolato$)]^{2+}$	4.1×10^{-2}	0.5	—	—	19
$[(NH_3)_5Co(thiodiglycolato)]^{2+}$	5.0×10^{-2}	0.5	—	—	19
$[(NH_3)_5Co(oxydiacetato)]^{2+}$	0.17	0.5	—	—	19
$[(NH_3)_5Co(mucochlorato)]^{2+}$	0.55	0.5	—	—	19
$[(NH_3)_5Co(o$-hydroxycinnamato$)]^{2+}$	3.5×10^{-2}	0.5	—	—	19
$[(NH_3)_5Co(4$-benzoylpyridino$)]^{3+}$	4.5	0.5	—	—	19

[a] Acid-dependent path; units are $l^2\ mol^{-2}\ s^{-1}$.

Gould[19] has studied the $[Ru(NH_3)_6]^{2+}$ reduction of a series of cobalt(III) oxidants which offer no sites for inner-sphere attack and therefore also react by an outer-sphere mechanism with V^{2+}, Eu^{2+}, and Cr^{2+}. The second-order rate constants for reduction of a common oxidant decrease in the order $k_{Ru} > k_V > k_{Eu} > k_{Cr}$. Moreover, linear relationships found are:

$$\log k_{Ru} = 1.05 \log k_V + 0.48$$

$$\log k_{Ru} = 1.05 \log k_{Eu} + 0.96$$

$$\log k_{Ru} = 1.05 \log k_{Cr} + 2.3$$

The widely studied relationship between $\log k_V$ and $\log k_{Cr}$ is discussed earlier (p. 13). In addition to their value in determining mechanisms, the relationships present good ways of storing large amounts of data, as shown by the Figure. Many of

Table 4 *Rate constants and activation parameters for miscellaneous redox reactions (for units see Table 1)*

Reaction	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$[Ru(NH_3)_5Cl]^{2+} + V^{3+}$	3.5×10^{-7}	1.0	—	—	69
$[(NH_3)_5CoO_2CC_5H_4NRu(NH_3)_4SO_4]^{2+}$	*ca.* 100	—	—	—	70[a,b]
$[(NH_3)_5CoO_2CCH_2C_5H_4NRu(NH_3)_4(H_2O)_2]^{4+}$	2.8×10^{-2}	1.0	—	—	70[a,b,c]
$[(NH_3)_5CoO_2CC_5H_4NRu(NH_3)_4(H_2O)_2]^{4+}$	8.2×10^{-3}	1.0	—	—	70[a,c,d]
$[(NH_3)_5CoO_2CCH_2C_5H_4NRu(NH_3)_4(H_2O)_2]^{4+}$	4.8×10^{-3}	1.0	—	—	70[a,c,d]
$(Hg^{I})_2 + [Ru(bipy)_3]^{3+}$	7×10^{-4}	3.0	21.2	−1.68	75
$(Hg^{I})_2 + [Fe(phen)_3]^{3+}$	*ca.* 5×10^{-4}	1.0	—	—	75
$Ti^{3+} + VO_2^+$	7.8×10^{3}	0.5	7.2	−16.6	76
$Ti^{3+} + VO_2^+$	8.3×10^{2}	0.5	14.7	4.1	76[e]
$Ag^{II} + VO^{2+}$	4.9×10^{3}	5.9	—	—	78[f]
$TiOH^{2+} + UO_2^{2+}$	1.01×10^{3}	0.5	—	—	79
$Sn^{II} + U^{VI}$	2.75×10^{-3}	1.0	18.1	−22.8	80[g]
$Am^{VI} + Np^{V}$	2.45×10^{4}	1.0	6.66	−16.2	81
$Am^{V} + Np^{V}$	—	—	15.2	−16	82
$MnO_4^- + [Mo(CN)_8]^{4-}$	3.76×10^{3}	1.0	10.8	−5.6	88[h]
$Tl^{2+} + Co^{2+}$	6.2×10^{3}	0.75	—	—	90
$Tl^{2+} + Fe^{3+}$	1.1×10^{6}	0.3	—	—	90
$Tl^{2+} + Fe^{2+}$	6.7×10^{6}	1.0	—	—	91[f]
$Tl^{3+} + Fe^{2+}$	1.39×10^{-2}	1.1	—	—	91

[a] Intramolecular reduction, units are s^{-1}. [b] *para*-Complex. [c] [NaCl] = 1 mol l^{-1}. [d] *meta*-Complex. [e] Acid-dependent pathway; units are s^{-1}. [f] T = 23 °C. [g] Units are l mol^{-1} h^{-1}, T = 30 °C. [h] [H$^+$] = 0.065 mol l^{-1}, T = 22.5 °C.

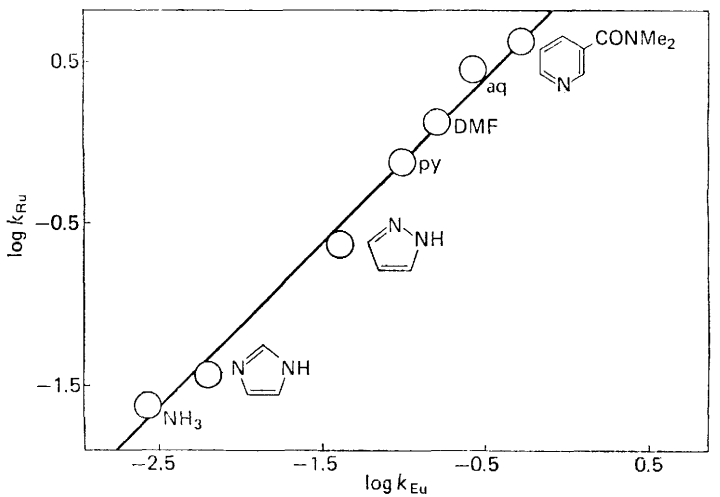
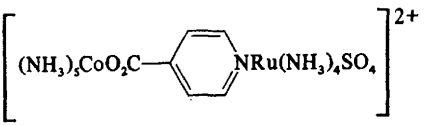


Figure *Log–log plot of the second-order rate constants for reduction by* $[Ru(NH_3)_6]^{2+}$ (k_{Ru}) *and* Eu^{2+} (k_{Eu}) *of common oxidants* $[R(NH_3)_5Co]^{2+}$ *with variable* R (Reproduced by permission from *Inorg. Chem.*, 1974, **13**, 2649)

the studies reported in this chapter relied on or presented new log–log plots (refs. 8, 11, 12, 16, 19—22, 35, 39). With the $[Ru(NH_3)_6]^{2+}$ relationships, Gould[19] was able to calculate outer-sphere components of reactions of V^{2+}, Eu^{2+}, and Cr^{2+} proceeding in the main by the inner-sphere mechanism. This is a particularly valuable approach with Eu^{2+} and V^{2+} where primary products of redox reactions are labile. Thus the V^{2+} reduction of 4-benzoylpyridinopenta-amminecobalt(III) was shown to proceed by a parallel outer-sphere path amounting to one-third of the reaction.

In the search for systems capable of yielding first-order rate constants for intramolecular electron transfer, Taube[70] appears to have had most success. Mixed dinuclear cobalt(III)–ruthenium(III) complexes have been prepared with pyridinecarboxylato-bridging ligands. Fast reduction by Eu^{2+} or $[Ru(NH_3)_6]^{2+}$ generates a cobalt(III)–ruthenium(II) dinuclear complex, which then disappears by a first-order process, taken to be intramolecular electron-transfer. The greatest rate from these early studies is found for the nicotinate complex (14). Some success has been



(14)

obtained[71] in reactions of cobalt(III) ammines containing unsaturated organic acids with Cu^{I}. Electron transfer was however extremely slow ($t_{1/2} > 50$ d) with propiolate and cinnamate ligands. No electron transfer was observed within the mixed dinuclear complexes described on p. 25. Another approach has been to prepare mononuclear complexes with oxidizable ligands, *e.g.* sulphito-[72,73] and hydrazino-ligands.[74] Results with the *trans*-$[Co(NH_3)_4(H_2O)SO_3]^+$ complex,[72] however, underline the uncertainty in observing first-order reaction rates. Except for the detection of slight curvature in $\log(OD_t - OD_\infty)$ *vs.* time plots, the rate would have been attributed to electron transfer, when in fact isomerization is the slow step. All the attempts to measure first-order rate constants are motivated by the need to make rate comparisons in the absence of factors involved in assembling reactants. We may have to revise our terminology when first-order rates for intramolecular electron transfer are commonplace since they will not be a measure of the rate of an electron being transferred!

It now seems likely that a distinction between one- and two-equivalent oxidants can be made on the basis of the rate law for reaction with mercury(I) dimer.[75] Both types of reaction are first-order in oxidant but in the case of two-equivalent oxidants an inverse $[Hg^{II}]$-dependence is observed. Thus with $[Ru(bipy)_3]^{3+}$ the reaction

[70] S. S. Isied and H. Taube, *J. Amer. Chem. Soc.*, 1973, **95**, 8198.
[71] J. K. Hurst and R. H. Lane, *J. Amer. Chem. Soc.*, 1973, **95**, 1703.
[72] M. A. Thacker, K. L. Scott, M. E. Simpson, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 647.
[73] K. L. Scott, *J.C.S. Dalton*, 1974, 1486.
[74] S. C. Chan and C. K. Lee, *Austral. J. Chem.*, 1973, **26**, 1923.
[75] R. Davies, B. Kipling, and A. G. Sykes, *J. Amer. Chem. Soc.*, 1973, **95**, 7250.

sequence and rate law are:

$$(Hg^{I})_2 + [Ru(bipy)_3]^{3+} \longrightarrow Hg^{I} + Hg^{II} + [Ru(bipy)_3]^{2+}$$

$$Hg^{I} + [Ru(bipy)_3]^{3+} \xrightarrow{fast} Hg^{II} + [Ru(bipy)_3]^{2+}$$

$$-d[Ru(bipy)_3^{3+}]/dt = 2k[(Hg^{I})_2][Ru(bipy)_3^{3+}]$$

Reaction with $[Fe(phen)_3]^{3+}$ is entirely analogous[75] and so are many of the previously studied systems. Two-equivalent oxidants, *e.g.* BrO_3^- and Tl^{III}, react according to the rate law

$$\text{Rate} = k[Hg^{I}_2][\text{oxid}][Hg^{II}]^{-1}$$

where the step $(Hg^{I})_2 \rightleftharpoons Hg^{0} + Hg^{II}$ is involved.

Another study[76] has been made of the reaction

$$V^{V} + Ti^{III} \longrightarrow V^{IV} + Ti^{IV}$$

in aqueous acid solution. A single stage is observed with rate law

$$-d[V^{V}]/dt = (k_1 + k_2[H^+]^{-1})[Ti^{III}][V^{V}]$$

and no interference from the much slower Ti^{3+} reduction of V^{IV}. Since good agreement was found between rate constants in NaCl and in LiCl and $LiClO_4$, runs were performed in HCl–NaCl media, thus eliminating storage difficulties due to Ti^{3+} reduction of perchlorate ion. However, it was found necessary to use Teflon as opposed to stainless-steel needles to prevent contamination of reactant solutions, and some of the complicated behaviour reported in an earlier study[77] can be explained on this basis. Considerably less importance of $[H^+]^{-1}$ terms compared with the analogous V^{III}–V^{V} reaction is noted, with the possibility that k_1 corresponds to a substitution-controlled process on Ti^{3+}. The rate of formation of V^{V} from the V^{IV} reduction of Ag^{II} is independent of $[H^+]$ in the range 1.0—5.8 mol l^{-1}.[78] Rates are greater than rates of substitution on V^{IV} and the mechanism could involve vanadyl-oxygen bridging or else be outer-sphere. A study[79] of the rate of Ti^{III} reduction of U^{VI} completes the series for reduction of d^0 metals. The rate law

$$-d[U^{VI}]/dt = \frac{k_1 k_a[Ti^{III}][U^{VI}]}{K_a + [H^+]}$$

reveals $TiOH^{2+}$ as the reactive species, with a mechanism

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

$$TiOH^{2+} + UO_2^{2+} \xrightarrow{k_1} TiO^{2+} + UO_2^{+} + H^+$$

$$TiOH^{2+} + UO_2^{+} + 3H^+ \xrightarrow{fast} TiO^{2+} + U^{4+} + 2H_2O$$

No evidence for a dinuclear complex of the type $[TiOHUO_2]^{4+}$ was forthcoming. This again raises the question of whether identification of a hydroxy-form as the reactive species, in this case $TiOH^{2+}$, indicates an inner-sphere mechanism with hydroxy-bridging or whether loss of protons occurs, to effect greater resemblance of activated complex to final product (TiO^{2+}), in which case the mechanism may well be outer-sphere. The reaction was also studied in the presence of V^{IV}. Inhibition occurs and

[76] J. D. Ellis and A. G. Sykes, *J.C.S. Dalton*, 1973, 2553.
[77] J. P. Birk and T. P. Logan, *Inorg. Chem.*, 1973, **12**, 580.
[78] E. Baumgartner and D. S. Honig, *J. Inorg. Nuclear Chem.*, 1974, **36**, 196.
[79] T. P. Logan and J. P. Birk, *Inorg. Chem.*, 1973, **12**, 2464.

V^{III} was identified as a product. Results were interpreted in terms of a competition with Ti^{III} for U^{V}. Sn^{II} reduction of U^{VI} has been studied[80] in 1—6M-HCl. Reactions, lasting from 2—10 days, were followed spectrophotometrically to 70—90% completion. The rate of formation of U^{IV} was found to be first order with respect to $[U^{VI}]$ and $[Sn^{II}]$. The dependence on $[H^+]$ was considerably more complicated and oscillatory behaviour was noted. In the regions 1—2M-HCl and 4—6M-HCl, the rate increases sharply with increase in $[H^+]$. In the medium acid range, an increase in acidity from 2 to 4M-HCl makes little difference to the rate; indeed at the highest temperature (50 °C) the rate actually decreases. In view of the numbers of uranyl and chlorotin complexes involved, a rationalization of rate behaviour in terms of specific complexes was not made. Activation parameters were therefore determined at constant $[H^+]$. Catalytic effects were investigated at 2M-HCl by adding NaCl, $FeCl_3$, and $CuCl_2$, the latter showing a pronounced effect attributed to further electron-transfer reactions involving Cu^{I}.

The rate of the reaction[81]

$$Am^{VI} + Np^{V} \longrightarrow Am^{V} + Np^{VI}$$

is independent of $[H^+]$ in the range 0.01—1.0 mol l^{-1}. Second-order rate constants are considerably higher than for Np^{V}–Np^{VI} exchange, with lower $\Delta H^{\ddagger}$ and more positive $\Delta S^{\ddagger}$. It is suggested that different numbers of water molecules may be present in the activated complexes. The Am^{V}–Np^{V} [82] and Am^{V}–Np^{IV} [83] reactions have also been studied, together with reactions of U^{IV} with Np^{VI},[84] Np^{V},[85] and Np^{IV} [85] and the Np^{VII}–V^{IV} reaction.[86]

Oxidation of Hg^{I} by Mn^{III} is catalysed by iridium and ruthenium sulphates of unknown composition, obtained by evaporating solutions of the complex chlorides in conc. H_2SO_4–Na_2SO_4.[87] The rate of the catalysed reaction is invariably independent of $[Hg^{I}]$. A first-order dependence on [catalyst] is observed up to *ca.* 10^{-6} mol l^{-1}, with little change in rate for increased catalyst. The dependence on $[Mn^{III}]$ is similar and the mechanism proposed is:

$$Ir^{III} + Mn^{III} \rightleftharpoons [Ir^{III}\text{–}Mn^{III}]$$
$$[Ir^{III}\text{–}Mn^{III}] \longrightarrow Ir^{IV} + Mn^{II}$$
$$Ir^{IV} + Hg^{I} \longrightarrow Ir^{III} + Hg^{II}$$

Maximum rates are observed in 8—10M-H_2SO_4 where the $[Mn(HSO_4)(H_2O)_5]^{2+}$ complex predominates. Oxidation of $[Mo(CN)_8]^{4-}$ by Mn^{VII} obeys[88] the rate law

$$-d[MnO_4^-]/dt = (k_1 + k_2[H^+])[MnO_4^-][Mo(CN)_8^{4-}]$$

[80] R. T. Mayhew and E. S. Amis, *J. Inorg. Nuclear Chem.*, 1973, **35**, 4245.
[81] M. Woods and J. C. Sullivan, *Inorg. Chem.*, 1974, **13**, 2774.
[82] A. G. Rykov, G. A. Timofeev, and V. M. Chistyakov, *Radiokhimiya*, 1973, **15**, 872 (*Chem. Abs.*, 1974, **80**, 64 270x).
[83] N. B. Blokhin, V. A. Ermakov, and A. G. Rykov, *Radiokhimiya*, 1974, **16**, 189 (*Chem. Abs.*, 1974, **81**, 54 794c).
[84] L. M. Frolova, G. A. Timofeev, and A. G. Rykov, *Radiokhimiya*, 1973, **15**, 867 (*Chem. Abs.*, 1974, **80**, 64 264y).
[85] N. B. Blokhin, V. A. Ermakov, and A. G. Rykov, *Radiokhimiya*, 1974, **16**, 355 (*Chem. Abs.*, 1974, **81**, 141 427d).
[86] K. O. Watkins, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1974, **13**, 1712.
[87] L. P. Tikhonova, K. B. Yatsimirskii, and G. V. Kudinova, *Russ. J. Inorg. Chem.*, 1974, **19**, 322.
[88] L. Thomas and K. W. Hicks, *Inorg. Chem.*, 1974, **13**, 749.

The kinetics of the electron-transfer reaction $[IrCl_6]^{2-}$–$[W(CN)_6]^{4-}$ have been studied in various media as a function of the concentration of alkali cations.[89] Rates increase in the order $Na^+ < K^+ < Rb^+ < Cs^+$ and in CsCl the rate is diffusion-controlled.

The powerful new technique of generating Tl^{2+} by flash photolysis has been used[90] to study the reactions of Tl^{2+} with Co^{2+} and Fe^{3+}:

$$Tl^{2+} + Co^{2+} \rightleftharpoons Tl^{+} + Co^{3+}$$
$$Tl^{2+} + Fe^{2+} \rightleftharpoons Tl^{3+} + Fe^{2+}$$

Reaction with Fe^{2+} has also been studied[19]:

$$Tl^{3+} + Fe^{2+} \longrightarrow Tl^{+} + Fe^{3+}$$

and in the Fe^{2+}–Tl^{3+} reaction the mechanism was confirmed to be[91]

$$Tl^{2+} + Fe^{2+} \rightleftharpoons Tl^{2+} + Fe^{3+}$$
$$Tl^{2+} + Fe^{2+} \longrightarrow Tl^{+} + Fe^{3+}$$

Standard reduction potentials have been calculated ($E^0 = +0.33$ V,[90] +0.3 V[91] for $Tl^{3+/2+}$ and $E^0 = +2.22$ V,[90] +2.22 V[91] for $Tl^{2+/1+}$) and this has caused some revision of the existing estimates. It has been shown that the Tl^{I}–Tl^{III} exchange is a two-electron transfer most likely by inner-sphere water bridging.

4 Electron Exchange Reactions

Very high rates of electron exchange between tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)-iron(II) and -iron(III) in acetonitrile[92] and between tris-(*NN*-dimethyldithiocarbamato)-iron(III) and -iron(IV) in CD_2Cl_2 [93] have been measured by n.m.r. line-broadening. Quantitative data for these and other exchange reactions are given in Table 5. The Fe^{II}–Fe^{III} exchange reaction has been studied in DMSO.[94] In the presence of added 0.03—0.15M-$HClO_4$, the apparent second-order rate constant is of the form

$$k_{app} = \frac{k_1 + k_2K[H^+]^{-1}}{1 + K[H^+]^{-1}}$$

with k_1 the same in DMF as it is in DMSO. The k_2 term can be rationalized in terms of complexes of the type $[Fe(OH)(H_2O)_{n-1}(DMF)_{6-n}]^{2+}$. With increased concentrations of water, the rate decreases but with added chloride ion, two further paths are evident.

The rate law for exchange between Cr^{2+} and the 4-pyridinomethylchromium(III) cation shows a single path, first order in reactant concentrations.[95] Decomposition in the absence of Cr^{2+} occurs therefore at a rate much lower than implied by the current mechanism, which also leads to an impossible rate for the back-reaction between Cr^{2+} and an organic radical. Marcus's theory has been tested following measurement of the $[Cr(bipy)_3]^{+}$–$[Cr(bipy)_3]$ exchange rate in DMF by e.s.r. line-broadening[96]

[89] J. Holzwarth and L. Strohmaier, *Ber. Bunsengesellschaft phys. Chem.*, 1973, **77**, 1145.
[90] B. Falcinella, P. D. Felgate, and G. S. Laurence, *J.C.S. Dalton*, 1974, 1367.
[91] H. A. Schwarz, D. Comstock, Y. K. Yandell, and R. W. Dodson, *J. Phys. Chem.*, 1974, **78**, 488.
[92] M.-S. Chan, J. B. De Roos, and A. C. Wahl, *J. Phys. Chem.*, 1973, **77**, 2163.
[93] M. C. Palazzotto and L. H. Pignolet, *Inorg. Chem.*, 1974, **13**, 1781.
[94] G. Wada, Y. Sahira, K. Ohsaki, and F. Shinoda, *Bull. Chem. Soc. Japan*, 1974, **47**, 851.
[95] J. H. Espenson and J. P. Leslie, *J. Amer. Chem. Soc.*, 1974, **96**, 1954.
[96] T. Saji and S. Aoyagui, *Bull. Chem. Soc. Japan*, 1973, **46**, 2101.

Table 5 *Electron-exchange reactions (for units see Table 1)*

Reaction	k (25 °C)	I/mol l^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
(3,4,7,8-tetramethyl-1,10-phen)$_3$Fe$^{2+/3+}$	1.7×10^{7}	*ca.* 0.1	—	—	92
(*NN*-dimethyldithiocarbamato)$_3$-Fe^{III}/Fe^{IV}	1.5×10^{8}	—	2.1	−11	93[a]
Fe^{II}/Fe^{III}	33.6	0.2	8.3	−24	94[b]
Fe^{II}/Fe^{III}	1.2×10^{2}	0.2	4.5	−34	94[b]
Fe^{II}/Fe^{III}Cl$_2$	*ca.* 10^{3}	0.2	—	—	94[b]
$[(H_2O)_5CrCH_2C_5H_4NH]^{3+}$ + Cr^{2+}	5.8×10^{-2}	1.0	—	—	95[c]
[Cr(bipy)$_3$] + [Cr(bipy)$_3$]$^{+}$	1.5×10^{9}	—	—	—	96[b]
$[(NH_3)_5CoSCN]^{2+}$ + $[Co(CN)_5]^{3-}$	$>10^{8}$, $<2\times10^{9}$	*ca.*0.11	—	—	102 102
[Co(acac)$_2$] + [Co*(acac)$_3$]	2.36	—	—	—	104[d]
$[MnO_4]^{2-}\rightarrow MnO_3$	1.08×10^{4}	0.1	12.7	2.5	108[e]
MnO_4^- + Mn^{2+}	10^{2}	—	—	—	109[f]
MnO_4^- + Mn^{2+}	19	—	—	—	109[g]
MnO_4^- + Mn^{2+}	63	—	—	—	109[h]
U^{V}/U^{V}	3.6×10^{2}	2.5	—	—	111[i]
Np^{V}/Np^{V}	8.1×10^{-2}	5.0	17.6	−24	112[j]
Tl$^{3+/1+}$	4.7	3.0	—	—	113[k]
Tl^{III} + Tl^{I}	2.13	3.0	—	—	113[l]
Tl^{2+} + Tl^{2+}	5.5×10^{8}	0.25	—	—	90
Tl^{2+} + Tl^{2+}	1.9×10^{8}	1.0	—	—	91[m]

[a] Reaction in CD_2Cl_2, T = −57 °C. [b] Reaction in DMF. [c] T = 55 °C. [d] Reaction in toluene, units are l mol^{-1} h^{-1}, T = 98 °C. [e] At 610 nm. [f] Units are l^2 mol^{-2} s^{-1}. [g] Units are l^3 mol^{-3} s^{-1}. [h] Units are l^4 mol^{-4} s^{-1}. [i] [H$^+$] = 0.75 mol l^{-1}, T = 20 °C. [j] Units are l^3 mol^{-3} min^{-1}, T = 92 °C. [k] Units are l mol^{-1} h^{-1}, T = 50 °C. [l] Units are h^{-1}, T = 50 °C. [m] T = 23 °C.

and measurement of the electrochemical rate by the galvanostatic double-pulse method.[97]

Gupta[98] has attempted to rationalize rates of electron-transfer reactions involving halogeno-metal complexes in terms of Sanderson's concept of partial charge. For reactions of the type Cr^{2+} or Eu^{2+} with CrX^{2+}, a linear free-energy relationship is found:

$$\log k = m \log \delta_{X^-} + c$$

A different approach in terms of donicity has been used to explain some ligand effects in redox reactions.[99] A correlation has been found[100] between the energy of the first *d–d* bands of a number of Cr^{III} complexes and their rates of electron exchange with Cr^{2+}. The tetragonal distortion of the Cr^{III} complex was evaluated from an analysis of the electronic spectrum and is manifested as a lower reorganization energy of the precursor complex.

Reactions of the type [LCo(Hdmg)$_2$X] + L′→[L′Co(Hdmg)$_2$X] + L have been studied,[101] where X = N- or S-bonded SCN^-, and shown to proceed only in the

[97] T. Saji and S. Aoyagui, *Bull. Chem. Soc. Japan*, 1974, **47**, 389.
[98] K. S. Gupta, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3879.
[99] V. Gutmann and R. Schmid, *Coordination Chem. Rev.*, 1974, **12**, 263.
[100] G. St. Nikolov, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1841.
[101] L. G. Marzilli, R. C. Stewart, L. A. Epps, and J. B. Allen, *J. Amer. Chem. Soc.*, 1973, **95**, 5796.

presence of catalytic amounts of $[LCo^{II}(Hdmg)_2]$. The mechanism is believed to involve an inner-sphere electron-transfer reaction. Furthermore, the evidence suggests that adjacent attack occurs more rapidly than remote attack in the reaction

$$[(4\text{-CNpy})(Hdmg)_2Co-SCN] + [Co(Hdmg)_2L] \longrightarrow \left[(4\text{-CNpy})(Hdmg)_2Co-\overset{\overset{CN}{|}}{S}-Co(Hdmg)_2L\right]$$

In the immeasurably fast reaction of $[(NH_3)_5CoSCN]^{2+}$ with $[Co(CN)_5]^{3-}$, the product spectrum closely corresponds to $[Co(CN)_5SCN]^{3-}$ and it has been estimated that adjacent attack at sulphur accounts for $>95\%$ reaction.[102] These studies, as with Cr^{2-} reduction,[103] show the high mediating action of the thiocyanate sulphur atom. The exchange reaction

$$[Co(acac)_2] + [Co^*(acac)_3] \longrightarrow [Co^*(acac)_2] + [Co(acac)_3]$$

is also proposed to proceed by an inner-sphere mechanism.[104]

The factor of 10^6 by which the self-exchange rate for $[Co([14]tetraeneN_4)(H_2O)_2]^{3+/2+}$ is faster than for the closely related diene complex has been traced to an unusually large difference in bond lengths between oxidized and reduced forms of the latter.[105] Anomalously low reorganizational barriers in other electron-transfer reactions of cobalt(III) suggest that such barriers are far more important in self-exchange reactions (k_{exch}).[106] The standard heterogeneous rate constants (k_S) for reduction of complexes of this type have been measured by the staircase voltammetric technique and whilst a good correlation, $\log k_{exch} \approx 2 \log k_S + 4$, exists for $Cr^{3+/2+}$, $Eu^{3+/2+}$, $V^{3+/2+}$, $[Fe(CN)_6]^{3-/4-}$, $[Ru(NH_3)_6]^{3+/2+}$, *etc.*, this does not extend to complexes of cobalt(III). Revised calculations of some earlier work have also been presented.[107]

Exchange reactions involving manganese include the disproportionation of manganate, which obeys different rate laws depending on whether the disappearance of manganate or appearance of permanganate is being observed,[108] and the reaction of the latter with Mn^{2+}, with rate law[109]

$$-d[MnO_4^-]/dt = \{k_0 + k_1[H^+] + k_2[H^+]^2\}[Mn^{2+}]^2[MnO_4^-]$$

The U^{VI}–U^{IV} exchange reaction has been studied in perchlorate and sulphate media.[110] In perchlorate, the rate is proportional to $[H^+]^{-3}$. At constant $[H^+]$, the rate is enhanced by addition of sulphate but inhibited by F^-, and with increasing $[H_2SO_4]$ the rate decreases initially but increases after reaching a minimum at *ca.* 1 mol l^{-1}. The much-studied disproportionation of U^V,

$$2UO + 4H^+ \longrightarrow U^{4+} + UO_2^{2+} + 2H_2O$$

has received further examination.[111] The retarding effect of U^{VI} is attributed to

[102] C. J. Shea and A. Haim, *Inorg. Chem.*, 1973, **12**, 3013.
[103] C. J. Shea and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 3055.
[104] J. R. McKellar and B. O. West, *J.C.S. Dalton*, 1974, 796.
[105] M. D. Glick, W. G. Schmonsees, and J. F. Endicott, *J. Amer. Chem. Soc.*, 1974, **96**, 5661.
[106] J. F. Endicott, R. S. Schroeder, D. H. Chidester, and R. D. Ferrier, *J. Phys. Chem.*, 1973, **77**, 2579.
[107] J. F. Endicott, *Inorg. Chem.*, 1973, **12**, 1712.
[108] J. H. Sutter, K. Colquitt, and J. R. Sutter, *Inorg. Chem.*, 1974, **13**, 1444.
[109] J. I. Morrow and S. Perlman, *Inorg. Chem.*, 1973, **12**, 2453.
[110] A. Ekstrom, G. E. Batley, T. M. Florence, and Y. J. Farrar, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2355.
[111] A. Ekstrom, *Inorg. Chem.*, 1974, **13**, 2237.

formation of a dinuclear U^{V}–U^{VI} complex, so that the rate constant for U^{V} reacting with the mononuclear (k_1) and dinuclear (k_2) forms of the complex is

$$k = (k_1 + k_2K[U^{VI}])(1 + K[U^{VI}])^{-2}.$$

In the range 0.25—2.0M-H^+, the dependence of k_1 on $[H^+]$ is not strictly first order and possible explanations are that significant concentrations of UO_2H^{2+} are formed or that U^{V} dimerizes and reacts with H^+ to form products. The reaction is strongly catalysed by SO_4^{2-} and by F^- and a marked dependence on ionic strength is shown with k_1 increasing by an order of magnitude on changing from $I = 0.5$ to 4.0 mol l^{-1}. Rates were also measured in D_2O with an isotope effect, $k_{D_2O}/k_{H_2O} = 1.29$. Disproportionation of Np^{V} in perchlorate media has been observed in the presence of N_2H_4 (there to scavenge NpO_2^{2+}) and found to be second order with respect to $[NpO_2^+]$ and $[H^+]$.[112] The rate of the Tl^{I}–Tl^{III} exchange reaction has been studied using ^{204}Tl in the presence of Ce^{III}.[113] The apparent rate constant, k_{app}, is of the form

$$k_{app} = k_1 + (k_2/[H^+]) + \{k_3 + (k_4/[H^+])\}[Ce^{IV}]$$

with k_3 and k_4 dominant. It is calculated that the equilibrium

$$Tl^+ + 2Ce^{IV} \rightleftharpoons Tl^{III} + 2Ce^{III} \qquad K$$

lies completely to the right (log $K = 15.6$). The authors accept a two-stage mechanism for this reaction but argue that in the absence of a one-electron oxidant, the Tl^{I}–Tl^{III} exchange must proceed by a single, two-electron step. The same conclusion is reached by Laurence and co-workers[90] and by a third group[91] who calculate that the exchange rate for Tl^{I}–Tl^{III} would be 6×10^{-17} l mol^{-1} s^{-1} if the intermediacy of Tl^{2+} were involved. The experimentally determined rate is greater by a factor of 2×10^8, proving that this mechanism plays no role in the exchange.

[112] V. S. Koltunov and M. F. Tikhonov, *Zhur. fiz. Khim.*, 1974, **48**, 860 (*Chem. Abs.*, 1974, **81**, 69 007x).
[113] G. Wada and K. Tamaki, *Bull. Chem. Soc. Japan*, 1974, **47**, 1422.

2
Metal Ion–Ligand Redox Reactions

BY A. McAULEY

In this chapter, the reactions of metal ions in a high oxidation state with inorganic and organic substrates are discussed. Investigations of this type provide extensive mechanistic data, and an important aspect is the evidence produced for inner-sphere reactions with the formation of metal-ion complex intermediates. Reactions with the metals in a reduced oxidation state are being increasingly studied as are the highly reactive species produced by pulse radiolysis and flash photolysis. The format is similar to that in previous volumes. Although a degree of selection has had to be imposed owing to the very large number of papers involving electron-transfer processes, an attempt has been made to cover as comprehensively as possible all the areas in which studies are currently being undertaken. Where possible compilations of data have been assembled to allow comparison of rate data.

1 Chromium(VI)

The kinetics and mechanism of the oxidation of hydrazinium ion have been studied over an extended hydrogen-ion concentration range[1] up to 2.2 mol l^{-1}. The rate law is first order with respect to [Cr^{VI}] but shows a small but distinct deviation from first-order behaviour at high [$NH_3NH_2^+$], consistent with the formation of an N-bonded chromate ester (H_3N^+—$NHCrO_3^-$) with $K_f = 3.2 \pm 0.3$ l mol^{-1}. At high [H^+] account must be taken of the presence of H_2CrO_4 in solution. The intermediate represents the first Cr^{VI} anhydride having a Cr—N bond for which a formation constant has been measured. The reaction is general acid catalysed (H^+, H_3PO_4, $H_2PO_4^-$, $HCrO_4^-$), and a mechanism consistent with the data may be formulated (HB = acid) as

$$HCrO_4^- + NH_3NH_2^+ \overset{K_f}{\rightleftharpoons} \overset{+}{N}H_3NHCrO_3^- + H_2O$$

$$\overset{+}{N}H_3NHCrO_3^- + H^+ \rightleftharpoons \overset{+}{N}H_3NHCrO_3H$$

$$\overset{+}{N}H_3NHCrO_3H + B^- \rightleftharpoons NH_2NHCrO_3H + HB$$

$$NH_2NHCrO_3H \longrightarrow Cr^{IV} + N_2H_2$$

$$2N_2H_2 \rightleftharpoons N_2H_4 + N_2$$

$$2Cr^{IV} \longrightarrow Cr^{V} + Cr^{III}$$

$$Cr^{V} + N_2H_4 \longrightarrow \tfrac{1}{2}N_2 + Cr^{III}$$

The initial nitrogen oxidation product is N_2H_2, which is thought to disproportionate. A bimolecular reaction takes place involving the Cr^{IV} formed in the two-electron redox step. Some Li^+ catalysis similar to that of H^+ occurs. By investigating the

[1] G. P. Haight, jun., T. J. Huang, and H. Platt, *J. Amer. Chem. Soc.*, 1974, **96**, 3137.

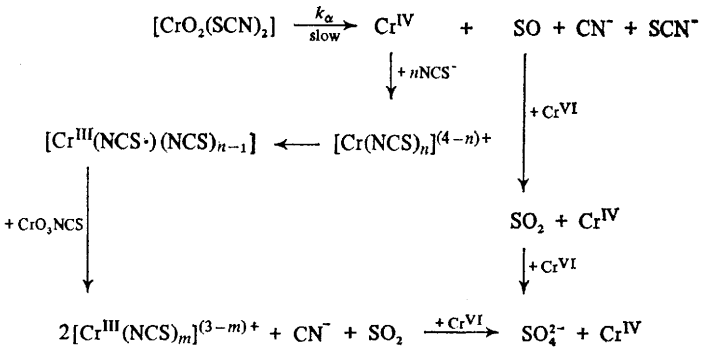
effect of Mn^{II} on the rate it appears that the Cr^{IV} disproportionation takes place before it is trapped by Cr^{VI}. From these data and from a comparison of the corresponding reaction with V^{V}, revised estimates of the Cr^{VI}/Cr^{V} and Cr^{V}/Cr^{IV} redox potentials have been proposed.

Oxygen-bonded ester formation is described in the reaction with hydroxylammonium ion[2] in the pH range 0.0—4.7. The initial stages of the kinetic runs are marked by a rapid increase in optical density, but the effect is too small for quantitative study. *O*-Methylhydroxylamine, in which any O-bonded-complex formation would be inhibited, reacts about two orders of magnitude more slowly at pH 4.7, although the rate is somewhat faster at higher H^+ concentrations. Again a two-electron oxidation is considered operative with Cr^{IV} formation, the reactive intermediate, HNO, being further oxidized primarily to HNO_2. The observed retardation of the rate by chloride ion is consistent with a transition state containing $HCrO_4^-$ ($HOCrO_3^-$) being more reactive than one with $ClCrO_3^-$ present. In the hydroxylammonium ion reaction, the products are markedly dependent on the ratio of initial reactant concentrations.

Two studies have been made of the chromium(VI) oxidation of thiocyanate,[3,4] in which the reported dependence of the ligand concentration is substantially different. In keeping with the earlier observation[5] that a complex between Cr^{VI} and SCN^- is sufficiently stable with respect to redox at low $[H^+]$ to allow temperature-jump studies to be made (and hence to yield a value for the formation constant), Muirhead and Haight[3] found an immediate increase in absorbance on mixing the reactants in the stopped-flow apparatus. The spectrum of the intermediate was derived using the continuous-flow method. Assuming the oxidation reaction to proceed *via* this complex, the rate law may be written in the form

$$\frac{-\mathrm{d}[Cr^{VI}]}{\mathrm{d}t} = k_0 \frac{[Cr^{VI}][SCN^-]^2[H^+]^3}{(1 + K_f[SCN^-][H^+])}$$

over the range $[H^+] = 0.025$—0.2 mol l^{-1}. The equilibrium constant, $K_f = 220$, is about an order of magnitude higher than for Cr^{VI}—N (and Cr^{VI}—O) bonded complexes and is probably indicative of a sulphur-bonded ester. The mechanism

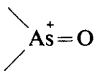


Scheme 1

[2] R. A. Scott, G. P. Haight, jun., and J. N. Cooper, *J. Amer. Chem. Soc.*, 1974, **96**, 4136.
[3] K. A. Muirhead and G. P. Haight, jun., *Inorg. Chem.*, 1973, **12**, 1116.
[4] U. Muralikrishna and K. V. Bapanaiah, *Z. phys. Chem.* (*Leipzig*), 1974, **255**, 1116.
[5] C. T. Lin and J. K. Beattie, *J. Amer. Chem. Soc.*, 1972, **94**, 3011.

consistent with the rate law (Scheme 1) satisfies the requirements that no Cr^{V} is observed in e.s.r. studies, that trapping of Cr^{IV} by Mn^{II} has no effect on the rate, and that the principal metal-ion-containing products are Cr^{III} thiocyanate complexes with only small amounts of the hexa-aquo-ion. In a separate study[4] under essentially similar experimental conditions, a 1 : 1 complex is postulated, but the suggested first-order dependence of ligand with no reference to the principal redox pathway *via* the 1 : 2 species must leave these findings open to question.

In the oxidation of arsenic(III) in perchlorate media[6] the reaction order of less than unity with respect to reductant is interpreted in terms of the formation of an unstable 1 : 1 intermediate. Activation parameters are essentially constant ($E_a = 9.3 \pm 0.5$ kcal mol^{-1}) at both high (excess) and low [Cr^{VI}] and the rate is increased on addition of sodium hydrogen phosphate. This latter observation may reflect an acid-catalytic route described earlier. The mechanism at low [Cr^{VI}] with reductant in excess is considered to involve the rate-determining decomposition of the 1 : 1 complex to give Cr^{IV} and an arsonium species of the type



An interesting paper[7] describes and attempts to quantify the processes associated with the capture of ligands by Cr^{III} in reductions of Cr^{VI}. The nature of the final Cr^{III} products is a function of both the ligand and hydrogen-ion concentrations and of the intermediate chromium species. Using systems in which the ligands are oxidized relatively slowly, the Cr^{VI} reduction was initiated by addition of either V^{IV}, a fast one-electron reductant, or $N_2H_5^+$, which undergoes a rapid two-electron transfer. In dilute perchloric acid with about a five-fold excess of ligand present and using $N_2H_5^+$ as initiator there is no ligand capture of the weakly co-ordinating species NO_3^-, Cl^-, or $MeCO_2^-$. Significant fractions of N_3^-, SO_4^{2-}, $H_2PO_2^-$, $H_2PO_3^-$, and $H_2PO_4^-$ are, however, identified in the Cr^{III} complexes under similar conditions whilst the chelating ligands oxalate and $H_2P_2O_7^{2-}$ show extensive ligand capture. Using the one-electron reagent, the potential ligands yield more highly substituted Cr^{III} products, the exception being oxalate ion. Where an excess of VO^{2+} is used to eliminate ligand oxidation, the co-ordination equilibria of V^{IV} and Cr^{IV} are believed to be rapid and the product distribution is considered to reflect the relative rates of reduction of the chromium(IV) precursors in the reaction (L = ligand)

$$V^{IV}L_m + Cr^{IV}L_n \xrightarrow{k_0} V^{V}L_m + Cr^{III}L_n$$

In the presence of oxidizable metal ions, however, (*e.g.* Ce^{III} or Mn^{II}) there is always the possibility of trapping the intermediates in competition with the ligands reacting to reduce the Cr^{IV}. Chromium(V) plays an important role in oxidations of this type and a long-lived Cr^{V} intermediate has been identified in the reaction with oxalic acid.[8] Using both e.s.r. and difference absorbance spectra, it has been shown that there is a significant build-up of a complex in moderately acidic media. The data

[6] K. K. Sen Gupta and J. K. Chakladar, *J.C.S. Dalton*, 1974, 222.
[7] J. N. Cooper, G. E. Standt, M. L. Smalser, L. M. Setto, and G. P. Haight, jun., *Inorg. Chem.*, 1973, **12**, 2075.
[8] V. Srinivasan and J. Rocek, *J. Amer. Chem. Soc.*, 1974, **96**, 127.

conform to a consecutive reaction sequence of the type

$$Cr^{VI} + S \xrightarrow{k_1} Cr^{V} + \text{products}$$

$$Cr^{V} + S \xrightarrow{k_2} Cr^{III} + \text{products}$$

where the substrate (S) is present in at least twenty-fold excess. One interesting finding is a considerable degree of independence of the ratio of the Cr^{VI} and Cr^{V} rate constants (k_1/k_2) to changing oxalic acid, hydrogen-ion, and chromium(VI) concentrations, and it is inferred that both oxidants have similar ligand and $[H^+]$ dependences. From such observations the conclusion is reached that Cr^{V} is only two to three times more reactive towards the substrate than is Cr^{VI}.

In the oxidation of oxalic acid, e.s.r. spectra run in acetic acid solutions showed enhancement of the Cr^{V} signal. Other similar studies have been carried out in this medium. The oxidation of cyclobutanol has been investigated in 97% acetic acid[9] and in aqueous media.[10] In the former study, a comparison of the data with those for the oxidation of isopropyl alcohol shows that both the rate of formation and the equilibrium constant for the chromate ester intermediate are larger for the ring compound. There is also evidence for the presence of 1 : 2 Cr^{VI}–substrate complexes. The spectrum of an intermediate Cr^{V} complex has been compiled and again, at a given acid concentration, the relative rates of Cr^{VI} and Cr^{V} reactions may be assessed. In this system, however, the higher oxidation state is apparently more reactive by a factor of about two. Precise data on equilibrium constants for the Cr^{V} species are required. Whereas Cr^{VI} and Cr^{V} react towards cyclobutanol to yield cyclobutanone, two groups have reported[9,11] that with Cr^{IV} cleavage of the C—C bonds occurs with ring-opening. The relative reactivities of Cr^{VI} and Cr^{V} towards aldehydes have been established in 96% acetic acid.[12] In this case both reagents behave as two-electron oxidants,

$$RCHO + Cr^{VI} \xrightarrow{k_\alpha} RCO_2H + Cr^{IV}$$

$$RCHO + Cr^{V} \xrightarrow{k_\beta} RCO_2H + Cr^{III}$$

and as in the former investigation again the Cr^{VI} appears to be about twice as active. Substitution of the phenyl ring has little effect on the reaction rate. Aliphatic aldehydes are, however, more rapidly oxidized by Cr^{V} than aromatic substrates. The oxidation of aliphatic aldehydes by Cr^{IV} generated *in situ* in aqueous solution from Cr^{VI} and V^{IV} has been studied.[13] Propionaldehyde is oxidized quantitatively to propionic acid. In this system, the rate scheme may be represented as

$$Cr^{VI} + V^{IV} \rightleftharpoons Cr^{V} + V^{V}$$

$$Cr^{V} + V^{IV} \xrightarrow[\text{determining}]{\text{rate}} Cr^{IV} + V^{V}$$

$$Cr^{IV} + V^{IV} \xrightarrow{k_x} Cr^{III} + V^{V}$$

$$Cr^{IV} + P \longrightarrow Cr^{III} + R\cdot$$

$$R\cdot + V^{V} \longrightarrow V^{IV} + \text{acid}$$

[9] K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, 1974, **96**, 6647.
[10] J. Rocek and A. E. Radkowsky, *J. Amer. Chem. Soc.*, 1973, **95**, 7123.
[11] F. Hasan and J. Rocek, *J. Amer. Chem. Soc.*, 1974, **96**, 534.
[12] K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, 1974, **96**, 1889.
[13] J. Rocek and C.-S. Ng, *J. Amer. Chem. Soc.*, 1974, **96**, 1522.

The invariance of the rate on aldehyde concentration is consistent with only Cr^{IV} acting as an oxidant for this substrate. Evidence has been presented for the reaction of this reagent with isopropyl alcohol[14] as an essential step in the Cr^{VI} oxidation of this substrate in acetic acid. A stable Cr^{IV} alkoxide of a secondary alcohol has been prepared.[15] The complex tetrakis-(3,3-dimethyl-2-butoxy)chromium(IV) is, however, sensitive to moisture and oxygen. The difference in its stability with respect to primary and secondary alcohols results from the presence of the bulky t-butyl groups which probably prevent the rearrangement of the molecule to the correct conformation required for hydrogen transfer in the oxidation step.

A feature of recent studies of oxidations by chromium(VI) has been the postulate that three-electron redox reactions are possible. If the reaction involving the co-oxidation of two substrates proceeds *via* an intermediate formed from one mole each of Cr^{VI} and the two organic compounds, then providing both a two-electron and a one-electron transfer can take place, the rate-determining step can lead to the production of Cr^{III} without the necessity of forming a Cr^{IV} species.[11] The synchronous nature of reactions of this kind has been elegantly demonstrated in the oxidation of glycollic acid,[16] in which there is a change in the reaction order depending on the concentration of the organic substrate. Also, the reaction of a mixture of isopropyl alcohol and glycollic acid results in co-oxidation leading to acetone and glyoxylic acid. In these reactions, only carbon–hydrogen bonds are broken,

$$Me_2CHOH + HOCH_2CO_2H + Cr^{VI} \rightleftharpoons \text{Intermediate}$$

$$\text{Intermediate} \xrightarrow{\text{slow}} Me_2CO + HO\dot{C}HCO_2H + Cr^{III}$$

and deuterium substitution may thus be used to examine whether the two steps are consecutive or simultaneous. If the slow step were a single oxidation leading to an intermediate oxidation state of chromium, only one isotope effect would be observed. Using both Me_2CDOH and $HOCD_2CO_2H$, however, the isotope effect is the product of that for the individual reactions, indicating that the two bond-breaking processes occur simultaneously. Since only a single step is involved and a change in geometry occurs between the tetrahedral Cr^{VI} and the octahedral Cr^{III} product, the structure of the transition state may be intermediate and the activation parameters for such a process will be of interest when determined. A similar mechanism has been postulated for the reaction with isopropyl alcohol and α-hydroxyisobutyric acid,[17] where the rate of reaction is about 4.5 times greater than that for the sum of the individual substrate pathways. In this case, the carbon dioxide which is eliminated derives from the free-radical intermediate and evolution can be suppressed by addition of acrylonitrile as a scavenger. The oxidation of malachite green in the presence of oxalic acid has been investigated by stopped-flow methods.[18] The Cr^{VI}–oxalic

[14] K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, 1974, **96**, 1884.
[15] G. Dyrkacz and J. Rocek, *J. Amer. Chem. Soc.*, 1973, **95**, 4756.
[16] F. Hasan and J. Rocek, *J. Amer. Chem. Soc.*, 1974, **96**, 6802.
[17] F. Hasan and J. Rocek, *J. Amer. Chem. Soc.*, 1973, **95**, 5421.
[18] A. Granzow, A. Wilson, and F. Ramirez, *J. Amer. Chem. Soc.*, 1974, **96**, 2454.

acid complex is considered to oxidize both the colourless and the coloured forms of malachite green.

An e.s.r. study has been reported[19] of the Cr^{V} complexes formed in the oxidation of diethylene glycol by Cr^{VI}. The reaction may be photo-induced, and with the ligand in large excess pseudo first-order conditions are operative. The mechanism involves the formation of essentially two complexes and proceeds *via* a primary reduction to give a Cr^{IV} centre followed by an intramolecular reaction to yield a Cr^{V} complex. The final reaction, with Cr^{III} and a carboxylic acid as products, is also photochemically sensitive.

2 Iron(III)

The reaction of iron(III) with hydroxylamine in strongly acid perchlorate media,

$$4Fe^{3+} + 2NH_3OH^+ \longrightarrow 4Fe^{2+} + N_2O + 6H^+ + H_2O$$

has been used in the quantitative determination of hydroxylamine and is sometimes enhanced by the presence of copper(II) as a catalyst. The kinetics of both the uncatalysed and catalysed pathways have been investigated,[20] the experimental rate law being complex. Both reactions are strongly inhibited by Fe^{II}, and in the absence of Cu^{II} the simplified rate law may be written as

$$\text{Rate} = \frac{k_1[Fe^{III}]^2[NH_2OH]^2}{[NH_2OH] + k_2[Fe^{II}]^2}$$

in which any hydrogen-ion dependences are neglected. In the presence of catalyst a concentration term in Cu^{II} replaces one of the Fe^{III} terms in the numerator of the above equation. The mechanism may involve the rapid formation of iron(III)– [and copper(II)–] hydroxylamine complexes followed by a dimerization to yield a dinuclear intermediate or activated complex containing two ligand bridges. The loss of two protons from the NH_3OH^+ molecules involved in this process accounts for the marked $[H^+]$ dependence observed.

In the reaction with catechol (*o*-dihydroxybenzene)[21] the equilibrium (1) and kinetics of formation of an intermediate complex have been studied in the pH range

$$Fe^{3+} + H_2cat \rightleftharpoons [Fe(cat)]^+ + 2H^+ \qquad (1)$$

1.00—2.00. The data are consistent with an I_d mechanism for ligand substitution. The complex $[Fe(cat)]^+$ undergoes a subsequent slow electron-transfer reaction. Under conditions of higher hydrogen-ion concentration, however, $1.0 > [H^+] \geqslant 0.1$ mol l^{-1}, the redox process may be studied[22a] using the stopped-flow method. In this acidity range, complex formation (1) is effectively suppressed and the mechanism proposed involves the intermediacy of semiquinone radicals,

$$Fe^{III} + H_2cat \underset{k_\beta}{\overset{k_\alpha}{\rightleftharpoons}} Fe^{2+} + Hcat\cdot + H^+$$

$$Fe^{3+} + Hcat\cdot \underset{k_\delta}{\overset{k_\gamma}{\rightleftharpoons}} Fe^{2+} + Q + H^+$$

[19] M. Mitewa, A. Malinovski, P. R. Bontchev, and K. Kabassanov, *Inorg. Chim. Acta*, 1974, **8**, 17.
[20] G. Bengtsson, *Acta Chem. Scand.*, 1973, **27**, 1717.
[21] E. Mentasti and E. Pelizzetti, *J.C.S. Dalton*, 1973, 2605.
[22] (*a*) E. Mentasti, E. Pelizzetti, and G. Saini, *J.C.S. Dalton*, 1973, 2609; (*b*) E. Pelizzetti, E. Mentasti, E. Pramauro, and G. Saini, *ibid.*, 1974, 1940.

where Q (= *o*-quinone) is the oxidized ligand product. The overall reaction is limited by the reversibility of the process. The rate constants k_α and k_β/k_γ vary with hydrogen-ion concentration, and from a detailed study of such dependences it is apparent that the reactive metal-ion species in the oxidation is in fact $FeOH^{2+}$. This complex ion then reacts with the undissociated ligand to produce the radical. In a later paper,[22b] the conditions being such that the oxidant was present in excess, the reaction rate is shown to be dependent on $[Fe^{III}]^n$ $(1 < n > 2)$, which is in turn a function of $[H^+]$. The higher-order terms are interpreted as resulting from the reaction of the 1 : 1 iron–catechol complex with iron(III):

$$\left.\begin{array}{l} [Fe(Hcat)]^{2+} \xrightarrow[k_0]{Fe^{III}} \\ \quad H^+ \Vert \\ [Fe(cat)]^{+} \xrightarrow[k_1]{Fe^{III}} \end{array}\right\} 2Fe^{2+} + Q$$

In the hydrogen-ion concentration range employed, some protonated complex is present and the dimeric species $[Fe{-}O{-}Fe]^{4+}$ represents only $\sim 1\%$ of the total iron(III). Participation of the dimer in the redox process is excluded since its formation rate is lower than the rate of the electron-transfer step. A similar scheme is postulated for the corresponding reaction of vanadium(V) (see below). The blue intermediate in the corresponding oxidation of 2-mercaptosuccinic acid (HORSH) has been characterized[23] and is described as having a chelated (O- and S-bonded) ring structure consistent with the observed equilibrium

$$Fe^{III} + HORSH \overset{K_1}{\rightleftharpoons} \left[\begin{array}{c} O \\ Fe \\ S \end{array}\!\!\begin{array}{l} \diagup \\ \diagdown \end{array}\!\!R\right]^{+} + 2H^+$$

Reactions of the oxo-bridged dimers $[L_2(H_2O)Fe{-}O{-}Fe(H_2O)L_2]$ (L = 2,2′-bipy or *o*-phen) with cyanide ion are pH-dependent and yield iron(II) complexes as products.[24] At pH 1.2—1.5 and ambient temperature these are $[Fe^{II}L_2(CN)_2]$. At higher pH's, however, there is initial replacement of H_2O by CN^- in the reactant dimeric complexes and a rapid colour change may be used to monitor the decomposition of these ions to monomers:

$$[L_2(CN)Fe{-}O{-}Fe(CN)L_2]^{2+} \xrightarrow{CN^-} [FeL_2(CN)_2]^+$$

Several studies have been reported of reactions of hexacyanoferrate(III). The oxidation of sulphite has been re-investigated.[25] Under conditions of higher ionic strength where $K_3[Co(CN)_6]$ and KCl were used to compensate for changes in $[K^+]$ caused by addition of $K_4[Fe(CN)_6]$, which is known to retard the rate, the following

[23] K. J. Ellis and A. McAuley, *J.C.S. Dalton*, 1973, 1533.
[24] B. J. C. Lima, F. David, and P. G. David, *J.C.S. Dalton*, 1974, 680.
[25] R. S. Murray, *J.C.S. Dalton*, 1974, 2381.

mechanism for formation of the intermediate is consistent with the data:

$$[Fe(CN)_6]^{3-} + SO_3^{2-} \underset{k_\beta}{\overset{k_\alpha}{\rightleftharpoons}} [Fe(CN)_6]^{4-} + SO_3^{-\cdot}$$

$$[Fe(CN)_6]^{3-} + SO_3^{-\cdot} \xrightarrow{k_\gamma} [Fe(CN)_5(CNSO_3)]^{4-}$$

The rate constant k_α is lowered by $\sim 5\%$ in the presence of dioxygen. The involvement of radicals in the reaction has been shown by the effects of allyl alcohol on the products. This scavenger has no effect on the rate of consumption of $[Fe(CN)_6]^{3-}$ but the relative proportions of intermediate to $[Fe(CN)_6]^{4-}$ decrease on increasing allyl alcohol concentration, presumably as a result of increasing competition for the radical anion (A = allyl alcohol):

$$A + SO_3^{-\cdot} \xrightarrow{k_\delta} ASO_3^{\cdot}$$

The relative rate constants k_β/k_γ and k_δ/k_γ are 5×10^{-3} and 8.3×10^{-2} respectively. The redox equilibrium

$$2H^+ + 2[Fe(CN)_6]^{3-} + HNO_2 + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} 2[Fe(CN)_6H_2]^{2-} + HNO_3 \quad (2)$$

is established rapidly in solution and has been investigated using both spectrophotometric and e.m.f. methods.[26] The extent of reaction is very sensitive to changes in hydrogen-ion concentration but there is little difference in measured K_1 values in $HClO_4$ and H_2SO_4 media over the range ~ 4—7 mol l^{-1}. Above this concentration of mineral acid, however, there is a dramatic change in the value of K_1 which may be due to protonation of the ferricyanide and/or increasing ionization of molecular nitrous acid to the nitronium ion. Low concentrations of HNO_2 and HNO_3 were employed to prevent a secondary stage involving attack by nitrogen dioxide on $[Fe(CN)_6]^{3-}$ to produce an intermediate similar to nitroprusside. In a further paper, however, studies of this latter reaction have been reported.[27] In 6M-HNO_3 in the presence of nitrous acid, the rate law may be expressed as

$$\text{Rate} = k[Fe(CN)_6{}^{3-}][HNO_2]^{1/2}$$

which is the same form as has been observed for the formation of the intermediate described. The half-order in $[HNO_2]$ is observed over a 10^3-fold range of concentration and cannot be explained as an average value resulting from parallel zero and first-order reactions. The mechanism proposed involves as a first stage the establishment of equilibrium (2) followed by a rate-determining attack by an equilibrium concentration of nitrogen dioxide on the oxidant:

$$H^+ + HNO_2 + NO_3^- \overset{\text{fast}}{\rightleftharpoons} N_2O_4 + H_2O$$

$$N_2O_4 \overset{\text{fast}}{\rightleftharpoons} 2NO_2$$

$$NO_2 + [Fe(CN)_6]^{3-} \xrightarrow{\text{slow}} \text{Intermediate} + \tfrac{1}{2}HCN$$

The intermediate species is not the $[Fe(CN)_5NO]^{2-}$ ion and is considered to be a bridged dinuclear complex, $[(NC)_5Fe—NO—Fe(CN)_4NO]^{3-}$, which subsequently decomposes.

[26] J. C. Bates, K. M. Davies, and G. Stedman, *J.C.S. Dalton*, 1974, 246.
[27] K. M. Davies and G. Stedman, *J.C.S. Dalton*, 1974, 2176, 2182.

Evidence has been presented whereby the proposed two-stage process in the transfer of an electron to a metal complex is substantiated. It is generally acknowledged that whilst ligands such as ammonia with no vacant low-energy orbitals may be considered as 'insulating', electron gain or loss may involve ligand participation if there is a vacant orbital to provide a low-energy pathway. Cyanide ion represents such a ligand and irradiation of pentacyanonitrosylferrate(II) in methanol as a glass[28] yields the paramagnetic ion $[(NC)_5Fe(NO)]^{2-}$ in the initial step. The reaction of photolysed pentacyanonitrosylferrate(II) and thiocyanate has been investigated in aqueous media.[29] After exposure to monochromatic radiation, the products were stored for 24 h before use to allow for establishment of the equilibrium

$$[Fe(CN)_5NO_2]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5(H_2O)]^{3-} + NO_2^-$$

When solutions were used immediately after irradiation, reproducible kinetics were not observed. The co-ordinated nitrite in the iron(II) complex is probably protonated under the conditions used and the formation of the product $[Fe^{III}(CN)_5SCN]^{3-}$ may best be rationalized by the scheme

$$[(NC)_5FeNO_2H]^{3-} + SCN^- \longrightarrow [(NC)_5FeSCN]^{4-} + NO_2H$$

$$[(NC)_5FeSCN]^{4-} + 2H^+ + NO_2^- \longrightarrow [(NC)_5FeSCN]^{3-} + NO + H_2O$$

in which the intermediate pentacyanothiocyanatoferrate(II) is oxidized by nitrite ion or nitrous acid. The reactivity of pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles has been described.[30] Ligand-exchange kinetics give clear evidence of a dissociative mechanism. Redox potentials of the Fe^{II}/Fe^{III} couples have been established and the iron(II) complexes may be reversibly oxidized by Ce^{IV} with disappearance of the characteristic charge-transfer band.

The reaction of hydrogen atoms with hexacyanoferrate(II) is independent of pH in the range 1—8.[31] After the reaction, two consecutive processes are observed one of which is first order, the second being the reaction of an intermediate with $[Fe(CN)_6]^{4-}$. The final product is aquapentacyanoferrate(II) and the reaction scheme may be written in the form shown in Scheme 2, where in the initial equilibrium it is considered that the hydrogen atom adds to the CN^- ligand to give the species $[(NC)_5$-

$$H\cdot + [Fe^{II}(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6H]^{4-} \longrightarrow [Fe^{I}(CN)_5HCN]^{4-}$$

$$\downarrow + [Fe^{III}(CN)_6]^{3-} \qquad \downarrow$$

$$2[Fe^{II}(CN)_6]^{4-} + H^+ \qquad [Fe(CN)_5]^{4-}$$

$$[Fe^{I}(CN)_5]^{4-} + [Fe^{II}(CN)_6]^{4-} \longrightarrow [Fe^{II}(CN)_5]^{3-} + [Fe^{I}(CN)_6]^{5-}$$

$$[Fe^{I}(CN)_5]^{4-} + [Fe^{III}(CN)_6]^{3-} \longrightarrow [Fe^{II}(CN)_5]^{3-} + [Fe^{II}(CN)_6]^{4-}$$

$$[Fe^{II}(CN)_5]^{3-} + H_2O \longrightarrow [(H_2O)Fe(CN)_5]^{2-}$$

Scheme 2

[28] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Chem. Comm.*, 1973, 917.
[29] P. A. Stoeri and D. X. West, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2347.
[30] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.
[31] D. Zehavi and J. Rabani, *J. Phys. Chem.*, 1974, **78**, 1368.

Fe—Ċ=NH]$^{4-}$. As shown, all the intermediates react with $[Fe(CN)_6]^{3-}$, and the iron(I) species, $[Fe(CN)_6]^{5-}$, is thought to undergo oxidation either by this reagent or by H_2O_2 produced in solution.

The oxidation of alcohols by ferrate(VI) ion has been reported.[32] This ion is a very strong oxidant,

$$FeO_4^{2-} + 8H^+ + 3e \longrightarrow Fe^{3+} + 4H_2O \qquad \varepsilon^0 = 2.2 \pm 0.03\ V$$

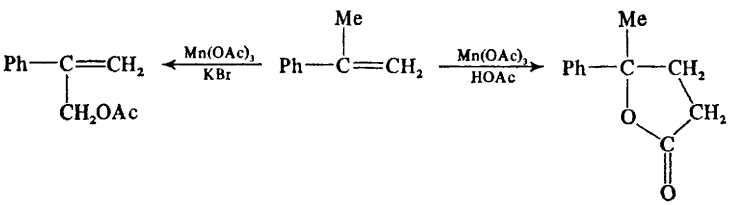
and is reduced by virtually all water-soluble substrates. A method of preparation of the potassium salt is described and in the reaction with polyhydric alcohols it is suggested that the iron(VI) reacts with the terminal functional groups in the initial step.

Polarographic evidence has been presented for the four-membered electron-transfer series $[M(Et_2dtc)_2(mnt)]^{z-}$, $z = -2 \rightarrow +1$, for the bis-(*NN*-disubstituted-dithiocarbamatodithiolene) complexes of iron and ruthenium.[33] In the case of the latter metal all steps are reversible. For the exchange $z = -1$ to $z = 0$ for iron, there is a decrease in electron density around the metal and there may be significant Fe^{IV} character in this species in which all six primary co-ordination sites are occupied by sulphur. Studies of the iron(II)/(III) couple in liquid ammonia[34] show the reaction to be almost completely reversible on vitreous carbon or reduced gold electrodes. The process is interpreted in terms of the spin states of the metal centres. Iron(III) carboxylate complexes have been postulated as catalysts in the reduction of iron(III) by phosphine in the presence of iodide in carboxylate media.[35]

3 Manganese(III) and Manganese(VII)

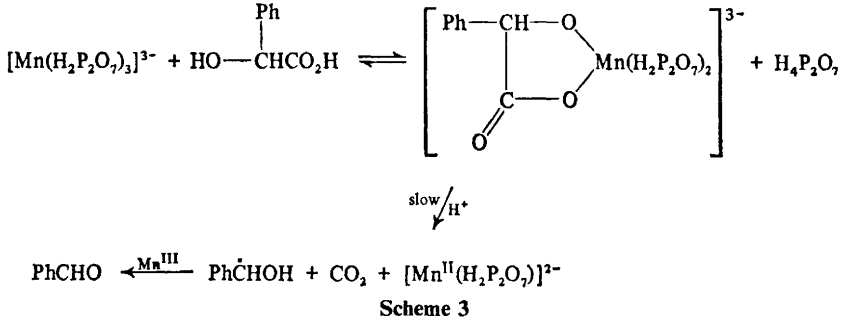
The kinetics and mechanism of the reduction of Mn^{III} at a platinum electrode in perchlorate media[36] have been reported and the new value derived for the redox potential, $\varepsilon^0 = 1.535 \pm 0.003$ V, is closely similar to that obtained by other workers. Previously, hydrolytic equilibria of these highly charged aquo-ions have been interpreted in terms of a $M^{III} \cdot OH^- \rightleftharpoons M^{II}OH$ charge-transfer resonance consistent with a correlation with M^{III} reduction potentials. A corresponding extent of charge transfer is inferred in the interpretation of the electrode mechanism.

The oxidation of α- and β-methylstyrenes by manganese(III) acetate is slow at 80 °C, but in the presence of KBr a rapid reaction leading to β-phenylallyl acetate is observed:[37]



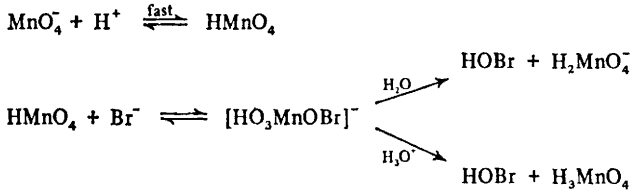
[32] D. H. Williams and J. T. Riley, *Inorg. Chim. Acta*, 1974, **8**, 177.
[33] L. H. Pignolet, G. S. Patterson, J. F. Weiher, and R. H. Holm, *Inorg. Chem.*, 1974, **13**, 1263.
[34] O. R. Brown and S. A. Thornton, *J.C.S. Faraday I*, 1974, **70**, 14.
[35] D. V. Sokol'skii, Ya. A. Dorfman, G. D. Rotopopova, *Russ. J. Inorg. Chem.*, 1973, **47**, 1116.
[36] D. R. Rosseinsky and R. J. Hill, *J.C.S. Faraday I*, 1974, **70**, 1140.
[37] A. Kasahara, R. Saito, and T. Izumi, *Bull. Chem. Soc. Japan*, 1973, **46**, 2610.

Tris(dihydrogen diphosphato)manganate(III) has also been widely used as an oxidant, and in the reaction with mandelic acid[38] in sulphuric acid media the initial step is the formation of a mixed Mn^{III} complex which undergoes hydrogen-ion-catalysed internal electron transfer to yield a radical. Further oxidation leads to benzaldehyde as the organic product (Scheme 3). The presence of Mn^{II} retards the rate, possibly as a result of competition for the radicals produced.



Scheme 3

In the oxidation of bromide by manganese(VII),[39] the stopped-flow method has been employed to monitor both the disappearance of MnO_4^- and the formation of Br_3^-. In the presence of excess bromide, rate plots show curvature, and the mechanism involves the reversible formation of a Mn^V–Br^I complex:

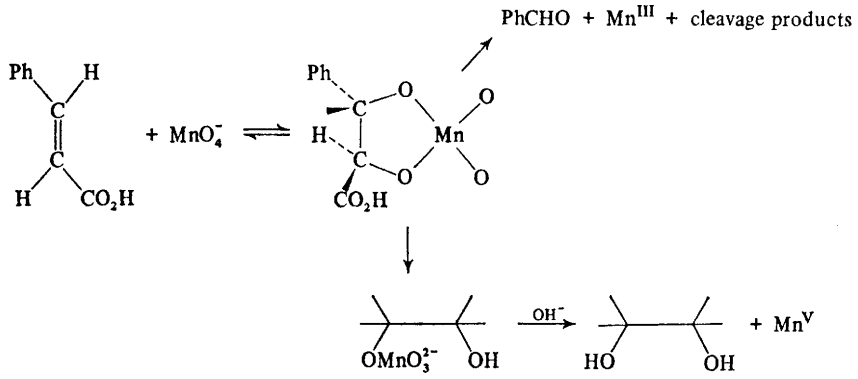


Any reaction in which MnO_4^- is reduced to Mn^{VI} whilst Br^- is oxidized to $\frac{1}{2}Br_2$ or HOBr is thermodynamically forbidden. It appears, however, that protonation sufficiently modifies the oxidant to allow the reaction to proceed. From an analysis of several systems the observation has been made that if the potential for the oxidation couple {*e.g.* I^-/I_2 or $[Fe(CN)_6]^{4-/3-}$} is less than that (+0.564 V) for MnO_4^-/MnO_4^{2-}, reaction may take place without $[H^+]$ dependence and by a relatively simple mechanism. If the oxidation couple is more negative than this value {*e.g.* Br^-/Br_2 or $[Fe(phen)_3]^{2+/3+}$}, the rate law exhibits a proton dependence and the more complex mechanism results in the need to overcome the unfavourable first step.

Intermediate complexes in the oxidation of cinnamic acid[40] and crotonic acid[41] have been characterized using spectroscopic techniques. In the former system, stopped-flow studies on the *trans*-isomer in perchloric acid indicate that the rates of disappearance of oxidant (λ = 530 nm) and of formation of the intermediate

[38] J. Barek and A. Berka, *Coll. Czech. Chem. Comm.*, 1974, **39**, 3278.
[39] S. A. Lawani and J. R. Sutter, *J. Phys. Chem.*, 1973, **77**, 1547.
[40] D. G. Lee and J. R. Brownridge, *J. Amer. Chem. Soc.*, 1973, **95**, 3033; 1974, **96**, 5517.
[41] K. B. Wiberg, C. J. Deutsch, and J. Rocek, *J. Amer. Chem. Soc.*, 1973, **95**, 3055.

hypomanganate ester (λ = 415 nm) are identical and that a slower secondary step is consistent with the decomposition to manganese(III) and benzaldehyde, together with some other cleavage products. Deuterium kinetic effects are suggestive of initial addition of the oxidant across the C=C double bond. The enthalpy of complex formation is low ($\Delta H^{\ddagger} \sim 4.2$ kcal mol^{-1}) whereas for the redox step the corresponding value is 11.9 kcal mol^{-1}. The rate of formation of the intermediate is relatively insensitive to substitution in the aromatic ring of the organic substrate. The differences in rates of the two stages are attributed to the fact that in the primary reaction there is cleavage of only one π-bond, whereas in the electron-transfer step three σ-bonds are broken (Scheme 4).



Scheme 4

In a comparable study in which unsaturated dicarboxylic acids (H_2A) were used as substrates,[42] activation enthalpies were observed for the formation of the intermediates remarkably similar to those above in reactions of both H_2A and HA^- with oxidant. The authors in this paper, however, chose to describe the ester intermediate as a manganese(v) complex, an observation which has been rejected on spectroscopic grounds.[40] In the reaction with crotonic acid,[41] the optical density changes at 525 nm and 420 nm paralleled those described above. The spectra both of Mn^{VII} and of the intermediates formed by the reactions

$$MeCH{=}CHCO_2^- + MnO_4^- \xrightarrow{k_1} [I_I]$$
$$[I_I] + HO^- \longrightarrow [I_{II}]$$

are presented and the substantial differences noted lead to the conclusion that I_I and I_{II} are, in fact, Mn^V intermediates. An interesting observation, if such is the oxidation state, is the relatively high stability of I_I in neutral solution. Manganate(v) is generally stable with respect to disproportionation only in strongly alkaline media. The stability of the intermediate may result, however, from its composition as a diester which is completely ionized even under neutral conditions. Kinetic analysis of the data indicate that I_I and I_{II} are, in fact, oxidized by MnO_4^- to a manganate(VI) state. The oxidation of aliphatic acids by Mn^{VII} has been studied in acidic media.[43] The

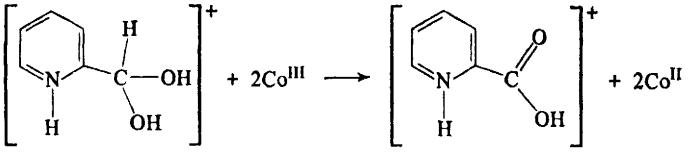
[42] L. J. Simandi and M. Jaky, *J.C.S. Perkin II*, 1973, 1856.
[43] K. K. Banerji, *Bull. Chem. Soc. Japan*, 1973, **46**, 3623.

reactions are autocatalytic, which may be due to the effects of Mn^{III} (or Mn^{IV}) in solution. Deuterium isotope effects are consistent with the rupture of the α-C—H bond as the rate-determining process.

The kinetics of disproportionation of manganate(VI) in acid solution have been studied.[44] The stopped-flow technique was used with manganate(VI) in basic solution in one syringe mixed with hydrogen ions to yield a known final $[H^+]$. Differing reaction orders are observed on monitoring the disappearance of MnO_4^{2-} (at 610 nm), where a first-order rate law is shown, and on the appearance of MnO_4^- (at 520 nm), where a second-order rate law obtains.

4 Cobalt(III)

The oxidation of 2-, 3-, and 4-pyridinecarboxaldehydes (PA) by aquocobalt(III) has been studied in perchlorate media.[45] The organic substrates are virtually completely N-protonated in acid solution but show differing degrees of hydration of the aldehydic group. The 2-PA and 4-PA systems are extensively hydrated whereas the 3-PA molecule is much less affected. The reactions are sufficiently slow to be monitored using conventional spectrophotometric techniques, and for the oxidations of all three aldehydes, *e.g.*



the observed rate law is

$$\text{Rate} = \{k_1 + k_2K_h/[H^+]\}[Co^{III}][PA] \qquad (3)$$

The values of k_1 at various $[H^+]$ and temperatures showed no systematic variation, the intercepts in the plots of observed rate constant against $[H^+]^{-1}$ being very small. The conclusion was reached that the only pathway involves the $CoOH^{2+}$ ion and the hydrated form of the aldehyde. Activation parameters show little differences between the various substrates and an inner-sphere mechanism is postulated, the rate-determining step being the fission of a C—H bond to yield a radical which is rapidly further oxidized by a cobalt(III) ion to the pyridine carboxylic acid. The study of the oxidation of thiourea and its N-substituted derivatives has been extended and re-investigated over a larger hydrogen-ion concentration range.[46] The rate law is as observed previously and is identical to that shown above. Unlike the pyridine aldehydes, however, the contribution from the reaction of $[Co(H_2O)_6]^{3+}$ [the k_1 pathway in (3)] is measurable, although still accounting for a relatively small percentage of the total reactivity. Activation parameters (Table 1) are, however, remarkably similar to those derived for the above reactions and for other inorganic systems and are consistent with a common (inner-sphere) mechanism. The rate constants are about an order of magnitude higher than for other reactions of this type and the possibility of some associative character cannot be completely excluded.

[44] J. H. Sutter, K. Colquitt, and J. R. Sutter, *Inorg. Chem.*, 1974, **13**, 1444.
[45] R. Giuntoli and H. S. Habib, *J. Inorg. Nuclear Chem.*, 1974, **36**, 363.
[46] A. McAuley and R. Shanker, *J.C.S. Dalton*, 1973, 2321.

Table 1 *Kinetic and thermodynamic data for oxidations by cobalt(III) ions*

Reaction	k(25 °C)/ l mol^{-1} s^{-1}	I/mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
$CoOH^{2+}$ + 2-PA	8.55×10^{-2}	1.03	24.8	22.3	45[a,b]
$CoOH^{2+}$ + 3-PA	23.6×10^{-2}	1.03	26.2	29.3	45[a,b]
$CoOH^{2+}$ + 4-PA	36.1×10^{-2}	1.03	26.9	32.8	45[a,b]
$CoOH^{2+}$ + $(NH_2)_2CS$	382	1.50	26.3	43	46
$CoOH^{2+}$ + $(MeNH)_2CS$	318	1.50	25.3	29	46
$CoOH^{2+}$ + $(MeNH)(NH_2)CS$	367	1.50	24.2	36	46
$CoOH^{2+}$ + $(EtNH)_2CS$	320	1.50	24.1	35	46
$CoOH^{2+}$ + $(CH_2NH)_2CS$	241	1.50	26.5	41	46
$CoOH^{2+}$ + VB	1.35×10^{4}	2.0	—	—	48[c]
$CoOH^{2+}$ + HL·	1.53×10^{4}	2.0	—	—	48[c,d]
Co^{3+} + $(NH_2)_2CS$	163	1.50	19.9	20	46
Co^{3+} + $(MeNH)_2CS$	270	1.50	18.8	18	46
Co^{3+} + $(MeNH)(NH_2)CS$	361	1.50	21.2	26	46
Co^{3+} + $(EtNH)_2CS$	300	1.50	15.6	7	46
Co^{3+} + $(CH_2NH)_2CS$	130	1.50	21.7	23	46

[a] PA = pyridinecarboxaldehyde. [b] T = 15 °C; [H$^+$] = 1.03 mol l^{-1}. [c] VB = variamine blue; [H$^+$] = 1.0 mol l^{-1}. [d] HL· = semiquinone form of VB.

They are, however, still substantially lower than the values for the reactions with hydroquinone and iodide ion which are thought to be outer-sphere.[47] The oxidation of variamine blue, *N*-(*p*-methoxyphenyl)phenylenediamine (L), has been studied in an excess of cobalt(III)[48] under anaerobic conditions. The reaction is biphasic, with a rapid initial step yielding Co^{II}. The rate law is essentially similar to equation (3) although there is some deviation from pseudo first-order behaviour even at very high oxidant concentrations. The overall reaction may be expressed as involving the protonated ligand,

$$CoOH^{2+} + HL^{+} \xrightarrow{k_1} Co^{II} + HL\cdot$$

$$CoOH^{2+} + HL\cdot \xrightarrow{k_2} Co^{II} + L_{ox}$$

where HL· is the iminoquinone form of variamine blue and L_{ox} is the oxidized product. The rate constants k_1 and k_2 are both much greater than other values obtained and an outer-sphere mechanism is postulated. It is of interest, however, that k_2 is only marginally greater than k_1.

Cobalt(III) trifluoroacetate is a strong oxidant formed by the equilibration of di-μ-hydroxo-diacetatocobalt(III) in trifluoroacetic acid (TFA).[49] In this medium facile oxidation of hydrocarbons is observed, in that benzene yields phenyl trifluoroacetate and ethylene is converted into ethyleneglycol ditrifluoroacetate:

$$CH_2{=}CH_2 + Co(O_2CCF_3)_3 \longrightarrow \overset{+}{C}H_2{-}\dot{C}H_2 + Co^{II}(O_2CCF_3)_3$$

$$\downarrow +HO_2CCF_3$$

$$CF_3CO_2CH_2\dot{C}H_2 \xrightarrow{Co^{III}} (CF_3CO_2CH_2)_2$$

[47] G. Davies and K. O. Watkins, *J. Phys. Chem.*, 1970, **74**, 3388.
[48] T. Imamura and M. Fujimoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 2774.
[49] R. Tang and J. K. Kochi, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3845.

The radical cation intermediate formed in the primary redox reaction has been characterized using e.s.r. techniques. The reaction of cobalt(III) acetate with *p*-toluic acid is autocatalytic in acetic acid,[50] the second-order dependence on oxidant concentration being seen to reflect the dimeric nature of the metal-ion reactant. The first step involves a redox equilibrium with one mole of Co^{II} released, which thus explains the observed inverse order of $[Co^{II}]$ on the rate. The radical intermediate in this system may then react with any O_2 present.

Electron-transfer reactions of cobalt(III) complexes with hydrazines have been investigated.[51] In dilute acid solution, the reaction

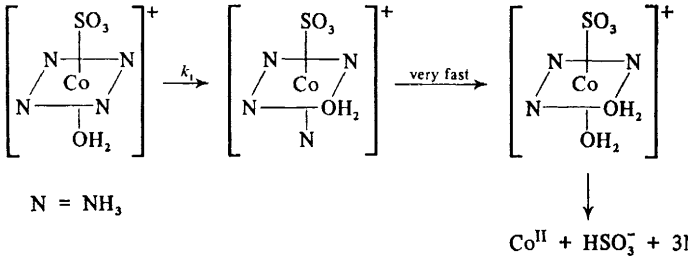
$$trans\text{-}[Co(en)_2Cl_2]^+ + N_2H_4 \longrightarrow [Co^{II}(en)_2]^{2+} + 2Cl^- + NH_4^+ + \tfrac{1}{2}N_2$$

is rapid and the liberation of N_2 is accompanied by a colour change from green to orange-yellow. The methylhydrazine complex *cis*-$[Co(en)_2(NH_2NHMe)Cl]^{2+}$ has also been prepared and undergoes spontaneous redox in aqueous solution, the rate-determining step being an electron transfer from the $MeNHNH_2$ to the cobalt(III) centre. The rate of the reaction

$$[Co(en)_2(H_2NNHMe)Cl]^{2+} \longrightarrow [Co^{II}(en)_2]^{2+} + Cl^- + MeNH_3^+ + \tfrac{1}{2}N_2$$

decreases with increasing perchloric acid concentration.

The redox decomposition of *trans*-tetra-ammineaquosulphitocobalt(III) in aqueous solution has also been studied.[52] These complexes containing oxidizable ligands are of interest in that they may be viewed as 'precursor' species capable of yielding first-order rate constants for electron transfer. The characterization of the *trans*-$[Co(NH_3)_4(H_2O)SO_3]^+$ ion has been described and, whilst first-order decomposition plots show some initial curvature, neither products nor radical scavengers affect the rate. Two stages are proposed, as shown in Scheme 5, the first being a



Scheme 5

trans→ *cis* isomerization and the second a faster loss of a (labilized) *trans*-ammine group with subsequent electron transfer. The loss of initial curvature and increased reaction rate in the presence of Fe^{II} are accounted for by reaction of this reducing agent with both the mono- and bis-aquo-sulphito-complexes. Products of the reactions of the monoaquosulphito-complex with $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, and $[Fe(CN)_5NO]^{2-}$ are μ-cyano mixed dinuclear species.[53] The pre-

[50] M. Kashima and Y. Kamiya, *Bull. Chem. Soc. Japan*, 1974, **47**, 481.
[51] S. C. Chan and C. K. Lee, *Austral. J. Chem.*, 1973, **26**, 1923.
[52] M. A. Thacker, K. L. Scott, M. E. Simpson, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 647.
[53] K. L. Scott, R. S. Murray, W. C. E. Higginson, and S. W. Foong, *J.C.S. Dalton*, 1973, 2335.

paration and characterization of *cis*- and *trans*-tetra-amminebis(sulphito)cobaltate-(III) ions have been reported.[54] This has enabled a re-definition to be made of the spectra of these isomers. In aqueous acidic solution ($HClO_4$) the aquation of the *trans*-complex is too rapid for study by conventional methods. The *cis*-species, however, under similar conditions shows an immediate change in the spectrum consistent with the rapid formation of $[Co(NH_3)_2(H_2O)_2(SO_3)_2]^-$, where *trans* labilization by the SO_3^{2-} group again appears to be important. This complex undergoes redox decomposition, and under air-free conditions the rate law over the $[H^+]$ range 0.02—0.2 mol l^{-1} is of the form

$$\text{Rate} = \{k_1[H^+] + k_2\}[Co^{III}]$$

where the contribution of k_2 is only about 3% of the observed rate constant. Although the second-order process

$$cis\text{-}[Co(NH_3)_2(H_2O)_2(SO_3)_2]^- + H^+ \longrightarrow Co^{II} + 2HSO_3^- + 2NH_4^+$$

implied by the k_1 term of the rate law may represent an electron-transfer step, it is not possible to exclude completely the possibility of a process involving some proton-assisted reaction with a very rapid subsequent redox interaction. The activation parameters for k_1 are similar in magnitude ($\Delta H^{\ddagger} = 26.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 23.4$ cal K^{-1} mol^{-1}) to typical values for substitution at a cobalt(III) centre and it may be that the essential process involved in an electron-transfer reaction of this type is similar to that in a substitution.

The kinetics of reduction of 1,2,6-triaquodipropylenetriamminecobalt(III), $[(H_2O)_3Co(dpt)]^{3+}$, in aqueous perchloric acid[55] have been studied over the range 60—80 °C. The first-order rate constant may be expressed as

$$k_{obs} = k_1 + k_\alpha/[H^+]$$

the inverse hydrogen-ion dependence arising from the reduction of the hydroxy-diaquo-complex:

$$[(H_2O)_3Co(dpt)]^{3+} \rightleftharpoons [(HO)(H_2O)_2Co(dpt)]^{2+} + H^+$$

$$\swarrow k_1 \qquad k_2 \searrow$$

$$Co^{II} + \text{oxidized products of dpt}$$

The consecutive reaction sequence in the hydrolysis of $[Co(NH_3)_5(OH_2)]^{3+}$ has been investigated[56] and it is found that spontaneous reduction of the red $[Co(NH_3)_3(H_2O)_3]^{3+}$ complex occurs. A hydrogen-ion dependence identical to that above is observed, again resulting from deprotonation of a co-ordinated water molecule. An extension of the investigations to *cis*-$[Co(NH_3)_2(H_2O)_4]^{3+}$ and *cis*-diaquobis(trimethylenediamine)cobalt(III), *cis*-$[Co(tmd)_2(OH_2)_2]^{3+}$, shows a similar behaviour pattern.[57] Including data from previous studies (see Table 2) an order of reduction rates for the k_2 pathway *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ < *cis*-$[Co(tmd)_2(OH_2)_2]^{3+}$ < 1,2,3-$[Co(dien)(OH_2)_3]^{3+}$ < 1,2,3-$[Co(NH_3)_3(OH_2)_3]^{3+}$ < 1,2,6-$[Co(dpt)(OH_2)_3]^{3+}$ < *cis*-$[Co(NH_3)_2(OH_2)_4]^{3+}$ has been established. A similar sequence, somewhat less well

[54] K. L. Scott, *J.C.S. Dalton*, 1974, 1486.
[55] S. Lunn, L. Ereshefsky, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2401.
[56] W. D. Stanley, S. Lunn, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3587.
[57] W. D. Stanley, T. Davies, T. D. Tullius, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3857.

Table 2 *Thermodynamic and kinetic parameters for the redox decomposition of cobalt(III) ammine complexes*

Complex	k/s^{-1}	I/mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
trans-$[Co(NH_3)_4(OH_2)(SO_3)]^+$	1.14×10^{-4}	1.00	26.5	12.5	52[a]
cis-$[Co(NH_3)_2(OH_2)_2(SO_3)_2]^-$	1.39×10^{-2}	1.00	26.5	23.4	54[b]
fac-$[Co(NH_3)_3(OH_2)_3]^{3+}$	1×10^{-6}	1.00	34.6	—	56[c]
cis-$[Co(NH_3)_2(OH_2)_4]^{3+}$	3×10^{-6}	1.00	—	—	57[d]
cis-$[Co(tmd)(OH_2)_2]^{3+}$	4×10^{-8}	1.00	—	—	57[d,e]
1,2,3-$[Co(dien)(OH_2)_3]^{3+}$	6.5×10^{-8}	1.00	36.7	—	56[d]
1,2,6-$[Co(dpt)(OH_2)_3]^{3+}$	2.5×10^{-6}	1.00	—	—	57[d,f]
cis-$[Co(en)_2(OH_2)_2]^{3+}$	$\ll 3 \times 10^{-8}$	1.00	—	—	57[d]

[a] T = 25 °C. [b] $[H^+]$-catalysed path; T = 25 °C. [c] Extrapolated data at T = 109.8 °C. [d] T = 80 °C. [e] tmd = tetramethylenediamine. [f] dpt = dipropylenetriamine.

defined, probably holds for the acid-independent pathway. The increase in redox rate thus appears to correlate with the increasing number of aquo-ligands. The results of a somewhat more detailed study on the ammonia complexes have been published. The initial step in the thermal decomposition of $[Co(NH_3)_6]^{3+}$ is the $[H^+]$-independent formation of $[Co(NH_3)_5(OH_2)]^{3+}$. An inverse hydrogen-ion dependence of the following steps has been substantiated,[58] and the primary reaction in the electron transfer involves oxidation of a water molecule to give ·OH:

$$[Co(NH_3)_3(OH_2)_3]^{3+} + H_2O \rightleftharpoons [Co(NH_3)_3(OH_2)_3]^{2+} + \cdot OH + H^+$$

Since it is known that ·OH does not in fact attack co-ordinated ammonia, a rapid dissociation of the Co^{II} ammine complex followed by attack by this radical on the ammonia released would then account for the formation of $\cdot NH_2$ radicals. The reaction products are Co^{2+}_{aq}, NH_4^+, N_2, N_2O, and a relatively small amount of O_2. The yields of N_2 and N_2O are close to those expected if NH_2OH were the intermediate giving rise to these gases. An interesting overlap on these studies is provided[59] by data on the rate of detachment of NH_3 from cobalt(III) complexes reduced by pulse radiolysis. The rate constant $k_0 = 8 \times 10^{10}$ l mol^{-1} s^{-1} for the process

$$e^- + [Co(NH_3)_6]^{3+} \xrightarrow{k_0} [Co(NH_3)_6]^{2+}$$

is consistent with a diffusion-controlled reaction. The resulting cobalt(II) complexes are unstable, and conductance measurements indicate loss of three NH_3 ligands to give $[Co(NH_3)_3(H_2O)_3]^{2+}$ within 2 μs. The individual rate constants for the three subsequent (rapid) steps to the hexa-aquo-ion have been determined. Similar kinetics were observed for $[Co(NH_3)_5Cl]^{2+}$ where one Cl and two NH_3 ligands are rapidly eliminated.

A Raman spectroscopic study of the hydrogenation of aqueous pentacyanocobaltate(II) has been reported.[60] In the presence of excess cyanide ion hydrogenation may be accompanied by the formation of some $[Co(CN)_6]^{3-}$. Also, the reaction of $[Co(CN)_5]^{3-}$ and BH_4^- is not an efficient method for the preparation of the hydrido-complex since the major product has been characterized as the hexacyano-species.

[58] A. M. Newton and T. W. Swaddle, *Canad. J. Chem.*, 1974, **52**, 2751.
[59] M. Simic and J. Lilie, *J. Amer. Chem. Soc.*, 1974, **96**, 291.
[60] H. J. Clase, A. J. Cleland, and M. J. Newlands, *J.C.S. Dalton*, 1973, 2546.

A reversible redox reaction has been identified involving nitrosyl-Co(2,2′-bipy)$_2$ complexes.[61] [Co(2,2′-bipy)$_2$]$^{2+}$ ions react with NO in halide or nitrite (X^-) media to give [Co(2,2′-bipy)$_2$XNO] as products, and it is suggested that the internal redox equilibrium $Co^{III}—NO^- \rightleftharpoons Co^{II} + NO$ exists. Under mild conditions, however, irreversible oxidation of co-ordinated NO to NO_2^- takes place.

5 Vanadium(V)

Hydrogen-ion dependences in the oxidation of hydroxylamine (L) have now been extended to cover the range 0.05—1.0 mol l^{-1}.[62] The two-stage reaction in more acidic media is now viewed as a limiting form of a three-stage system as a result of a pathway which becomes important at [H$^+$] < 0.2 mol l^{-1}. Under these conditions, there is evidence for two complexes,

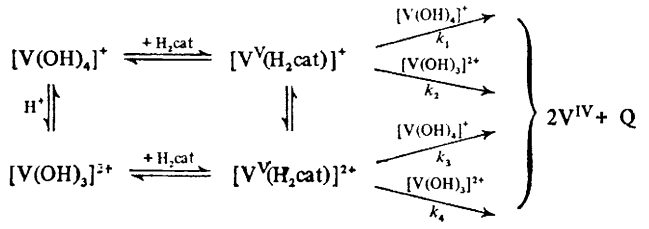
$$\begin{array}{ccccc} V^V + L & \rightleftharpoons & V^VL & \overset{+L}{\rightleftharpoons} & V^VL_2\,(+2H^+) \\ & & \downarrow k_3 & & \downarrow k_4 \end{array}$$

the second being formed more slowly than the first. The second equilibrium has an associated [H$^+$]^2 dependence and in strongly acid solutions the equilibrium is displaced to the left-hand side so that the k_3 term predominates. Some dependence of k_3 and k_4 on [H$^+$] is reported, the latter rate showing a slight decrease with increasing hydrogen ions. There is, however, still some uncertainty as to exactly which protons are eliminated in the second equilibrium step.

The kinetics of the reaction with phosphorous acid have been investigated.[63] The rate is greater in sulphuric than in perchloric acid and in both cases is first order in substrate and in vanadium(v). At [H$^+$] $\leqslant$ 5.5 mol l^{-1}, the order with respect to hydrogen ion is two. From an analysis of the activation parameters of several reactions, differing features are apparent depending on whether V^V is acting as a one-electron or a two-electron oxidant. In the case of H_3PO_3, the mechanism involves the formation of a complex which undergoes intramolecular electron transfer to yield V^{IV} and a free radical $(HO)_2\dot{P}O$ which subsequently reacts with a further mole of the metal ion to give the P^V product. Complex formation has also been observed in the reaction with catechol (*o*-dihydroxybenzene).[64] In the range [H$^+$] = 0.3—0.5 mol l^{-1} and in an excess of oxidant stopped-flow traces show an immediate increase in absorbance consistent with the presence of the protonated species $[V^VH_2cat]^+$. The reaction order with respect to [V^V] is greater than unity and is indicative of several reaction pathways (Scheme 6). The corresponding reaction with quinol[64] shows essentially similar behaviour except that the reactions involving the internal redox of the 1 : 1 complexes have also been identified (Q = quinone).

Protonated carboxylic acid complexes of vanadium(v) have been identified as catalysts in the oxidation of aniline by chlorate.[65] The oxidation of ascorbic acid

[61] A. Vlcek and A. A. Vlcek, *Inorg. Chim. Acta*, 1974, **9**, 165.
[62] G. Bengtsson, *Acta Chem. Scand.*, 1973, **27**, 3053.
[63] K. K. Sen Gupta, B. B. Pal, and D. C. Mukherjee, *J.C.S. Dalton*, 1974, 226.
[64] E. Pelizzetti, E. Mentasti, E. Pramauro, and G. Saini, *J.C.S. Dalton*, 1974, 1940.
[65] A. Vanni and P. Amico, *Gazzetta*, 1974, **104**, 747.



Scheme 6

(H_2A) in excess vanadium(v),

$$2V^{V} + H_2A \rightleftharpoons 2V^{IV} + A + 2H^{+}$$

has been studied[66] over the range $[H^+] = 0.2—1.0\ mol\ l^{-1}$. A spectrum of the transient intermediate has been obtained ($\lambda_{max} = 425\ nm$, $\varepsilon_{max} = 4.31 \times 10^3\ l\ mol^{-1}\ cm^{-1}$). Kinetics of the reaction are described by a rate law which is first order in $[H_2A]$ but which involves the equilibrium constant for the complex formation. The mechanism may be represented as

$$V^{V} + H_2A \overset{K}{\rightleftharpoons} V^{V}H_2A \xrightarrow[k_0]{\text{slow}} V^{IV} + HA\cdot$$

$$V^{V} + HA\cdot \xrightarrow{\text{fast}} V^{IV} + H^{+} + A$$

where $K = 488 \pm 28\ l\ mol^{-1}$ and $k_0 = 12.1 \pm 0.2\ s^{-1}$. A two-electron transfer to vanadium(III) followed by the reaction $V^{V} + V^{III} \rightarrow 2V^{IV}$ is ruled out since the k_0 value is at least twenty-fold greater than would be expected if the vanadium(IV) were formed *via* this route.

6 Thallium(III)

The oxidation of arsenic(III) by thallium(III) is inhibited by chloride ions,[67] the reactivity sequence following the order $Tl^{3+} > TlCl^{2+} > TlCl_2^{+} > TlCl_3 > TlCl_4^{-}$. The order with respect to both Tl^{III} and As^{III} is unity and at any constant ratio of $[Cl^-]/[Tl^{III}]$ the rate is inversely dependent on $[H^+]$. Using a large range of $[Cl^-]$, rate constants have been derived for all the chlorothallium(III) reactions. The data are consistent with the formation of an intermediate ($n = 0—3$):

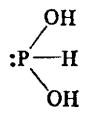
$$Tl^{3+} + H_2O \rightleftharpoons TlOH^{2+} + H^{+}$$

$$\left.\begin{aligned} TlOH^{2+} + H_3AsO_3 &\rightleftharpoons H_2O + [TlH_2AsO_3]^{2+} \xrightarrow{k_\alpha} \\ TlCl_n^{(3-n)+} + H_3AsO_3 &\rightleftharpoons H^{+} + [TlCl_nH_2AsO_3]^{(2-n)+} \xrightarrow{k_{n'}} \end{aligned}\right\} \text{products}$$

Complex formation is considered essential for the redox process. The role of the chloride ions as inhibitors is that they act as competitors in blocking the co-ordination sites on the metal ion. The situation is clearly more complicated than this, however. In a study from the same laboratory, the reverse order of reactivity of Tl^{III} chloro-complexes has been observed in the oxidation of hypophosphite.[68] The explanation for this behaviour involves a unique reaction of hypophosphite in that

[66] K. Kustin and D. L. Toppen, *Inorg. Chem.*, 1973, **12**, 1404.
[67] P. D. Sharma and Y. K. Gupta, *Austral. J. Chem.*, 1973, **26**, 2115.
[68] K. S. Gupta and Y. K. Gupta, *Inorg. Chem.*, 1974, **13**, 851.

its 'reactive' form (1) could interact in a chloride-like bridged transition state and so be closer in nature to the situation which prevails when the halide ion mediates in the interaction of two metal cations. The oxidation of catechol by aquothallium(III)



(1)

has been investigated in both an excess of reductant[69] and an excess of oxidant.[64] Unlike the corresponding reactions of iron(III) and vanadium(V),[64] there is no change in the reaction order when either Tl^{III} or organic substrate is present in excess. There is no evidence in the stopped-flow traces for the existence of intermediate complexes. The rate dependence on $[H^+]^{-1}$ is similar to that observed previously and is attributed to $TlOH^{2+}$ as the reactive species. Reactions carried out in the presence of Tl^{I} show that there is no equilibrium involving this ion, and at present there is no clear way of distinguishing between a two-electron and two single-electron transfer steps.

The reactions of thallium(III) with phenylethylenes have been investigated in methanol,[70] and the corresponding oxidation of styrene[71] involves the formation of an intermediate, $PhCH(OMe)CH_2Tl(OAc)_2$ (2). The kinetics of the decomposition of this complex have been studied in a MeOH–H_2O mixture and are dependent on $[H^+]$, [HOAc], and $[OAc^-]$. The organothallium(III) compound (2) is shown to dissociate at low concentrations, yielding two species, RTl^{2+} and $RTlOH^+$, the reactivity of the former being about three orders of magnitude greater than that of the latter. The e.s.r. technique has been used in the study of reactions where thallium(III) acts as a one-electron oxidant for arenes.[72] With the tristrifluoroacetate salt the reaction

$$Tl(O_2CCF_3)_3 + ArH \longrightarrow ArTl(O_2CCF_3)_2 + CF_3CO_2H$$

takes place and there is evidence for arene cation radicals as intermediates. This is one of the few instances of this oxidant behaving as a single-electron acceptor, a feature which is not unexpected in view of the instability of Tl^{II} in aqueous media.

7 Cerium(IV)

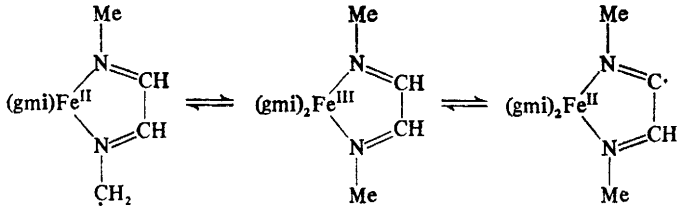
This reagent continues to attract attention as an oxidant for both organic and inorganic substrates. The choice of reaction medium ($HClO_4$ or H_2SO_4) seems to play an important part in the mode of oxidation, probably as a result of the competition in the latter system between the reacting substrate and SO_4^{2-} as ligands in the formation of any intermediate complexes. In nitrate media, however, the situation seems more akin to that in perchlorate in that over the nitrate concentration range 0.5—10 mol l^{-1} only one complex, $[Ce(NO_3)]^{3+}$, is present in equilibrium with the uncomplexed metal ion.[73] The evaluation of the equilibrium constant $K_1 = 0.14 \pm 0.1$ l mol^{-1} confirms that the observation of metal–ligand intermediates in the presence

[69] E. Pelizzetti, E. Mentasti, and G. Saini, *J.C.S. Dalton*, 1974, 721.
[70] L. Nadon, M. Zador, and S. Fliszar, *Canad. J. Chem.*, 1973, **51**, 2366.
[71] L. Nadon and M. Zador, *Canad. J. Chem.*, 1974, **52**, 2667.
[72] I. H. Elson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 5060.
[73] I. A. Lebedev, B. F. Myasvedov, and V. Y. Frenkel, *Russ. J. Inorg. Chem.*, 1973, **18**, 1716.

of this anion is much more likely. The reaction with phosphorous acid,[74]

$$2Ce^{IV} + H_3PO_3 \xrightarrow{H_2O} 2Ce^{III} + H_3PO_4$$

has been studied at 70 °C in 1—2M-sulphuric acid. There are no complexes formed between the Ce^{IV} and phosphorus(III) although other oxidations of this substrate by metal ions have shown such species to exist. The rate is markedly dependent on $[HSO_4^-]$ and a principal pathway involves the reaction of $Ce(SO_4)_2$. No metal-ion complexes have been found in the oxidation of thiols by cerium(IV),[75] where a study of the stoicheiometry of these reactions has confirmed that over-oxidation may take place depending both on the concentration of the thiol and on the presence of a free β-carboxylate group in the organic substrate. The oxidation of the ligands in iron(II) di-imine complexes has been reported.[76] Tris(glyoxalbismethylimine)iron(II), $[Fe(gmi)_3]^{2+}$ (gmi = MeN=CH—CH=NMe), is oxidized stoicheiometrically by Ce^{IV} in 10M-H_2SO_4 to the iron(III) complex. At lower mineral acid concentrations ($\sim$1—4M-H_2SO_4) the reaction with one equivalent of oxidant results in the formation of two ligand-oxidized species $[Fe(gmi)_2(ga)]^{3+}$ and $[Fe(gmi)_2(gh)]^{2+}$ (ga = MeN=CH—CONHMe and gh = MeN=CH—CH=NCH$_2$OH). The reaction proceeds *via* the formation and disproportionation of $[Fe(gmi)_3]^{3+}$, and these systems may be considered as limiting cases in an induced-electron-transfer mechanism. In this case the two-electron oxidation of a ligand occurs by the concomitant action of an internal and an external one-electron oxidant. In general, the internal oxidant is the central metal ion (in the higher oxidation state) bound to the ligand to be oxidized and the external oxidant is another complexed metal ion in its higher oxidation state. The $[Fe(gmi)_3]^{2+}$ complexes represent a system where both metal ions are identical. The radical complex when formed may be present in several redox equilibrium forms which then react to yield the observed products (Scheme 7).



Scheme 7

The cerium(IV) oxidation of variamine blue (VB) has been shown[48] to proceed *via* a two-step mechanism which involves the formation of an intermediate imino-quinone (I):

$$Ce^{IV} + VB \xrightarrow{k_\alpha} Ce^{III} + I$$

$$Ce^{IV} + I \xrightarrow{k_\beta} Ce^{III} + (VB)_{ox}$$

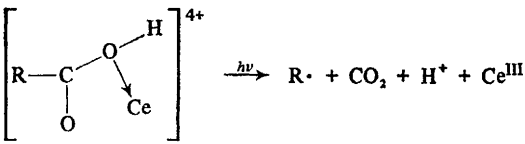
[74] S. K. Mishra, P. D. Sharma, and Y. K. Gupta, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1845.
[75] D. K. Lavalee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 1440.
[76] H. Li Chum and P. Krumholz, *Inorg. Chem.*, 1974, **13**, 514, 519.

Unusually, the rate is independent of $[H^+]$ in the range 0.2—2.0 mol l^{-1}, and the rate constants k_α and k_β are 1.7×10^5 and 2.4×10^5 l mol^{-1} s^{-1} respectively, suggesting an inner-sphere mechanism. In the reaction with malic acid (HL) a different mechanism has been proposed.[77] In this case, an intermediate complex has been characterized spectroscopically, the formation constant being obtained from both optical density and kinetic data. A feature of this study is the re-investigation of the first hydrolysis constant, K_h, for cerium(IV). The value determined, 0.2 ± 0.02 at 25 °C, compares favourably with that derived previously.[78] Many workers have, however, made use of the data of Hardwick and Robertson,[79] whose value is considerably higher and who also found evidence for dimer formation. If the cerium(IV) is prepared electrolytically there appears to be little tendency for this to occur in the range $\leqslant 3 \times 10^{-3}$ mol l^{-1}. In the presence of malic acid, the rate data are consistent with Scheme 8. From kinetic studies over the range $[H^+] = 0.25$—1.45 mol l^{-1}, it is suggested that the only significant pathway is that involving the deprotonated complex $[CeL]^{3+}$.

$$\begin{array}{ccccc} Ce^{4+} + HL & \overset{K_1}{\rightleftharpoons} & [Ce(HL)]^{4+} & \xrightarrow{k_a} & Ce^{III} + HL\cdot \\ {\scriptstyle H^+}\Big\downarrow{\scriptstyle K_h} & & {\scriptstyle H^+}\Big\downarrow{\scriptstyle K_2} & & \\ [Ce(OH)]^{3+} + HL & \overset{K_2}{\rightleftharpoons} & [CeL]^{3+} & \xrightarrow{k_b} & Ce^{III} + L\cdot \end{array}$$

Scheme 8

E.s.r. studies have been undertaken on the photo-induced U^{VI} and Ce^{IV} reactions with organic compounds.[80] Whereas in the former case the photo-oxidation is predominantly (though not exclusively) by H-atom abstraction from a carbon atom α to the activating site (*e.g.* OH or CO_2H), Ce^{IV} reacts by C—C bond fission. In the oxidative decarboxylation of RCO_2H, for instance, the reaction reported involves the decomposition of a complex:



In the oxidation of 1,2-diarylethanes, using ammonium ceric nitrate in 70% aqueous acetonitrile,[81] the mechanism involves the rate-determining formation of radical cation intermediates. Cleavage of the C—C bond then takes place to produce a benzyl radical and a benzyl cation. Hydrogen atom abstraction is unimportant here as seen from the reaction of 2,3-diphenyl-2,3-dimethylbutane which, although having no α-hydrogen atoms, reacts about five times faster than the parent compound. The same oxidant has been used in the reactions with substituted phenylacetic acids in

[77] Z. Amjad and A. McAuley, *J.C.S. Dalton*, 1974, 2521.
[78] H. G. Offner and D. A. Skoog, *Analyt. Chem.*, 1966, **38**, 1520.
[79] T. J. Hardwick and E. Robertson, *Canad. J. Chem.*, 1951, **29**, 818.
[80] D. Greatorex, R. J. Hill, T. J. Kemp, and T. S. Stone, *J.C.S. Faraday I*, 1974, **70**, 216.
[81] W. S. Trahanovsky and D. W. Brixius, *J. Amer. Chem. Soc.*, 1973, **95**, 6778.

aqueous acetonitrile.[82] A linear free-energy relationship has been established for the rates of *m*- and *p*-substituted acids and the mechanism proposed involves a one-electron rate-determining decomposition of a cerium(IV) carboxylate complex to yield a benzyl radical and CO_2.

The reaction of cerium(IV) complexes with phosphine has been investigated.[83] Halide complexes are reduced at least ten times faster than sulphate or perchlorate analogues. There is no direct reaction between the oxidant and phosphine, and the reaction

$$X_3^- + PH_3 \longrightarrow 2HX + PH + X^-$$

is followed by further reaction of the trihalide ion with the intermediate PH.

8 Copper(II)

The kinetics of the oxidation of ascorbic acid (H_2A) have been studied in acetate media.[84] In the pH range 4—6, with the metal ion in excess, stopped-flow data are consistent with the rate law

$$-d[HA^-]/dt = k_1[Cu^{II}]^2[HA^-] + k_2[Cu^{II}]^2[A^-]$$

Under nitrogen, using quenched-flow e.s.r., there is no evidence for the formation of ascorbate ion radicals, and the mechanism involves the reaction of a copper(II) complex with a second mole of copper(II),

$$Cu^{II}HA \xrightarrow{+Cu^{II}} 2Cu^{I} + DA + H^+$$

$$\Big\downarrow H^+$$

$$Cu^{II}A \xrightarrow{+Cu^{II}} 2Cu^{I} + DA$$

where DA = dehydroascorbate anion. E.s.r. and spectroscopic studies have been made on the copper(I) complex formed in the redox reaction with thiourea,[85] in 0.1M-HNO_3. Even in a three-fold excess of reductant, however, there is still some evidence for copper(II).

The catalytic influence of copper(II) on the reactions of iron(III) complexes continues to receive attention. The oxidation of sulphur(IV) by hexa-aquoiron(III) in acid perchlorate[86] in the presence of excess ligand follows an empirical rate law of the form Rate = $k_0[Fe^{III}]^2$, where k_0 is a complex term involving $[Fe^{II}]$, $[H^+]$, $[HSO_3^-]$, and $[SO_2]$. (A somewhat simpler expression is observed in the presence of excess oxidant.) In solutions containing copper(II) and excess sulphur(IV), the rate equation is

$$\frac{-d[Fe^{III}]}{dt} = k_\alpha \frac{[Cu^{II}][HSO_3^-][Fe^{III}]/[H^+]}{\{a[Fe^{II}] + b[Cu^{II}] + c[Cu^{II}]^2/[H^+]\}}$$

The results are interpreted in terms of a multistep mechanism in which an electron transfer takes place within the inner-sphere complex $FeSO_3^+$ and there is the forma-

[82] W. S. Trahanovsky, J. Cramer, and D. W. Brixius, *J. Amer. Chem. Soc.*, 1974, **76**, 1077.
[83] D. V. Sokol'skii, Ya. A. Dorfman, and R. I. Rogoza, *Russ. J. Phys. Chem.*, 1974, **48**, 341.
[84] K. Hayakawa, S. Minami, and S. Nakamura, *Bull. Chem. Soc. Japan*, 1973, **46**, 2788.
[85] H. M. Ratajczak and L. Pajdowski, *J. Inorg. Nuclear Chem.*, 1974, **36**, 459.
[86] D. W. Carlyle and O. F. Zeck, *Inorg. Chem.*, 1973, **12**, 2978.

tion of a sulphur(v) intermediate which reacts further with Fe^{3+}, $FeOH^{2+}$, or Cu^{2+}. The observation of a mixture of dithionate and sulphate as ligand oxidation products is consistent with this scheme. In the presence of 1M-chloride ions, however, only the latter ion is produced,[87] the Fe^{III}–S^{IV} electron transfer being rate determining. In this system there is rapid oxidation of S^V by Cu^{II}. In the oxidation of sulphur(IV) by copper(II) under the same conditions, the rate law is first order with respect to the reactants but shows a complex $[H^+]$ dependence. A feature of this study, however, is the spectroscopic evidence for the formation in solution of a sulphur dioxide complex with chlorocopper(I). The presence of small amounts of copper(II) as impurities in solutions of hexacyanoferrate(III) and thiols has a marked effect on both the rate and the mechanism of the reaction.[88] A similar observation has been made in the corresponding reaction with hydroxylamine.[89] In this case the catalysis is consistent with the scheme

$$Cu^{2+} + NH_2OH \overset{K}{\rightleftharpoons} [Cu(NH_2OH)]^{2+}$$

$$[Cu(NH_2OH)]^{2+} + [Fe(CN)_6]^{3-} + H_2O \xrightarrow{k_2} [Cu(NH_2O)]^{2+} + [Fe(CN)_6]^{4-} + H_3O^+$$

$$[Cu(NH_2O)]^{2+} + NH_2OH \xrightarrow{k_3} Cu^+ + N_2 + H_3O^+ + H_2O$$

$$Cu + [Fe(CN)_6]^{3-} \xrightarrow{k_4} Cu^{2+} + [Fe(CN)_6]^{4-}$$

in which k_2 represents the rate constant for the rate-determining step. This reaction scheme also satisfactorily represents the situation when the iron(III)–edta complex acts as a catalyst. The oxidation of hydroxylamine by peroxodisulphate[90] has been shown to be catalysed by copper(II). The reaction involves the formation of a copper(II) peroxodisulphate complex which then reacts with the hydroxylamine:

$$CuS_2O_8 + H_2NOH \longrightarrow Cu^{2+} + 2SO_4^{2-} + HNO$$

$$HNO \xrightarrow{\text{fast}} \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O$$

A scheme in which the persulphate complex undergoes decomposition to yield $SO_4^{-\bullet}$ radicals, which rapidly react with the substrate, would give the same rate law. A puzzling feature of the kinetic data is a deviation from this behaviour at low $[NH_2OH]$ which the authors have not elucidated. The catalytic activity of copper(II) is enhanced when Mn^{II} is present, although there is no effect of Mn^{II} in the absence of the copper ion.

Two separate mechanisms dependent on the reactant concentrations have been found in the copper-catalysed reaction between oxalate and peroxodisulphate.[91] In an excess of oxalate, ox^{2-}, the rate law may be written as

$$\text{Rate} = k_0[Cu^{II}]^{1/2}[S_2O_8^{2-}][ox^{2-}]^0$$

The reaction is completely inhibited by 1% acrylonitrile and only less markedly so by molecular oxygen. In this case the active copper species is thought to be dioxalatocuprate(II). In low concentrations of oxalic acid, however, the rate is almost zero

[87] O. F. Zeck and D. W. Carlyle, *Inorg. Chem.*, 1974, **13**, 34.
[88] G. J. Bridgart, M. W. Fuller, and I. R. Wilson, *J.C.S. Dalton*, 1973, 1274; G. J. Bridgart and I. R. Wilson, *ibid.*, 1974, 1281.
[89] G. J. Bridgart, W. A. Waters, and I. R. Wilson, *J.C.S. Dalton*, 1973, 1582.
[90] R. Swaroop and Y. K. Gupta, *J. Inorg. Nuclear Chem.*, 1974, **36**, 169.
[91] M. Kimura, *J. Phys. Chem.*, 1973, **77**, 1265.

order in [Cu^{II}], first order in [$S_2O_8^{2-}$], and half-order in oxalic acid. Under these conditions, the inhibiting effect of O_2 becomes extremely small. Both SO_4^- and CO_2^- radicals are involved in a complex reaction scheme. Iron(III) is a strong inhibitor of the reaction and manganese(II) reacts in a similar manner, probably by acting as a competitor for the radical anions.

A stopped-flow kinetic study has been made of the decomposition of copper(II) cyanide in water and methanol–water mixtures.[92] The reaction is second order in [Cu^{II}] and inversely proportional to uncomplexed cyanide. The rate constant k_2 for the reaction

$$[Cu(CN)_3]^- + [Cu(CN)_4]^{2-} \xrightarrow{k_2} C_2N_2 + 2Cu^I$$

decreases from 470 l mol^{-1} s^{-1} in H_2O to 1.23 l mol^{-1} s^{-1} in 80% methanol–water solutions. The reaction of copper(II) with $HO_2\cdot$ radicals has been investigated using flash-photolysis–e.s.r. techniques.[93] Using Th^{IV} as a spin trap for the $HO_2\cdot$ radicals the formation of a [Th^{IV}–$HO_2\cdot$] complex is complete within 1 ms, and if no copper(II) is present this decays slowly, mainly *via* a second-order process. Addition of minute amounts of copper(II) dramatically increases the decomposition rate, consistent with the formation of a [$CuHO_2\cdot]^{2+}$ complex,

$$Cu^{2+} + HO_2\cdot \overset{K}{\rightleftharpoons} [CuHO_2\cdot]^{2+} \xrightarrow{k_0} \text{products}$$

where $K = 5 \times 10^7$ l mol^{-1} and $k_0 = 30$ s^{-1}. The redox reactions of copper(II) [and iron(II)/(III)] with radicals derived using Fenton's reagent have been described.[94] The mode of oxidation of alkyl radicals in the case of Cu^{II} involves the formation of an organo-copper(III) complex followed by insertion of a neighbouring ligand (H_2O) and reduction to copper(I) rather than β-proton loss, a pathway which may occur in non-aqueous media. Radical oxidation by iron(III), on the other hand, is an electron-transfer process,

$$R\cdot + Fe^{III} \rightleftharpoons R^+ + Fe^{II}$$

and this equilibrium will lie to the right only for those radicals which yield relatively stable carbonium ions.

Rhus vernicifera laccase is known to incorporate four tightly bound copper atoms distributed in three distinct sites. Type 1 copper is responsible for the intense blue colouration, and a second form of metal ion, type 2, is not associated with any specific spectroscopic absorption bands but has been inferred from e.s.r. studies. This centre is known to function as a strong anion-binding site. Type 3 copper is non-detectable by e.s.r. and is characterized by a u.v. absorption band (λ_{max} *ca.* 330 nm). Anaerobic stopped-flow studies with hydroquinone (H_2Q) have been made to investigate the mode of reduction at these centres.[95] The type 1 and type 3 copper ions are reduced in parallel at comparable rates over a wide range of substrate concentrations and pH. The rate data are consistent with the mechanism

$$H_2Q \rightleftharpoons HQ^- + H^+$$

$$\left.\begin{aligned} HQ^- + Cu(1) &\xrightarrow{k_1} \\ HQ^- + Cu(3) &\xrightarrow{k_3} \end{aligned}\right\} \text{products}$$

[92] G. Nord and H. Matthes, *Acta Chem. Scand.*, 1974, **A28**, 13.
[93] D. Meisel, H. Levanon, and G. Czapski, *J. Phys. Chem.*, 1974, **78**, 779.
[94] C. Walling, G. M. El-Taliawi, and R. A. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 113.
[95] R. A. Holwerda and H. B. Gray, *J. Amer. Chem. Soc.*, 1974, **96**, 6008.

where $k_1 = 1.5 \times 10^5$ l mol^{-1} s^{-1} and $k_3 = 7.2 \times 10^5$ l mol^{-1} s^{-1} respectively. Fluoride and azide inhibition results at pH 6 are suggestive of inner-sphere complex formation between type 2 copper and HQ^-, in that reduction rates of type 1 and 3 sites are similar when hydroquinone attacks the type 2–laccase–fluoride complex. The data for the reduction of the type 2–laccase–azide complex are, however, different from those of the fluoride-bound system. The first-order dependence of $[N_3^-]$ in the reduction of the type 2–laccase–azide species is accounted for by a type 1 to type 2 electron-transfer step catalysed by bridging azide ion.

9 Miscellaneous Redox Reactions

Quantitative data for metal-ion–ligand reactions are presented in Table 3.

Table 3 *Metal-ion–ligand redox reactions*

Reaction	k(25 °C)/ l mol^{-1} s^{-1}	I/mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
$[IrCl_6]^{2-} + SO_3^{2-}$	2×10^4	0.2	—	—	98
$Pu^{VI} + H_2Q$	1.6×10^3	1.0	15.1	6.8	101[a]
$Pu^{IV} + H_2Q$	9.6×10^4	1.0	11.6	2.5	101[a]
$Np^{VI} + H_2Q$	4.52×10^4	1.0	8.2	−9.4	102[a]
$Np^{VI} + MeH_2Q$	6.26×10^4	1.0	9.2	−5.8	102[a]
$Np^{VI} + HO_2CCH_2S^-$	2×10^8	1.0	—	—	103
$Np^{VI} + HO_2CCH_2SH$	3.5	1.0	6	14.2	103
$Np^{VI} + {}^-O_2CCH_2SH$	1.5×10^5	1.0	—	—	103
$Np^{VI} + MeO_2CCH_2SH$	58	1.0	—	—	103
$Np^{VI} + MeO_2CCH_2S^-$	2.7	1.0	—	—	103
$RuO_4^- + H_2PO_2^-$	248	0.3	1.9	−41	109[b]
$Fe^{2+} + BrO_3^-$	0.37	0.50	—	—	124[c]
$[Fe(CN)_6]^{4-} + BrO_3^-$	0.19	0.50	—	—	125[d]
$Br^- + BrO_3^-$	2.86	0.50	—	—	125[d]
$ClO_2 + BrO_3^-$	1.7	1.93	10.7	—	128

[a] H_2Q = hydroquinone. [b] Third-order rate law incorporating $[HO^-]$ term. [c] Value of 13.4 may be obtained depending on mechanistic interpretation. [d] Units of rate constant are mol^3 l^{-3} s^{-3} since a term in $[H^+]^2$ is involved.

The kinetics and mechanism of the reaction between peroxodisulphate and formate ions have been studied over the pH range 0.7—12.6.[96] In three concentration ranges of $[HCO_2^-]$, the rate law assumes three different forms. At $[HCO_2^-] < 0.01$ mol l^{-1} and $[S_2O_8^{2-}] \sim 4 \times 10^{-3}$ mol l^{-1}, in the pH range 4.5—7 and in the absence of oxygen, the rate law is

$$-d[S_2O_8^{2-}]/dt = k_a[HCO_2^-]^{1/2}[S_2O_8^{2-}]$$

the rate being a maximum in this pH range. At both lower and higher $[H^+]$ values the rate decreases owing to the presence of differing radicals formed under these conditions. In order to account fully for the pH profile, the reactivity order of the radicals has been postulated to be $HCO_2H^{+\bullet} < HCO_3^{\bullet} < CO_2^{-\bullet} > O_2CO_2^{-\bullet} > HO_2^{\bullet} > O_2^{-\bullet}$. Iron(III) is found to inhibit the rate through interaction with these transient species. SO_4^- radical ions have been shown to be reactive[97] in the oxidation of phenyl-substituted alcohols and ethers by $S_2O_8^{2-}$.

[96] M. Kimura, *Inorg. Chem.*, 1974, **13**, 841.
[97] M. E. Snook and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1974, **96**, 860.

The oxidation of sulphur(IV) by hexachloroiridate(IV) has been investigated[98] in the pH range 4—6 and for the net reactions

$$2[IrCl_6]^{2-} + HSO_3^- + H_2O \longrightarrow 2[IrCl_6]^{3-} + SO_4^{2-} + 3H^+$$

and

$$2[IrCl_6]^{2-} + 2HSO_3^- \longrightarrow 2[IrCl_6]^{3-} + S_2O_6^{2-} + 2H^+$$

the rate law may be written as

$$\text{Rate} = k_0[IrCl_6^{2-}][HSO_3^-]/[H^+]$$

In accord with the qualitative evidence that both reactions proceed at comparable rates, the mechanism proposed involves a rate-determining one-electron transfer to yield Ir^{III} and S^V and is probably outer-sphere. The S^V intermediate is then further oxidized by Ir^{IV} or is involved in a dimerization to dithionate. Experiments in the presence of copper(II) show negligible catalytic activity.

Several studies have been made using Pb^{IV} as an oxidant. The reaction with methanol[99] yields formaldehyde with rupture of a C—H bond as the rate-limiting step. Whereas the product is reportedly stable in the presence of $Pb(OAc)_4$, in fact further reaction takes place to yield methyl formate. The mechanism of decarboxylation of 2-hydroxycarboxylic acids, ROH, in anhydrous acetic acid has been investigated using several techniques.[100] The rate law is of the form

$$\text{Rate} = k_0[Pb^{IV}][ROH]/[HOAc]$$

and the observation of an inverse linear dependence on [HOAc] coupled with solvent deuterium isotope effects ($k_H/k_D \sim 0.63$) is suggestive of a chelated Pb^{IV} intermediate which is formed prior to the rate-determining ring-opening. Activation entropies are also consistent with this mechanism.

The oxidation of hydroquinone by Pu^{VI} and Pu^{IV} has been studied.[101] Despite the apparent simplicity of the reactions, for example

$$2Pu^{VI} + H_2Q \longrightarrow 2Pu^V + Q$$

the kinetics are complex and data have been derived from initial rates. Inhibition by product Pu^V but not by quinone has been observed, and the rate law,

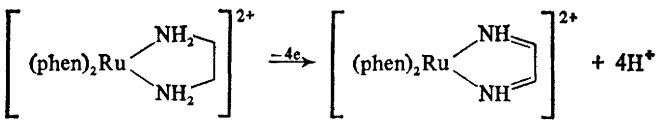
$$\frac{-d[H_2Q]}{dt} = \frac{k_1[Pu^{VI}][H_2Q]}{1 + a[Pu^V]/[Pu^{VI}] + b\{[Pu^V]/[Pu^{VI}]^2\}}$$

is essentially similar to that for the Pu^{IV} reaction. The parameter a is slightly dependent on hydrogen-ion concentration. Comparison of the activation parameters for k_1 with those for other systems shows a decrease in $\Delta H^{\ddagger}$ in the order $Fe^{III} > Pu^{VI} > Pu^{IV} > Np^{VI}$. In the latter reaction, in contrast with the plutonium system, the rates are first order with respect to reactants with no hydrogen-ion dependence in the range 0.05—1.0 mol l^{-1}.[102] A similar rate law obtains for *p*-toluhydroquinone, where the rate constant is only ~30% higher. These data have been interpreted in terms of a Marcus cross-relation equation for electron transfer. Stoicheiometric studies on

[98] E. L. Stapp and D. W. Carlyle, *Inorg. Chem.*, 1974, **13**, 834.
[99] Y. Pocker and B. C. Davis, *J.C.S. Chem. Comm.*, 1974, 803.
[100] Y. Pocker and B. C. Davis, *J. Amer. Chem. Soc.*, 1973, **95**, 6216.
[101] T. W. Newton, *J. Inorg. Nuclear Chem.*, 1974, **36**, 639.
[102] K. Reinschmeidt, J. C. Sullivan, and M. Woods, *Inorg. Chem.*, 1973, **12**, 1639.

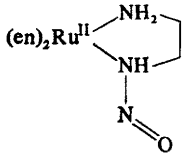
the Np^{VI} oxidation of thiols have been reported,[75] and it is of interest that whereas there appears to be little effect of O_2 on the reactions with Ce^{IV}, in the case of Np^{VI} marked differences in the stopped-flow traces are observed. The kinetics of the oxidation of free and co-ordinated thioglycollic acid by this metal ion have been investigated.[103] The former reactions are relatively simple, in marked contrast to those of other metal ions, *e.g.* iron(III), copper(II), and vanadium(V), where there is substantial evidence for the formation of intermediate complexes. A useful comparison has been made between the oxidation of the α-mercapto-carboxylic acid and the corresponding methyl ester which eliminates the ambiguity concerning the dissociation of a weak carboxylic acid as a possible source of inverse hydrogen-ion effects. The data have been interpreted in terms of a net rate of oxidation of the thioglycollic acid deprotonated at the carboxy-group being 12 times greater than that for a substrate deprotonated at a sulphydryl group. The oxidations of co-ordinated thiols are more complex and involve either a one-equivalent electron transfer or a multistep process, where there is oxidation of the carbon chain of the thiol.

The preparations of dinuclear ruthenium ammine complexes have been reported.[104] The ion $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ (3) has been identified as a product in the reaction of $[(H_3N)_5RuOH_2]^{3+}$ with sulphurizing agents such as COS or C_2H_4S or in the oxidation of a mixture of the corresponding Ru^{II} complex and H_2S. Reduction of (3) with Eu^{2+} requires four moles of reductant and yields Ru^{II} and H_2S with no detectable formation of any intermediates. Reaction with CN^-, however, yields initially $[(H_3N)_5RuSCN]^+$, which on acidification and exposure to air shows a shift in the spectrum to give the isomeric N-bonded form. From spectroscopic considerations, the structure favoured for (3) is that of two Ru^{III} centres bridged by S_2^{2-}. Ethylenediamine co-ordinated to ruthenium(II) is readily oxidized by sodium hypochlorite at approximately neutral pH to the co-ordinated di-imine ligand:[105]

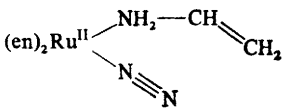


The reaction using ClO^- is not quantitative. When alkaline $[Fe(CN)_6]^{3-}$ is used, however, four equivalents of oxidant are required. The ruthenium(II) complexes may, however, be oxidized to Ru^{III} both by cyclic voltammetry and by titration with Ce^{IV}. In the latter case, however, some over-oxidation occurs since five moles of oxidant are necessary for complete reaction. Dinitrogen complex formation has been postulated[106] from the cleavage of a C—N bond in a co-ordinated ethylenediamine of ruthenium(III). Treatment of $[Ru(en)_3]^{3+}$ with NO in alkaline media yields as one product $[(en)_2Ru(N_2)(OH_2)]^{2+}$. An initial rapid reaction may be associated with reduction of the metal to the +2 oxidation state and the reaction may proceed *via* either (4) or (5) as intermediates.

[103] C. J. Weschler, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, 1974, **13**, 2360.
[104] C. R. Brulet, S. S. Isied, and H. Taube, *J. Amer. Chem. Soc.*, 1973, **95**, 4759.
[105] D. F. Mahoney and J. K. Beattie, *Inorg. Chem.*, 1973, **12**, 2561.
[106] S. Pell and J. N. Armor, *J.C.S. Chem. Comm.*, 1974, 259.



(4)



(5)

The formation of co-ordinated nitrene and rhodium(II) intermediates has been postulated in the photolysis of $[(H_3N)_5RhN_3]^{2+}$ in 1.00M-HCl.[107] A suggested mechanism involves the transient existence of $[(H_3N)_5RuN]^{2+}$ and $N_3^{\bullet}$. The former ion then rapidly protonates and further reaction leads to $[(H_3N)_5RuNH_2Cl]^{3+}$ as a primary product. In an extension of studies on systems of this type[108] it is proposed that species of the type $[(H_3N)_5MNH]^{3+}$ (M = Co, Rh, or Ir) behave like a singlet nitrene, being very susceptible to nucleophilic attack. The synthesis of sulphamato-complexes may then be seen to be the result of sulphite ion acting as a nitrene trap:

$$[(H_3N)_5IrNH]^{3+} + H^+ + SO_3^{2-} \longrightarrow [(H_3N)_5IrNH_2SO_3]^{2+}$$

The reaction between perruthenate and hypophosphite ion, $H_2PO_2^-$, has been studied in basic media.[109] The rate law is of the form

$$\text{Rate} = k_2[RuO_4^-][OH^-][H_2PO_2^-]$$

and the kinetic data are consistent with a rapid pre-equilibrium between OH^- and $H_2PO_2^-$ followed by a rate-determining step between the phosphorus(I) species and the oxidant to form a P^{II} intermediate. Further rapid reaction takes place to yield the phosphite ion:

$$H_2PO_2^- + HO^- \rightleftharpoons H_3PO_3^{2-} + RuO_4^- \xrightarrow{k_2} P^{II} + RuO_4^{2-}$$

$$P^{II} + RuO_4^- + 3OH^- \xrightarrow{\text{fast}} H_2PO_3^- + RuO_4^{2-} + 2H_2O$$

The large negative $\Delta S^{\ddagger}$ associated with the reaction is, however, also consistent with a $[RuO_4^-\text{–}P^I]$ intermediate containing both tetrahedral Ru and P atoms linked by a hydroxo- or aquo-bridge.

The reaction of hydroxylamine and tetracyanonickelate(II) in an inert atmosphere involves the sequence[110]

$$[Ni(CN)_4]^{2-} + NH_2OH \rightleftharpoons [Ni(CN)_3(NH_2OH)]^- + CN^-$$

$$\downarrow NH_2OH\text{-}OH^-$$

$$H_2O + [Ni(CN)_4]^{2-} + N_2 + OH^- \xleftarrow{NH_2OH\text{-}CN^-} [Ni(CN)_3NO]^{2-} + NH_3 + 2H_2O$$

in which the tricyanonitroso-complex is considered as an intermediate. There is no evidence for N_2O, which might be expected if nitroxyl radicals were formed. The rates of NH_3 and N_2 formation are equal and are a linear function of $[NH_2OH]$. Nickel(I) and cobalt(I) complexes have been postulated as intermediates in the mechanism of reduction of the corresponding bivalent halides with tetrahydroborate

[107] J. L. Reed, H. D. Gafney, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 1363.
[108] T. R. Weaver and F. Basolo, *Inorg. Chem.*, 1974, **13**, 1535.
[109] S. J. Paton and C. H. Brubaker, jun., *Inorg. Chem.*, 1973, **12**, 1402.
[110] J. Veprek-Siska and S. Lumak, *Coll. Czech. Chem. Comm.*, 1974, **39**, 41.

ion in the presence of phosphine ligands.[111] The oxidation of acetylacetone by hexahalogenoplatinum(IV) complexes has been shown to result in the formation of Pt^{II} diketonate species.[112]

The oxidative reactivities of silver(II) and silver(III) have been compared.[113] The first- and second-order terms in $[Ag^{II}]$ in various reactions have been assessed and an attempt has been made to resolve the apparent reverse of reactivity between the bi- and ter-valent silver ions, depending on the substrate. A reaction scheme for the oxidation of water has been presented and the data are consistent with a reactive dimeric form of Ag^{II}. The hydrolysis constant of Ag^{II} is also considered to be less than 3 l mol^{-1}. The properties of octaethylporphyrins show the Ag^{III} complex to be stable,[114] and cyclic voltammetric studies show reversibility in the $+3 \leftrightarrow +2$ redox steps. In the gold(III) (as $AuCl_4^-$) oxidation of methionine,[115] there is stereospecificity in the reaction, the product being the corresponding sulphoxide with no evidence for a sulphone. The reaction is biphasic, with an initial complex formation which is too rapid for study by conventional techniques followed by a slower intramolecular redox reaction leading to gold(I). The rate of this latter process is dependent on the methionine concentration. The oxidation also takes place when the substrate is part of a peptide chain.

The sulphur-bridged ion $[Mo_2S_2O_2]^{2+}$ has been prepared[116] by dissolving $[Mo_2S_2O_2(\text{cysteine})_2]^{2-}$ in 1M-HCl. Passage through an ion-exchange column removes the liberated cysteine. The ion is particularly stable towards strong acids, probably as a result of a strong Mo—S interaction. The reaction of di-μ-oxo-bis[oxo-(L-cysteinato)]molybdate(VI) $[Mo_2O_4(cys)_2]^{2-}$ with cysteine has been investigated in the pH range 8—10.[117] The reaction is first order with respect to each reactant, and cysteine is catalytically regenerated. The products are Mo^V species and a temperature-dependent equilibrium mixture of mono-oxo-bridged molybdenum dimers with a monomeric Mo^V cysteine complex. In model systems for nitrogenase,[118] the reduction of dinitrogen to ammonia has been shown to take place in the presence of molybdate with thiols of this type. The reductant is BH_4^-, and addition of substrate concentrations of ATP significantly increases the rate but also leads to di-imide products. The reduction of CN^-, N_3^-, N_2O, and N_2 by molybdocysteine catalysts in the presence of nucleoside phosphates under conditions similar to the above have also been reported.[119] Again the use of ATP as a co-factor greatly enhances the rates.

10 Halogens and Halogenate Ions

The formation of free radicals in the reaction of iron(II) with chlorate ion[120] has been described and the effect of alcohols on the oxidation rate provides evidence for $OCl^{\bullet}$

[111] D. G. Holah, A. N. Hughes, and B. C. Hui, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 427.
[112] C. Oldham and A. P. Ketteringham, *Inorg. Chim. Acta*, 1974, **9**, 127.
[113] C. F. Wells, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3856.
[114] J. H. Furhop, K. M. Kadish, and D. G. Davis, *J. Amer. Chem. Soc.*, 1973, **95**, 5140.
[115] E. Bordignon, L. Cattalini, G. Natile, and A. Scatturin, *J.C.S. Chem. Comm.*, 1973, 878.
[116] B. Spivak and Z. Dori, *J.C.S. Chem. Comm.*, 1973, 909.
[117] R. F. Stephenson and F. A. Schultz, *Inorg. Chem.*, 1973, **12**, 1762.
[118] G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. A. Doemeny, *J. Amer. Chem. Soc.*, 1974, **96**, 641.
[119] G. N. Schrauzer, G. W. Kiefer, P. A. Doemeny, and H. Kisch, *J. Amer. Chem. Soc.*, 1973, **95**, 5582.
[120] W. C. E. Higginson and M. E. Simpson, *J.C.S. Chem. Comm.*, 1974, 817.

and Cl· intermediates. The presence of alcohols (ROH) produces marked curvature in the kinetic plots, and the reaction scheme

$$Fe^{2+} + ClO_3^- + 2H^+ \longrightarrow Fe^{3+} + \cdot ClO_2 + H_2O$$
$$Fe^{2+} + ClO_2\cdot + H^+ \longrightarrow Fe^{3+} + HClO_2$$
$$Fe^{2+} + HClO_2 + H^+ \longrightarrow Fe^{3+} + OCl\cdot + H_2O$$
$$Fe^{2+} + OCl\cdot + H^+ \xrightarrow{k_4} Fe^{3+} + HOCl \quad (4)$$
$$Fe^{2+} + HOCl + H^+ \longrightarrow Fe^{3+} + Cl\cdot + H_2O \quad (5)$$
$$Fe^{2+} + Cl\cdot \xrightarrow{k_6} Fe^{3+} + Cl^- \quad (6)$$
$$ROH + OCl\cdot \xrightarrow{k_7} RO\cdot + HOCl \quad (7)$$
$$ROH + Cl\cdot \xrightarrow{k_8} RO\cdot + H^+ + Cl^- \quad (8)$$
$$RO\cdot + Fe^{3+} + H_2O \xrightarrow{k_9} ROH + Fe^{2+} + H^+ \quad (9)$$

represents all the reactions taking place under these conditions. At methanol concentrations of 1—2 mol l^{-1}, a limiting rate is reached where $k_{obs} = \frac{3}{2}k_0$ (k_0 = the observed constant in the absence of ROH), and in this case reaction (6) is completely replaced by reactions (8) and (9). In 1M-propan-2-ol, however, a drop in k_{obs} to $\frac{1}{2}k_0$ is reported, there being partial replacement of (4) by (7) and (9), *i.e.* the free-radical OCl· is not sufficiently active to react with MeOH in the presence of iron(II). There is no reaction of $\cdot ClO_2$ with alcohols and little effect of chloride ion up to ~1.2 mol l^{-1}. The same radical intermediates have been postulated in a separate study of this reaction in the absence of alcohols.[121] In this case, the rate law may be expressed in the form

$$\text{Rate} = (k_1K_a + k_2)[Fe^{II}][ClO_3^-] + k_3K_a[FeCl^+][ClO_3^-][H^+]$$

where K_a is the formation constant of chloric acid and the second term derives from reactive $FeCl^+$ formed during the course of the reaction. In the corresponding reaction with iodate, however,[122] there is no evidence for a rate term involving the reductant. The mechanism involves the reactions

$$H^+ + IO_3^- \overset{\text{fast}}{\rightleftharpoons} HIO_3 \overset{\text{slow}}{\rightleftharpoons} [IO_2^+ \cdot OH^-]$$

in which there is a slow transformation to an iodine(V) complex which rapidly reacts with Fe^{II}. IO·, IO^-, and HIO are considered intermediates in the reaction scheme. In the case of bromate,[123] however, the situation is somewhat closer to chlorate, in that the rate-limiting steps are those involving the reactions of iron(II) with both BrO_3^- and Br_2. Under conditions of large excess of oxidant, however, only the reaction with bromate is significant.[124] Studies carried out over the $[H^+]$ range 0.01—0.30 mol l^{-1} are consistent with the rate law

$$\text{Rate} = [Fe^{II}][BrO_3^-](k_1 + k_2[H^+])/(k_3 + [H^+])$$

The mechanism has not been fully elucidated but the data provide evidence for an inner-sphere path, probably involving substitution on Fe^{II} rather than on BrO_3^-.

[121] R. Mitzner, G. Fischer, and P. Leupold, *Z. phys. Chem.* (*Leipzig*), 1973, **253**, 81.
[122] R. Mitzner, G. Fischer, and P. Leupold, *Z. phys. Chem.* (*Leipzig*), 1973, **253**, 161.
[123] R. Mitzner, G. Fischer, and P. Leupold, *Z. phys. Chem.* (*Leipzig*), 1973, **253**, 193.
[124] J. P. Birk, *Inorg. Chem.*, 1973, **12**, 2468.

The corresponding reaction with $[Fe(CN)_6]^{4-}$ is partially autocatalytic[125] but involves as the first step the reaction

$$[Fe(CN)_6]^{4-} + BrO_3^- \xrightarrow[k_1]{2H^+} [Fe(CN)_6]^{3-} + BrO_2 + H_2O$$

where the $[H^+]^2$ term associated with other reactions of this oxidant is observed. The reaction of iodate with hexacyanoferrate(II),

$$6[Fe(CN)_6]^{4-} + IO_3^- + 6H^+ \longrightarrow 6[Fe(CN)_6]^{3-} + I^- + 3H_2O$$

has been investigated[126] at pH 1.76—2.65, and although the order with respect to the Fe^{II} and I^V species is unity, as in the case of the bromate reaction a complex hydrogen-ion dependence obtains. Some protonation of the reductant takes place and the ambiguities in the reactions of protonated species, *e.g.*

$$[HFe(CN)_6]^{3-} + IO_3^- \longrightarrow \quad \text{or} \quad [Fe(CN)_6]^{4-} + HIO_3 \longrightarrow$$

are again highlighted.

The $[H^+]^2$ term in bromate reactions referred to above has been confirmed in the reaction with bromide.[125] A similar observation has been made in the reaction with the mercury(I) dimer species.[127] In this case the mechanism is

$$[Hg^I]_2 \overset{K}{\rightleftharpoons} Hg^0 + Hg^{2+}$$

$$Hg^0 + BrO_3^- \xrightarrow[2H^+]{k_0} Hg^{II} + BrO_2^- + H_2O$$

The first-order dependence on oxidant has been substantiated. A small hydrogen-ion-independent pathway is also described. The stoicheiometry of the reaction of chlorous acid with bromate in perchlorate media has been determined.[128] In the presence of allyl alcohol, which acts as a scavenger for the hypobromous acid intermediate, the reaction may be represented as

$$BrO_3^- + HClO_2 + H^+ \xrightarrow{k_1} BrO_2 + ClO_2 + H_2O$$

$$BrO_2 + HClO_2 \longrightarrow HBrO_2 + ClO_2$$

$$BrO_2 + ClO_2 + H_2O \longrightarrow HBrO_2 + ClO_3^- + H^+$$

$$HBrO_2 + HClO_2 \longrightarrow HOBr + ClO_3^- + H^+$$

In this case a single proton is required for the k_1 pathway, the second hydrogen ion probably being derived from the chlorous acid.

Several studies have been reported in which the halogens have been used as oxidants. The oxidation of iron(II) by Br_2 is complex[129] and involves the formation of the tribromide ion as a reagent. The corresponding reaction with iodine has been studied in acetate media[130] and whilst the reaction order with respect to $[Fe^{II}]$ and $[I_2]$ is unity, a term in $[MeCO_2^-]$ and retardation by I^- and H^+ are also observed. The reaction scheme

$$FeOAc^+ + I_2 \rightleftharpoons [Fe^{III}MeCO_2I]^{2+} + I^-$$

$$[Fe^{III}MeCO_2I] \longrightarrow Fe^{III}OAc + I\cdot$$

[125] J. P. Birk and S. G. Kozub, *Inorg. Chem.*, 1973, **12**, 2460.
[126] Y. Sulfab and H. A. Elfaki, *Canad. J. Chem.*, 1974, **52**, 2001.
[127] R. Davies, B. Kipling, and A. G. Sykes, *J. Amer. Chem. Soc.*, 1973, **95**, 7250.
[128] R. C. Thompson, *Inorg. Chem.*, 1973, **12**, 1905.
[129] R. Mitzner, G. Fischer, and P. Leupold, *Z. phys. Chem.* (*Leipzig*), 1973, **253**, 179.
[130] R. K. Srivastava, M. N. Srivastava, and B. B. L. Saxana, *Z. phys. Chem.* (*Leipzig*), 1974, **255**, 133.

is considered to represent one of the rate-limiting reaction paths. Preliminary experiments on the Br_2–$[Fe(CN)_6]^{4-}$ reaction show it to be rapid,[125] with a rate constant of $\sim 10^3$—10^5 l mol^{-1} s^{-1}, which is about four orders of magnitude greater than for either the Br^-–BrO_3^- or the Fe^{II}–BrO_3^- systems.

A kinetic study has been made of the rapid oxidative substitution of $[(H_3N)_5CoBr]^{2+}$ by Cl_2, HOCl, and HOBr.[131] In the presence of excess [HOBr], the rate law is of the form

$$-d[Co^{III}]/dt = k[HOBr][H^+][Co^{III}]$$

When HOCl is the reactant, however, an additional $[H^+]$-independent term is also evident. With chloride as oxidant, there is no dependence on $[H^+]$ in the range 0.05—1.0 mol l^{-1}, but chloride-ion catalysis has been observed. Hypobromous acid and hypobromite ion have been used as reactants in the oxidation of bivalent metal aminopolycarboxylate ($M^{III}L$) complexes.[132–134] In the reaction of $[Co^{II}L]^{2-}$ by Br_2,[132] the kinetically important form of the oxidizing agent changes with pH from Br_2 and Br_3^- to HOBr and then to OBr^-. The rate law is first order with respect to each reactant, the final products being $Co^{III}L$ and Br^-. A mechanism consistent with these findings may be written for HOBr as

$$[Co^{II}L]^{2-} + HOBr \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [LCo^{II}\cdots\overset{H}{\overset{|}{O}}\!-\!Br] \xrightarrow{k_2} [Co^{III}L(OH_2)^-] + Br\cdot$$

$$[CoL(OH_2)]^- \xrightarrow[\text{closure}]{\text{ring}} [Co^{III}L]^- + H_2O$$

There appears to be no significant inner-sphere pathway *via* the Br end of the molecule since no $[Co^{III}LBr]^{2-}$ product is detected. In an extension of the work to other metal ions, aminopolycarboxylates, and oxidants it is reported[133,134] that, whereas the rates of oxidation of $[Fe^{II}L]^{2-}$ by Br_2, Br_3^-, and I_2 appear to be controlled by the rate at which the oxidant enters the primary co-ordination sphere of the metal ion (Table 4), the rates of oxidation of $[Fe^{II}L]^{2-}$ by I_3^- and of $[Co^{II}L]^{2-}$ and $[Mn^{II}L]^{2-}$ by I_2, I_3^-, Br_2, and Br_3^- are limited by electron-transfer steps subsequent to co-ordination of the oxidant. Linear free-energy relationships for these reactions have been presented in terms of a Marcus correlation.[134] In the cleavage reactions of alkyl-chromium(III) cations $[RCr(H_2O)_5]^{2+}$ by Br_2 (R = alkyl, halogeno-alkyl, or 4-pyridinomethyl) the overall stoicheiometric reaction,

$$[RCr(H_2O)_5]^{2+} + Br_2 \longrightarrow [Cr(H_2O)_6]^{3+} + Br^- + RBr$$

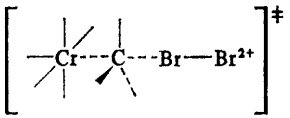
proceeds *via* a rate law first order in both reactants with no hydrogen-ion dependence.[135] The rates are in the order R = Me > Et > Pr^n > Pr^i > CH(Cl)Me > CH_2Cl > CH_2Br, and it is suggested that the reactions are best described as S_E2 in which there is an 'open' transition state since no $CrBr^{2+}$ is formed. The rates are strongly dependent on electronic effects from halogen substitution in that although the substituents

[131] J. M. Malin, H. E. Toma, and E. Giesbrecht, *Inorg. Chim. Acta*, 1973, **7**, 423.
[132] W. H. Woodruff, D. W. Margerum, M. J. Milano, H. L. Pardue, and R. E. Santini, *Inorg. Chem.*, 1973, **12**, 1490.
[133] W. H. Woodruff, B. A. Burke, and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2573.
[134] W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2578.
[135] J. H. Espenson and D. A. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 1008.

Table 4 *Rate and thermodynamic parameters for reactions of metal–amino-polycarboxylate ions with halogens*

Reaction	k(25 °C)/ l mol^{-1} s^{-1}	I/mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
Fe^{II}edta + I_2	1.6×10^{6}	0.2	7.5	−5	134
Fe^{II}edta + I_3^-	4.4×10^{3}	0.2	17	15	134
Fe^{II}cydta + I_2	1.24×10^{6}	0.2	7.7	−5	134
Fe^{II}cydta + I_3^-	5.0×10^{3}	0.2	21	28	134
Fe^{II}cydta + Br_2	9.3×10^{6}	1.1	—	—	134
Fe^{II}cydta + Br_3^-	1.16×10^{6}	1.1	—	—	134
Co^{II}cydta + I_2	6.4×10^{-5}	1.0	21.0	−7.3	133
Co^{II}cydta + I_3^-	2.2×10^{-5}	1.0	21.1	−9	133
Co^{II}edta + I_2	5.2×10^{-4}	1.0	23	1	133
Co^{II}edta + I_3^-	3.1×10^{-5}	1.0	24	5	133
Co^{II}cydta + Br_2	2.0×10^{-3}	1.1	18.3	−9.5	133
Co^{II}cydta + Br_3^-	1.11×10^{-3}	1.1	18.0	−12	133
Co^{II}edta + Br_2	7.3×10^{-2}	1.1	—	—	133
Co^{II}edta + Br_3^-	5.4×10^{-2}	1.1	—	—	133
Mn^{II}edta + Br_2	7.8×10^{-3}	1.1	—	—	134
Mn^{II}edta + Br_3^-	2.5×10^{-4}	1.1	—	—	134

CH_2Cl and CH_2Me are similar in size they show a rate difference of 4×10^{5}. On the basis of the present evidence the form of the transition state favoured is (6), leading



(6)

to inversion of configuration. Substituent effects in the electrophilic cleavage reactions of *p*-substituted benzylpenta-aquochromium(III) cations by molecular halogens have also been observed.[136] Again $[Cr(H_2O)_6]^{3+}$ is the only metal-ion product.

The oxidation of V^{II} and Cr^{II} by di-iodide, dibromide, and dichloride ions X_2^- has been investigated.[137] These studies are a continuation of those reported[138,139] with Co^{2+}. The radical anions, X_2^-, are generated by flash photolysis. In the reaction

$$Co^{II} + Cl_2^- \xrightarrow{k_1} Co^{II} + 2Cl^-$$

the initial product[138] is $CoCl^{2+}$, the spectrum reported being identical to that described previously. There is some evidence for dissociation to Co^{3+} and Cl^-, but this is slower than the oxidation process. The reaction Co^{2+}–Cl_2^- is inner-sphere-substitution controlled (Table 5) and there is no evidence for a corresponding reaction with Br_2^-. The oxidations of Mn^{II} by Br_2^- and Cl_2^- have been studied[139] and whilst the reactions are first order in [Mn^{II}] at low concentrations, a tendency to zero order at

[136] J. C. Chang and J. H. Espenson, *J.C.S. Chem. Comm.*, 1974, 233.
[137] G. S. Laurence and A. T. Thornton, *J.C.S. Dalton*, 1974, 1142.
[138] A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 1632.
[139] G. S. Laurence and A. T. Thornton, *J.C.S. Dalton*, 1973, 1637.

higher values is consistent with the formation of metal-ion–radical-ion complexes,

$$X_2^- + Mn^{II} \overset{K_0}{\rightleftharpoons} [Mn^{II}X_2]^+ \overset{k_1}{\longrightarrow} Mn^{III} + 2X^-$$

the values of K_0 being 39 ± 15 and 68 ± 30 l mol^{-1} for Br_2^- and Cl_2^- respectively. These complexes are thought to be inner-sphere and the oxidation reactions are not considered to be inner-sphere-substitution controlled. The mechanisms for these reactions together with rate data are presented in Table 5. In the case of V^{II} as reductant in the reactions with all three dihalide anions an outer-sphere mechanism is proposed,[137] whereas for Cr^{2+} with I_2^- and Br_2^- an inner-sphere pathway is indicated. In the oxidation of Cr^{2+} by Cl_2^-, however, there appears to be an equal probability of both inner-sphere and outer-sphere reactions.

Table 5 *Reactions of transition-metal ions with dihalide ions* (X_2^-)

Reaction	k(25 °C)/ l mol^{-1} s^{-1}	I/mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
$Co^{2+} + Cl_2^-$	1.4×10^6	0.3	6.9	7.4	138[a]
$Mn^{2+} + Cl_2^-$	8.5×10^6	0.21—0.25	7.6	1.7	139[b]
$Mn^{2+} + Br_2^-$	6.3×10^6	0.21—0.25	14.0	1.3	139[b]
$Fe^{2+} + Cl_2^-$	1.0×10^7	0.2	8.4	18.4	140[c]
$Fe^{2+} + Cl_2^-$	4×10^6	0.2	6.9	9.6	140[a]
$Fe^{2+} + Br_2^-$	3.6×10^6	0.2	9.5	18.6	140[a]
$V^{2+} + Cl_2^-$	1.95×10^9	~0.3	—	—	137[d,e]
$V^{2+} + Br_2^-$	1.48×10^9	~0.3	—	—	137[d,e]
$V^{2+} + I_2^-$	1.43×10^8	~0.3	—	—	137[d,e]
$Cr^{2+} + Cl_2^-$	2.4×10^9	~0.3	—	—	137[d,e,f]
$Cr^{2+} + Br_2^-$	1.9×10^9	~0.3	—	—	137[e,f]
$Cr^{2+} + I_2^-$	1.5×10^9	~0.3	—	—	137[e,f]

[a] Inner-sphere substitution. [b] Inner-sphere electron transfer. [c] Outer-sphere reaction. [d] Outer-sphere diffusion controlled. [e] T = 22 °C. [f] Inner-sphere diffusion controlled.

The oxidation of nitrite by aqueous bromine[141] and chlorine[142] has been studied using stopped-flow methods. In acetate-buffered media, over the pH range 4.5—5.8, the rate law in the reaction with Br_2 [141] is

$$-d[Br_2]_{tot}/dt = (a + b/[Br^-])[Br_2][NO_2^-]^2$$

where $[Br_2]_{tot} = [Br_2] + [Br_3^-]$. At lower pH's, however, further terms in $[HNO_2]$ are required to describe the reaction. The rate data may be interpreted in terms of an initial reversible reaction,

$$NO_2^- + Br_2 \rightleftharpoons NO_2Br + Br^- \qquad (10)$$

followed by attack of NO_2^- on the NO_2Br or on dimerization to yield $N_2O_4^{2-}$ followed by a rate-determining reaction with Br_2. In the oxidation by chlorine,[142] reaction (10) is again considered operative with two subsequent parallel reactions, one a unimolecular decomposition and the other an attack by HNO_2 on NO_2Cl. A study of the rapid reactions of cysteine and cystine by the same oxidants,[143] and comparison of the rates with cysteine *SS*-dioxide, suggests that the latter is not an

[140] A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 804.
[141] J. N. Pendelbury and R. H. Smith, *Austral. J. Chem.*, 1973, **26**, 1847.
[142] J. N. Pendelbury and R. H. Smith, *Austral. J. Chem.*, 1973, **26**, 1857.
[143] P. G. Gordon, *Austral. J. Chem.*, 1973, **26**, 1771.

intermediate in these oxidations. The rates of reactions of substituted benzyl dimethylamines with Br_2 in 50% aqueous acetic acid[144] are decreased if electron-withdrawing substituents are present. The rate-determining step is the cleavage of an α-C—H bond and general base catalysis is observed. The rate law for the oxidation of phenol by chlorine dioxide in acidic media may be expressed in the form[145]

$$-d[ClO_2]/dt = (k_\alpha + k_\beta)[ClO_2][PhOH]$$

A complex dependence on hydrogen-ion concentration is reported, and from stoicheiometry studies it is suggested that ClO_2 undergoes a one-electron reduction to form chlorous acid in the rate-determining step. This species then undergoes a bimolecular disproportionation to yield $[Cl_2O_2]$, which reacts with the excess phenol present to give the observed chlorophenol product. The kinetics and mechanism of the oxidation of allyl alcohol by chloramine T in HCl media have been investigated.[146] The reaction involves an initial hydrolysis of the *N*-chlorotoluene-*p*-sulphonamide to give HOCl, which rapidly reacts with the allyl alcohol. The oxidation of thiocyanate by iodine[147] has been studied over the pH range 9.2—12.5. The reaction is general base (B) catalysed, and a mechanism consistent with the rate data may be written as

$$I_2 + SCN^- \rightleftharpoons ISCN + I^-$$

$$ISCN + H_2O + B \xrightarrow{\text{slow}} HOSCN + I^- + HB$$

A further rapid bimolecular reaction of HOSCN then probably takes place, although further oxidation of this intermediate by I_2 cannot be eliminated. In the reaction of iodine monochloride with alcohols,[148] the slow step is the attack of I^+ on the alcohol to yield ROI. There is no evidence for any chlorinated product. An n.m.r. study of the exchange between Cl^- and Cl_2 in aqueous solution has been reported[149] and comparisons have been made with other halogen exchange processes. The reduction of perchlorate to chloride by molecular hydrogen in the presence of tungsten carbide catalysts has also been described.[150]

11 Metal Ion Reductions

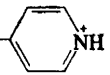
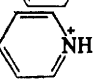
Quantitative data for metal ion reduction reactions are presented in Table 6.

The mechanisms of the reduction of nitric and nitrous acids by aquochromium(II) have been investigated.[151] Stoicheiometries of four moles of reductant per mole of HNO_3 and two moles of metal ion reacting with HNO_2 are consistent with the previous findings of Swaddle.[152] In the former reaction the products are essentially a 1 : 1 : 1 mixture of Cr^{3+}, $CrNO^{2+}$, and $[Cr(OH)_2Cr]^{4+}$ when $[HNO_3] > [Cr^{II}]$, although if these concentrations are reversed the product distribution is dependent on $[NO_3^-]$. The rate law for the reaction,

$$\text{Rate} = \frac{k_1 + k_2K_a^{-1}[H^+]}{1 + K_a^{-1}[H^+]}[NO_3^-]_{tot}[Cr^{II}], \qquad K_a = [H^+][NO_3^-]/[HNO_3]$$

[144] D. G. Lee and R. Srinavasan, *Canad. J. Chem.*, 1973, **51**, 2546.
[145] E. Grimley and G. Gordon, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2383.
[146] D. S. Mahadevappa and H. M. K. Naidu, *Austral. J. Chem.*, 1974, **27**, 1203.
[147] G. T. Briot and R. H. Smith, *Austral. J. Chem.*, 1973, **26**, 1863.
[148] C. R. Das and A. N. Bose, *Bull. Chem. Soc. Japan*, 1973, **46**, 818.
[149] H. W. Dodgen, A. D. Jordan, and R. B. Jordan, *J. Phys. Chem.*, 1973, **77**, 2149.
[150] G. Horanyi and G. Vertes, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 767.
[151] H. Ogino, K. Tsukahara, and N. Tanaka, *Bull. Chem. Soc. Japan*, 1974, **47**, 308.
[152] T. W. Swaddle, *J. Amer. Chem. Soc.*, 1967, **89**, 4338.

Table 6 *Metal-ion reduction reactions*

Reaction	k(25 °C)/ l mol^{-1} s^{-1}	I/mol l^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
$Cr^{II} + HNO_3$	2.2×10^{2}	1.0	—	—	151
$Cr^{II} + NO_3^-$	<0.2	1.0	—	—	151
$Cr^{II} + HNO_2$	4.5×10^{3}	1.0	—	—	151
$Cr^{II} + NO_2^-$	$<5\times10^{4}$	1.0	—	—	151
$Cr^{II} + NO$	$>4.5\times10^{3}$	1.0	—	—	151
$Cr^{II} + HN_3$	8.95	1.0	4.6	−35.6	154[a]
$Cr^{II} + PhCHO$	6.3×10^{-4}	1.0	1.8	−68.3	155[b]
$Cr^{II} + PhCHO$	7.2×10^{-4}	1.0	1.4	−70	155[c]
Cr^{II} + 	16.9	1.0	—	—	156[d]
Cr^{II} + 	$\sim6\times10^{5}$	1.0	—	—	156[d]
$Cr^{II} + CrNO^{2+}$	0.49	1.3	9.6	−27.1	153
$Cr^{II} + H\cdot$	1.5×10^{9}	—	—	—	178
$V^{II} + NH_2OH$	1.8×10^{3}	1.0	9.2	−13	162
$Ti^{III} + NH_2OH$	1.48×10^{6}	1.0	—	—	163
$U^{III} + PhCHO$	3.7	0.1	3.4	−44	170[e]

[a] T = 15 °C. [b] In 50% aqueous MeOH. [c] In 50% aqueous HOAc. [d] T = 55 °C. [e] Hydrogen-ion-dependent pathway; data for salicylaldehyde similar.

is consistent with the mechanism involving the reduction of NO_3^- (k_1) and HNO_3 (k_2) by the metal ion (Table 6). In the corresponding reaction with HNO_2, however, no $[H^+]$ dependence is observed. The reaction is first order with respect to both reactants and in an excess of nitrous acid the products are equivalent amounts of Cr^{3+} and $CrNO^{2+}$. The reaction scheme is

$$Cr^{2+} + HNO_2 \xrightarrow{k_0} Cr^{3+} + NO + OH^- \quad (11)$$

$$Cr^{2+} + NO \xrightarrow{\text{fast}} CrNO^{2+} \quad (12)$$

Reaction (12) has recently been the subject of an independent investigation.[153] Provided a slight excess of NO is present the only product is $CrNO^{2+}$ and the spectrum of this complex has been determined. The chromium(II) reduction of hydrazoic acid has been found to be second order overall[154] and catalysis by simple anions X^- (SO_4^{2-}, Br^-, Cl^-, I^-) is the result of a parallel competing pathway ($CrX^+ + HN_3 \rightarrow$). In the case of F^- and SCN^-, however, rate enhancement is considerable. The Cr^{II} reduction of benzaldehyde has been studied polarographically[155] in 50% aqueous HOAc and 50% aqueous MeOH. The results are markedly different in that in acetate solutions a rate dependence on $HClO_4$ is observed passing through a minimum at $[H^+]$ = 0.2—0.3 mol l^{-1}. In methanol a direct proportionality to $[H^+]$ is confirmed in the range 0.05—1.5 mol l^{-1}. Cr^{III} has a retarding effect on the reaction and an intermediate α-hydroxybenzylchromium(III) cation has been

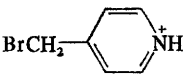
[153] J. N. Armor and M. Buchbinder, *Inorg. Chem.*, 1973, **12**, 1086.
[154] P. Sevcik and D. Biresova, *Coll. Czech. Chem. Comm.*, 1974, **39**, 2168.
[155] P. Sevcik and J. Cieker, *Coll. Czech. Chem. Comm.*, 1973, **38**, 2855.

characterized. The data are consistent with mechanism

$$[Cr(H_2O)_6]^{2+} + PhCHOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Cr(H_2O)_6]^{3+} + Ph\dot{C}HOH$$

$$Cr^{II} + Ph\dot{C}HOH \xrightarrow{fast} \left[PhCH(OH)-Cr^{III}(OH_2)_5\right]^{2+} \longrightarrow Cr^{III} + PhCH_2OH$$

Despite differing $[H^+]$ dependences in the two media, the rates and activation parameters are remarkably similar (Table 6). A radical intermediate has been postulated in the reduction of the 4-pyridinobromomethyl cation (7) ($\equiv$Br—R).[156]



(7)

In the two-step mechanism,

$$Cr^{II} + R-Br \xrightarrow{k_1} CrBr^{2+} + R\cdot \xrightarrow[+Cr^{II}]{k_2} [(H_2O)_5Cr-R]^{2+}$$

there is a slight variation of k_1 with $[H^+]$. The rate law is, however, first order with respect to both reactants. An estimate of $k_2 > 10^5$ l mol^{-1} s^{-1} for the reaction of the radical with Cr^{II} is also consistent with the data. Several studies have been reported on the Cr^{II} reductions of tropylium cations.[157,158] The one-electron reduction of tropylium fluoroborate has been investigated using a flow method. Whereas Cl^-, Br^-, and SO_4^{2-} show a rate-enhancing effect, BF_4^- and ClO_4^- retard the reaction. From these data, together with an examination of the Cr^{III} products, it is concluded that the reduction proceeds *via* an electron-transfer step where the anion acts as a mediator, in a manner analogous to the more familiar inner-sphere mechanism between two metal-ion reactants. The effect of substitution on the tropylium ring has been described and a linear relationship observed between log k_2 (the second-order rate constant) and pK_{trop^+} values, implying a parallelism between the electrophilicity and electron affinity of these stable carbonium ions. In the corresponding reduction of aryl- and n-alkyl-tropylium ions,[159] a correlation between log k_2 and the charge-transfer energy bands of these ions relative to pyrene as a standard electron donor supports the assumption that the reducibility of these ions with Cr^{II} may be regarded as a relative criterion of the electron affinities of these species in solution. Further data on cyclopropenium ions have also been reported.[160]

The chromium(II) reduction of co-ordinated nitrosyl has been investigated in the reaction with $CrNO^{2+}$.[153] In the presence of excess reductant, a simultaneous two-electron step yields NH_3OH^+ and a Cr^{III} dimer. The rate law may be written

$$-d[CrNO^{2+}]/dt = (k_1 + k_2/[H^+])[Cr^{II}][CrNO^{2+}]$$

156 J. H. Espenson and J. P. Leslie, *J. Amer. Chem. Soc.*, 1974, **96**, 1954.
157 K. Okamoto, K. Komatsu, S. Tsukada, and O. Murai, *Bull. Chem. Soc. Japan*, 1973, **46**, 1780.
158 K. Okamoto, K. Komatsu, O. Murai, O. Sakaguchi, and Y. Matsui, *Bull. Chem. Soc. Japan*, 1973, **46**, 1785.
159 K. Okamoto, K. Komatsu, M. Fujimori, and S. Yasuda, *Bull. Chem. Soc. Japan*, 1974, **47**, 2426.
160 K. Okamoto, K. Komatsu, and A. Hitomi, *Bull. Chem. Soc. Japan*, 1973, **46**, 3881.

and the mechanism involves attack by the reductant on $CrNO^{2+}$ to produce a species which reacts further with Cr^{II} to yield the dimer directly. The mechanism is not totally elucidated since if Cr^{II} reduced the ligand in a two-electron step, the product distribution of $\frac{1}{3}Cr^{III}$ and Cr^{IV} would be expected, leading through further reaction of Cr^{IV} with Cr^{II} to only $\frac{2}{3}Cr^{III}$ dimer. The ruthenium nitrosyl complex $[Ru(NH_3)_5NO]^{3+}$ is very stable in solution[161] and requires six moles of reductant to give the hexa-ammineruthenium(II) ion,

$$[Ru(NH_3)_5NO]^{3+} + 6Cr^{II} \xrightarrow[H^+]{Cl^-} [Ru(NH_3)_6]^{2+} + 6Cr^{III}$$

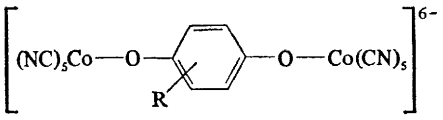
Preliminary stopped-flow studies indicate the presence of several short-lived intermediates. The corresponding cobalt(III) complex, however, yields (quantitatively) $CrNO^{2+}$ and Co^{II}. An examination of these data thus provides three possible reaction pathways for the reaction of this co-ordinated ligand with a common reductant.

The reduction of hydroxylamine by vanadium(III) has been studied over the pH range 0—2.[162] The rate law

$$\text{Rate} = k_1[V^{III}][NH_2OH]$$

is considered evidence for attack on the unprotonated form of the ligand. The reaction products are VO^{2+} and NH_3, and in the absence of radical scavengers it is suggested that the $\cdot NH_2$ radical is an intermediate. The rate constant $k_1 = 1.8 \times 10^3$ l mol^{-1} s^{-1} is somewhat higher than that for the solvent exchange rate on this ion but the possibility of an inner-sphere reaction is not totally excluded by the authors. A comparison with the corresponding reaction with Ti^{III} [163] indicates that in this case the rate is several orders of magnitude higher than the exchange rate and an outer-sphere mechanism is favoured. A second-order rate law has been derived in the reduction of alkyl halides by $[VCl_2(py)_4]$ in THF–HCl media.[164] The reaction of titanium(III) with maleic acid has been investigated using a titrimetric technique.[165] In excess reductant the reaction product is succinic acid (together with Ti^{IV}) whereas with organic acid in excess the product is fumaric acid, probably owing to isomerization. In this regard the reaction behaviour parallels that of vanadium(II) found previously. E.s.r. studies on the Ti^{III} ion in the pH range 1.0—3.5 are consistent[166] with the active species in solution being the $[Ti(OH)_2(H_2O)_4]^+$ ion.

The reaction of various substituted 1,4-benzoquinones with pentacyanocobaltate(II) has been shown to proceed *via* a redox–addition mechanism.[167] In the mole ratio $2Co^{II}$: 1 benzoquinone, a bridged species of the type (8) is formed. These bridged



(8)

[161] J. Armor, *Inorg. Chem.*, 1973, **12**, 1959.
[162] R. Tomat and A. Rigo, *J. Inorg. Nuclear Chem.*, 1974, **36**, 611.
[163] R. Tomat and A. Rigo, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1972, **35**, 21.
[164] T. A. Cooper, *J. Amer. Chem. Soc.*, 1973, **95**, 4158.
[165] R. D. Foust and P. C. Ford, *J. Inorg. Nuclear Chem.*, 1974, **36**, 920.
[166] P. I. Premovic and R. P. West, *Canad. J. Chem.*, 1974, **52**, 2919.
[167] J. Hanzlik and A. A. Vlcek, *Inorg. Chim. Acta*, 1974, **8**, 247.

species decompose in a two-step mechanism:

$$(8) \xrightarrow{k_1} [Co(CN)_5OH_2]^{2-} + [Co(CN)_5QH]^{3-} \xrightarrow{k_2} [Co(CN)_5OH_2]^{2-} + QH_2$$

The dependences of both k_1 and k_2 pathways on pH and ionic strength have been determined. Aqueous cobalt(II) ions have been shown[168] to react with 1-nitroso-2-naphthol-3,6-disulphonate under anaerobic conditions in a four-electron reduction of the ligand to the 1-amino-derivative. At lower pH's, however, the ligand appears to act as a two-electron oxidant.[169]

The redox reactions of uranium(III) with benzaldehyde and salicylaldehyde (L) have been investigated[170] in perchloric acid media. Two moles of reductant are required for complete reaction and U^{IV} is found to retard the rate. The rate law is of the form

$$\text{Rate} = k[U^{III}][L][H^+]$$

and a mechanism consistent with the data involves an initial redox equilibrium followed by a rapid reaction of the radical produced,

$$L + U^{III} + H^+ \rightleftharpoons U^{IV} + HL\cdot \xrightarrow[+H^+]{U^{III}} L' + U^{IV}$$

where L′ represents the corresponding alcohol.

The reduction of silver(I) by ascorbic acid, AH_2, has been investigated using a titrimetric method.[171] The rate is inversely dependent on hydrogen ion and the mechanism proposed,

$$AH_2 \rightleftharpoons H^+ + AH^- \xrightarrow{Ag^+} AH\cdot + Ag^0$$

involves the formation of ascorbic acid radicals which subsequently react in a rapid step with Ag^I. No appreciable ionic-strength effects have been observed.

12 Pulse Radiolysis Studies

The reaction of e^-_{aq} and $[Co^{III}(bipy)_3]^{3+}$ has been examined[172] at low concentrations of the cobalt(III) complex ($\sim 4 \times 10^{-5}$ mol l^{-1}) in order to monitor spectroscopic changes in the region $\lambda \sim 400$ nm. An intense transient is observed at $\lambda_{max} \sim 300$ nm and identical (transient) absorptions are obtained using CO_2^- and $Me_2\dot{C}OH$ radicals as reductants. The decay of the intermediate is first order with $k \sim 3.5$ s^{-1}. A virtually identical species is produced with $[Cr(bipy)_3]^{3+}$ as oxidant, the decay rate constant having the same value. The species are not as yet characterized but they are not considered to be excited spin states of the metal centres nor may they be described simply as radical anions of the bipy ligands. The rates of reduction of Co^{III} complexes $[Co(NH_3)_5X]^{2+}$ by CO_2^- radicals have been studied.[173] For a large series of ligands X, varying from OH^-, NH_3, and OAc^- to p-$O_2NC_6H_4CH_2CO_2^-$ the rate constants are in the range $\sim 4 \times 10^{-7}$ to 1.9×10^9 l mol^{-1} s^{-1}. The CO_2^- radical is kinetically more selective than e^-_{aq}, the faster reactions involving aromatic nitro-complexes being compatible with the strongly electrophilic character of the NO_2^-

[168] G. C. Lalor and G. A. Taylor, *J. Inorg. Nuclear Chem.*, 1973, **35**, 4221.
[169] S. A. Bajue and G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1973, **35**, 4231.
[170] L. Adamcikova and L. Treindl, *Coll. Czech. Chem. Comm.*, 1974, **39**, 1264.
[171] S. P. Mushram, M. C. Agrawal, R. M. Mehrotra, and R. Sanehi, *J.C.S. Dalton*, 1974, 1460.
[172] M. Z. Hoffman and M. Simic, *J.C.S. Chem. Comm.*, 1973, 640.
[173] M. Z. Hoffman and M. Simic, *Inorg. Chem.*, 1973, **12**, 2471.

group. The reactivity of the radical is, however, considered as being governed more by the nature of the complex as a whole than by the properties of any individual free ligand. Two classifications are presented, (*a*) where there is direct attack of CO_2^- on the complex and electron transfer to an available orbital localized on the ligand and (*b*) where the reactivity is somewhat lower and the only available orbitals are anti-bonding in character and of high energy. In the reaction of $\cdot CH_2OH$ with $[Co(NH_3)_6]^{3+}$ in acidic media less than 10% of the stoicheiometrically expected cobalt(II) is in fact produced.[174] At neutral pH's, however, yields of Co^{II} and CH_2O are quantitative. The generation of only small amounts of Co^{II} in the former conditions is thought to be kinetic rather than thermodynamic. The mechanism proposed involves an associative process between the metal complex and the radical such that there occurs the transfer of an electron from the associated radical to the e_g^* acceptor orbital of the metal. The requirement of reorganization of the primary co-ordination sphere and electronic excitation is indicative of a low intramolecular rate process with a high activation barrier, especially when the radical remains protonated in aqueous acidic media. In a study of various cobalamins[175] it has been shown that whilst e_{aq}^- reduces cyanocobalamin to vitamin B_{12r}, the radical ion CO_2^- does not. CO_2^- will, however, reduce hydroxocobalamin and B_{12r} (almost specifically) to B_{12s}. The reaction of $\cdot OH$ with cyanocobalamin leads to a yellow–brown complex which is as yet uncharacterized. The reduction of haemotoporphyrin (H_2P) and the corresponding zinc complex, ZnP, by radicals has been described.[176] In alkaline conditions for both compounds, three intermediates are observed prior to the formation of stable products. In the reaction of ZnP with Me_2CO^-, four consecutive reactions have been identified, in which the first step is a one-electron reduction by the radical ion, followed by a dimerization:

$$Me_2CO^- + ZnP \xrightarrow{k_1} ZnP^{\bullet -}$$

$$2ZnP^{\bullet -} \xrightarrow{k_2} (ZnPH)_2$$

Rearrangement within the dimer then takes place, with a photochemically accelerated reaction as the final step. Absorption spectra of the intermediates have been obtained. In contrast, the reduction of haemin by e_{aq}^- or $MeCHO^-$ proceeds *via* a direct redox reaction involving a single-step transfer from Fe^{III} to Fe^{II}.

The rate constants for the reactions of aliphatic radicals, $\cdot RH$, with $[Cr(H_2O)_6]^{2+}$ have been measured.[177] The rate data were obtained by measuring the absorption changes resulting on the formation of Cr—C bonds. No hydrogen-ion dependences were observed. Using Cr^{II} concentrations such that $[(H_2O)_5Cr^{III}RH]$ complexes were formed, it has been shown that substitution of an α-hydrogen by an electron-donating methyl group decreases the rate, whereas substitution by an electron-withdrawing group, CH_2OR, is associated with an increase. The hydrolysis rate constants are $\sim 10^9$ lower that the formation rates and studies are suggestive of a heterolytic reaction in which the metal ion remains in the +3 oxidation state. The reaction of H• atoms with $[Cr(H_2O)_6]^{2+}$ has been studied,[178] the product being

[174] K. R. Olson and M. Z. Hoffman, *J.C.S. Chem. Comm.*, 1974, 938.
[175] R. Blackburn, A. Y. Erkol, G. O. Phillips, and A. J. Swallow, *J.C.S. Faraday I*, 1974, **70**, 1693.
[176] Y. Harel and D. Meyerstein, *J. Amer. Chem. Soc.*, 1974, **96**, 2720.
[177] H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434.
[178] H. Cohen and D. Meyerstein, *J.C.S. Dalton*, 1974, 2559.

$[(H_2O)_5CrH]^{2+}$. A comparison of the spectrum of this species with those derived for the Cr—C bonded systems described above shows them to be very similar. The hydrido-complex decomposes almost exclusively *via* a $[H^+]$-dependent pathway to yield $[Cr(H_2O)_6]^{3+}$ and H_2 ($k = 1.8 \times 10^4$ l mol^{-1} s^{-1} at 22 °C). At neutral pH, e^-_{aq} + Cr^{II} yields Cr^+_{aq} as product. The absorption spectrum of this ion has been derived and the major pathway for its decomposition is *via* the first-order reaction

$$Cr^+_{aq} + H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + H_2$$

with little evidence for any disproportion to Cr^0 and Cr^{II}. The observed rate for this process is independent of $[Cr^{II}]$, $[H^+]$, $[ClO_4^-]$, and $[Cr^{III}]$ present. Pulse radiolysis of nickel(II) sulphate gives Ni^I as product.[179] Both optical and conductance measurements have been used to investigate the reactions of this species with organic radicals (*e.g.* aliphatic alcohols). If these are present in solution the formation of Ni—C bonds is observed, the rates resulting from reactions of the type $Ni^+ + R\bullet \rightarrow [NiR^+]$, with no evidence for disproportionation of the univalent complex ion under these conditions. Using $\bullet CH_2OH$ (derived from the reaction of $\bullet OH$ + MeOH) the reaction sequence is

$$Ni^+ + \cdot CH_2OH \longrightarrow [Ni-CH_2OH]^+ \longrightarrow Ni^{II} + MeOH + H^+$$

where the second stage is slow relative to the first on the time-scale employed. Hydrated electrons are produced by the flash photolysis of M^+ (M = Co, Zn, Ni, or Cd) ions.[180] At $\lambda \sim 260$ nm the yield of e^-_{aq} is high and it is considered that these observations are consistent with the assignment of the near-u.v. absorption bands as accompanying charge-transfer-to-solvent transitions in these univalent ions.

The oxidation of Ti^{III} to Ti^{IV} by $\bullet OH$ radicals is observed on the pulse radiolysis of titanium(III) solutions.[181] When formic acid is present, however, the formate radical $\bullet CO_2H$ is produced and the Ti^{III} is reduced to Ti^{II} ($k \sim 5 \times 10^6$ l mol^{-1} s^{-1} at pH 1.4). A similar reaction is observed with Eu^{III} ($k \gg 7 \times 10^6$ l mol^{-1} s^{-1}), but not with Yb^{III}, Cr^{III}, or Sc^{III}. Although, in the case of Cr^{III}, reduction is possible on the basis of oxidation potentials, the outer-sphere electron transfer $Cr^{III} \rightarrow Cr^{II}$ is not kinetically favoured since one requirement is the reorganization energy accompanying the formation of the tetragonally distorted Cr^{II} ion. *In situ* radiolysis of malonic acid in 0.4M-sulphuric acid solutions has shown that 90% of the $\bullet OH$ reaction is associated with the abstraction of a CH hydrogen to yield $\bullet CH(CO_2H)_2$, the remaining 10% leading to $\bullet CH_2CO_2H$ *via* a decarboxylation.[182] Reactions with Ti^{III} show that whereas this complex ion will react with the former radical it shows no reactivity towards the latter. An additional finding is that whilst radicals derived from alcohols and carboxylic acids as well as those from alkanes will oxidize Ti^{III}, only those of the type $R^1R^2\dot{C}(CO_2H)$ will oxidize Fe^{II}. 1-hydroxy-1-methylethyl radicals react with O_2 to form the species $Me_2C(OH)O_2^\bullet$ (= $RO_2^\bullet$) and the resulting dioxygen radical oxidizes Fe^{II}.[183] The product is an iron(III) complex $FeRO_2^-$ and the kinetic data are

[179] M. Kelm, J. Lilie, A. Henglein, and E. Janata, *J. Phys. Chem.*, 1974, **78**, 882.
[180] N. Basco, S. K. Vidyarthi, and D. C. Walker, *Canad. J. Chem.*, 1974, **52**, 343.
[181] J. D. Ellis, M. Green, A. G. Sykes, G. V. Buxton, and R. M. Sellers, *J.C.S. Dalton*, 1973, 1724.
[182] D. Behar, A. Samuni, and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 2055.
[183] J. Butler, G. G. Jayson, and A. J. Swallow, *J.C.S. Faraday I*, 1974, **70**, 1394.

consistent with the scheme

$$\begin{array}{ccc} Fe^{III}RO_2^{\cdot} + Fe^{II} & \rightleftharpoons & Fe^{III}RO_2^{\cdot}Fe^{II} \\ \downarrow k_\alpha & & \downarrow k_\beta \\ Fe^{III} + RO_2^{\cdot} & & Fe^{III} + RO_2^{\cdot} + Fe^{II} \end{array}$$

The oxidized metal complexes are considered to be outer-sphere. In the pulse radiolysis of Fe^{II} sulphate solutions, oxidation to iron(III) complexes is observed.[184] In the absence of SO_4^{2-}, the oxidant is the hydroperoxyl radical, the product being $[Fe^{III}HO_2]^{-}$. In the presence of SO_4^{2-}, an equilibrium is established between this ion and the iron(III) complex. Hydroxyl radicals have been shown to act as oxidants in the reactions with transition-metal cyanide complexes.[185] The rate constants for the reactions (M = Fe, Ru, or Os)

$$[M(CN)_6]^{4-} + HO\cdot \longrightarrow HO^- + [M(CN)_6]^{3-}$$

and for that with $[Mo(CN)_8]^{4-}$ are all of the order of 10^9—10^{10} l mol^{-1} s^{-1}, in contrast with those for the pentacyanonitrosyl complexes which react more slowly. Comment has been made[186] on the mode of interaction of the oxidant ·OH. The rates of reaction with the aquo-ions of Fe^{II}, Mn^{II}, Ce^{III}, Cr^{III}, and Cu^{II} are all similar despite a large variation in E° values. The mechanism is considered to be inner-sphere with possible H· abstraction. A similar mechanism is proposed for the Tl^+ ion but that for Tl^{III} is outer-sphere and comparable to the $[Fe(CN)_6]^{3-}$ reaction. A study has been made of the copper(II) catalysis of the disproportionation of peroxy- and hydroperoxy-radicals.[187] Cu^{2+} reacts with O_2^- ($k = 8 \times 10^9$ l mol^{-1} s^{-1}) and with $HO_2\cdot$ ($k \sim 1 \times 10^8$ l mol^{-1} s^{-1}) and catalysis involves alternate redox reactions of the metal ion:

$$Cu^{II} + O_2^- \xrightarrow{k_1} CuO_2^+ \longrightarrow Cu^+ + O_2$$

$$Cu^+ + O_2^- \xrightarrow{+2H_2O} Cu^{II} + H_2O_2 + 2OH^-$$

The u.v. spectrum of the Cu^I ion has been measured in formate and in methanol solutions. The reaction of ·OH with Cl^- has been investigated[188] and the series of equilibria deriving from the initial reaction has been characterized. The scheme may be represented as

$$\cdot OH + Cl^- \overset{K_1}{\rightleftharpoons} HOCl^- \qquad K_1 = 0.70 \text{ l mol}^{-1}$$

$$HOCl^- + H^+ \overset{K_2}{\rightleftharpoons} Cl\cdot + H_2O \qquad K_2 = 1.6 \times 10^7$$

$$Cl\cdot + Cl^- \overset{K_3}{\rightleftharpoons} Cl_2^- \qquad K_3 = 1.9 \times 10^5 \text{ l mol}^{-1}$$

Absorption spectra of both Cl_2^- and $HOCl^-$ have been measured in the range λ = 230—450 nm. Cl_2^- and $Cl\cdot$ oxidize Fe^{II}, the reactions being studied by the pulse radiolysis of solutions containing $Fe(ClO_4)_2$ and NaCl. It is not possible,

[184] G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J.C.S. Faraday I*, 1973, **69**, 1079.
[185] W. L. Waltz, S. S. Akhtar, and R. L. Eager, *Canad. J. Chem.*, 1973, **51**, 2525.
[186] V. M. Berdnikov, *Russ. J. Phys. Chem.*, 1973, **47**, 1547.
[187] J. Rabani, D. Klug-Roth, and J. Lilie, *J. Phys. Chem.*, 1973, **77**, 1169.
[188] G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J.C.S. Faraday I*, 1973, **69**, 1597.

however, to characterize $Fe^{III}Cl^-$ as a primary product although Fe^{III} is present within 1 μs of pulsing.

Thallium(II) has been generated in the pulse radiolysis of Tl^I and Tl^{III} in 1M-$HClO_4$.[189] The rates of the reaction of Tl^I + ·OH and Tl^{III} + H· have been measured, and from data on the Fe^{II}–Tl^{II} reaction, the free energy of formation of Tl^{II} has been shown to be 42 kcal mol^{-1}. Tl^{II} plays no part in the Tl^I–Tl^{III} exchange. Three chloride complexes of Tl^{II} have also been characterized by radiolytic techniques.[190] Absorption spectra for $TlCl^+$, $TlCl_2$, and $TlCl_3^-$ have been reported. In the complex formation reaction

$$Tl^{II} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TlCl^+$$

k_1 and k_{-1} have values of 9×10^9 l mol^{-1} s^{-1} and 1.4×10^5 s^{-1} respectively. The oxidation of Tl^I by Cl_2^- has been described, and the rates of reaction of $TlCl_2^+$, $TlCl_3$, and $TlCl_4^-$ with H· are greater than that for Tl^{3+}_{aq}, contrary to considerations based on free energies. The preferred mechanism for reduction is *via* ligand abstraction. In support of this proposal the product of the reaction of H· with $TlCl^{2+}$ is not $TlCl^+$ but Tl^{II}.

The pulse radiolysis of penicillamine (RSH) and penicillamine disulphide (RSSR) in aqueous solutions has been described.[191] The rate constant for the reaction e^-_{aq} + RSSR decreases by a factor of 9 over the pH range 7—10 whilst the first-order rate constant for decay of the resulting radical anion $RSSR^-$ increases by a factor of 4 over the same range. These pH effects are attributed to deprotonation of the amino-groups on the substrates. Absorption spectra of RS· and $RSSR^-$ have been obtained, the latter having a pronounced absorbance in the visible range (ε_{max} = 7.5×10^3 l mol^{-1} cm^{-1} at λ = 450 nm). The reaction of the solvated electron with the hydrogen sulphide ion has been investigated[192] and a rate constant k_1 = 3×10^7 l mol^{-1} s^{-1} evaluated, in contrast to an earlier report that the substrate was unreactive. A comparison of the reactions of e^-_{aq} towards HS^- and HSe^- suggests that the reactivity reflects the ability of the substrate atom to accept an electron, rather than its ability to donate a proton to the reductant.

The kinetics of the reaction of sodium with alkyl sulphides in liquid ammonia have been reported.[193] The overall reaction may be represented as

$$RSR + 2Na \xrightarrow{NH_3} NaSR + RH + NaNH_2$$

The rate law is first order with respect to both $[e^-]$ and $[R_2S]$, where R = Me, Et, or Pr^n. The technique of continuously mixing solutions of solvated electrons (Na dissolved in NH_3) with substrates in the cavity of an e.s.r. spectrometer continues to be used.[194] Radical anions have been characterized in the reactions with acrylic acid and with some dicarboxylic acids.

[189] H. A. Schwartz, D. Comstock, J. K. Yandell, and R. W. Dodson, *J. Phys. Chem.*, 1974, **78**, 488.
[190] R. W. Dodson and H. A. Schwartz, *J. Phys. Chem.*, 1974, **78**, 892.
[191] J. W. Purdie, H. A. Gillis, and N. V. Klassen, *Canad. J. Chem.*, 1973, **51**, 3132.
[192] R. L. Eager, V. Kabachia, W. L. Waltz, R. J. Woods, and K. J. MacCallum, *Canad. J. Chem.*, 1973, **51**, 1920.
[193] R. L. Jones and R. R. Dewald, *J. Amer. Chem. Soc.*, 1974, **96**, 2315.
[194] I. H. Elson, T. J. Kemp, D. Greatorex, and H. D. B. Jenkins, *J.C.S. Faraday II*, 1973, **69**, 1402.

3

Reactions of Oxygen and Hydrogen Peroxide

BY A. McAULEY

The nature of the interactions between metal complexes and dioxygen continues to be examined using a variety of techniques. The metal centre still most favoured in terms of research effort is cobalt and much work is currently being undertaken to identify the factors involved both in reversible oxygenation and in the oxidation process which may follow. The identification of the oxidation state of the metal centre and of the types of bonding in the complexes are also currently under investigation. Structural factors have been introduced in the reactions of iron(II), and in some cases oxidation to the +3 state has been prevented.

A review[1] has been published of the thermodynamic and kinetic aspects of the oxygenation of cobalt(II) complexes. The correlation between electronic structure and oxygenation of cobalt(II) salen complexes has been discussed[2] and a mechanism for oxygenation proposed. An interesting mixed-ligand complex has been shown to be an effective oxygen[3] carrier at low pH (2—3). Addition of solid-state cobalt terpyridyl dichloride [Co^{II}(terpy)Cl_2] to a solution of 1,10-phenanthroline leads to the formation of the complex $[ML^1L^2]^{2+}$, $[Co(terpy)(phen)(H_2O)]^{2+}$, in solution. Reaction of two moles of complex with one mole of dioxygen yields an adduct of high thermodynamic stability. The rate of formation has been characterized using stopped-flow techniques, the reaction orders being unity and two with respect to $[O_2]$ and $[(ML^1L^2)^{2+}]$ respectively. The mechanism consistent with the data is

$$CoL^1L^2 + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CoL^1L^2O_2$$

$$CoL^1L^2O_2 + CoL^1L^2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (CoL^1L^2)_2O_2$$

Under pseudo first-order conditions,

$$\frac{d[(CoL^1L^2)_2O_2]}{dt} = \frac{k_1k_3[CoL^1L^2]^2[O_2]}{(k_2 + k_3[CoL^1L^2])} = k_{obs}[O_2]$$

In this case, $k_2 \gg k_3[CoL^1L^2]$, unlike most of the previous systems studied where the reverse inequality holds leading to a first-order term in complex. Such a situation is that reported in the reaction[4] of cobalt(II) tetrasulphophthalocyanine [Co(tsp)] with O_2. Again a 2 : 1 adduct is formed, stable in anaerobic and aerobic conditions. The reaction is first order with respect to [Co(tsp)], and the rate-limiting step is the forma-

[1] E. I. Ochiai, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3375.
[2] E. I. Ochiai, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1727.
[3] D. H. Huchital and A. E. Martell, *J.C.S. Chem. Comm.*, 1973, 868.
[4] D. M. Wagnerova, E. Schwertnerova, and J. Veprek-Siska, *Coll. Czech. Chem. Comm.*, 1974, **39**, 1980.

tion of the 1 : 1 adduct. There is, however, evidence for a [Co(tsp)] monomer–dimer equilibrium. The reversible formation of a high-spin cobalt(II) complex,

$$[Co(pfp)_2(H_2O)_2]^{2-} \overset{O_2}{\rightleftharpoons} [Co(pfp)(pfpH)O_2]^-$$

(where pfp^{2-} = perfluoropicolinato dianion) has been investigated and a stable tetra-alkylammonium salt of the adduct isolated.[5] Evidence has been presented for hydrogen-bonding with the co-ordinated oxygen in the amine complexes of cobalt(II) protoporphyrin(IX) dimethyl ester.[6] In toluene the reaction is first order in [Co^{II}] and in [O_2] but less than first order in amine. The evaluation of the thermodynamic data for the reversible oxygenation in these protoporphyrin systems has been criticized.[7] The methods used involved graphical solutions, and the initial data were considered too poorly defined for any numerical analysis to be significant.

Two studies have been made of the crystal structures of the adducts formed between $[Co(CN)_5]^{3-}$ and O_2. In the 2 : 1 adduct[8] $[(NC)_5Co—O—O—Co(CN)_5]^{6-}$ a planar arrangement of the Co—O—O—Co system is shown and the σ-bonded oxygen is consistent with a superoxide structure of cobalt(III). The CoOO bond angle of 119° is similar to that for other peroxo-complexes. The Raman spectra of these μ-peroxo-complexes[9] exhibit an intense peak at ~800 cm^{-1}, assigned to the O_2^{2-} stretching which is in resonance with the band at ~360 nm associated with the $O_2^{2-} \rightarrow Co^{III}$ charge transfer. The crystal structure of the 1 : 1 adduct containing the ion $[Co(CN)_5O_2]^{3-}$ has been determined[10] using the tetraethylammonium salt. This complex is prepared by exposure to air of an anhydrous solution of $(NEt_4)_3[Co(CN)_5]$ in DMF. The oxygen adduct is six-co-ordinate, the dioxygen being σ-bonded. The formulation proposed by the authors is of a nearly linear superoxide complex of Co^{III} in which the CoOO bond angle is 175°. From these data and by comparing them with biological systems, *e.g.* oxycobaltmyoglobin, and other model compounds it appears that dioxygen binds to Fe^{II} and Co^{II} through only one oxygen atom. The question of cleavage of the O—O bond on oxygenation has been discussed.[11] Whereas with Mn^{II}, Cr^{II}, V^{II}, and Fe^{II} the products of oxygenation are $M^{III}—O^{2-}—M^{III}$ species resulting from O—O bond rupture, there is little evidence for a similar effect with Co^{II}. In thermodynamic terms the $M^{III}—O^{2-}—M^{III}$ species should be most stable, and if the mechanism of oxygenation involves the reaction scheme represented by reactions (1)—(3) (formal charges are neglected for clarity)

$$M + O_2 \rightleftharpoons MO_2 + M \rightleftharpoons M^+O_2^{2-}M^+ \quad (1)$$

$$M^+O_2^{2-}M^+ \rightleftharpoons 2M^+O^{\cdot -} \quad (2)$$

$$M^+O^{\cdot -} + M \rightleftharpoons M^+O^{2-}M^+ \quad (3)$$

the O—O bond rupture in step (2) which takes place is likely to be of the same order in energy as that for H_2O_2 (51.1 kcal mol^{-1}). In the formation of the final product allowance must therefore be made for this energy barrier. The most important factor in the stabilization of the $M^+O^{\cdot -}$ state is the interaction between the d_π electron on

[5] C. J. Willis, *J.C.S. Chem. Comm.*, 1974, 117.
[6] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, 1973, **95**, 1142.
[7] R. M. Guidry and R. S. Drago, *J. Amer. Chem. Soc.*, 1973, **95**, 6645.
[8] F. R. Fronczek and W. P. Schaefer, *Inorg. Chim. Acta*, 1974, **9**, 143.
[9] T. B. Freedman, C. M. Yoshida, and T. M. Loehr, *J.C.S. Chem. Comm.*, 1974, 1016.
[10] L. D. Brown and K. N. Raymond, *J.C.S. Chem. Comm.*, 1974, 470.
[11] E. I. Ochiai, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 453.

M^+ and the odd electron on $O^{\cdot -}$. In the case of Cr^{II}, for example, the electron may be accommodated in a bonding orbital, but for a d^6 system, as in the oxygenation of Co^{II}, the electron has to occupy an antibonding orbital, providing no stabilization of the $M^+O^{\cdot -}$ state.

Thermodynamic data have been reported[12] for the reversible oxygenation of several cobalt(II) Schiff-base ($Co^{II}L$) complexes. A linear correlation has been described between the equilibrium constants K_1 for the reactions

$$Co(L)B + O_2 \overset{K_1}{\rightleftharpoons} Co(L)BO_2$$

where B = a unidentate ligand in the axial position, and the ease of oxidation of Co^{II} to Co^{III} as measured by cyclic voltammetry. The effects of both axial and equatorial ligands have been discussed, and the origin of the linear free-energy relationship is seen to derive from the redox potential being a measure of the electron density around the metal centre, which in turn is the most important factor governing oxygen affinity. Electronegativity and π-withdrawing groups together with π-delocalization of the electron density are important aspects of the equatorial interaction but both π-bonding and the basicity of the (N) donor axial ligand *trans* to O_2 must also be considered. Similar effects have been reported for chelate complexes, including vitamin B_{12r}.[13] In the latter case, however, the K_1 value is smaller than expected. A linear correlation similar to that described above has been derived and used to identify the efficiency of these complexes as oxygen carriers and as phosphine oxidation catalysts.[14] Three groups of compounds have been characterized, and those in which there is a ready transfer of the electron to give a superoxide ion and cobalt(III) show no catalytic activity. Greatest acceleration of the rate of formation of Ph_3PO was observed when the redox potentials were neither too high to preclude metal–oxygen interaction nor low enough to allow facile oxidation. Evidence against the superoxide formation in cobalt(II) adducts of dioxygen has been provided from e.s.r. studies.[15] Using the quinquedentate Schiff-base ligand bis-(salicylidene-γ-iminopropyl)methylamine the e.s.r. spectra of the O_2 and CO adducts are virtually identical and, since there is little evidence for the reduction of the latter ligand, it appears that the best description is one where the unpaired electron is largely in the Co^{II} orbital rather than a π^*-orbital of the oxygen. The reaction of superoxide with vitamin B_{12a} [cobalt(III) aquocobalamin] in DMF leads, however, to the formation of superoxocobalamin.[16] The same complex may also be formed by the reaction of vitamin B_{12r} with dioxygen. This reaction appears to be reversible at low temperatures.[17]

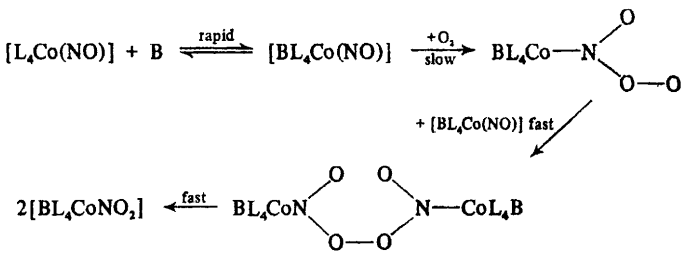
The reduction of co-ordinated oxygen by organic substrates has been investigated.[17] Oxygen adducts of 3-methoxysalen-Co^{II} in pyridine are formed reversibly, and reaction takes place with substrates (RH_2) such as thiols, ascorbic acid, and *NN'*-tetramethyl-*p*-phenylenediamine (tmpd). Since the latter has no significant ligand properties and Wurster's blue radical cation is formed in the course of reaction as confirmed by e.s.r. and u.v., it is suggested that the reaction proceeds without

[12] M. J. Carter, D. P. Rillema, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 392.
[13] M. J. Carter, L. M. Engelhardt, D. P. Rillema, and F. Basolo, *J.C.S. Chem. Comm.*, 1973, 810.
[14] R. P. Hanzlik and D. F. Smith, *J.C.S. Chem. Comm.*, 1974, 528.
[15] B. S. Tovrog and R. S. Drago, *J. Amer. Chem. Soc.*, 1974, **96**, 6765.
[16] J. Ellis, J. M. Pratt, and M. Green, *J.C.S. Chem. Comm.*, 1973, 781.
[17] E. W. Abel, J. M. Pratt, R. Whelan, and P. J. Wilkinson, *J. Amer. Chem. Soc.*, 1974, **96**, 7119.

prior co-ordination of the reductant to the cobalt. Second-order kinetic behaviour is observed initially, although after 70% reaction deviations from this behaviour are apparent. The initial step involved is

$$[LCo^{II}O_2] + RH_2 \longrightarrow [LCo^{III}O_2H]^- + \cdot RH$$

followed by reactions of the radicals and HO_2^-. In the case of the superoxocobalamin complex, the $[LCo^{III}O_2H]$ complex has been characterized spectroscopically. In the reactions of nitrosyl–Schiff-base–cobalt(II) $[L_4Co(NO)]$ complexes with oxygen in the presence of base, B (*e.g.* pyridine), the formation of nitro-complexes has been reported.[18] Kinetic studies show the reaction to be first order in $[O_2]$ and cobalt complex. Quantitative uptake of 0.5 mole of dioxygen per mole of complex observed is in accord with the scheme



This mechanism parallels that postulated for the gas-phase reaction between NO and O_2. The reaction rates do, however, increase with increasing base concentration, reaching a limiting rate at high value.

In contrast with these findings for cobalt(II) complexes of octahedral configuration, the interaction of O_2 with a cobalt(II) histidine complex has been investigated in strongly basic media.[19] In solutions of 1M-NaOH, the spectrum of the cobalt(II) species is consistent with that of a tetrahedral complex with four nitrogen donors. The rate law for the reaction is

$$\text{Rate} = k_{obs}[O_2] = \{k_1 + k_2[\text{his}]\}[Co(\text{his})_2][O_2]$$

although the mechanism of the k_2 pathway is at present uncertain. The product differs from those derived under less basic conditions and may be a doubly bridged μ-(O_2,OH) dinuclear species.

The reversible binding of dioxygen to iron(II) in solution has been reported.[20] By incorporating into the ligand a steric effect which prevents dimerization and the formation of a μ-oxo-bridged structure of iron(III), it has been shown that the formation of 1 : 1 adducts takes place at low temperatures. A similar 1 : 1 complex with carbon monoxide has also been identified. Using an essentially similar approach,[21] a paramagnetic dioxygen complex of an iron(II) porphyrin has been isolated. In this case, however, a solid–gas reaction was employed (see Part III of this Report). The kinetics of dissociation of iron(II) tetraphenylporphine–oxygen adducts containing axial bases have been investigated in methylene chloride at −79 °C.

[18] K. L. Watters and R. G. Wilkins, *Inorg. Chem.*, 1974, **13**, 752.
[19] S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 1973, **12**, 1528.
[20] J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 1973, **95**, 5757.
[21] J. P. Collman, R. R. Gagné, and C. A. Reed, *J. Amer. Chem. Soc.*, 1974, **96**, 2629.

Using the bases py, piperidine, and 1-methylimidazole, no rate dependence on base concentration was observed, suggesting a first-order dissociative mechanism.[22] The axial base exerts a *trans* influence, the lability of the co-ordinated O_2 decreasing in the order py > piperidine ≫ 1-methylimidazole. This latter finding is surprising in view of the presence of an imidazole in haem proteins. The Fe—O bond is considered to involve both σ- and π-bonding, and within these model systems the axial ligand *trans* to the O_2 will compete for the π-electron density on the iron. Several other papers have been published in which differing aspects of the iron(II) oxygenation reactions are discussed. Spectroscopic effects on oxygenation of protohaem complexes have been monitored[23] at various temperatures with several axial basic ligands. One result which is of interest is that an imidazolyl-type base is not unique in its ability as an axial ligand to effect the formation of the oxyhaem complex. Simple dioxygen–haem complexes are formed in DMF.[24] Solvent effects on reversible formation and oxidative stability of species of this type have been described[25] using as a model a ligand with marked steric hindrance on one side of the complex. The reversible binding of O_2 to mesoporphyrin IX has also been investigated at low temperatures.[26,27]

The oxidation of $[Cu(R\text{-phen})_2]^+$ (R = substituents) by molecular oxygen has been investigated in nitromethane.[28] Although the solid Cu^I complex is stable in air, treatment of dark brown solutions of this cation in nitromethane with oxygenated solvent leads to a colour change to green. The product ion has some anion incorporated in the primary co-ordination sphere since 1 : 1 electrolyte behaviour is observed. The oxidation step is followed by the reaction

$$[Cu(R\text{-phen})_2]^{2+} + CH_2NO_2^- \longrightarrow [Cu(R\text{-phen})_2(CH_2NO_2)]^+$$

a process which has been verified by the action of the copper(II) salt with sodium nitromethane. The oxidation of uranium(IV) by O_2 in sulphate media has been investigated.[29] Logarithmic plots against time show an initial induction period followed by a linear dependence. Increasing the sulphuric acid concentration strongly diminishes the oxidation rate. The final product is UO_2^{2+} and a first-order dependence on $[O_2]$ is observed. The overall scheme is, however, clearly more complicated than that presented by the authors and more work is required on this system for a fuller understanding of all the effects. The oxidation of Ti^{III} has been studied in sulphuric acid media over the concentration range $[H^+]$ = 1—5 mol l^{-1}.[30] The rate is first order with respect to both reactants and there is little effect of $[SO_4^{2-}]$ on the process. The reaction proceeds about ten-fold faster than the corresponding oxidation in chloride media, suggesting that chloride-ion complexing retards the reaction. In this respect, the reaction is very similar to the corresponding iron(II) oxidation previously studied. Molecular oxygen and $TiCl_3$ react in anhydrous pyridine to give the oxo-bridged Ti^{IV} complex $Cl_3Ti—O—TiCl_3$,4py in quantitative

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[29] K. Juznic and S. Fedina, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2609.
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yield.[31] The rate law is first order with respect to both [Ti^{III}] and [O_2] and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 10 kcal mol^{-1} and -31 cal mol^{-1} K^{-1} respectively. The mechanism is virtually identical to that proposed above in the formation of μ-oxo-bridged species in that a rate-determining electron transfer occurs (solvated py omitted for clarity),

$$O_2 + TiCl_3 \xrightarrow{k_1} Cl_3Ti^{IV}O_2^{\cdot -} + TiCl_3 \xrightarrow{k_2} 2TiCl_3O^{\cdot}$$

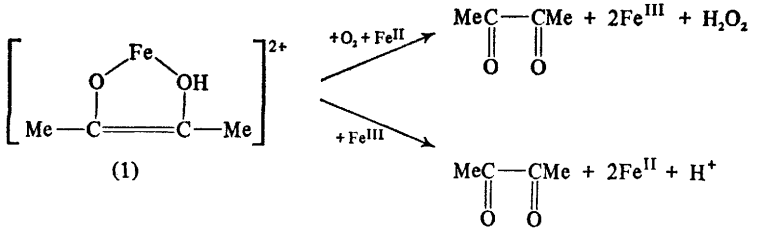
$$Cl_3TiO^{\cdot} + TiCl_3 \longrightarrow \text{product}$$

with the formation of a superoxide ion.

The reaction of cobalt(II) complexes with 1-nitroso-2-naphthol-3,6-disulphonate in the presence of O_2 leads to cobalt(III) complexes.[32] The oxidation of hydroxylamine by molecular oxygen is catalysed by cobalt(II) tetrasulphophthalocyanine (CoTSP) at pH >10.[33] The reaction products are N_2, N_2O, and NO_2^-, whilst O_2 is reduced to H_2O and H_2O_2. The mechanism invoked requires the formation of a ternary complex of NH_2OH, CoTSP, and O_2 within which the electron-transfer process occurs without the liberation of free radicals. Manganese(II) Schiff-base complexes react with O_2,[34] the overall process being governed by the geometry of the ligand. The products are considered not to be low-spin Mn^{III} species on the basis of magnetic data, and the uptake of oxygen is slightly less than that theoretically required for a 2 : 1 Mn : O_2 complex. In the catalysis of the oxidation of ascorbic acid (AH_2) by copper(II) ions,[35] the reaction is first order with respect to [AH_2] and [Cu^{II}] but is more complex in other reagents ($[H^+]^{-1}$ and $[O_2]^{0.5}$). There is evidence for the accumulation of hydrogen peroxide and this may be involved in a side reaction. The overall rate is much lower in anaerobic conditions, and the authors conclude that when O_2 is present their data are best represented by a chain mechanism. The iron(II)- and iron(III)-catalysed oxidation of acetoin (Ac) has been investigated in perchloric acid solutions in the range [H^+] = 0.125—2.00 mol l^{-1}.[36] In aqueous ethanolic (1 : 1 v/v) media the data are essentially similar to those in water, and a mechanism consistent with the rate law

$$\text{Rate} = \frac{-d[O_2]}{dt} = \frac{k_1[Ac][Fe^{III}][H^+]}{k_2/k_3[H^+] + [Fe^{III}]} + \frac{k_4[Ac][Fe^{III}]}{[H^+]}$$

involves the formation of the complex (1), which undergoes decomposition *via* two predominant pathways:



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Reaction of Fe^{II} with H_2O_2 yields ·OH radicals which are further involved in redox processes with the organic substrate, thus increasing the complexity of the overall system. The autoxidation of triphenylphosphine is catalysed by iron(III) and iron(IV) dithiolate complexes.[37] Both complexes provide good catalytic pathways, one mole of $[Fe^{IV}(mnt)_3]^{2-}$ (mnt^{2-} = *cis*-1,2-dicyanoethylene-1,2-dithiolate) producing 15 moles of Ph_3PO in pure O_2 and 20 moles in air. No simple kinetic behaviour is observed, however, even in the presence of large (~10%) concentrations of catalyst. Cobalt(II) complexes of the same ligand catalyse the aerial oxidation of thiols to disulphide with the formation of H_2O_2.[38] In a previous study,[39] the anaerobic oxidation of iodide ion by vanadium(V) was reported.[39] An extension of the data to include the oxygen-dependent pathway has now been published.[40] The complete rate law is of the form Rate = $a + b[O_2]$, where $b = k[H_4VO_4^+][I^-]^2[H^+]^2$, and the mechanism for this pathway,

$$[H_4VO_4]^+ + 2H^+ \rightleftharpoons [V(OH)_2]^{3+} + 2H_2O$$

$$[V(OH)_2]^{3+} + I^- \rightleftharpoons [V(OH)_2I]^{2+} \overset{+I^-}{\rightleftharpoons} [V(OH)_2I_2]^+$$

$$O_2 + [V(OH)_2I_2]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [O_2V(OH)_2I_2]^+ \xrightarrow{k_2} [VO(O_2)]^+ + I_2 + H_2O$$

$$[VO(O_2)]^+ + 2I^- + 2H^+ \xrightarrow{\text{fast}} VO_2^+ + I_2 + H_2O$$

involves the formation of the oxoperoxovanadium(V) ion which is unstable and reacts further with iodide. It is considered that the ability of V^V complexes to take up oxygen is dependent on the electron-donating capacity of the ligands co-ordinated to the metal centre. Hydroxide ion and water are not sufficiently good donors whereas iodide allows the reaction to proceed, probably *via* a polarization of the ligand.

The reversible uptake of O_2 (and CO) by a copper(II) polyoxime complex containing 1,2-bis(hydroximino)trimethylene units has been reported.[41] Stereoregularity on the structure of the polymer may impart properties which are not observed in monomeric copper(II) dimethylglyoxime complexes.

The kinetics of the reactions of sodium dithionate with O_2 and H_2O_2 have been re-investigated.[42] Using the stopped-flow method to study the O_2 reaction, it was found that with either reagent in excess the kinetics were consistent with the rate-determining dissociation of $S_2O_4^{2-}$ into $2SO_2^-$.

Two studies using ozone as oxidant have been reported. The mechanism of the oxidation of alkenes shows stereospecific effects[43] and the reaction has been studied in the presence and absence of iron(III). In the oxidation of sodium thiosulphate, the products are dependent on the conditions.[44] At neutral pH, SO_4^{2-}, SO_3^{2-}, and tri- and tetra-thionates are formed whereas in alkaline solutions sulphite is an intermediate which is oxidized to sulphate.

The E° for the Am^{VI}/Am^V couple of 1.60 V in perchloric acid shows that Am^{VI} is

[37] N. Sutin and J. K. Yandell, *J. Amer. Chem. Soc.*, 1973, **95**, 4847.
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[40] S. Celsi, F. Secco, and M. Venturini, *J.C.S. Dalton*, 1974, 793.
[41] S. J. Kim and T. Takizawa, *J.C.S. Chem. Comm.*, 1974, 356.
[42] C. Cretz and N. Sutin, *Inorg. Chem.*, 1974, **13**, 2041.
[43] T. M. Hellman and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1974, **96**, 1531.
[44] M. Takizawa, A. Okuwari, and T. Okabe, *Bull. Chem. Soc. Japan*, 1973, **46**, 3785.

a stronger oxidant than either Pu^{VI} or Np^{VI}. The oxidation of hydrogen peroxide by Am^{VI} has been investigated[45] using the stopped-flow method,

$$2AmO_2^{2+} + H_2O_2 \longrightarrow 2AmO_2^{+} + 2H^+ + O_2$$

the reaction being first order with respect to both $[H_2O_2]$ and $[Am^{VI}]$. The predominant pathway is hydrogen-ion-independent, with the possibility of a small $[H^+]$ contribution. The simplicity of the rate law is thus in marked contrast with those for the corresponding reactions of Np^{VI} and Pu^{VI}, where in the former case inhibition by Np^{V} is observed and in the latter a term in $[H^+]^{-1}$ is involved.

The reaction of hydrogen peroxide with 1,2-diaminocyclohexanetetra-acetatomanganate(III) $[Mn^{III}L]^-$ is found to be second order in metal complex and first order in reductant.[46] A mechanism consistent with the observed $[H^+]^{-1}$ and $[Mn^{II}L]^{2-}$ dependences may be written as

$$[LMn^{III}OH_2]^- + H_2O_2 \overset{K}{\rightleftharpoons} [LMn^{III}O_2H]^{2-} + H^+ + H_2O$$

$$[LMn^{III}O_2H]^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Mn^{II}L]^{2} + HO_2\cdot$$

$$[LMn^{III}OH_2]^- + HO_2\cdot \overset{k_3}{\longrightarrow} [Mn^{II}L]^{2-} + O_2 + H^+$$

The pH dependence of the pseudo-second-order rate constant shows deviations from linearity at both low and high values. At pH < 3, some free Mn^{II} may be present resulting from dissociation of $[MnL]^{2-}$, and at pH $> \sim 4$ some proton dissociation of the $HO_2\cdot$ radical is expected ($pK_a = 4.8$). An e.s.r. study of the complexation of metal ions with $HO_2\cdot$ has been made.[47] Formation reactions,

$$M^{n+} + HO_2\cdot \overset{K}{\rightleftharpoons} [MHO_2]^{n+}$$

have been investigated in a flow system with K values in the range 10^3—10^5 l mol^{-1} for M^{IV} = Th, U, Zr, and Ti. The mechanism of decay of $MHO_2\cdot$ complexes is dependent on the extent of equilibrium since a pathway involving $HO_2\cdot$ has been detected.

Oxidation of co-ordinated thiocyanate in $[Co(en)_2(NH_3)NCS]^{2+}$ has been reported.[48] Reaction with H_2O_2 leads to the formation of *cis*- and *trans*-$[Co(en)_2(NH_3)CN]^{2+}$ and -$[Co(en)_2(NH_3)_2]^{3+}$ ions. The isomeric cyano-ammine species have been characterized spectroscopically. The extent of conversion into the *trans*-isomer is greatest at lower concentrations of the reacting complex, whilst $[H_2O_2]$ is in the range 1.5—2.5 mol l^{-1}. The kinetics of formation of H_2O_2 induced by the decomposition of trioxalatocobaltate(III) in the presence of manganese(II) and O_2 have been studied.[49] Although manganese(III) oxalate is formed as an intermediate, there appears to be little evidence for its reaction with the peroxide under the conditions obtaining. A method of estimating rate constants for the aquation (at low acidities) of iron(II) complexes of the type $[FeL_3]^{2+}$ (L = phen or 2,2'-bipy) and of Schiff-base ligand complexes has been found using H_2O_2. The zero-order dependence on the substrate corresponds to a rate-limiting dissociation of the $[FeL_3]^{2+}$ species followed by rapid reaction of

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[46] T. E. Jones and R. E. Hamm, *Inorg. Chem.*, 1974, **13**, 1940.
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[48] A. R. Norris and J. W. L. Wilson, *Canad. J. Chem.*, 1973, **51**, 4152.
[49] M. Kimura and Y. Monma, *Bull. Chem. Soc. Japan*, 1973, **46**, 2246.

$[FeL_2]^{2+}$ and L with H_2O_2. For the complex tris-3-(2-pyridyl)-5,6-bis-(4-phenylsulphonato)-1,2,4-triazineiron(II), $[Fe(ppsa)_3]^{2+}$, however, this mechanism does not apply.[50] The rate is $[H_2O_2]$-dependent and probably reflects the attack by this oxidant on the co-ordinated ligand. The retardation of the iron(III)-catalysed decomposition of H_2O_2 by an iron(II) di-imine complex, tris(glyoxal)bis(methylimine)-iron(II), $[Fe(gmi)_3]^{2+}$, has been investigated.[51] In the reaction, $HO_2\cdot$ radicals formed react with $[Fe^{II}(gmi)_3]^{2+}$, regenerating H_2O_2. The iron(III) complexes so produced can undergo an internal redox (see Part 1, Chapter 2 of this Report), yielding a radical at the ligand, and further reaction with $HO_2\cdot$ (or $HO\cdot$) radicals leads to the formation of labile ligand-oxidized species. A number of organic substrates also retard the iron(III)–H_2O_2 reaction.[52] The results with acetone, acetic acid, and t-butyl alcohol are consistent with the assumption that these species act as a trap for the $HO\cdot$ radicals. The reactivity towards the radicals is t-butyl alcohol > acetone > HOAc. These data are generally in accord with the redox chain mechanism postulated previously, but the authors do note that their conclusions relate only to acidic media. Complexes of iron(III) in less acid conditions show a considerable variation in rate with H_2O_2 and concurrent oxidation of the ligands is frequently observed. The effects of NO_3^- and ClO_4^- on the rate of catalytic decomposition of H_2O_2 by iron(III) have been reported,[53] the reaction in nitrate media being about 17% slower than in perchlorate. In these systems, the reaction rates have been monitored using tetranitromethane as an indicator, since the reaction of this substrate with any intermediate O_2^- leads to the coloured nitro-form ion $C(NO_2)_3^-$. The reaction of the iron(III) triethylenetetramine complex with H_2O_2 is considered as an 'inorganic' analogue of catalase.[54] Additions of 2,2′-bipy and allyl alcohol have been used to confirm that iron(II) complexes are formed during the course of this reaction. The mechanism proposed is one in which no $\cdot OH$ radicals are produced but instead a two-electron transfer takes place to yield an iron(IV) species:

$$[(trien)Fe^{II}] + H_2O_2 \longrightarrow 2OH^- + [(trien)Fe^{IV}]$$

$$[(trien)Fe^{IV}] + HO_2^- \longrightarrow [(trien)Fe^{II}] + O_2 + H^+$$

There is no evidence for any O_2^- ions being generated since addition of $C(NO_2)_4$ shows no effect on the rate. The mechanism of the corresponding reaction with iron(III) edta complexes has been investigated.[55] A linear inverse hydrogen-ion dependence is consistent with the principal pathway involving the reaction

$$[Fe(edta)]^- + HO_2\cdot \longrightarrow [Fe(edta)]^{2-} + H^+ + O_2^-$$

the pH conditions (≤ 2) being such that no proton dissociation of the radical is considered. As in other reactions of this type a chain mechanism is proposed. The increase in the reaction rate when compared with the aquoiron(III) ion is, however, thought to constitute an example of the situation where the change in lability of the co-ordination sphere of the ion plays as important a role in catalysis as the change in redox potential.

[50] E. R. Gardner, F. M. Mekhail, J. Burgess, and J. M. Rankin, *J.C.S. Dalton*, 1973, 1340.
[51] H. L. Chum and M. L. de Castro, *J. Amer. Chem. Soc.*, 1974, **96**, 5278.
[52] C. Walling and A. Goosen, *J. Amer. Chem. Soc.*, 1973, **95**, 2987.
[53] B. Erofeev and V. A. Plakhotnik, *Russ. J. Phys. Chem.*, 1973, **47**, 1237, 1238.
[54] T. P. Vorob'eva, V. G. Isak, A. P. Purmal, and A. Ya. Sychev, *Russ. J. Phys. Chem.*, 1974, **48**, 844.
[55] T. P. Vorob'eva, Y. N. Kozlov, and A. P. Purmal, *Russ. J. Phys. Chem.*, 1974, **48**, 846.

The catalytic decomposition of H_2O_2 by copper(II) ammine complexes has been studied using a variety of physical techniques.[56] Two reaction pathways have been identified. At low ammonia concentrations, $[NH_3] \sim 0.04$ mol l^{-1}, there is a linear rate of evolution of O_2 during which a brown intermediate is formed. This species has been characterized as a peroxocopper(III) complex which decomposes on standing. Under these conditions, however, e.s.r. studies are consistent with the formation of the O_2^- radical anion. At higher ammonia concentrations, however, there is no linearity in the rate of O_2 evolution and a more complex $[H_2O_2]$ dependence is reported. A reaction scheme consistent with the data may be represented by reactions (4)—(7).

$$\begin{array}{ccccc} & & [Cu^{II}(NH_3)_n] + OH^- & \rightleftharpoons & [Cu^{II}(NH_3)_3OH]^+ \\ & & (7)\ \uparrow +NH_3 & & (5)\ \downarrow +H_2O_2 \\ Cu^{II} + 2H_2O + O_2 & \xleftarrow[(4)]{+2H_2O_2} & [Cu^{II}(NH_3)_3(OH)]^+ & \xleftarrow[(6)]{+NH_3,-O_2} & [\text{peroxo}Cu^{III}\ \text{complex}] \end{array}$$

At low $[NH_3]$ reaction (4) is the main pathway, and reaction (5) is much more rapid than (6). When large excesses of ammonia are present, however, the rates of reactions (6) and (7) are much greater than (5) so no build-up of the peroxocopper(III) species is detected. The oxidations of *N*-methyl-*p*-aminophenol, resorcinol, and pyrocatechol by H_2O_2 are catalysed by aquocopper(II) ions and by the corresponding nitrilotriacetate and edta complexes.[57] Ternary complex intermediates are formed during the course of the reaction. An interpretation of the data based on a mechanism where the catalysing ion and the substrate form a complex which is then oxidized by H_2O_2 has been shown to be incorrect. In keeping with the observation that increase of the complexing agent (*e.g.* edta) lowers the rate of reaction, a scheme has been proposed in which only the aquo-metal ion is reactive, the retardation being seen to result from competition by the various potential ligands for co-ordination sites on the metal ion. The fact that different metal ions affect to differing extents the rates of oxidation of substrates by H_2O_2 is seen to be the result not of a radical mechanism but of the variation of stabilities of the ternary complexes.

[56] K. Hayakawa and S. Nakamura, *Bull. Chem. Soc. Japan*, 1974, **47**, 1162.
[57] K. Eckschlager, I. Horsak, and J. Veprek-Siska, *Coll. Czech. Chem. Comm.*, 1974, **39**, 2353.

Part II

SUBSTITUTION AND RELATED REACTIONS

By
J. BURGESS
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G. STEDMAN

1
Non-metallic Elements

BY G. STEDMAN

The plan for this chapter is similar to that used in previous volumes of this Report, including substitution, addition, dissociation, and intramolecular rearrangements. A few reactions of metallic elements in Groups III—V have been included. Inevitably some papers could properly be reported in more than one section of this volume, and among the non-metallic elements there is overlap with organic reaction mechanisms and with material covered in other Specialist Periodical Reports. A degree of overlap seems preferable to the alternative, the omission of papers that are of interest.

1 Group III

Boron.—*Boron–Hydrogen Compounds.* Theoretical calculations have been made[1] of likely sites for electrophilic and nucleophilic attack in a number of boranes and related anions. Electrophilic benzoylation of $[B_{10}H_{10}]^{2-}$ to form $[2\text{-}B_{10}H_9COPh]^{2-}$ follows simple second-order kinetics in acetonitrile. Reaction is inhibited by acid, and a kinetic analysis suggests[2] that it is due to conversion of $[B_{10}H_{10}]^{2-}$ into the unreactive conjugate acid $[B_{10}H_{11}]^{-}$, with $K = 4.6$ mol dm^{-3}. The reaction of $[2\text{-}B_{12}H_{12}]^{2-}$ with acetone + alkyl sulphoxides involves[3] electrophilic attack by $(RCH_2)_2\overset{+}{S}OCOMe$.

Nuclear magnetic resonance studies have been used to demonstrate[4] intramolecular exchange of terminal and bridge hydrogens in $[B_2H_7]^{-}$ in methylene chloride, the migration of basal hydrogens in B_6H_{10} and its 2-methyl and 2-bromo-derivatives,[5] the exchange[6] of bridge hydrogen atoms in $[B_{10}H_{15}]^{-}$, and the interconversion[7] of two polytopal isomers of $2Na^{+}[B_8H_8]^{-}$ in 1,2-dimethoxyethane. The thermal rearrangements of non-icosahedral cobaltacarbaboranes have been shown[8] to have rather similar $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. These rearrangements occur more readily than those of the neutral carbaboranes of the same geometry. A set of rules summarizing the results has been outlined.

The thermal rearrangement of 9,12-dichloro-*CC'*-dimethyl-*o*-carbaborane yields 5,12-dichloro-*CC'*-dimethyl-*m*-carbaborane as a major product, probably by a

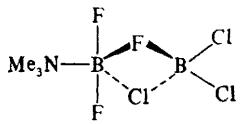
[1] J. H. Hall, D. S. Marynick, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1974, **96**, 770.
[2] P. A. Wegner, D. M. Adams, F. J. Callabretta, L. T. Spada, and R. G. Unger, *J. Amer. Chem. Soc.*, 1973, **95**, 7513.
[3] J. Wright and A. Kaczmarczyk, *Inorg. Chem.*, 1973, **12**, 1453.
[4] R. K. Hertz, H. D. Johnson, jun., and S. G. Shore, *Inorg. Chem.*, 1973, **12**, 1875.
[5] V. T. Brice, H. D. Johnson, jun., and S. G. Shore, *J. Amer. Chem. Soc.*, 1973, **95**, 6629.
[6] R. R. Rietz, A. R. Siedle, R. O. Schaeffer, and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 2100.
[7] E. L. Muetterties, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1973, **95**, 7520.
[8] D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1974, **96**, 3085.

mechanism involving a cuboctahedral intermediate. A large number of other, minor, products are formed, possibly arising from triangle rotations in the intermediate.[9] A one-ring-flip mechanism describes[10] the conformational dynamics of alkoxydiarylboranes, but a two-ring-flip mechanism is required[11] for the isomerization of the triarylboranes, and this is supported by direct evidence. A quenched-flow reactor has been devised for producing reactive intermediates which can be stabilized by a sudden change in conditions, and the $[BH_3OH]^-$ ion was produced[12] in 50—90% yield in the hydrolysis of $[BH_4]^-$. An acid-catalysed hydrolysis of $RbBH_4$ has been reported[13] to follow second-order kinetics, first order in each reactant, with an activation energy of 13.8 kcal mol^{-1}.

Boron–Nitrogen Compounds. The reactions of various boron Lewis acids with amines continue to attract interest. The halogen scrambling between Me_3N,BX_3 and BY_3 is suggested[14] to occur without boron–nitrogen bond fission, but by a mechanism involving a five-co-ordinate boron species (1), where X = F and Y = Cl. For Me_3N,BI_3 an ionic mechanism is suggested:

$$Me_3N,BI_3 \longrightarrow I^- + Me_3N,BI_2^+ \xrightarrow{Cl^-} Me_3N,BI_2Cl$$

An ionization mechanism has also been proposed for the scrambling reactions between the adducts of various amines and BCl_3 and $BPhCl_2$. Unimolecular ionization of a boron–chlorine bond occurs,[15] and not dissociation of the boron–nitrogen linkage. A similar intermediate to (1), but with bridging methyl groups instead of



(1)

halogens, has been proposed[16] for the exchange between $Me_3P,AlMe_3$ and Al_2Me_6, whereas the exchange between Me_3P,BMe_3 and BMe_3 is suggested to occur by a dissociative mechanism. This contrasts with earlier work[17] on $Me_3P,GaMe_3$. The hydrolysis of $Na[BPh_nL_{4-n}]$ (L = 1-pyridyl) follows second-order kinetics and is catalysed by acid. A mechanism involving addition of H_3O^+, elimination of HL, and reaction with water is proposed.[18]

The hydrolyses of cyanoborane adducts with morpholine and with dimethylaniline,

$$R_2NHBH_2CN + 2H_2O + 2OH^- \longrightarrow R_2NH + [B(OH)_4]^- + 2H_2 + CN^-$$

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[10] P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, 1973, **95**, 7029.
[11] J. P. Hummel, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, 1974, **96**, 3679; J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *ibid.*, 1973, **95**, 7019.
[12] J. W. Reed, H. H. Ho, and W. L. Jolly, *J. Amer. Chem. Soc.*, 1974, **96**, 1248.
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[15] J. R. Blackborow, M. N. Stuart-Hill, and S. Kumar, *J.C.S. Dalton*, 1974, 411; J. R. Blackborow, *ibid.*, 1973, 2139.
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[18] J. Emri, B. Gyori, and P. Szarvas, *Z. anorg. Chem.*, 1973, **400**, 321 (*Chem. Abs.*, 1973, **79**, 129 632t).

give[19] simple second-order kinetics. In contrast, trimethylamine and *N*-methylmorpholine react very much more slowly and with a rate law independent of [OH^-]. An S_N1cb mechanism is proposed for the first two processes. The thermal decomposition of BH_3,N_2H_4 and BH_3,N_2H_4,BH_3 has been reported[20] to follow first-order kinetics, with rate constants $1.13 \times 10^8 \exp(-22.5/RT)\ s^{-1}$ and $6.34 \times 10^7 \exp(-24.1/RT)\ s^{-1}$ respectively.

Boron–Oxygen Compounds. The rate constant for the formation of HBF_4 from $B(OH)_3$ and HF has been measured.[21] The kinetics of complex formation between $PhB(OH)_2$ and lactic acid have been studied by the temperature-jump method, and the reactivity of the lactate ion was found[22] to be about ten times that of lactic acid. N.m.r. has been used[23] to show that although in Me_2O,BX_3 the rate of dissociation of the boron–oxygen bond is much greater than the rate of the halogen redistribution reaction, with Me_2S,BX_3, there is a very rapid dissociation of the boron–sulphur bond. In the co-ordination with the boron trihalides of $MeCO_2Me$ and the analogous compounds with one or both oxygens replaced by sulphur, it is found that there is preferential donation by the doubly bonded atom, =O or =S. Again the rate of bond breaking for sulphur seems to be much greater than for oxygen. The order of acceptor strengths is $BBr_3 > BCl_3 > BFBr_2 > BFCl_2 > BF_2Br > BF_2Cl > BF_3$. The Lewis-acid-catalysed dealkyloxyboronation of *trans*-2-ethoxycyclohexaneboronate occurs[24] by a concerted *anti*-elimination reaction with relative catalytic efficiencies $BCl_3 > BF_3 > AlCl_3 \gg SbCl_3$.

Aluminium.—A review of aluminium chemistry includes[25] some mechanistic material. The use of ^{27}Al n.m.r. has shown[26] the existence of $[Al(BH_4)_4]^-$, $[Al(BH_4)_2Br_2]^-$, and $[Al(BH_4)Br_3]^-$ as intermediate species in the self-exchange reaction of $[Bu^n_4N]^+[Al(BH_4)_3Br]^-$ in THF. Kinetic parameters for the bridge–terminal interconversion reaction in Al_2Et_6 and $Al_2Pr^n_6$ have been obtained[27] and are similar to those observed for Al_2Me_6. The methyl and ethyl compounds undergo intramolecular exchange, whereas the n-propyl compound reacts partly by an intermolecular mechanism in cyclopentane. In toluene solution all three compounds undergo partial intermolecular exchange, probably because solvation stabilizes the monomer. The monomer–dimer equilibrium for the liquid n-alkyl aluminiums has been studied,[28] and from propyl to octyl there is little change in ΔH. Some material related to the above-mentioned studies was discussed[29] in an earlier review of aluminium chemistry. The interconversion of dimers, trimers, and tetramers of $Al(OPr)_3$

[19] C. Weidig, S. S. Uppal, and H. C. Kelly, *Inorg. Chem.*, 1974, **13**, 1763; V. V. Zakharov, A. F. Zhigach, G. B. Manelis, and G. N. Nechiporenko, *Zhur. fiz. Khim.*, 1974, **48**, 492 (*Chem. Abs.*, 1974, **81**, 41 971h).

[20] V. V. Zakharov, A. F. Zhigach, G. B. Manelis, G. N. Nechiporenko, B. M. Esel'son, and V. S. Nitkin, *Zhur. fiz. Khim.*, 1974, **48**, 499 (*Chem. Abs.*, 1974, **81**, 41 973k).

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[23] M. J. Bula and J. S. Hartman, *J.C.S. Dalton*, 1972, 1405; *ibid.*, 1973, 1047; M. J. Bula, J. S. Hartman, and C. V. Raman, *ibid.*, 1974, 725.

[24] D. J. Pasto and P. E. Timony, *J. Organometallic Chem.*, 1973, **60**, 19.

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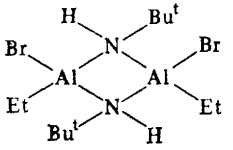
[29] J. P. Oliver, *J. Organometallic Chem.*, 1973, **62**, 190.

has been studied.[30] In view of the role of alkyl aluminiums in the polymerization of alkenes there is interest in a paper[31] on the kinetics of addition of triethylaluminium to styrene or 2-methylhept-1-ene in hydrocarbon solution, which follow the equation

$$-d[CH_2=CR^1R^2]/dt = k[Al_2Et_6]^{1/2}[CH_2=CR^1R^2]$$

Steric factors have an important effect on the Arrhenius parameters and with a sterically encumbered alkene one can observe a rate-determining formation of a π-complex.

The thermal stability of adducts of the type $Et_2XAl,NHMe_2$ and Et_2XAl,NH_2Bu^t towards thermal elimination of C_2H_6 follows[32] the order X = Et < Cl < Br < I. The stability seems to depend upon the negative charge density on the α carbon atom of the ethyl group, not on the acidity of the proton on the nitrogen. The interconversion of (2) and (3) to an equilibrium mixture of isomers occurs much more rapidly than



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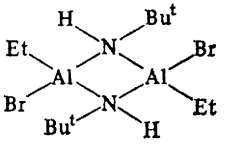

(3)

for iodo-compounds. The mechanism is thought[33] to be complex and involve many transient species. Isotopic studies (^{14}C) of exchange between [Al(dmb)$_3$] and Hdmb in THF (dmb^- = the anion of the enol form of dibenzoylmethane) follow the rate law

$$\text{Rate} = [\text{complex}](k_2[H_2O] + k_3'[\text{acid}] + k_3[\text{acid}][H_2O])$$

The mechanism is thought[34] to involve an intermediate with a unidentate ligand, and the breaking of the remaining bond is rate determining.

Gallium.—The rate of extraction of Ga^{3+} into chloroform containing thenoyltrifluoroacetone (A) to form the tris-complex GaA_3 follows the rate law below, and is thought[35] to involve $GaOH^{2+}$ and A^-.

$$\text{Rate} = k[Ga^{3+}][HA]_{org}[H^+]^{-2}$$

Indium.—The rates and equilibria involved in the disproportionation reaction of $3In^I$ to $In^{III} + 2In$ have been studied[36] in aqueous media.

2 Group IV

Carbon.—The suggestion that the mechanisms of nucleophilic substitution at carbon, S_N1 and S_N2, might merge into an ion-pair mechanism has been further

[30] D. C. Kleinschmidt, V. J. Shiner, and D. Whittaker, *J. Org. Chem.*, 1973, **38**, 3334.
[31] P. E. Allen and R. M. Lough, *J.C.S. Faraday I*, 1973, 849.
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[33] R. E. Bowen and K. Gosling, *J.C.S. Dalton*, 1974, 964.
[34] K. Matsuzawa and K. Saito, *Bull. Chem. Soc. Japan*, 1973, **46**, 2777.
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[36] L. F. Kozin and A. G. Egorova, *Zhur. neorg. Khim.*, 1974, **19**, 1077 (*Chem. Abs.*, 1974, **81**, 30 168a); *Izvest. Akad. Nauk Kazakh S.S.R., Ser. khim.*, 1974, **24**, 23 (*Chem. Abs.*, 1974, **81**, 41 968n).

studied. A study of the $^{35}Cl/^{37}Cl$ isotope effect in the hydrolysis of *p*-methoxybenzyl-chloride in the presence of sodium azide has shown[37] that it varies from 1.00786 ± 0.00010 to 1.01049 ± 0.00025 with change in azide concentration. It is claimed that these results are consistent with an ion-pair mechanism, and not with simultaneous reaction by S_N1 and S_N2 routes. A contrary view based upon ^{14}C and α-deuterium isotope effects in a variety of hydrolysis reactions in the presence of sodium azide is interpreted[38] in favour of a classical S_N2 transition state and against the ion-pair idea. The authors offer an alternative explanation of the results mentioned above. The kinetics of conversion of carbon disulphide and sodium azide into 1,2,3,4-thiatriazol-5-thiolate ($CS_2N_3^-$) has been briefly investigated.[39] There was also a short study of its stability as a function of pH; optimum stability at pH 6.8 was found. Flash photolysis has been used[40] to generate CO_3^- and HCO_3 from $[Co(NH_3)_4CO_3]^+$. By studying the reactivity of these species as a function of pH, a value of 9.6 was obtained for the pK of HCO_3. A stopped-flow study of the formation of cyanogen from $[Cu(CN)_4]^{2-}$ shows a rate law second order in $[Cu(CN)_4^{2-}]$ and inversely proportional to $[CN^-]$; a reaction between $[Cu(CN)_4]^{2-}$ and $[Cu(CN)_3]^-$ is suggested.[41]

Silicon.—A review[42] of molecular rearrangements of organosilicon compounds includes some mechanistic material. Recent developments in Fourier-transform n.m.r. spectroscopy enable ^{29}Si to be studied in solution.[43] Different signals for end and mid-chain atoms can be detected, and tacticity effects can be observed[44] for short-chain (Si_5) silicones. This is likely to be a valuable tool for silicon chemistry in the future. A review of the evidence for the existence of siliconium ions has appeared, which concludes that there is no need to invoke them in mechanistic studies, although it is conceded[45] that their possible existence cannot be excluded. *Ab initio* calculations on silyl-substituted carbonium ions show[46] that such species are destabilized by an α-silyl group, but stabilized by a β-silyl group. In contrast, the stabilities of alkanes and radicals are little affected by α- or β-replacement. These calculations are consistent with the rates of the S_N1 solvolysis of trimethylsilylalkyl halides Other authors comment[47] that in the elimination of HBr from Me_3SiCMe_2Br the trimethylsilyl group is much poorer at stabilizing a carbonium ion than the t-butyl group. These calculations also suggest that the energy of a bridged, non-classical carbonium ion may be *ca.* 12 kcal mol^{-1} lower than for an open-chain structure, and it is interesting to note that a non-classical structure has been suggested[48] for $SiH_3CH_2CH_2^+$.

A rather detailed study of the solvolysis of $XC_6H_4NHSiEt_3$, $PhNHSi(C_6H_4Y)_3$, and $PhNHSiR_3$ in alkaline aqueous methanol has been reported.[49] In the transition

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[49] M. Ali, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1974, **78**, 83.

state the O—Si bond is virtually fully formed, the Si—N bond some 20—50% broken, and the N—H bond (H from the solvent) about 10—30% formed. There is also a report[50] of the solvolysis of $XC_6H_4SiMe_2(NC_4H_4)$ in absolute ethanol. The kinetics of solvolysis of $Me_3SiCHCl_2$, $Me_3SiCHBr_2$, Me_3SiCHI_2, and Me_3SiCCl_2Me have been followed in aqueous n-propanol, using an ammonia–ammonium chloride buffer, and yield the rate law

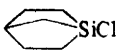
$$\text{Rate} = (k_1 + k_2[NH_3])[NH_3][Me_3SiCHX_2][NH_4Cl]^{-1}$$

Two parallel reaction schemes are proposed:[51] (*a*) a slow bimolecular attack of Pr^nO^- forming Me_3SiOPr^n and CHX_2^-, the latter rapidly abstracting a proton from the solvent, and (*b*) a general base-catalysed nucleophilic attack by ammonia involving a transition state $[RO\cdots H\cdots NH_2\cdots SiMe_3\cdots CHX_2]^-$. A study of the alkaline hydrolysis of silicon phthalocyanine, $Cl_2SiC_{32}H_{16}N_8$, has been reported to occur much more slowly than for the other organochloro-silanes. This is interpreted[52] in terms of an increase in covalent character of the silicon–chlorine bond, and $(p–d)\pi$ overlap of the lone pairs on the nitrogen with the empty 3*d*-orbitals on silicon. One is also, of course, comparing compounds of different geometries.

The acid-catalysed hydrolysis of Bu_3SiOPh in aqueous organic solvents shows[53] kinetics that are at least second order in stoicheiometric water concentration:

$$Bu_3SiOPh + H^+ \rightleftharpoons Bu_3Si\overset{+}{O}HPh \xrightarrow[\text{slow}]{H_2O} Bu_3SiOH + PhOH + H^+$$

A report has appeared[54] stating that the hydrolysis and methanolysis of R_3SiOAr proceed by different mechanisms. A study of nucleophilic substitution at bridgehead organosilicon compounds involves retention of configuration by an S_N2-Si mechanism. The reactivity sequence is $(4) > (Me_3SiCH_2)_3SiCl > Me_3AdBr > Me_3AdCl$, where Ad = the adamantate structure with a silicon atom in the 4-position and Me_3Ad represents Ad with three methyl substituents. A transition state (5) is



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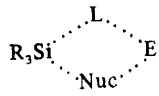

(5)

proposed,[55] in which L = leaving group, Nuc = nucleophile, and E = electrophile. Displacement of chloride ion by hydride ion by the reduction of 1,2-dimethyl-1-chloro-1-silacyclobutane occurs with more than 95% retention of configuration,[56] in contrast to earlier reports.[57]

The reduction of optically active $R_3Si^*OPr^i$ and R_3Si^*F with Bu^i_2AlH has been

[50] B. Bøe, *J. Organometallic Chem.*, 1974, **73**, 297.
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[56] B. G. McKinnie, N. S. Bhacca, and F. K. Cartledge, *J. Amer. Chem. Soc.*, 1974, **96**, 2637.
[57] J. Dubac, P. Mazerolles, and B. Serres, *Tetrahedron Letters*, 1972, 3495.

claimed[58] to show a correlation of stereochemistry with mechanism, retention of configuration for S_N1-Si and inversion for S_N2-Si. The racemization of chlorosilanes in mixed solvents (*e.g.* 0—2% DMF in toluene) is second order in the active component of the solvent. An increase in co-ordination number to 5 or 6 is envisaged,[59] but pseudorotation is ruled out as the mechanism for racemization. Similar conclusions are reached for the optically active bromosilanes studied. The racemization of the trisacetylacetone silicon(IV) ions follows[60] the rate laws

$$\text{Rate} = [\text{complex}](k_1 + k_2[\text{acid}]) \qquad \text{trichloroacetic acid in trichloroethane}$$

$$\text{Rate} = [\text{complex}](k_3 + k_4[\text{base}]) \qquad \text{2,6-lutidine in acetonitrile}$$

There is no isotopic exchange with ^{14}C-labelled acetylacetone, and racemization proceeds intramolecularly, probably by a one-ended dissociation mechanism.

A feature of mechanistic studies of silicon chemistry in the gas phase has been the possible formation of intermediates of the type $R^1R^2Si{=}CR^3R^4$. Evidence for such a species in solution has come[61] from the photolysis of $Me_3SiCN_2CO_2Et$ in alcohol solution. A similar intermediate may be involved[62] in the base-catalysed β-elimination reactions of $(Me_3SiOSiMe_2CH_2)_3B$ and $(PhMe_2SiOSiMe_2CH_2)_3B$. Theoretical studies on the stability of such species have been reported.[63] The exchange of halogen for methoxyl between Bu^n_3SnOMe and Et_3SiF and also Me_3GeBr has been investigated,[64] together with the reaction between $(Bu^n_3Sn)_2O$ and Me_3SiCl and Me_3GeBr. Exchange reactions between the silanes R_3SiH and alkoxy-tin compounds $R^1_3SnOR^2$ follow second-order kinetics and result in retention of configuration at an asymmetric silicon atom. The rate of reaction is enhanced by election-withdrawing substituents on the silicon and electron-releasing groups on the tin. Steric effects are substantial in this system. An S_N1-Si mechanism is postulated[65] with a four-centre Sn–O–Si–H transition state in which the O—Si bond is more developed than the Sn—H bond.

Mechanistic studies of other reactions of the silanes include the methoxide-catalysed methanolysis of triphenylsilane. Solvent isotope effects in mixtures of methanol and *O*-deuteriomethanol suggest[66] a transition state with two solvent molecules with stronger hydrogen bonds than in the bulk solvent, in addition to the proton-donor methanol molecule. Another isotopic study of this type of reaction is interpreted[67] as the rapid reversible formation of a five-co-ordinate silicon intermediate, followed by a rate-determining cleavage of the Si—H bond, with a bent Si···H···H geometry in the transition state.

Germanium.—The redistribution reactions in mixtures of tetra-alkylgermanes with germanium tetrachloride or tin tetrachloride follow second-order kinetics and occur

[58] L. H. Sommer, C. M. Golino, D. N. Roark, and R. D. Bush, *J. Organometallic Chem.*, 1973, **49**, C3.
[59] R. J. P. Corriu and M. Henner-Leard, *J. Organometallic Chem.*, 1974, **65**, C39.
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[61] W. Ando, T. Hagiwara, and T. Migita, *J. Amer. Chem. Soc.*, 1973, **95**, 7518.
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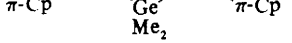
[65] J. Pijselman and M. Pereyre, *J. Organometallic Chem.*, 1973, **63**, 139.
[66] C. R. Howie, J. K. Lee, and R. L. Schowen, *J. Amer. Chem. Soc.*, 1973, **95**, 5286.
[67] C. Eaborn and I. D. Jenkins, *J. Organometallic Chem.*, 1974, **69**, 185.

by electrophilic substitution at the carbon atom, with a polar transition state.[68] The reaction of trichloracetic acid and trifluoracetic acid with hexaphenyldigermane gives $Ge_2Ph_5OCOCX_3$ and $GePh_2(OCOCX_3)_2$. Reaction occurs by electrophilic attack at the aromatic carbon atom of the Ph—Ge bond, rather than by nucleophilic attack on the metal.[69] $Ge(CH_2Ph)_4$ does not react with trifluoracetic acid, in contrast to $GePh_4$. $Ge_2(C_6F_5)_6$ is much more reactive than $Ge_2(C_6H_5)_6$ towards cleavage in THF of the germanium germanium bond[70] by a variety of reagents, *viz.* H_2O, MeOH, HCl, $MeCO_2H$, CF_3CO_2H, $HgCl_2$, S, and Se. The acid-catalysed hydrolysis of R_3GeOPh proceeds to equilibrium[71] in aqueous dioxan. The reaction is at least second order in $[H_2O]$, and Bu_3GeOPh is at least 5×10^5 times as reactive as Bu_3SiOPh. Optically active compounds $R^1{}_3Ge^*OR^2$ react with saturated reagents such as Bu^nLi to give retention of configuration, whereas with allyl- or benzyl-lithium inversion is observed.[72] The reaction of triphenylgermane with sodium methoxide in methanol has been studied. There is an exchange reaction of the hydrogen with the solvent, but there does not seem to be any significant amount of decomposition with the liberation of dihydrogen.[73] This is in contrast to an earlier report.[74] Two n.m.r. studies of fluxional behaviour in germanium derivatives have been reported.[75] One is concerned with cyclopentadiene derivatives of germane; spin-coupling data show the GeH_3 group to be mobile. The other[76] involves *cis–trans* interconversion in (6), by opening of one side of the germanium and carbonyl bridges.



(6)

Tin.—The stereochemistry, kinetics, and mechanism of the cleavage of Sn–C bonds have been reviewed,[77] and several other papers[78] include summaries or reviews of other mechanistic studies. Ligand-exchange reactions continue to be a popular field of study. A ^1H n.m.r. study of the exchange of acetylacetone (acac) between $[Ph_2Sn(acac)_2]$ and $[Me_2Sn(acac)_2]$ in deuteriochloroform and in bromoform gives kinetics that are first order in the former and zero order in the latter component. A rate-determining fission of a tin–oxygen bond in the phenyl compound to form a five-co-ordinate species with a unidentate acetylacetone is proposed.[79] A similar

[68] E. J. Bulten and W. Drenth, *J. Organometallic Chem.*, 1973, **61**, 179.
[69] F. Glockling and R. E. Houston, *J.C.S. Dalton*, 1973, 1357.
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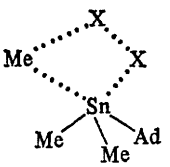
[74] R. Fuchs and H. Gilman, *J. Org. Chem.*, 1957, **22**, 1009.
[75] P. C. Angus and S. R. Stobart, *J.C.S. Dalton*, 1973, 2374.
[76] R. D. Adams, M. D. Brice, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1080.
[77] M. Gielen, *Accounts Chem. Res.*, 1973, **6**, 198.
[78] A. G. Davies and B. P. Roberts, *Accounts Chem. Res.*, 1972, **5**, 415; E. B. Milovskaya, *Uspekhi Khim.*, 1973, **42**, 881; P. G. Harrison, *J. Organometallic Chem.*, 1974, **79**, 17.
[79] N. Serpone and R. Ishayek, *Inorg. Chem.*, 1974, **13**, 52.

species may be involved[80] in the exchange reactions of the methyl groups of acetylacetone in non-equivalent sites in the complexes *cis*-[$X_2Sn(acac)_2$] (X = F, Cl, Br, or I). The data for the chloro-compound are very different from those reported earlier.[81]

^{1}H n.m.r. studies show[82] that halogen exchange among the trimethyltin halides occurs by ionization to Me_3Sn^+. The solvolysis of the methyltin chlorides, $Me_{4-x}SnCl_x$, in 100% sulphuric acid and in fluorosulphonic acid has been studied by n.m.r. and also by measurement of the Mössbauer spectrum of samples rapidly frozen to a glass. The species Me_3Sn^+, $MeSnCl_2^+$, Me_2Sn^{2+}, and $MeSnCl^{2+}$ have been identified.[83] Metal–proton and metal–metal exchange reactions for a range of aryl thiols and PhHg, Ph_3Sn, and Ph_3Pb derivatives in chlorobenzene and in pyridine have been reported[84] to occur by an associative mechanism. Studies on dissymmetric tetra-alkyl-tin(IV) compounds by ^{1}H n.m.r. show that these compounds are stereochemically stable.[85] There have been a number of papers on electrophilic sutstitution of tetra-alkyl-tin(IV) compounds in methanol and t-butyl alcohol by mercury(II) compounds. In the case of mercury(II) acetate reaction occurs by an open S_E2 mechanism with retention of configuration. It is claimed that a reactivity sequence (due to steric effects) may be used to distinguish between S_E2 open (inversion) and S_E2 open (retention). The results have been applied to the reactions of mercury(II) acetate with the alkylcobaloximes, where it was originally suggested that inversion took place, but it is now concluded that retention occurs.[86] Other studies of mercury(II) electrophilic substitutions on tetra-alkyl-tins have been reported.[87] Electrophilic attack on the 1-adamantyl derivative Me_3SnAd by bromine and iodine gives 48% and 66% cleavage of the methyl–tin bond respectively,[88] and involves a transition state (7). The cleavage of $ArSnMe_3$ by acetic acid and of



(7)

$ArSiMe_3$ by trifluoroacetic acid has been reported.[89] High values of the product isotope effect, using deuteriated reagents, are found, 5—6.5, and it is suggested that proton transfer to form a Wheland-type intermediate is more than half complete in each case. The solvent isotope effect has also been used as a mechanistic

[80] R. W. Jones and R. C. Fay, *Inorg. Chem.*, 1973, **12**, 2599.
[81] Y. Kawasaki, T. Tanaka, and R. Okawara, *Spectrochim. Acta*, 1966, **22**, 1571.
[82] S. O. Chan and L. W. Reeves, *Inorg. Chem.*, 1973, **12**, 1704.
[83] T. Birchall, P. K. H. Chan, and A. R. Pereira, *J.C.S. Dalton*, 1974, 2157.
[84] D. N. Kravtsov, A. S. Peregudov, E. M. Rokhlina, and L. A. Fedorov, *J. Organometallic Chem.*, 1974, **77**, 199.
[85] K. S. A. Kandil and C. E. Holloway, *J.C.S. Dalton*, 1973, 1421.
[86] M. H. Abraham and P. Grellier, *J.C.S. Perkin II*, 1973, 1132.
[87] M. H. Abraham and F. J. Dorrel, *J.C.S. Perkin II*, 1973, 444; M. H. Abraham, D. F. Dadjour, and C. J. Holloway, *J. Organometallic Chem.*, 1973, **52**, C27.
[88] R. M. G. Roberts, *J. Organometallic Chem.*, 1973, **63**, 159.
[89] C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 596.

tool in the alkaline cleavage of $XC_6H_4CH_2SnMe_3$ by methoxide ion in methanol. It is proposed[90] that there is a rate-determining proton transfer from the solvent to the carbon atom of the tin–carbon bond which is breaking, and that a free carbanion is not involved. A similar conclusion seems likely to apply to the analogous silicon compounds. A number of publications 91—94 deal with radical reactions involving tin compounds.

Lead.—Kinetic studies of the exchange of radioactive lead show[95] that the disproportionation of Pb_2Ph_6 to $PbPh_4$ and $PbPh_2$ does not occur at low temperature, where Pb_2Ph_6 is stable. The kinetics of ligand exchange of the pdta and ethylenediamine-*NN'*-diacetic and -*NN'*-dipropionic acid complexes of cadmium, zinc, and lead have been studied by n.m.r. line-broadening.[96]

3 Group V

Nitrogen.—An indirect method of determining the electrophilic reactivity of nitrosyl chloride towards various substrates in aqueous solution has been proposed.[97] The action of nitrosyl chloride, bromide, and thiocyanate or nitrosating agents in micellar systems has been studied,[98] and the results were interpreted in terms of the competition of anions present in solution for sites at the surface of a cationic micelle. The kinetics of the oxidation of nitrite to nitrate by chlorine and bromine are complex[99] and have been interpreted in terms of mechanisms involving the nitryl halides as intermediates:

$$-\mathrm{d}[Cl_2]/\mathrm{d}t = (k_a + k_b[HNO_2])[Cl_2][NO_2^-][Cl^-]^{-2}$$

$$-\mathrm{d}[Br_2]/\mathrm{d}t = (k_c + k_d[Br^-]^{-1})[Br_2][NO_2^-]^2 \quad \text{(pH range 4.2—5.8)}$$

$$-\mathrm{d}[Br_2]/\mathrm{d}t = [HNO_2]^2[Br_2](k_e + k_f[Br^-]^{-1})/(1 + k_g[H^+][Br_2]) \quad \text{(pH range 0.8—2.5)}$$

Two unusual species have been postulated for the reaction with bromine in the pH range 4.2—5.8:

$$NO_2^- + NO_2^- \rightleftharpoons N_2O_4^{2-}$$

$$N_2O_4^{2-} + Br_2 \longrightarrow N_2O_4Br_2^{2-}$$

$$N_2O_4Br_2^{2-} + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+ + 2Br^-$$

The mechanism of the reaction of iodine with nitrite is discussed, and earlier results[100] are suggested to be compatible with a scheme proposed for bromine. A study of the oxidation of iodide by nitrous acid has led to a rate law containing a new term, not previously reported.[101] Another oxidation of nitrite to nitrate, this time by dioxygen

[90] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 490.
[91] A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1973, 1777.
[92] P. M. Digiacomo and H. G. Kuivila, *J. Organometallic Chem.*, 1973, **63**, 251.
[93] H. J. Albert, W. P. Neumann, and K. Schneider, *Chem. Ber.*, 1973, **106**, 411.
[94] M. L. Poutsma and P. A. Ibarbia, *J. Amer. Chem. Soc.*, 1973, **95**, 6000.
[95] G. Plazzogna, V. Peruzzo, and G. Tagliavini, *J. Organometallic Chem.*, 1973, **60**, 229.
[96] B. J. Fuhr and D. L. Rabenstein, *Inorg. Chem.*, 1973, **12**, 1868.
[97] D. L. H. Williams, *J.C.S. Chem. Comm.*, 1974, 324.
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[99] J. N. Pendlebury and R. H. Smith, *Austral. J. Chem.*, 1973, **26**, 1847, 1857.
[100] G. G. Durrant, R. O. Griffith, and A. McKeown, *Trans. Faraday Soc.*, 1936, **32**, 999.
[101] L. Dozsa, I. Szilassy, and M. T. Beck, *Magyar Kém. Folyóirat*, 1974, **80**, 267 (*Chem. Abs.*, 1974, **81**, 141 475t).

in a potassium nitrate–sodium nitrate melt, has been studied kinetically.[102] The mechanism proposed is

$$NO_2^- + O_2 \xrightarrow{\text{slow}} NO_3^- + O$$

$$NO_2^- + O \xrightarrow{\text{fast}} NO_3^-$$

Traces of peroxide and superoxide have very large catalytic effects, and here the reaction is thought[103] to proceed by at least four or five parallel pathways!

A study of the exchange of ^{15}N between nitric oxide and nitric acid has been continued, and the results are held[104] to fit essentially the same mechanism as that originally proposed by Abel for the disproportionation of nitrous acid. Nitrogen dioxide appears to be the active intermediate in the reaction of 30% nitric acid with hexacyanoferrate(III). It oxidizes cyanide to cyanate, reduces iron(III) to iron(II), and introduces a nitrosyl ligand. An intermediate $[(CN)_5Fe—NO—Fe(CN)_4NO]^{3-}$ is postulated.[105] The rate of formation of the nitronium ion from nitric acid in sulphuric acid has been measured; an early result on the zero-order kinetics observed in aromatic nitration studies in acetic anhydride, and thought to be due to a rate-determining formation of the nitronium ion, has been shown to be complicated by a strong medium effect.[106] A series of papers describing a very thorough investigation of the reaction of hydroxylamine-*O*-sulphonate with a variety of nucleophiles has appeared.[107] These reactions occur through the free base $NH_2OSO_3^-$ in most cases; for some reagents there is an acid-catalysed term in the rate law, due to protonation on the nitrogen. In all cases SO_4^{2-} is the leaving group. The reactivity order is $EtS^- > Ph_3P > (NH_2)_2CS > {}^-O_3SS^- > I^- (> Br^- > Cl^-) > Et_3N > HONH_2 > OH^-$. This order qualitatively parallels the order observed[108] with nucleophilic substitutions at CH_3I and *trans*-$[Pt(py)_2Cl_2]$ and with H_2O_2. It is suggested that for substitution at NH_2X the nitrogen behaves as a soft electrophile, and that polarizibility and not basicity plays a major role in determining reactivity. Several interesting features in these reactions are worth noting. In the substitutions by NH_2OH and OH^-, di-imide, HN=NH, is formed,[107] and it was necessary[108] to attempt to minimize kinetic complications by scavenging with fumarate ion:

$$2HN=NH \longrightarrow N_2H_4 + N_2$$

$$N_2H_4 + NH_2OSO_3^- \longrightarrow HN=NH + NH_3 + H^+ + SO_4^{2-}$$

For the substitution by $S_2O_3^{2-}$ an intermediate $NH_2—S—SO_3^-$ is formed according to the rate law

$$\text{Rate} = 0.55[NH_2OSO_3^-][S_2O_3^{2-}] \text{ mol l}^{-1} \text{ s}^{-1} \text{ at } 20.4\ ^\circ\text{C}$$

for which $\Delta H^{\ddagger} = 10.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -23$ cal K^{-1} mol^{-1}. This species undergoes reaction with a second thiosulphate ion at a rate given by

$$\text{Rate} = 7.3 \times 10^7[NH_2SSO_3^-][S_2O_3^{2-}][H^+] \text{ mol l}^{-1} \text{ s}^{-1}$$

[102] P. Paniccia and P. G. Zambonin, *J. Phys. Chem.*, 1973, **77**, 1810.
[103] P. Paniccia and P. G. Zambonin, *J. Phys. Chem.*, 1974, **78**, 1693.
[104] D. Axente, G. Lacoste, and J. Mahenc, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2057.
[105] K. M. Davies and G. Stedman, *J.C.S. Dalton*, 1974, 2176; J. C. Bates, K. M. Davies, and G. Stedman, *ibid.*, p. 2182.
[106] J. W. Chapman and A. N. Strachan, *J.C.S. Chem. Comm.*, 1974, 293; N. C. Marziano, J. H. Rees, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 601.
[107] J. H. Krueger, B. A. Sudbury, and P. F. Blanchet, *J. Amer. Chem. Soc.*, 1974, **96**, 5733.
[108] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319; B. A. Sudbury and J. H. Krueger, *Inorg. Chem.*, 1974, **13**, 1736.

With a low concentration of thiourea, 10^{-5} mol l^{-1}, the product of substitution is $(NH_2)_2CSNH_2^+$. In the presence of higher concentrations of thiourea, 10^{-3} mol l^{-1}, formamidine disulphide is a product:

$$(NH_2)_2CS + (NH_2)_2CSNH_2^+ + 2H^+ \longrightarrow [(NH_2)_2CSSC(NH_2)_2]^{2+} + NH_4^+$$

Replacement of $NH_2OSO_3^-$ by $MeNHOSO_3^-$ decreases the rate of the first of these reactions with thiourea by a factor of a thousand.[109] This is similar to the results observed[110] in substitution at $NH_2OSO_3^-$, $MeNHOSO_3^-$, and $PhCONHOSO_3^-$ by Ph_3P and I^-, and steric effects are thought to be large. One of the intermediates mentioned above, di-imide, has been studied[111] in liquid ammonia solution from -38 to -65 °C by following the absorbance at 400 nm. Its decay follows first-order kinetics ($A = 1.9 \times 10^3$ s^{-1} and $E = 6.6$ kcal mol^{-1}), but in all cases is preceded by a more rapid initial decay process of higher order. The rapid initial decay may be a bimolecular process involving the *cis*-isomer of di-imide, while the slow reaction may involve a *cis* to *trans* isomerization.

The decomposition of hydroxylamine in alkaline medium has been reported[112] to follow the rate law

$$-d[NH_2OH]/dt = k[NH_2OH][OH^-]^3$$

A range of cations, notably Fe^{II}, catalyse the reaction and also reduce the ratio N_2/N_2O in the product. It is claimed that when such cations are completely complexed, decomposition does not occur. A mechanism involving decomposition of hydroxylamine complexes of Fe^{II}, Cu^{II}, or Co^{II} is preferred. Calorimetric determinations of the heat of solution of a range of alkylhydrazines in water, and in 0.1 mol dm^{-3} hydrochloric acid, have been correlated in terms of σ^* constants and hydration parameters. This enables calculations of the relative basicities of the two nitrogen atoms in an unsymmetrical alkylhydrazine to be made. This may be of value in interpreting the mechanism of oxidation of the alkylhydrazines.[113] The mechanisms involved in the synthesis of $NF_4^+[AsF_6]^-$ from NF_3, AsF_5, and F_2 have been discussed,[114] and an alternative mechanism to that suggested earlier has been proposed for the thermal decomposition of $NF_4^+[AsF_6]^-$.[115]

Phosphorus.—*Oxoanions.* The hydrolysis of pyro- and tripoly-phosphates in mixtures of water and various organic solvents is thought[116] to occur by an S_N2 mechanism. There have been several reports[117] of studies of the condensation equilibria of the orthophosphates, including a study[118] showing clearly the existence of branched-chain species. The substitution of pyrophosphate into the hydration shell of the magnesium ion occurs[119] by parallel paths involving $[P_2O_7]^{4-}$, $[HP_2O_7]^{3-}$, and $[H_2P_2O_7]^{2-}$. The decomposition of pentamolybdodiphosphates, $[Mo_5P_2O_{23}]^{6-}$,

[109] P. F. Blanchet and J. H. Krueger, *Inorg. Chem.*, 1974, **13**, 719.
[110] J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, 1973, **12**, 2714.
[111] R. A. Back and C. Willis, *Canad. J. Chem.*, 1974, **52**, 2513.
[112] S. Lunak and J. Veprek-Siska, *Coll. Czech. Chem. Comm.*, 1974, **39**, 391.
[113] F. E. Condon, R. T. Reece, D. G. Shapiro, D. C. Thakkar, and T. B. Goldstein, *J.C.S. Perkin II*, 1974, 1112.
[114] K. O. Christie, R. D. Wilson, and A. E. Axworthy, *Inorg. Chem.*, 1973, **12**, 2478.
[115] I. J. Solomon, J. N. Keith, and A. Snelson, *J. Fluorine Chem.*, 1972, **2**, 129.
[116] M. Watanabe, *Bull. Chem. Soc. Japan*, 1974, **47**, 2048.
[117] A. J. R. Costello, T. Glonek, T. C. Myers, and J. R. Van Wazer, *Inorg. Chem.*, 1974, **13**, 1225.
[118] T. Glonek, J. R. Van Wazer, R. A. Kleps, and T. C. Myers, *Inorg. Chem.*, 1974, **13**, 2337.
[119] R. C. Patel and R. S. Taylor, *J. Phys. Chem.*, 1973, **77**, 2318.

in alkali is first order in hydroxide-ion concentration.[120] Turning to the esters of orthophosphoric acid, the exchange of $(MeO)_3PO$ with $[Be\{(MeO)_3PO\}_4]^{2+}$ in methylene chloride has been investigated[121] by ^1H n.m.r. A dissociative mechanism is proposed, with $\Delta H^{\ddagger} = 13.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.5$ cal K^{-1} mol^{-1}. The heats of hydrolysis of some simple diesters of phosphoric acid have been measured[122] and an enzyme that catalyses this hydrolysis has also been isolated.[123] The acid-catalysed dealkylation of trialkyl phosphites in dioxan depends upon the square of the hydrogen chloride concentration, and the mechanism below has been suggested.[124] Trineopentyl phosphite is very unreactive.

$$(RO)_3P + HCl \rightleftharpoons (RO)_3P\cdots H{-}Cl$$

$$(RO)_3P\cdots H{-}Cl + HCl \rightleftharpoons (RO)_3PH^+ + HCl_2^-$$

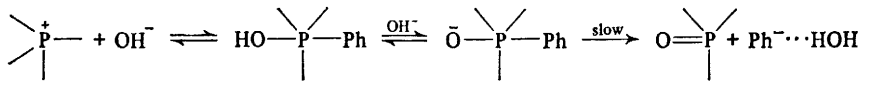
$$(RO)_3PH^+ + HCl_2^- \longrightarrow RCl + (RO)_2P(O)H + HCl$$

The hydrolysis of $(PhO)_5P$ and its phenyl-substituted derivatives fits the rate law

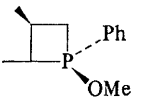
$$\text{Rate} = (k + k'[H^+] + k''[OH^-])[(PhO)_5P]$$

There are large steric effects for the neutral and alkaline reactions; reaction is postulated to proceed through a six-co-ordinate phosphorus species.[125] Previous work on the oxidation of orthophosphorous acid by Ag^{II} has been re-interpreted,[126] avoiding the need to postulate Ag^{III} as an intermediate.

The alkaline decomposition of tetraphenylphosphonium chloride to triphenylphosphine oxide and benzene has been studied as a function of temperature in a wide range (0—80%) of aqueous dioxan mixtures. The rate law is first order in phosphonium ion and second order in hydroxide ion; the rate is greatly increased by increasing the dioxan content: $k = 19.6 \exp(-33\,500/RT)$ in H_2O and $10.7 \exp(-10\,630/RT)$ in 80% dioxan (k in mol^{-2} dm^6 s^{-1}). The mechanism proposed is as follows:[127]



This agrees well with previous work.[128] Another hydrolytic study, of (8), has shown[129] reaction to occur by a rate-limiting hydration around pH 7, but by a rate-determin-



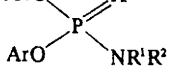
(8)

[120] R. Mellström and N. Ingri, *Acta Chem. Scand.*, 1974, **A28**, 703.
[121] J. Crea and S. F. Lincoln, *J.C.S. Dalton*, 1973, 2075.
[122] J. M. Sturtevant, J. A. Gerlt, and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1973, **95**, 8168.
[123] J. A. Gerlt and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1974, **95**, 8167.
[124] H. R. Hudson and J. C. Roberts, *J.C.S. Perkin II*, 1974, 1575.
[125] W. C. Archie and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1973, **95**, 5955.
[126] C. F. Wells, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3857.
[127] F. Y. Khalil and G. Aksnes, *Acta Chem. Scand.*, 1973, **27**, 3832.
[128] W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1964, **86**, 2378.
[129] D. R. Gorestein, *J. Amer. Chem. Soc.*, 1973, **95**, 8060.

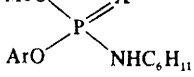
ing breakdown of a quinquecovalent intermediate in acid solution, possibly due to an encounter-controlled proton transfer.

Oxygen-18 exchange has been investigated in a series of phosphine oxides as a function of pH. By using geometrically constrained compounds it was found that there were two types of rate *versus* pH profile, characteristic of two types of trigonal-bipyramidal intermediate, one in which both oxygens were axial and another in which one was axial and one equatorial. In acid media there is a rate-limiting hydration. It is claimed[130] that the evidence is in favour of a turnstile rotation rather than a simple Berry pseudorotation in compounds reacting *via* the latter intermediate.

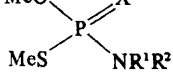
Compounds with Nitrogen. A number of mechanistic studies of the phosphinanilides and phosphinamides have been reported. The acid-catalysed hydrolysis of ArPhP(O)-NHAr occurs by an *A*-1 mechanism, but evidence for a merging of the *A*-1 and *A*-2 mechanisms has been obtained; in one case, evidence for an *A*-2 mechanism was obtained.[131] Cyclopropyl groups normally stabilize electron-deficient centres, and might be expected to enhance the rate of *A*-1 mechanisms. In a study[132] of alkylphenylphosphinanilides hydrolysed in 2.08 mol l^{-1} HCl (R = Et, cyclopropyl, Pr^i, methylcyclopropyl, or Bu^t) the reaction showed a marked sensitivity to steric effects, and $\Delta S^{\ddagger}$ was in the range -21.5 to -24 cal K^{-1} mol^{-1}. This was held to support an *A*-2-type mechanism. Another study of (−)-(*S*)-methylphenylphosphinanilide covered a wide range of acidity, 7×10^{-3} mol l^{-1} HCl to 9.4 mol l^{-1} H_2SO_4, and was claimed[133] to show a merging of *A*-1 and *A*-2, with a trend towards increased *A*-1 character at high acidities. The acid-catalysed hydrolysis of phosphinamides, $R_2P(O)NR_2$, seems to involve labilization of the phosphorus–nitrogen bond by N protonation and to occur by an *A*-2 mechanism; a displacement reaction is preferred, rather than a five-co-ordinate intermediate of significant stability. For the alkaline hydrolysis, ^{18}O studies show some exchange into the unreacted phosphinamide, with $k(\text{hyd})/k(\text{exch}) \approx 70$. A five-co-ordinate intermediate may be involved.[134] It has generally been thought that the base-catalysed solvolysis of fully esterified derivatives of phosphoramidic acid with good leaving groups occurs by an *E*1cb mechanism. This view has been questioned[135] on the basis of a study of the methyphosphoramidates and methyl phosphoramidothiates (9), (10), and (11). From the



(9)



(10)



(11)

relative rates and direction of cleavage, it is concluded that there is no appreciable amount of reaction by an *E*1cb process. The alkaline hydrolysis of phosphinate esters involves nucleophilic attack on the phosphorus, with the reversible formation of an intermediate, which breaks down in the rate-determining step. No ^{18}O ex-

[130] R. B. Wetzel and G. L. Kenyon, *J. Amer. Chem. Soc.*, 1974, **96**, 5199.
[131] D. A. Tyssee, L. P. Bausher, and P. Haake, *J. Amer. Chem. Soc.*, 1973, **95**, 8066.
[132] M. J. P. Harger, *J.C.S. Chem. Comm.*, 1973, 774.
[133] T. Koizumi, Y. Kobayashi, and E. Yoshii, *J.C.S. Chem. Comm.*, 1974, 678.
[134] T. Koizumi and P. Haake, *J. Amer. Chem. Soc.*, 1973, **95**, 8073.
[135] N. K. Hamer and R. D. Tack, *J.C.S. Perkin II*, 1974, 1184.

change with the P=O group is observed.[136] A different mechanism, a rate-determining proton transfer, has been suggested[137] for the acid-catalysed hydrolysis of the phosphoroguanidines.

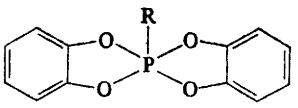
Phosphazanes. The fluorination of $P_5N_5Cl_{10}$ by potassium fluorosulphite forms a range of products $P_5N_5Cl_{10-x}F_x$ (x = 1—9). None of these products contains more than one PFCl group. The geminal substitution is attributed to electrostatic or σ-inductive effects. For the process

$$PCl_2 \xrightarrow{k_1} PClF \xrightarrow{k_2} PF_2$$

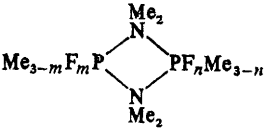
the ratio k_2/k_1 is assigned values of *ca.* 8, 100, and 7 for $(PNCl_2)_3$, $(PNCl_2)_4$, and $(PNCl_2)_5$ respectively. The importance of π-inductive effects in determining the-rate of reaction is emphasized.[138] Another study,[139] involving fluorination of $P_3N_3Cl_5NMe_2$, showed preferential attack at the PCl_2 group. However, with SbF_3 there is attack at $PClNMe_2$. The fluorination of $(PNClNMe_2)_4$ and $[(PNClNMe_2)_3PN(NMe_2)_2]$ by SbF_3 has been studied, and found[140] to involve the formation of an SbF_3 adduct.

Reaction of $P_3N_3Cl_{6-n}(NMe_2)_n$ with C_6H_6 and $AlCl_3$ produces[141] a mixture of compounds $P_3N_3Ph_m(NMe_2)_nCl_{6-m-n}$. Here replacement occurs more readily at $PNMe_2Cl$ than at PCl_2.

Intramolecular Processes. X-Ray work has shown the existence of a square-pyramidal structure (12). The n.m.r. data on spirocyclic oxyphosphoranes have been discussed,[142] and were concluded to be consistent with the *X*-ray data. Mechanisms for intramolecular exchange processes are proposed. The rate of pseudorotation in XPF_4 increases in the sequence $Me_2N < SR$, $H < Cl < Me$, F. It was concluded[143] that even if a square pyramid were an intermediate in pseudorotation, it would not be possible to detect it directly with present-day equipment. However, in a study of the ^1H n.m.r. spectrum of 2-isopropylphenylbis-(4,4′-dimethyl-2,2′-biphenylene) phosphorane, it is suggested[144] that pseudorotation does not occur by a simple Berry mechanism, but involves a square-pyramidal intermediate. An n.m.r. study of (13)



(12)



(13)

[136] R. D. Cook, C. E. Diebert, W. Schwarz, P. C. Turley, and P. Haake, *J. Amer. Chem. Soc.*, 1973, **95**, 8088.
[137] G. W. Allen and P. Haake, *J. Amer. Chem. Soc.*, 1973, **95**, 8080.
[138] N. L. Paddock and J. Serreqi, *Canad. J. Chem.*, 1974, **52**, 2546.
[139] B. Green, *J.C.S. Dalton*, 1974, 1113.
[140] D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 1973, 2649.
[141] S. Das, R. A. Shaw, and B. C. Smith, *J.C.S. Dalton*, 1973, 1883.
[142] R. R. Holmes, *J. Amer. Chem. Soc.*, 1974, **96**, 4143.
[143] M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 5385.
[144] G. M. Whitesides, M. Eisenhut, and W. M. Bunting, *J. Amer. Chem. Soc.*, 1974, **96**, 5398.

and the corresponding methoxy-species shows[145] that in only two cases is axial–equatorial exchange slow on the n.m.r. time-scale.

Arsenic.—Oxygen exchange between arsenate and water follows a complex rate law:

$$10^6 \times \text{Rate} = 100[H_2AsO_4^-] + 12[HAsO_4^{2-}] + 1.5[AsO_4^{3-}] + 74\,000[H_2AsO_4^-]^2 + 6400[H_2AsO_4^-][HAsO_4^{2-}] + 8.5[HAsO_4^{2-}]^2 \text{ mol dm}^{-3}\text{ s}^{-1} \text{ at } 30\ ^\circ\text{C}$$

The second-order terms are probably due to a condensation reaction, a pyro-arsenate species being formed and hydrolysed.[146] The exchange is also catalysed by arsenite. The rate law was first order in both arsenite and arsenate and was interpreted[147] in terms of the mechanism

$$H_2AsO_4^- + H_3AsO_3 \rightleftharpoons H_3As_2O_6^- + H_2O$$

The exchange of oxygen between arsenate and water of crystallization has also been studied by the same authors.[148] The mechanism of formation of $[Co(NH_3)_5HAsO_4]^+$ by substitution of $[Co(NH_3)_5H_2O]^{3+}$ upon $HAsO_4^{2-}$ and $H_2AsO_4^-$ occurs with oxygen–arsenic bond cleavage. A dissociative release of H_2O from a $[Co(NH_3)_5H_2O]^{3+}$,$[HAsO_4]^{2-}$ ion pair is suggested[149] to be too slow (by a factor of 2.6) to be an acceptable explanation, and an associative mechanism is preferred. This contrasts with the corresponding reaction involving phosphate, where Co—O bond fission occurs. The hydrolysis of the arsenate complex occurs by several paths and is complicated by an acid–base equilibrium of the arsenate ligand. The rate law is reported to be

$$\text{Rate} = [\text{arsenate complex}](Kk_1 + k_2[H^+] + k_3[H^+]^2)/(K + [H^+])$$

where K, the ionization constant for $[Co(NH_3)_5H_2AsO_4]^{2+}$, has a value of $10^{-3.3}$. The rate laws for the forward and reverse reactions between arsenious acid and iodine respectively are[150]

$$\text{Rate} = (f + g[H^+]^{-1} + h[H^+]^{-2})[H_3AsO_3][I_3^-][I^-]^{-2}$$

$$\text{Rate} = (u[H^+] + v[H^+]^2)[H_3AsO_4][I^-]$$

The mechanism involves the rapid establishment of the equilibrium

$$H_3AsO_3 + I_2 \rightleftharpoons H_3AsO_3I^+ + I^-$$

followed by rate-determining attack by water on $H_3AsO_3I^+$, H_2AsO_3I, and $HAsO_3I^-$.

A very different type of work is an e.s.r. investigation[151] of the decay of arsenyl radicals, $Ph_3\dot{A}sOBu^t$ and $Ph_2\dot{A}s(OBu^t)_2$, in organic solvents. The rate law shows first-order dependence upon radical concentration, and reaction is thought to be due to α-scission from an apical position. For the second compound, a rate-determining pseudorotation may be involved.

Antimony.—The preparation[152] of an optically active stibine, PhMeEtPr^{i}SbI, may be useful for future mechanistic studies. A ^{19}F n.m.r. study has shown[153] rapid

[145] R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912.
[146] A. Okumara and N. Okazaki, *Bull. Chem. Soc. Japan*, 1973, **46**, 2937.
[147] A. Okumara, N. Yamamoto, and N. Okazaki, *Bull. Chem. Soc. Japan*, 1973, **46**, 3633.
[148] A. Okumara and N. Okazaki, *Bull. Chem. Soc. Japan.*, 1973, **46**, 2981.
[149] T. A. Beech, N. C. Lawrence, and S. F. Lincoln, *Austral. J. Chem.*, 1973, **26**, 1877.
[150] J. N. Pendlebury and R. H. Smith, *Internat. J. Chem. Kinetics*, 1974, **6**, 663.
[151] E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1973, **95**, 6574.
[152] S. Sato, Y. Matsumura, and R. Okowara, *J. Organometallic Chem.*, 1973, **60**, C9.
[153] Yu. A. Buslaev and V. V. Peshkov, *Russ. J. Inorg. Chem.*, 1973, **18**, 803.

exchange between the various antimony(III) fluoride complexes in aqueous solution. The hydrolysis of hydrogen tartaroantimonate(V) has been studied[154] and also the reduction of Sb^V by I^- in the presence of α-hydroxy-acids.[155]

Bismuth.—The rate of formation of Bi^I in an aqueous solution of $BiCl_3$ in HCl in contact with metallic bismuth is[156] a first-order process, occurring by two stages. The first stage is faster than the second and is a diffusion-controlled reaction with an activation energy of 1.8 kcal mol^{-1}. The kinetics of formation and dissociation of $[Bi_6(OH)_{12}]^{6+}$ have been investigated.[157] Under equilibrium conditions the pressure-jump method gives a rate law

$$d[Bi_6(OH)_{12}{}^{6+}]/dt = k_f[Bi^{3+}]^3[H^+]^{-5} - k_d[Bi_6(OH)_{12}{}^{6+}]^{1/2}[H^+]$$

For the dissociation at high acidities,

$$-d[Bi_6(OH)_{12}{}^{6+}]/dt = -(k_1 + k_2[H^+])[Bi_6(OH)_{12}{}^{6+}] - k_4[Bi_6(OH)_{12}{}^{6+}]^{1/2}[H^+]$$

An intermediate species, $[Bi_3(OH)_5]^{4+}$, is thought to be involved.

4 Group VI

Oxygen.—A study of the exchange of ^{18}O between gaseous dioxygen and molten sodium hydroxide follows[158] simple first-order kinetics, $v = kp_{O_2}$, with $E_{act} = 18 \pm 3$ kcal mol^{-1}. It is not thought to involve the formation of peroxide, although the latter is thought to be formed when dioxygen is in contact with molten sodium hydroxide. The kinetics of the oxidation of various alcohols, ketones, and acids by high pressures (up to 136 atmospheres) of dioxygen have been studied.[159] In all cases simple second-order kinetics are observed, first order in substrate and in dioxygen. Two non-chain mechanisms are proposed: (*a*) the reaction of dioxygen with an enol to form a peroxy intermediate; and (*b*) the reaction of dioxygen with an alcohol to form an unstable intermediate whose structure is not discussed.

Sulphur.—The oxidation of thiocyanate by iodine is general base catalysed:[160]

$$I_2 + SCN^- \overset{\text{fast}}{\rightleftharpoons} ISCN + I^-$$

$$ISCN + H_2O + B \xrightarrow{\text{slow}} HOSCN + I^- + BH^+$$

$$HOSCN \xrightarrow{\text{fast}} H_2SO_4 + HCN$$

The reaction of triphenylphosphine with aryl disulphides occurs by a nucleophilic substitution:

$$Ph_3P + ArSSAr \rightleftharpoons Ph_3\overset{+}{P}SAr + ArS^-$$

$$H_2O + Ph_3\overset{+}{P}SAr \longrightarrow Ph_3PO + ArS^- + 2H^+$$

At high and/or low pH the first step can be rate determining, but at intermediate pH values the reverse of the first step becomes important, and the kinetics become

[154] J. Mazieres and J. Lefebvre, *Rev. Chim. minérale*, 1973, **10**, 457 (*Chem. Abs.*, 1974, **81**, 30 107e)
[155] A. Bahsoun and J. Lefebvre, *Rev. Chim. minérale*, 1973, **10**, 591 (*Chem. Abs.*, 1974, **81**, 30 154t).
[156] A. G. Egorova, R. Kh. Kuraklaeva, and L. F. Kozin, *Izvest. Akad. Nauk Kazakh. S.S.R., Ser. khim.*, 1974, **24**, 75.
[157] V. Frei, G. Mages, and H. Wendt, *Ber. Bunsengesellschaft phys. Chem.*, 1973, **77**, 243.
[158] Y. U. Baikov, *Russ. J. Phys. Chem.*, 1973, **47**, 720.
[159] J. E. Taylor and J. C. Weygandt, *Canad. J. Chem.*, 1974, **52**, 1925.
[160] G. T. Briot and R. H. Smith, *Austral. J. Chem.*, 1973, **26**, 1863.

complex. Mechanisms involving biphilic attack by the phosphine on both sulphur atoms of the disulphide to form a five-co-ordinate phosphorus species are rejected.[161] The alkaline hydrolysis of bis-2-nitro-4-trifluoromethylphenyl disulphide occurs by nucleophilic substitution at sulphur.[162] The disproportionation of the tetrasulphide anion in alkali involves[163] the equilibrium

$$4S_3S^{2-} + 8OH^- + H_2O \rightleftharpoons 3S_2O_3^{2-} + 10SH^-$$

The exchange of sulphur atoms between thiourea and diphenyl tetrasulphide has been studied[164] and is thought to involve homolytic fission to PhSS·. A similar reaction can account for the fact that both the central sulphur atoms in diethyl tetrasulphide exchange with the central sulphur in diethyl trisulphide.

A mechanism has been proposed[165] for the reaction of cyanide ion with thiocyanogen, selenocyanogen, sulphur dicyanide, and selenium dicyanide in acetonitrile on the basis of studies using ^{13}C as a tracer:

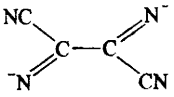
$$(SCN)_2 + {}^*CN^- \xrightarrow[\text{fast}]{} SCN^- + S({}^*CN)CN \xrightarrow[\text{slow}]{{}^*CN^-} S({}^*CN)_2CN \xrightarrow[\text{slow}]{} 0.33SCN^- + 0.66S{}^*CN^- + (CN)_2$$

The species $S(CN)_3^-$ may be trigonal bipyramidal, and it was assumed that fast pseudorotation makes all three cyanide groups equivalent:

$$(SeCN)_2 + {}^*CN^- \xrightarrow[\text{fast}]{} SeCN^- + Se({}^*CN)CN \underset{a}{\rightleftharpoons} Se({}^*CN)_3^-$$

$$Se({}^*CN)_3^- \xrightarrow[\text{slow}]{} 0.2SeCN^- + 0.8Se{}^*CN^- + (CN)_2$$

Reaction *a* is thought to involve a rapid exchange with three $^*CN^-$ ions. In each case the cyanogen reacts rapidly with the cyanide ions to form (14). The nucleophilicity



(14)

of the cyanide ion towards bivalent sulphur or selenium appears to be much greater than that of thiocyanate or selenocyanate ion. This is in contrast to the situation in water, where cyanide and selenocyanate ions have comparable nucleophilicities towards selenium.[166] The transient red colour observed in the preparative procedure

$$2CS(NH_2)_2 + 2HNO_2 \longrightarrow 2NO + [(NH_2)_2C-S-S-C(NH_2)_2]^{2+}$$

for making formamidine disulphide has been identified[167] as the *S*-nitroso-compound $(NH_2)_2C{=}\overset{+}{S}{-}NO$.

The equilibrium constant for its formation from thiourea and nitrous acid has been

[161] L. E. Overman, D. Matzinger, E. M. O'Connor, and J. D. Overman, *J. Amer. Chem. Soc.*, 1974, **96**, 6081.
[162] D. R. Hogg and J. Stewart, *J.C.S. Perkin II*, 1974, 436.
[163] W. F. Giggenbach, *Inorg. Chem.*, 1974, **13**, 1730.
[164] G. Peyronel, R. Battistuzzi, and G. Marcotrigiano, *J.C.S. Perkin II*, 1974, 896.
[165] T. Austad, *Acta Chem. Scand.*, 1974, **A28**, 806.
[166] S. Hauge, *Acta Chem. Scand.*, 1971, **25**, 3081.
[167] K. Y. Al-Mallah, P. Collings, and G. Stedman, *J.C.S. Dalton*, 1974, 2469.

measured. A parallel reaction, the formation of isothiocyanic acid and nitrogen, follows the rate law

$$(d[HNCS]/dt)_0 = k[HNO_2][CS(NH_2)_2]$$

and it is thought to occur by an S to N migration of the nitrosyl group in the conjugate base of $(NH_2)_2C{=}\overset{+}{S}{-}NO$. Nucleophilic substitutions by iodide ion and thiourea at $MePh\overset{+}{S}NH_2$ follow the rate law

$$\text{Rate} = k[MePh\overset{+}{S}NH_2][Nuc][H^+]$$

$$MePh\overset{+}{S}NH_2 + 3I^- + 2H^+ \longrightarrow PhSMe + NH_4^+ + I_3^-$$

$$MePh\overset{+}{S}NH_2 + 2CS(NH_2)_2 + 2H^+ \longrightarrow PhSMe + NH_4^+ + [(NH_2)CSSC(NH_2)_2]^{2+}$$

Protonation is thought to occur at the nitrogen of the substrate with nucleophilic attack on the sulphur and with ammonia as the leaving group. The intermediate, $MePh\overset{+}{S}Nuc$ then undergoes further rapid reaction with a second mole of nucleophile.[168] A correlation between the nucleophilic reactivity of a series of compounds containing the C=S group and the ionization potentials of the lone-pair electrons on the sulphur, as determined by photoelectron spectroscopy, has been reported.[169] The effect of substituents on the reactivity of the thiophenoxide ion closely parallels the effect on their basicities.[170]

Discrepancies in the kinetics of the reaction between dithionite and dioxygen have been resolved in a recent investigation.[171] Reaction occurs by a rate-determining dissociation:

$$S_2O_4^{2-} \longrightarrow 2SO_2^{-\bullet}$$

Earlier work appears to have been complicated by the fact that reaction solutions were not saturated with dioxygen, as the investigators had thought.[172] Some evidence for a change in stoicheiometry with dithionite concentration was reported. In addition, a rate law for the reaction with hydrogen peroxide was reported:

$$\text{Rate} = k[H_2O_2][S_2O_4^{2-}]^{1/2} + k'[HO_2^-][S_2O_4^{2-}]^{1/2}$$

The reaction of cyanide ion with tetrathionate in acetonitrile occurs with a 2 : 1 stoicheiometry, and it is proposed that the SO_3CN^- ion may be formed.[173] This species, or its conjugate acid, has been postulated as an intermediate in the hydrolysis of thiacyanogen and in the sulphur dicyanide–thiosulphate reaction. A study of the analytical determination of microamounts of hexathionate has included[174] some kinetic work on the reaction

$$S_6O_6^{2-} + 3SO_3^{2-} \longrightarrow 3S_2O_3^{2-} + S_3O_6^{2-}$$

The hydrolysis of sulphuryl fluoride in alkali follows the rate law

$$\text{Rate} = [SO_2F_2](k_w + k[OH^-])$$

[168] J. H. Krueger and R. J. Kiyokane, *Inorg. Chem.*, 1974, **13**, 2522.
[169] M. Arbelot, J. Metzger, M. Chanon, C. Guimon, and G. Pfister-Guillouzo, *J. Amer. Chem. Soc.*, 1974, **96**, 6217.
[170] M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1974, 238.
[171] N. Suten and C. Creutz, *Inorg. Chem.*, 1974, **13**, 2041.
[172] R. G. Rinker, D. M. Mason, R. R. Sakaida, W. H. Corcoran, and T. P. Gordon, *J. Phys. Chem.*, 1960, **64**, 573.
[173] T. Austad, *Acta Chem. Scand.*, 1974, **A28**, 693.
[174] T. Koh and T. Taniguchi, *Analyt. Chem.*, 1974, **46**, 1679.

Reaction involves[175] nucleophilic displacement of F^- by OH^-. For reaction in buffer solutions (other than borate) there appears to be nucleophilic catalysis. Experiments in the presence of cyanide showed that if $SO_2(CN)_2$ is formed it must be very rapidly hydrolysed. This is of interest in view of the postulated presence of HSO_3CN in the disproportionation reaction converting HOSCN into H_2SO_4 + HCN. The acid-catalysed hydrolysis of $ArNHSO_3^-Na^+$ to $ArNH_3^+HSO_4^-$ occurs by an *A*-2 mechanism involving nucleophilic attack upon sulphur.[176] A previous claim[177] for a likely S_N1 mechanism in substitution at an aromatic sulphonyl chloride has been re-investigated. It is claimed[178] that the reaction rate depends upon $[OH^-]$, contrary to previous reports. Kinetic studies of *para*-substituted benzenesulphonylchlorides show that nucleophilic substitution at sulphur has an S_N2 mechanism and is general base catalysed.[179] Halogen substitution in these compounds also occurs by an S_N2 process.[180] The reaction of hydrogen peroxide with n-butyl methanesulphonate at pH values greater than 11 occurs by C—O and not S—O bond fission, and presumably does *not* involve nucleophilic attack on the sulphur atom.[181]

The kinetics of the formation of chlorosulphonic acid from sulphuric acid have been followed[182] in a heterogeneous system; the activation energy is 23.8 kcal mol^{-1}. The hydrolysis of sulphite esters in carboxylate buffer has been examined[183] as a model for the corresponding pepsin-catalysed process. The carboxylate anion acts as a nucleophile, attacking the sulphur, with the formation of a mixed anhydride. The rate of the alkaline hydrolysis of *para*-substituted ethyl benzenesulphinates has been studied. This reaction, which occurs with S—O bond fission,[184] occurs by nucleophilic attack on sulphur to form a tetrahedral intermediate. The value of $\Delta S^{\ddagger} \sim -30$ cal K^{-1} mol^{-1} and $\rho = +1.60$. It is concluded that $k_2 \gg k_{-1}$, and the reaction is

$$Ar{-}\underset{\downarrow}{S}{-}OEt + HO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar{-}\underset{O^-}{\overset{OH}{S}}{-}OEt \xrightarrow{k_2} ArSO_2^- + EtOH$$

indistinguishable from an S_N2 process. For the acid-catalysed hydrolysis $\log k$ is proportional to H_0. The $\rangle S{=}O$ group is protonated and nucleophilic addition of water is followed by loss of ethanol. Experiments on partial hydrolysis in ^{18}O-enriched water showed no exchange with the unreacted ester, again providing no clear evidence for the presence of an intermediate.[185] The base-catalysed hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphinate occurs by a kinetically interest-

[175] **G. H. Cady** and S. Misra, *Inorg. Chem.*, 1974, **13**, **837.**
[176] W. J. Spillane, N. Regan, and F. L. Scott, *J.C.S. Perkin II*, 1974, 445.
[177] R. V. Vizgert, *Zhur. obshchei Khim.*, 1962, **32**, 628 (*Chem. Abs.*, 1963, **58**, 428f).
[178] L. Senatore, L. Sagramora, and E. Ciuffarin, *J.C.S. Perkin II*, 1974, 722.
[179] W. K. Kim and I. Lee, *Daehan. Hwahak, Hwoejee.*, 1973, **17**, 163 (*Chem. Abs.*, 1973, **79**, 41 582r).
[180] J. E. Yie and I. Lee, *Daehan. Hwahak. Hwoejee.*, 1973, **17**, 154 (*Chem. Abs.*, 1973, **79**, 46 203c).
[181] N. A. Radomsky and M. J. Gibian, *J. Amer. Chem. Soc.*, 1973, **95**, 8713.
[182] R. G. Makitra, Ya. N. Pyrig, and M. N. Didyck, *Russ. J. Inorg. Chem.*, 1973, **18**, 1541.
[183] L. H. King and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1974, **96**, 1410.
[184] C. A. Bunton and B. N. Hendy, *J. Chem. Soc.*, 1962, 2562.
[185] M. Kobayaski, R. Nishi, and H. Minato, *Bull. Chem. Soc. Japan*, 1974, **47**, 888.

ing mechanism:[186]

$$ArSX + OH^- \longrightarrow ArSOH + X^-$$

$$2ArSO^- + H_2O \rightleftharpoons Ar{-}S(O){-}S(OH)Ar + OH^-$$

$$ArSO_2H + ArS^- \longleftarrow Ar{-}S(\underset{\downarrow}{O}){-}SAr + OH^-$$

No exchange of ^{35}S between sulphur dioxide and thionyl fluoride was observed in liquid mixtures, but the addition of antimony pentafluoride did catalyse exchange.[187]

Selenium.—The reaction of triphenylmethyl isoselenocyanate with a variety of tervalent phosphorus compounds,

$$Ph_3CNCSe + PX_3 \longrightarrow Ph_3CNC + Se{=}PX_3$$

follows second-order kinetics and has been examined in cyclohexane and acetonitrile. The rate is enhanced by solvent polarity, but the enhancement is very dependent upon the nature of the tervalent phosphorus compound. There remains considerable uncertainty about the details of the mechanism.[188]

Tellurium.—The hydrolysis of tellurium hexafluoride has been shown[189] to involve $TeF_4(OH)_2$, $TeF_3(OH)_3$, and $TeF_2(OH)_4$ as intermediate species. Hydrolysis to $Te(OH)_6$ is very slow. The reactivity of the tellurocyanate ion as a nucleophile towards benzyl bromide in acetonitrile has been compared with that of selenocyanate and thiocyanate.[190] The kinetics are second order in each case, and k_2 values in $mol^{-1}\ dm^3\ s^{-1}$ at 21 °C are $NCTe^-$ 1.20, $NCSe^-$ 0.195, and NCS^- 0.00324; polarizability appears to be an important factor.

5 Group VII

Fluorine.—The kinetics and mechanism of at least one socially significant reaction, between fluoride and hydroxyapatite, has been studied.[191] An n.m.r. study of the exchange time between the axial and equatorial positions in $OClF_3$ has been carried out.[192]

Chlorine.—The anion-catalysed hydrolysis of $ArOSO_2Cl$ occurs by nucleophilic attack on the chlorine, and gives a reactivity sequence $S_2O_3^{2-} > CN^- > I^- > SO_3^{2-} > Br^-, Cl^-, F^- > OAc^-$. It is concluded[193] that the chlorine acts as a 'soft' electrophile:

$$ArOSO_2Cl + Nuc^- \longrightarrow ArOSO_2^- + ClNuc$$

$$ArOSO_2^- + H_2O \longrightarrow ArOH + HSO_3^-$$

$$ClNuc + HSO_3^- + H_2O \longrightarrow Nuc^- + Cl^- + HSO_4^- + 2H^+$$

A detailed stoicheiometric and kinetic study of the reaction of bromate with chlorous acid indicates[194] that reaction proceeds by the formation of a sizeable concentration

[186] D. R. Hogg and J. Stewart, *J.C.S. Perkin II*, 1974, 43.
[187] P. B. deGroot and T. H. Norris, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1123.
[188] L. J. Stangeland, T. Austad, and J. Songstad, *Acta Chem. Scand.*, 1973, **27**, 3918.
[189] G. W. Fraser and G. D. Meikle, *J.C.S. Chem. Comm.*, 1974, 624.
[190] T. Austad, S. Esperås, and J. Songstad, *Acta Chem. Scand.*, 1973, **27**, 3594.
[191] Z. S. Liang and W. I. Higuchi, *J. Phys. Chem.*, 1973, **77**, 1704.
[192] M. Alexandre and P. Rigny, *Canad. J. Chem.*, 1974, **52**, 3676.
[193] E. Buncel, A. Raoult, and L. A. Lancaster, *J. Amer. Chem. Soc.*, 1973, **95**, 5964.
[194] R. C. Thompson, *Inorg. Chem.*, 1973, **12**, 1905.

of chlorine dioxide. This species is also formed in the decomposition of chlorous acid, for which two pathways are suggested:[195]

$$Cl^- + HClO_2 \longrightarrow HCl_2O_2^- \longrightarrow HClO + ClO^-$$
$$HClO_2 + Cl_2 \longrightarrow ClO_2\cdot + Cl^- + H^+ + Cl\cdot$$
$$HClO_2 + Cl\cdot \longrightarrow ClO_2\cdot + Cl^- + H^+$$
$$HClO_2 + ClO^- \longrightarrow ClO_3^- + Cl^- + H^+$$

The kinetics of this last reaction have been studied[196] as a function of pH. Another reaction in the complex series of interactions among the oxoacids of chlorine, the disproportionation of chlorine dioxide to chlorate and chlorite, follows[197] the rate law below, with $E = 10.8$ kcal mol^{-1}:

$$-d[ClO_2\cdot]/dt = 3.0\times10^{-5}[ClO_2\cdot] + 36[ClO_2\cdot][ClO^-]$$

There is also mention of a study of the thermal decomposition of perchloric acid (65.9—84.8%) at temperatures above 120 °C, where second-order kinetics have been observed.[198]

Bromine.—The oxidation of bromide ion by permanganate is thought[199] to involve an initial addition reaction:

$$MnO_4^- + H^+ + Br^- \rightleftharpoons HO_3MnOBr^-$$

This is followed by two slow reactions with H_2O and H_3O^+ respectively to form hypobromous acid and Mn^V. A number of oxidations by bromate are postulated to involve nucleophilic substitution at $H_2BrO_3^+$, and the oxidation of iodide in aqueous DMSO obeys[200] a rate law that agrees with earlier work:

$$\text{Rate} = (k_I[I^-] + k_{nuc}[Nuc])[BrO_3^-][H^+]^2$$

Tungstates have been found[201] to catalyse this reaction. The oxidation of hexacyanoferrate(II) is suggested[202] to involve an intermediate $[(CN)_5Fe{-}CN{-}BrO_2]^{3-}$ in one pathway; a parallel outer-sphere electron-transfer process is also postulated. A number of reactions of dihalogen radical anions with bivalent transition-metal ions involve substitution processes at some stage.[203]

6 Group VIII

Xenon.—The decomposition of xenon trioxide in aqueous media can be followed spectrophotometrically[204] and obeys first-order kinetics with $k_1 = 10^{13.4}\exp(-28\,100/RT)$ s^{-1}.

[195] R. Mitzner, P. Leupold, and G. Fischer, *Z. phys. Chem.* (*Leipzig*), 1973, **253**, 273.
[196] H. Imagawa, M. Fukogawa, and Y. Tanaka, *Nippon Kogaku Kaishi*, 1974, 238 (*Chem. Abs.*, 1974, **80**, 113 158c).
[197] G. von Heijne and A. Teder, *Acta Chem. Scand.*, 1973, **27**, 4018.
[198] Y. I. Rubtsov, G. B. Manelis, Z. I. Grigorivich, and V. Ya. Rosolovskii, *Zhur. fiz. Khim.*, 1974, **48**, 1394 (*Chem. Abs.*, 1974, **81**, 141 481s).
[199] S. A. Lawani and J. R. Sutter, *J. Phys. Chem.*, 1973, **77**, 1547.
[200] J. H. Krueger and T. R. Webb, *Inorg. Chem.*, 1973, **12**, 1587.
[201] C. M. Wolff and J. P. Schwing, *Bull. Soc. chim. France*, 1973, 3255.
[202] J. P. Birk and S. G. Kozub, *Inorg. Chem.*, 1973, **12**, 2460.
[203] A. T. Thornton and G. S. Laurence, *J.C.S. Dalton*, 1973, 804, 1632, 1637; *ibid.*, 1974, 1142.
[204] B. L. Korsunski, N. N. Abeinikov, F. I. Dubovitskii, and L. I. Gurino, *Bull. Acad. Sci., U.S.S.R.*, 1974, **23**, 14.

2

Inert Metal Complexes: Co-ordination Numbers Four and Five

BY J. S. COE

This chapter follows broadly the pattern set in earlier Reports. The description 'inert' has been interpreted somewhat liberally in the brief sections on Cu^{II} and on the tetrahedral and five-co-ordinate complexes, and is perhaps justified on the grounds that a small amount of overlap is preferable to the existence of gaps.

1 Square-planar Complexes

Platinum(II).—*General.* Several review articles cover one or more aspects of mechanistic studies on platinum(II) complexes. Cleare[1] has reviewed the use of transition-metal complexes in cancer chemotherapy and a general review[2] of the unidentate amine complexes of Pt^{II} includes an account of kinetic and mechanistic studies with specific references to their role as anti-cancer agents. Belluco and co-workers[3] confine attention to reactions in which the entering groups are bidentate ligands whereas Peloso[4] gives a broadly based account of kinetic studies on Ni, Pd, and Pt complexes, including all the common oxidation states (0, II, and IV) and references to both substitution and redox reactions.

Aquation and Hydrolysis. Close inspection of individual reactions often reveals complexities in apparently straightforward situations. In their kinetic and equilibrium studies on the aquation of $[Pt(en)Cl_2]$, Coley and Martin[5] have found, and have accounted for, discrepancies with the work of other authors. The rate constant for the replacement of the first chloride is greater than that for the corresponding reaction of *cis*-$[Pt(NH_3)_2Cl_2]$, and it is interesting that the anation of $[Pt(en)Cl(H_2O)]^+$ by Cl^- is slow enough to be measured by conventional techniques ($k = 1.54 \times 10^{-2}$ l mol^{-1} s^{-1} at 25 °C). Vranckx and Vanquickenborne[6] have shown that the rate constants for aquation reactions of platinum(II) chloro- and bromo-complexes are in the same sequence as predicted by ligand-field activation-energy calculations in which only the relative σ-bonding abilities of the ligands are taken into account. The alkaline hydrolyses of *cis*- and *trans*-$[PtX_2(SEt_2)_2]$ (X = Cl, Br, or I) have been studied in 1 : 1 aqueous alcohol and in alcoholic solutions.[7] The observed

[1] M. J. Cleare, *Coordination Chem. Rev.*, 1974, **12**, 349.
[2] K. P. Beaumont and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **8**, 105.
[3] P. Uguagliati, G. Carturan, and U. Belluco, *Chimica e Industria*, 1974, **56**, 287.
[4] A. Peloso, *Coordination Chem. Rev.*, 1973, **10**, 123.
[5] R. F. Coley and D. S. Martin, *Inorg. Chim. Acta*, 1973, **7**, 573.
[6] J. Vranckx and L. G. Vanquickenborne, *Inorg. Chim. Acta*, 1974, **11**, 159.
[7] V. A. Valyaeva and S. P. Derendyaev, *Prir. Kompleksy Udmurt ASSR*, 1972, **107** (*Chem. Abs.*, 1974, **80**, 31 008q).

first-order rate constants decrease with increasing concentration of alkali. For the *cis*-complexes k_{obs} decreases in the order of X values Cl > Br > I, and in each case is greater than the value found for the corresponding *trans*-complex. These data give information on the *trans* effect of Et_2S, but the conclusions are obscured by the fact that values of the rate constants vary with the time of preliminary storage of the complex solutions.

N-*Donor Ligands as Entering Groups.* Amines showing a variety of basic and steric properties continue to be popular as entering groups. Extension of earlier studies to the reactions (in methanol)

$$trans\text{-}[Pt(PEt_3)_2(o\text{-tolyl})Cl] + am \rightleftharpoons trans\text{-}[Pt(PEt_3)_2(o\text{-tolyl})am]^+ + Cl^-$$

(am = pyridine derivative) reveal the relative efficiencies of Cl^- and am in capturing the intermediate solvent complex.[8] A variety of amines (am) has been used[9] in studying the forward and reverse steps in the reactions

$$[PtCl_3(DMSO)]^- + am \rightleftharpoons trans\text{-}[PtCl_2(DMSO)(am)] + Cl^-$$

and[10]

$$cis\text{-}[PtCl_2(DMSO)(am)] + am \rightleftharpoons cis\text{-}[PtCl(DMSO)(am)_2]^+ + Cl^-$$

The reverse reactions are unusual in studies of Pt^{II} substitution reactions in that they give information about processes in which an amine is a leaving group. The results are discussed in terms of the basicities and, in the latter case, the *cis* effects of the amines. The reactions of $(Et_3NH)_2PtCl_4$ with NH_3, $MeNH_2$, and $EtNH_2$ in methanol have also been investigated.[11] It is stated that the results show that the reaction rates decrease in the presence of high concentrations of LiCl, which points to the conclusion that a solvent complex is involved—contrary to the case of the corresponding reactions in aqueous solution. However, the translation of this paper is difficult to understand in parts. For example, the reactions appear to have been followed by measuring the concentration of entering amine (which is in several-fold excess of the substrate) and are said to be complicated by the 'redox' reactions

$$Et_3NH^+ + am \rightleftharpoons Et_3N + amH^+$$

Reactions of pyridine with some complexes containing S-bonded ligands[12] {*e.g.* $M(EtOCS_2)_2$ and $M[(EtO)_2P(S)S]_2$; M = Pt or Pd} show the normal behaviour for ligand-substitution reactions of Pt^{II} complexes.

S-*Donor Ligands as Entering Groups.* Kukushkin *et al.* have investigated the effects of sulphoxides in several reactions. These include the replacement of halide ions by DMSO from $[PtBr_4]^{2-}$, $[PtBr_3(DMSO)]^-$, and $[PtCl_3(DMSO)]^-$ [13] and the rate of chloride exchange in $[Pt(R_2SO)Cl_3]^-$ [R = Pr^n or Pr^i or R_2 = $(CH_2)_4$].[14] In the latter case the rate of displacement of the Cl^- *cis* to R_2SO decreased with increasing

[8] V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 927.
[9] R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1991.
[10] P. D. Braddock, R. Romeo, and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1170.
[11] Yu. N. Kukushkin and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, 1973, **18**, 560.
[12] M. Nanjo, *Tohoku Daigaku Senko Seiren Kenkyusho Iho*, 1971, **27**, 67 (*Chem. Abs.*, 1972, **77**, 106 085m).
[13] Yu. N. Kukushkin and V. V. Kirillov, *Russ. J. Inorg. Chem.*, 1973, **18**, 756.
[14] Yu. N. Kukushkin, M. A. Kuz'mina, and V. N. Spevak, *Radiokhimiya*, 1973, **15**, 716 (*Chem. Abs.*, 1974, **80**, 19 898x).

bulkiness of the R radicals. Exchange of Cl^- *trans* to R_2SO occurs instantaneously and all these sulphoxides have very strong *cis* and *trans* effects. It is also reported[15] that exchange of DESO is much slower in $[PtCl(DESO)(en)]^+$ than in $[PtCl_3(DESO)]^-$, the differences being attributed to the weak *trans* effect of NH_2, the difference in charges, and the effect of a cyclic group (en) in preventing the formation of an intermediate. Exchange of DESO in $[PtCl_3(DESO)]^-$ is also influenced by β-radiation from ^{35}S.[16] Treatment of $K[PtpyX_3]$ (X = Cl or Br) with thiourea gave *cis*-$[Pt(tu)(py)X_2]$. However, the reaction of thiourea with K_2PtCl_4 in dilute aqueous hydrochloric acid gives a chloride-bridged dimer, $[PtCl_2(tu)]_2$.[17]

Steric Effects. Steric effects of entering amines have been investigated[18] for reactions in which one chloride is displaced from $Pt(oz)Cl_2$ [oz = biacetyl bis-(*N*-methyl-*N*-phenyl)osazone). These reactions are compared with the corresponding reactions of $[Pt(bipy)Cl_2]$. The discriminating abilities of the two substrates are about the same and, as might be expected, the osazone complex is more sensitive than the bipy complex to steric retardation. However, the osazone complex is considerably more reactive towards unhindered amines, and it is suggested that this could be attributed to interactions between the leaving Cl^- and one of the *ortho* hydrogens of the ligand phenyl groups. Steric effects of methyl groups *ortho* to the donor atom in the *trans*-ligand have been studied by using as substrate complexes of the type $[Pt(PEt_3)_2(R)X]^{n+}$ (R = Ph, *o*-MeC_6H_4, or 2,4,6-$Me_3C_6H_2$). Although the original data on the reactions of *cis*- and *trans*-$[Pt(PEt_3)_2(R)Cl]$ with pyridine require reinterpretation, the new data,[19] with CN^- as attacking ligand, support the original view that the transition state has a trigonal-bipyramidal structure. The additional steric effects of methyl groups in the entering nucleophile are revealed[20] by the measurement of activation parameters for the reactions of *trans*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ with a series of pyridine derivatives and for the reactions of *trans*-$[Pt(PEt_3)_2(R)Cl]$ with thiourea derivatives. In general terms, the effect of structural changes on the rate of reaction is in the direction that might be predicted knowing that the mechanism is associative. However, this work demonstrates the importance of measuring activation parameters. The variation of the free energies of activation is far less than the variations in activation entropies and enthalpies, which in most cases have compensating effects.

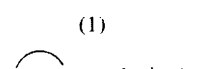
Bidentate Entering Groups. Carturan and Rizzardi[21] have studied the reaction of [Pt(L-methionine)Cl_2] with L-methionine. Although the latter acts as a bidentate ligand in this reaction it is potentially terdentate and the mechanism is rather complicated. Analysis of the kinetic data gives values of rate constants for the successive displacement of the two chlorides, the first being displaced by co-ordination of the sulphur atom and the second by the nitrogen of the amino-group in a fast step ($k = 25.1 \pm 0.9\ s^{-1}$ at 35 °C). In the reactions of the DL-α-alanine anion with

[15] Yu. N. Kukushkin and V. V. Golosov, *Russ. J. Inorg. Chem.*, 1973, **18**, 752.
[16] Yu. N. Kukushkin and V. V. Golosov, *Russ. J. Inorg. Chem.*, 1973, **18**, 248.
[17] Yu. N. Kukushkin, V. V. Sibirskaya, T. K. Mikhal'chenko, and Yu. V. Fadeev, *Zhur. obshchei. Khim.*, 1973, **43**, 1327.
[18] G. Annibale, L. Cattalini, L. Maresca, G. Michelon, and G. Natile, *Inorg. Chim. Acta*, 1974, **10**, 211.
[19] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 1376.
[20] R. Romeo, M. L. Tobe, and M. Trozzi, *Inorg. Chim. Acta*, 1974, **11**, 231.
[21] G. Carturan and G. Rizzardi, *Inorg. Chim. Acta*, 1973, **7**, 484.

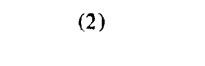
Zeise's anion, $[Pt(C_2H_4)Cl_3]^-$, and with *trans*-$[Pt(C_2H_4)(H_2O)Cl_2]$, the first step in each case involves replacement of Cl^- or H_2O by the amino-group of the entering ligand.[22] The rate constants (25 °C) for these processes are $6.1 \pm 3.5 \times 10^3$ and $1.70 \pm 0.15 \times 10^5$ l mol^{-1} s^{-1} respectively, whilst for the common intramolecular ring-closure reaction the rate constant is much smaller ($k = 6.11 \pm 0.14 \times 10^{-3}$ s^{-1}). A comparison of the reactions of Pt^{II} and Pd^{II} tetrahalogeno-complexes (MX_4^{2-}; X = Cl or Br) with 1,10-phenanthroline shows that, after adjusting the values of rate constants for the Pd^{II} reactions to 55 °C, the trends were as expected,[23] *viz.* (*a*) the palladium reactions were faster by a factor of 2×10^4—10^5, (*b*) the $[M(H_2O)X_3]^-$ complexes were more reactive than $[MX_4]^{2-}$, and (*c*) reactions with X = Br were faster than those with X = Cl.

Displacement of Bidentate Groups. This type of reaction is always potentially complicated. The reactions of Cl^- and Br^- with $[Pt(C_2O_4)]^{2-}$ involve slow replacement of the first oxalate group *via* a singly bonded, protonated intermediate and a parallel step independent of acid.[24] Activation parameters for these reactions are reported. The corresponding reactions of $[Pd(C_2O_4)]^{2-}$ are fast. The oxalate ligands in the platinum complex are not easily replaced by thiosulphate ion.[25] Both chelate rings are opened, however, to give the extraordinary species *trans*-$[Pt(C_2O_4)_2(S_2O_3)_2]^{6-}$, which was isolated as its hydrated sodium salt. Reactions in aqueous solution of $[Pt(NH_3)(L)Cl]$[26] (HL = glycine; the ammine and amido-groups are in *trans*-positions) in the presence of Hg^{2+} proceed through the formation of a stable intermediate, $[Pt(NH_3)(L)(Cl)Hg]^{2+}$, which is aquated to form $[Pt(NH_3)(L)(H_2O)]^+$.

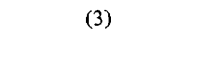
Ring Closure. Russian workers have continued their studies of ring-closure reactions involving amino-acid ligands. Volshtein *et al.*[27] have given a summary of much of the earlier work in this field and have related the results to *cis* and *trans* effects of ligands. In the intramolecular conversion of *trans*-dibromobis(glycine)platinum(II) into bis(glycinato)platinum(II) the slow process is the closure of the second ring.[28] This may occur *via* the two intermediates (1) and (2), but the corresponding aquo-ions (H_2O in place of Br) are not important intermediates. For the corresponding reactions of *cis*-$[Pt(N\frown OH)_2Cl_2]$ the intermediate (3) can be isolated and the second ring closure studied separately.[29] As in the case of the bromo-complex[28] there is a



(1)



(2)



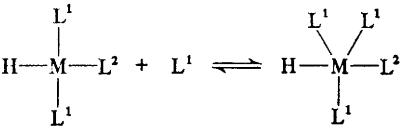
(3)

N O = glycinate anion

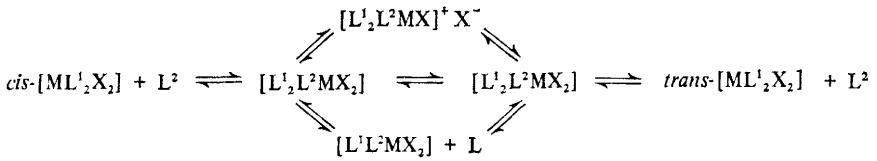
[22] G. Carturan, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1974, **13**, 542.
[23] J. V. Rund, *Inorg. Chem.*, 1974, **13**, 738.
[24] D. Banerjea and P. Banerjee, *Z. anorg. Chem.*, 1973, **401**, 189.
[25] A. Giacomelli, M. Spinetti, and A. Indelli, *Gazetta*, 1973, **103**, 459.
[26] A. B. Venediktov and A. V. Belyaev, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1974, 46 (*Chem. Abs.*, 1974, **80**, 115 565g).
[27] L. M. Volshtein, L. L. Krylova, and A. V. Belyaev, *Russ. J. Inorg. Chem.*, 1973, **18**, 562.
[28] G. D. Mal'chikov, T. R. Lastushkina, and L. M. Volshtein, *Russ. J. Inorg. Chem.*, 1972, **17**, 1414.
[29] G. D. Mal'chikov and V. I. Kazbanov, *Russ. J. Inorg. Chem.*, 1973, **18**, 1387.

two-path process for each ring closure, but for the chloro-complex the second ring closure is slightly faster (at 40 °C) than the first.

Isomerization. The controversy over the mechanism of the catalysed *cis–trans* isomerization of dichlorobis(triethylphosphine)platinum(II) has been revived by the publication of new evidence[30] that is said to support the fluxional-rotation scheme and by a rapid riposte[31] showing how this evidence can be rationalized on the basis of the alternative consecutive-displacement mechanism. The latter type of mechanism is favoured by Roulet and Barkey[32] for the *cis–trans* isomerization of dihalogenobis(dialkyl sulphide)platinum(II) complexes. In a study of the equilibria and kinetics of isomerization of $[Pt(Me_2S)_2Cl_2]$ in the presence of Me_2S they show that the reactions are second order. Ligand exchange in complexes of the type HML_3^+ (L = PEt_3, M = Pt, Pd, or Ni) has also been studied using n.m.r. techniques.[33] In the cases where M = Pt exchange of L occurs by an associative process,



with the position of equilibrium in favour of the reactants. For M = Pd some intramolecular rearrangement occurs in the five-co-ordinate species, and for M = Ni this intramolecular rearrangement occurs more rapidly than the loss of a ligand. As most of the evidence appears to be explicable on either the fluxional-rotation or the consecutive-displacement mechanism, it may be that the differences between the two views are not sufficiently sharp to constitute a real controversy. Indeed, it has been pointed out[34] that it may be 'a matter of taste whether one chooses to call $[PtX_2L_3]$ a five-co-ordinate complex or an ion pair'. Redfield and Nelson[35] suggest a third mechanism for the isomerization and conclude that one of three mechanisms (see Scheme 1) may be operative depending upon the conditions.

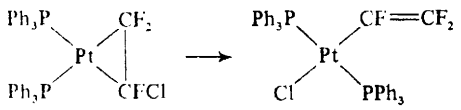


Scheme 1

There have also been some investigations of *cis–trans* isomerization reactions in the absence of catalysts. For the isomerization of *cis*-$[Pt(NH_3)_2Cl_2]$[36] the first-order

[30] W. J. Louw, *J.C.S. Chem. Comm.*, 1974, 353.
[31] J. Powell and D. G. Cooper, *J.C.S. Chem. Comm.*, 1974, 749.
[32] R. Roulet and C. Barkey, *Helv. Chim. Acta*, 1973, **56**, 2179.
[33] P. Meakin, R. A. Shunn, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 277.
[34] R. G. Pearson, W. Louw, and J. Rajaram, *Inorg. Chim. Acta*, 1974, **9**, 251.
[35] D. A. Redfield and J. H. Nelson, *J. Amer. Chem. Soc.*, 1974, **96**, 6219.
[36] Yu. G. Breusova-Baidala, N. N. Zheligovskaya, and V. I. Spitsyn, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, 1239 (*Chem. Abs.*, 1974, **81**, 98 708g).

rate constant at 20 °C is 1.77×10^{-5} s^{-1}. For several di-iododiamines[37] (PtA_2I_2; A = NH_3, $MeNH_2$, $EtNH_2$, or py) the heat of isomerization is in the range 1—7 kcal mol^{-1}. For these and complexes of the type *trans*-[$Pt(R_2SO)(A)Cl_2$], which isomerize in molten form, the isomerization appears to be through a tetrahedral intermediate. Green and Parker[38] have studied some interesting rearrangements, exemplified by the process



These may occur through a mechanism that involves formation of a tight ion pair by fission of the C—Cl bond and its collapse to give a co-ordinated chloride.

cis *and* trans *Effects*. Hartley[39] has given a concise and general review of *cis* and *trans* effects of ligands. There have also been more specific reviews of *cis* effects in substitution reactions of Pt^{II} complexes[40] and of the measurement and significance of the *trans* influence.[41] Several techniques have been used to investigate the influences of *cis*- and *trans*-ligands on the ground-state properties of Pt^{II} complexes. The ^{129}I Mössbauer spectra of complexes of general formula [PtL_2I_2] show that the Pt—I bond strength increases with changes in the nature of L in the order N-donor < S-donor < P-donor.[42] The *cis* influence therefore operates in opposition to the *trans* influence, a result contrary to that suggested by molecular orbital calculations.[43] ^{129}I Mössbauer parameters have also been used[44] to investigate the order of *trans* influence of the ligands X and L in the complexes *trans*-[$Pt(PPheMe_2)_2IX$] and *trans*-[$Pt(PPhMe_2)_2IL]^+$. The orders found were (for X) $Me > H > CF_3 \gg I$ and (for L) $P(OMe)_3 > EtNC > P(OMe)_2Ph \sim p\text{-}MeOC_6H_4NC > Ph_3As > Ph_3P$. Direct comparison of these conclusions with those reached by others is not always possible because of ambiguities in some of the earlier work, but the order for ligands X is consistent with that established[45] unambiguously in a ^{13}C n.m.r. study of the complexes [(cod)PtX_2]. Another approach[46] is to use values of $^3J_{PtF}$ coupling constants in *trans*- and *cis*-[$PtX(SCF_3)(PEt_3)_2$] to establish scales of *trans* and *cis* influence for the X ligands. The results show a good inverse linear correlation between the two scales for a series of anionic ligands, but it appears that, for unknown reasons, the correlation cannot be extended to neutral ligands or to scales constructed on the basis of coupling constants between directly bound nuclei. (Unfortunately, pages 374 and 375 of this paper have been printed in the wrong order.) Infrared data have been used to

[37] Yu. N. Kukushkin, *Kem. Koslem.*, 1972, **37**, 389 (*Chem. Abs.*, 1973, **78**, 23 413m).
[38] M. Green and G. J. Parker, *J.C.S. Dalton*, 1973, 2099.
[39] F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163.
[40] B. I. Peshchevitskii, G. D. Mal'chikov, and R. L. Shchekochikhina, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1974, 39 (*Chem. Abs.*, 1974, **81**, 30 039j).
[41] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coordination. Chem. Rev.*, 1973, **10**, 335.
[42] B. W. Dale, R. J. Dickinson, and R. V. Parish, *J.C.S. Chem. Comm.*, 1974, 35.
[43] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 6669.
[44] G. M. Bancroft and K. D. Butler, *J. Amer. Chem. Soc.*, 1974, **96**, 7208.
[45] M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Amer. Chem. Soc.*, 1972, **94**, 5087.
[46] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 373.

demonstrate *cis* influences[47] and *trans* influences[48] in several Pt^{II} complexes. From an examination of the i.r. spectra of *trans*-$[Pt(NH_3)_2(L)Cl]$ (L = Ph_3P or Ph_3Sb), the acid ionization constants of the corresponding aquo-ions, and the stability constants for $[Pt(NH_3)_2(L)Cl]^+$ and $[Pt(NH_3)_3L]^{2+}$, it is concluded[49] that the *trans* effect of Ph_3P is greater than that of Ph_3Sb. The *cis* and *trans* effects of dialkyl sulphoxides have been related to acidities of Pt^{II} aquo-ions containing these ligands.[50] The *trans*-influence sequence for some C-bonded ligands is established as σ-carbyl > carbene > isonitrile > CO from measurements of Pt—C bond lengths.[51] This order is the exact reverse of the π-acidity sequence and the suggestion is, therefore, that the *trans* influence of these C-donor ligands (L) depends mainly on the extent of M→L π-back-bonding. It is also concluded that the *trans* influence for ligands with both σ-donor and π-acceptor properties should take both these factors into account. A simple qualitative explanation of the results is possible on the basis that the *trans* influence on Pt—C bonds is largely electrostatic in nature.

Kinetic studies[52] on the replacement of Cl^- by NH_3 in $[Pt(en)(L)Cl]^+$ show that the relative *cis* effects of ligands L are diethyl sulphide ≈ dipropyl sulphoxide < diethyl sulphoxide < dimethyl sulphoxide. Theoretical studies have also contributed to a further understanding of *cis* and *trans* effects. An attempt has been made to give, for both σ- and π-bonding ligands, a general theoretical description of the nature of the *trans* effect (for Pt^{II} complexes) by means of a molecular orbital approach.[53] For a wide variety of ligands (C_2H_4, PH_3, CO, H_2S, NH_3, H_2O, H^-, CN^-, CH_3^-, Br^-, Cl^-, OH^-, and NO_2^-) the results confirm the general picture of contributions from ground-state and transition-state effects. The overwhelming effect is π-bonding in the transition state, and for σ-bonding ligands the *trans* influence is more important than σ-bonding in the transition state when the two effects do not reinforce each other. The authors believe that the Pt $d_{x^2-y^2}$-orbital is more important than the p_x-orbital when σ-bonding effects in the transition state are considered. In another theoretical analysis[54] ligand-field activation energies (LFAE), which make an important contribution to total activation energies, are shown to have an inverse correlation with *trans* effects in Pt^{II} complexes. LFAE may be calculated from two parameters, Δ, the octahedral field splitting, and τ, a measure of the relative importance of σ- and π-bonding in a given M—L bond. Thus, the *trans* effects appear to result from the interplay of these two parameters. For a series of ligands with a given value of τ the order of *trans* effects would be opposite to the order of the ligands in the spectrochemical series. Variation in LFAE is twice as great for *trans* substitutions as for *cis* substitutions, a result that is in qualitative agreement with the fact that *cis* effects are generally much smaller than *trans* effects.

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[53] D. R. Armstrong, R. Fortune, and P. G. Perkins, *Inorg. Chim. Acta*, 1974, **9**, 9.
[54] L. G. Vanquickenborne, J. Vranckx, and C. Görler-Walrand, *J. Amer. Chem. Soc.*, 1974, **96**, 4121.

Bridged Complexes. Harris and Gray[55] have characterized the cyclopropenium salts of the dinuclear anion $[M_2Cl_6]^{2-}$ (M = Pt or Pd) and have studied equilibria in the reactions

$$[M_2Cl_6]^{2-} + 2L \overset{K}{\rightleftharpoons} 2[MCl_3L]^-$$

where L is acetonitrile or cyclo-octene. The equilibria are established much more quickly in the palladium systems and these also have much smaller values of K [*e.g.*, for L = MeCN at 21 °C, $K = 5 \times 10^{-2}$ l mol^{-1} (M = Pd) and 10^4 l mol^{-1} (M = Pt)]. A more complicated series of reactions involving dinuclear complexes has been studied kinetically by employing n.m.r. line-broadening techniques.[56] The formation of bi-heterometallic complexes [*e.g.* $PdPtCl_4(PBu_3)_2$] on mixing chloroform solutions of bi-homometallic complexes $[M_2Cl_4(PBu_3)_2$; M = Pd or Pt] occurs *via* attack of dimer on dimer to form a tetrameric intermediate with each metal ion of the two dimers bonded to one of the bridging chlorides. The *trans* effect of methanethiol as a bridging ligand has been investigated by measuring the rates of chloride exchange in $[Pt_2(SMe)Cl_5]^{2-}$. One *trans*-Cl^- exchanges rapidly in a zero-order reaction whereas the second *trans*-Cl^- and the remaining chlorides exchange much more slowly by a first-order process.[57]

Miscellaneous. Hynes and Moran[58] have carried out kinetic studies on substitution reactions of Pt^{II} dithiolate complexes with CN^- and with several dithiolate ions. In the reactions with the bidentate ligands the mechanism is similar to that proposed for the corresponding reactions of the nickel and palladium complexes, and the order of reactivities is Ni : Pd : Pt = 10^5 : 10^2 : 1. Evidence for an unusual mechanism in some reactions of Pt^{II} complexes has been reported[59] in the case of the process

$$[Pt(CO)(PPh_3)(I)Me] + L \longrightarrow [Pt(PPh_3)(L)(I)COMe]$$

[L = $AsPh_3$, $As(p\text{-}MeC_6H_4)_3$, $AsMe(o\text{-}MeC_6H_4)_2$, or $SbPh_3$]. The first step in the mechanism involves formation of the three-co-ordinate species $[Pt(PPh_3)(I)(COMe)]$ and thus differs from most substitution reactions of square-planar complexes in that it does not involve the incoming ligand (L) or the solvent.

Palladium(II).—Reference has been made above to several publications[4, 12, 23, 55, 56] in which both platinum(II) and palladium(II) complexes have been studied.

Unidentate Entering Groups. Elding[60] has continued his comprehensive study of the aquation and halide anation reactions of palladium(II) halide and aquo-halide complexes with a report on the reactions of *cis*- and *trans*-$[PdX_2(H_2O)_2]$ (X = Cl or Br). The Pd^{II} complexes react *ca.* 5×10^4—5×10^5 times faster than the analogous Pt^{II} complexes, and the activation enthalpies are 8—10 kcal mol^{-1} smaller for Pd^{II} (see Table). The relative *trans* effects (Cl/H_2O and Br/H_2O) are six times smaller for Pd^{II} than for Pt^{II}, and the *cis* effects (H_2O/Cl and H_2O/Br) somewhat greater. Equilibrium constants for the *cis–trans* equilibria in $[PdX_2(H_2O)_2]$ are 2.1 ± 0.3

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[58] M. J. Hynes and A. J. Moran, *J.C.S. Dalton*, 1973, 2280.
[59] C. J. Wilson, M. Green, and R. J. Mawby, *J.C.S. Dalton*, 1974, 1293.
[60] L. I. Elding, *Inorg. Chim. Acta*, 1973, **7**, 581.

Table *Rate constants* (25 °C) *and activation parameters for anation and aquation reactions of palladium*(II) *and platinum*(II) *complexes* (*from reference* 60). *Ionic strength* 1.00 mol l^{-1} (Pd) *and* 0.50 mol l^{-1} (Pt). *Values of* $\Delta H^{\ddagger}$ *in* kcal mol^{-1} (*with standard deviation* ±1). *Values of* $\Delta S^{\ddagger}$ *in* cal K^{-1} mol^{-1} (*with standard deviation* ±3)

	M = Pd			M = Pt			
*Anation reactions**	k/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k_{Pd}/k_{Pt}
$MCl^+ + Cl^- \rightarrow$ *cis*-MCl_2	$(5.1 \pm 1.3) \times 10^2$	—	—	$\sim 2 \times 10^{-3}$	—	—	$\sim 3 \times 10^5$
$MBr^+ + Br^- \rightarrow$ *cis*-MBr_2	$(4 \pm 3) \times 10^3$	—	—	—	—	—	—
$MCl^+ + Cl^- \rightarrow$ *trans*-MCl_2	$(3.5 \pm 0.9) \times 10^4$	—	—	$\sim 5 \times 10^{-1}$	—	—	$\sim 7 \times 10^4$
$MBr^+ + Br^- \rightarrow$ *trans*-MBr_2	$(6.9 \pm 1.6) \times 10^5$	—	—	—	—	—	—
trans-$MCl_2 + Cl^- \rightarrow MCl_3^-$	21.7 ± 0.2	13	−9	4.6×10^{-5}	23	−2	5×10^5
trans-$MBr_2 + Br^- \rightarrow MBr_3^-$	$(8.3 \pm 0.4) \times 10$	11	−14	1.8×10^{-4}	20	−10	5×10^5
cis-$MCl_2 + Cl^- \rightarrow MCl_3^-$	$(5.4 \pm 0.6) \times 10^3$	10	−7	7.5×10^{-2}	18	−4	7×10^4
cis-$MBr_2 + Br^- \rightarrow MBr_3^-$	$> 2 \times 10^5$	—	—	3.3	14	−9	$> 6 \times 10^4$
*Aquation reactions**	k/s^{-1}			k/s^{-1}			
cis-$MCl_2 \rightarrow MCl^+ + Cl^-$	$(3.9 \pm 1.6) \times 10^{-1}$	—	—	$\sim 3 \times 10^{-7}$	—	—	$\sim 1 \times 10^6$
cis-$MBr_2 \rightarrow MBr^+ + Br^-$	—	—	—	—	—	—	—
trans-$MCl_2 \rightarrow MCl^+ + Cl^-$	$(5.6 \pm 0.5) \times 10$	12	−9	$\sim 1 \times 10^{-4}$	—	—	$\sim 6 \times 10^5$
trans-$MBr_2 \rightarrow MBr^+ + Br^-$	$(2.6 \pm 0.2) \times 10^2$	9	−17	—	—	—	—
$MCl_3^- \rightarrow$ *trans*-$MCl_2 + Cl^-$	$(2.7 \pm 0.9) \times 10^{-2}$	—	—	2.8×10^{-8}	24	−12	1×10^6
$MBr_3^- \rightarrow$ *trans*-$MBr_2 + Br^-$	$(5.9 \pm 1.5) \times 10^{-3}$	—	—	1.4×10^{-8}	26	−8	4×10^5
$MCl_3^- \rightarrow$ *cis*-$MCl_2 + Cl^-$	$(1.4 \pm 0.3) \times 10$	—	—	6×10^{-5}	20	−11	2×10^5
$MBr_3^- \rightarrow$ *cis*-$MBr_2 + Br^-$	$> 1 \times 10^2$	—	—	6×10^{-4}	21	−3	$> 1 \times 10^5$

* Water molecules have been omitted from the equations.

(X = Cl) and 6.0 ± 0.8 (X = Br) at 25 °C in 1.00 mol l^{-1} perchloric acid. It is pointed out that, owing to the small *trans* effect of water, the usual statement that water is an excellent leaving ligand is not true when the leaving ligand is a water molecule *trans* to another water molecule. Nucleophilic reactivity constants (n^0_{Pd}) have been determined for the first time for some ligands in substitution reactions of Pd^{II} complexes.[61] The procedure followed is similar to that used for the calculation of n^0_{Pt} values, except that the standard substrate used is *trans*-$[Pd(PPr^n_3)_2(NO_2)_2]$. The same sequence is found as for Pt^{II} $[Cl^- < N_3^- < Br^- < I^- < SCN^- < (NH_2)_2CS]$ and the palladium substrates also obey the linear free-energy relation that allows calculation of nucleophilic discrimination factors for Pd^{II} complexes. The effects of several solvents on the kinetics of aquation of *trans*-$[Pd(NO_2)_2(NH_3)_2]$ have been investigated.[62] The activation parameters for the reactions are very similar for solvent water and for aqueous methanol and aqueous dioxan but show significantly different values in aqueous acetone. The dissociation of $[Pd(CN)_4]^{2-}$ is slow ($k = 4.3 \times 10^{-5}$ s^{-1} at 25 °C).[63]

Bidentate Entering Groups. The reaction of Na_2PdCl_4 with ethylenediamine in aqueous acetate buffer[64] occurs by three parallel pathways, each involving the reaction of enH^+ with one of the following three species in equilibrium: $[PdCl_4]^{2-}$, $[PdCl_3(H_2O)]^-$, and $[PdCl_3(OAc)]^{2-}$. Rate constants and activation parameters are given. Comparison with the results of Reinhardt and Monk[65] shows that the reactions of enH^+ with the tetrachloro- and trichloro-aquo-ions are slightly faster than the corresponding reactions of NH_3 with these species. In most cases the reactions of *N*-methyl-substituted ethylenediamines[66] [in buffered aqueous tetrachloropalladate(II)] are similar to those of ethylenediamine, involving rate-determining reactions of the monoprotonated amine with $[PdCl_4]^{2-}$ and $[PdCl_3(H_2O)]^-$. {No$[PdCl_3(OAc)]^{2-}$ is present under the conditions of lower buffer concentration used in these experiments.} However, tetramethylethylenediamine reacts by a slightly different mechanism that includes formation of ion pairs from the protonated amine and chloride ions. This process is common to the reactions of the substituted ethylenediamines with gold(III) chloro-complexes.[67] Reactions of several amino-acids (glycine, DL-α-alanine, L-proline, L-asparagine, and DL-serine) with $[Pd(tu)_4]Cl_2$ follow the normal two-term rate law for square-planar substitutions.[68] This is not the case, however, for DL-valine and DL-threonine.

Isomerization. A detailed investigation has been reported[69] of catalysed and uncatalysed *cis–trans* and linkage isomerization reactions of $[PdL_2(tet)_2]$ (L = a phosphine, tet = 5-methyl or 5-trifluoromethyl tetrazolate). This leads to the postulation of general mechanisms, involving five-co-ordinate transition states, that

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[65] R. A. Reinhardt and W. W. Monk, *Inorg. Chem.*, 1970, **9**, 2026.
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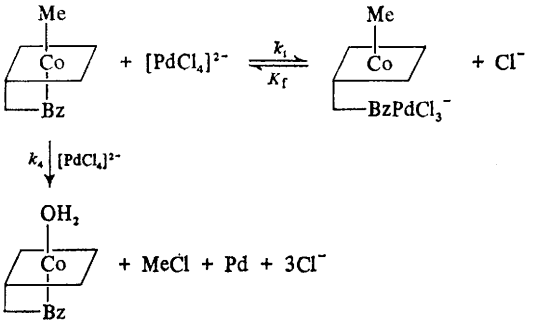
[67] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 1974, **8**, 253.
[68] O. Farook and A. U. Malik, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3410.
[69] D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1974, **96**, 6298.

account for the effects of solvent, anion, basicity, catalysts, and steric factors. Contrary to the case of the corresponding Pt^{II} complexes (referred to above) the addition of dimethyl sulphide to *trans*-$[Pd(Me_2S)_2Cl_2]$ results in fast ligand exchange but no isomerization.[32] Also, in a thermal study of bis-sulphide complexes of Pd^{II} the expected *trans*→ *cis* isomerization did not occur.[70]

Miscellaneous. The reaction of $[PdCl_4]^{2-}$ with methyl-cobalamin (Me-B_{12}) is complicated, involving both substitution and oxidation-reduction (Scheme 2).[71] At 20 °C



Bz = 5,6-dimethylbenzimidazole

Scheme 2

$k_1 = 0.90\ l\ mol^{-1}\ s^{-1}$, $K_f = 91$, and $k_4 = 7.7 \times 10^{-3}\ l\ mol^{-1}\ s^{-1}$. The rate constants are considerably smaller than in the analogous reactions of Hg^{II} with Me-B_{12}.

Nickel(II).—The slow rate of dissociation of $[Ni(CN)_4]^{2-}$ has been measured by using molecular iodine as a scavenger for the cyanide ion, thus causing a favourable displacement of the dissociation equilibrium.[63] Comparison with the tetracyano-complexes of palladium and cadmium (tetrahedral) shows the expected trends. At 25 °C the rate constants for dissociation of the Ni, Pd, and Cd complexes are, respectively, 4.8×10^{-4}, 4.3×10^{-5}, and $> 10^3\ s^{-1}$. The rapid substitution of CN^- by several ligands (L) was also measured[72] in the presence of I_2 (L = en, pn, trien, Htrien$^+$, H_2trien^{2+}, tu, *N*-Me-en, *NN'*-diMe-en, *NN*-diMe-en, NH_3, or glycinate). It is concluded that chelation by the incoming nucleophile is not necessary for rapid displacement of CN^- and that substitution occurs with a five-co-ordinate transition state. The reaction of bis-(1,5-diazacyclo-octane)nickel(II) with cyanide ion is fast.[73] The mechanism is an associative one and involves two measurable stages with the intermediate formation of the isolable [Ni(1,5-diazacyclo-octane)$(CN)_2$]. The reaction rates are dependent upon the hydrogen-ion concentration and, at pH values below 8, the rate equations become more complicated owing to the intervention of HCN as a reagent.

[70] Yu. N. Kukushkin, S. I. Bakhireva, L. V. Konovalov, E. A. Andronov, and R. A. Vlasova, *Russ. J. Inorg. Chem.*, 1973, **18**, 1732.
[71] W. M. Scovell, *J. Amer. Chem. Soc.*, 1974, **96**, 3451.
[72] W. C. Crouse and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 1437.
[73] E. J. Billo, *Inorg. Chem.*, 1973, **12**, 2783.

Gold(III).—Rate constants and activation parameters have been measured[74] for the aquation reactions of $[AuBr_4]^-$ and $[AuBr_3(OH)]^-$ and for the reaction of $[AuCl_4]^-$ with Br^-. The results show support for Cattalini *et al.*[75] in the view that bond formation and bond breaking are both of importance in substitution reactions of Au^{III} complexes. The aquation reactions of the tetrabromo-complex is similar to that of the tetrachloro-complex in that the aquation of $[AuBr_4]^-$ is *ca.* 10^3 times as fast as that of $[PtBr_4]^{2-}$. The same authors have also measured rate constants and activation parameters for the reactions of $[AuCl_4]^-$ with various methyl-substituted ethylenediamines (am). The dependence of the observed rate constants on hydrogen- and chloride-ion concentrations is not the same for these reactions as for the corresponding reactions of ethylenediamine and diethylenetriamine. The difference is attributed to formation of ion pairs of the type $[AuCl_3(amH^+\ Cl^-)]$ for the methyl-substituted reactants, but the reason for this special behaviour is not known. (Similar ion pairs were postulated to account for the reaction of tetramethylethylenediamine with $[PdCl_4]^{2-}$.[66]) It has been pointed out[76] that the relatively large Au—Cl distance for the chlorine *trans* to the phosphine in $[Au(PPh_3)Cl_3]$ and the deviation of the structure from planar geometry are related to the high rate at which the complex undergoes chloride substitution. These properties may be attributed to a *trans* effect of PPh_3 analogous to that observed in Pt^{II} complexes. The replacement of bipy in $[Au(bipy)X_2]^+$ to form $[AuX_4]^-$ (X = Cl or Br) has been studied kinetically.[77] Kinetic equations for this type of reaction are notoriously complicated and the present one is no exception. The mechanism appears to involve two simultaneous reaction paths in one of which a six-co-ordinate species is formed by addition of two halide ions to the substrate. In contrast to complexes of the type $[PtCl_2L_2]$, the rate of *cis–trans* isomerization of (trialkyl)(triphenylphosphine)gold(III) complexes is unaffected by the presence of an excess of triphenylphosphine.[78] This suggests that the process occurs by a unimolecular mechanism. These complexes also undergo isomerization of alkyl groups {*e.g.* t-butyl to iso-butyl in *trans*-$[Au(Bu^t)Me_2(PPh_3)]$} and reductive elimination reactions (to form dialkyls and Au^I).

Rhodium(I).—Initial studies[79] on reactions of 2,2′-bipyridyl with a series of chloro(cod)aminerhodium(I) complexes gave no indication of a five-co-ordinate intermediate, such as found earlier[80] for some reactions of Rh^I complexes. However, reactions of [Rh(cod)Cl(piperidine)] in which piperidine is displaced by an amine (Y) showed some interesting features.[81] The reactions obey the normal expression of the form $k_{obs} = k_1 + k_2[Y]$, but values of k_1 (commonly taken to represent the rate constant for the nucleophilic reaction of solvent with substrate) are different for unidentate and for bidentate amines. An explanation of this anomaly is given in terms of a mechanism in which the leaving group (X) competes successfully with the entering group for the intermediate solvo-complex. If the rate constants for these competing reactions are k_{-s} and k_f, $k_1 = k_s + (k_Y k_{-s}/k_f)[X]$, where k_s is the rate constant for

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[78] A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 6140.
[79] W. Robb and C. G. Nicholson, *Inorg. Chim. Acta*, 1973, **7**, 645.
[80] L. Cattalini, R. Ugo, and A. Orio, *J. Amer. Chem. Soc.*, 1968, **90**, 4800.
[81] C. G. Nicholson and W. Robb, *Inorg. Chim. Acta*, 1974, **8**, 41.

the solvent path when bipy is the entering group. Values of k_{-s}/k_f are calculated for several entering amines, but the method appears to be based on the assumption that the concentration of X is equal to that of the complex.

Copper(II).—Activation parameters for the formation of the mono-complex of Cu^{II} with a number of ligands have been reported[82] and a rather extensive comparison has been made with the corresponding reactions of Ni^{2+}(aq). 'Normal' behaviour (*i.e.* ligand–water interchange within an outer-sphere complex, leading to formation of the inner complex) is characterized by a ratio of observed rate constants, k_{Cu}/k_{Ni}, approximately equal to 10^5. In some cases (*e.g.* when the reacting ligand is monoprotonated 2-aminomethylpyridine, N⌒NH$^+$) 'abnormal' behaviour ($k_{Cu}/k_{Ni} \simeq 10^2$) is found and is explicable on the basis that proton loss from the singly bonded intermediate [Cu—N⌒NH]$^{3+}$ may be rate-determining. In other cases it is more likely that low k_{Cu}/k_{Ni} values arise from small values of equilibrium constants for formation of the outer-sphere complexes. Rate constants have also been measured[83] for the two stages of the reactions,

$$2L^- + Cu^{2+} \xrightarrow{k_1} CuL^+ + L^- \xrightarrow{k_2} CuL_2$$

where L = glycine, α-alanine, valine, or *NN*-dihydroxyethylglycine. These reactions differ from those of Ni^{II} and Co^{II} in that, for the Cu^{II} species, k_1 is generally greater than k_2. Rate constants are known approximately from values of equilibrium constants.

2 Tetrahedral Complexes

Very little has been reported on substitution reactions of inert complexes in this category. N.m.r. studies[84] on the dissociation of the Ni^0 complexes NiL_4,

$$NiL_4 \rightleftharpoons NiL_3 + L$$

for a number of phosphine and phosphite ligands (L) show that the extent of dissociation and rate of exchange (indicated by lineshape effects) may be correlated with the electronic and steric properties of the ligand. In general, phosphines and phosphinites dissociate more rapidly than phosphites. Reactions of the substrates $[M(PEt_3)_4]$ with fluorohalogenobenzenes (C_6H_4FX) involve oxidative addition as well as substitution, and the rates decrease in the sequences Ni > Pd > Pt (for M) and I > Br > Cl > CN ≫ F (for X).[85] Que *et al.*[86,87] have studied some interesting ligand-substitution reactions of the type

$$[Fe_4S_4(SR^1)_4]^{2-} + nR^2SH \rightleftharpoons [Fe_4S_4(SR^1)_{4-n}(SR^2)_n]^{2-} + nR^1SH$$

The iron complexes have a cubane-type stereochemistry with four-co-ordinate Fe and three-co-ordinate S atoms occupying alternate corners of the 'cube'. No detailed kinetic measurements were reported but it is stated that in all cases equilibrium appeared to be established within several minutes or less – implying that not all the

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[85] G. W. Parshall, *J. Amer. Chem. Soc.*, 1974, **96**, 2360.
[86] L. Que, M. A. Bobrik, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, 1974, **96**, 4168.
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reactions are very rapid. In the later paper brief reference is made to the order of magnitude ($1—10^3$ l mol^{-1} s^{-1} at ambient temperature) of rate constants for the reactions with R^1 = Bu^t, R^2 = aryl, and n = 1.

3 Five-Co-ordinate Complexes

Reactions of iron and cobalt dithioline complexes,[88] $[M(mnt)_2X]^-$ {mnt = $[S_2C_2(CN)_2]$, X = a phosphine or phosphite}, with unidentate nucleophiles (L) give five-co-ordinate products, $[M(mnt)_2L]^-$, and with bidentate nucleophiles (L—L) give six-co-ordinate products, $[M(mnt)_2(L—L)]^-$. In each case the iron complexes react more rapidly than those of cobalt and the mechanism involves both dissociative and, unusually for five-co-ordinate substrates, associative pathways. The kinetic equations are necessarily complicated but the experimental results are consistent with the predictions in limiting cases. Kinetic studies have been carried out on the ligand-exchange reactions[89]

$$[NiL_3X_2] \rightleftharpoons [NiL_2X_2] + L$$

[L = Ph_2POEt, $P(OEt)_3$, $PhPMe_2$, or $PhP(OEt)_2$; X = Cl, Br, or CN]. Results with the cyano-complexes show the mechanism to be a dissociative one and thus confirm Tolman's prediction that, in such reactions, any intermediate in significant concentration must contain 16 or 18 valence electrons. A qualitative comparison shows that, for L = $PhPMe_2$, the rate constants for the dissociation step increase with changing X^- in the order $CN^- < Br^- < Cl^-$. A study of ligand exchange in $[Ni(2,6\text{-lutidine oxide})_5]^{2+}$ by n.m.r. spectroscopy[90] indicates that two exchanging species are present in solution, the results being best interpreted in terms of dissociation of a species with a trigonal-bipyramidal structure. Rate constants and equilibrium constants for the rapid dissociation of $[NiLCl_2]$ have been measured,[91] where L is the terdentate ligand 1,1,7,7-tetraethyldiethylenetriamine. The process occurs *via* the formation of an ion pair:

$$[NiLCl_2] \rightleftharpoons NiL^+ Cl^- \rightleftharpoons [NiLCl]^+ + Cl^-$$

Rearrangement in a five-co-ordinate species, from a trigonal bipyramid to a square pyramid, has been effected[92] by increasing pressure on the $[Cr(en)_3]^{3+}$ salt of $[Ni(CN)_5]^{3-}$.

[88] D. A. Sweigart, *Inorg. Chim. Acta*, 1974, **8**, 317.
[89] C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, 1974, **13**, 971.
[90] P. M. Enriquez and S. S. Zumdahl, *Inorg. Chem.*, 1973, **12**, 2475.
[91] H. Horohara, K. J. Ivin, J. J. McGarvey, and J. Wilson, *J. Amer. Chem. Soc.*, 1974, **96**, 4435.
[92] L. J. Basile, J. R. Ferraro, M. Choca, and K. Nakamoto, *Inorg. Chem.*, 1974, **13**, 496.

3

Inert Metal Complexes: Co-ordination Numbers Six and Higher

BY P. MOORE

1 Introduction

This chapter is concerned with substitution reactions of inert metal ions of co-ordination number six or higher. Where a metal ion is sometimes inert and sometimes labile {*e.g.* iron(II) which is inert in its low-spin complexes such as $[Fe(bipy)_3]^{2+}$ (t_{2g}^6) but labile when high-spin (*e.g.* $[Fe(H_2O)_6]^{2+}$ $t_{2g}^4 e_g^{*2}$)} only references to the inert complexes will be found here, and readers should refer to Chapter 4 for references to labile systems. Conversely, where a metal ion is normally labile, a few references will be found in this chapter to those systems in which relatively slow reactions have been observed. For example, exchange of multidentate ligands between bivalent metal ions which are normally labile often comes into this category.

For the sake of continuity the format adopted by the previous Reporter[1] will be largely adhered to in the present volume. Therefore, all the studies of a particular metal ion will not be found in one section, but instead the chapter is subdivided in the first instance according to reaction type. Aquation reactions are covered first, followed by sections on base hydrolysis, formation, exchange and replacement, and isomerization. The sections concerned with aquation reactions have been widened somewhat to include references to related dissociation studies. Section headings are further subdivided according to the central metal ion, beginning with cobalt(III) and chromium(III), which are still the most widely studied systems. Some headings are dealt with more fully in later chapters (*e.g.* solvent effects in Chapter 5) and only brief mention will be made of them here. In this introduction highlights of some of the interesting developments during the past eighteen months will be made, and references will be found to reviews or other publications of a general nature. This Report covers literature through to December 1974.

Although cobalt(III) and chromium(III) continue to be kinetically the most widely investigated inert metal ions, some progress has been made in recent years towards our understanding of the rarer metals. The continuing efforts of Taube and his associates are particularly noteworthy in the field of ruthenium chemistry, and several interesting publications from them dealing with aspects of ruthenium(II) and ruthenium(III) complexes have appeared recently.[2-5] The photochemical studies of

[1] J. Burgess, in 'Inorganic Reaction Mechanisms', ed. J. Burgess, Specialist Periodical Reports, The Chemical Society, London, 1974, Vol. 3, p. 163.
[2] S. E. Diamond and H. Taube, *J.C.S. Chem. Comm.*, 1974, 622.
[3] R. J. Sundberg, R. F. Bryan, I. F. Taylor, and H. Taube, *J. Amer. Chem. Soc.*, 1974, **96**, 381.
[4] S. Isied and H. Taube, *Inorg. Chem.*, 1974, **13**, 1545.
[5] M. J. Clarke and H. Taube, *J. Amer. Chem. Soc.*, 1974, **96**, 5413.

ruthenium and closely related metal ions [*e.g.* rhodium(III), iridium(III), and osmium(II)] are also noteworthy, especially the photolysis of azido-complexes where reactive nitrene intermediates are postulated.[6,7] Two reviews on photochemical aspects have appeared,[8] one of which deals specifically with octahedral complexes of these heavy-metal ions. Ruthenium(II) is well known for its ability to stabilize unusual ligands (*e.g.* dinitrogen) and there have been a number of reports of the way in which co-ordination to ruthenium ions can markedly affect the reactivity of a ligand. Some recent studies of ruthenium(III) systems indicate how in one case a ligand is deactivated by co-ordination, whereas in a further example substantial activation occurs. Thus, ruthenium(III) nucleosides are more stable towards acid-catalysed hydrolysis of the sugar–purine bond,[5] whereas the co-ordination of a nitrile RCN (R = Me or Ph) increases its reactivity towards base hydrolysis [reaction (1); M = Ru^{III}] by a factor of *ca.* 10^8.

$$[(NH_3)_5M(NCR)]^{n+} + OH^- \longrightarrow [(NH_3)_5M(NHCOR)]^{(n-1)+} \quad (1)$$

The ruthenium(II) analogue is *ca.* 10^6 times less reactive and although the reduction in charge is no doubt partly responsible for this rate difference, this cannot be the sole reason because even the rhodium(III) compound [which is isoelectronic with the ruthenium(II) complex] is *ca.* 10^2 times less reactive than when M = ruthenium(III).[9] One of the reasons why kinetic and mechanistic studies of ruthenium complexes have been rather limited until recent years must lie with the difficult synthetic chemistry. Molybdenum is another metal which is kinetically difficult to study for the same reason. However, some further kinetic reports have appeared in this area,[10] and the aqueous chemistry of molybdenum in oxidation states +2 to +6 has been discussed.[11] Studies of the $[Mo(H_3O)_6]^{3+}$ ion ($4d^3$) are particularly interesting in comparison with the widely investigated $[Cr(H_2O_6]^{3+}$ ion ($3d^3$). The former species is much more reactive than the latter, and for molybdenum(III) the limited results are best interpreted in terms of an associative interchange (I_a) mechanism.[10] This mechanism is to be expected for the larger molybdenum ion since recent evidence supports an I_a mechanism for substitutions at the smaller chromium(III) ion. As pointed out in Volume 3 of this series,[1] substitutions at cobalt(III) invariably proceed *via* a dissociative (I_d or *D*) mechanism, and although for many years chromium(III) was believed to show parallel behaviour, recent evidence (*e.g.* measurements of volumes of activation and transition enthalpies)[1,12] indicate that this is not the case. Even quantum mechanical calculations are claimed[13] to support an S_N2 mechanism for anation of $[Cr(H_2O)_6]^{3+}$ ion. The point is well substantiated in a recent review of the subject[12] in which the author argues that for most tervalent metal ions, except cobalt(III), I_a mechanisms are probably more important than I_d, and the problem

[6] H. D. Gafney, J. L. Reed, and F. Basolo, *J. Amer. Chem. Soc.*, 1973, **95**, 7998; 1974, **96**, 1363.
[7] G. Feraudi and J. F. Endicott, *Inorg. Chem.*, 1973, **12**, 2389.
[8] P. C. Ford, J. D. Petersen, and R. E. Hintze, *Coordination Chem. Rev.*, 1974, **14**, 67; D. Phillips, in 'Photochemistry', ed. D. Bryce-Smith, Specialist Periodical Reports, The Chemical Society, London, 1973, Vol. 4, p. 355.
[9] A. W. Zanella and P. C. Ford, *J.C.S. Chem. Comm.*, 1974, 795.
[10] Y. Sasaki and A. G. Sykes, *J.C.S. Chem. Comm.*, 1973, 767; *J. Less-Common Metals*, 1974, **36**, 125; *J.C.S. Dalton*, 1974, 1468.
[11] M. Ardon and A. Pernick, *J. Amer. Chem. Soc.*, 1973, **95**, 6871; G. P. Haight and D. R. Boston, *J. Less-Common Metals*, 1974, **36**, 95; M. Lamache, *ibid.*, p. 179.
[12] T. W. Swaddle, *Coordination Chem. Rev.*, 1974, **14**, 217.
[13] E. D. German, Z. D. Urushadze, and V. K. Khidureli, *Chem. Abs.*, 1974, **81**, 30 110a.

may be to explain why cobalt(III) is anomalous! If this latter point were correct the situation would be truly ironic since cobalt(III) substitutions have been assumed for a long time to typify tervalent metal ions in general.

Another feature of substitution reactions of chromium(III) which has been recognized in recent years is the influence that co-ordinated oxoanions XO_m^{n-} (X = S, N, P, As, *etc.*) can exert upon neighbouring *cis*-ligands.[1] *cis*-Activation has been further investigated[14] in $[Cr(NH_3)_5(ONO_2)]^{2+}$, where the immediate products of acid hydrolysis contain more *cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ than $[Cr(NH_3)_5(OH_2)]^{3+}$. Also, several steps in the stepwise aquation of $[Cr(NH_3)_6]^{3+}$ have been shown to be much slower in perchlorate than in a nitrate medium.[15] Furthermore, O-bonded sulphite, nitrate, and acetate ions have been reported to labilize anions (X^-) in complexes of the type $[Cr(H_2O)_5X]^{2+}$ (X = OAc, N_3, or F) by *cis*-activation.[16] In the latter study a seven-co-ordinate intermediate or transition state is postulated to be formed by chelation of the labilizing anion,[16] and since associative mechanisms are rarely (if ever) found for cobalt(III) this is perhaps why activation of this type is not so common in cobalt(III) complexes. Some time ago a somewhat different *cis*-activation mechanism was postulated in nitrito-complexes of the type *cis*-$[CrA_4(ONO)X]^+$ (A = NH_3 or A_2 = en; X = Cl, Br, or NCS) in which the nitrito-group assisted in the release of X^- by anchimeric assistance (neighbouring group participation), with NOX envisaged as the leaving group.[17] This mechanism is only possible with oxoanions like nitrite ion where the nitrogen–oxygen bond is more labile than the oxygen–metal bond and it should be equally applicable to cobalt(III) and chromium(III) complexes. It differs from the *cis*-activation reported recently in that the nitrite ion does not need to co-ordinate to the metal centre to affect labilization. *trans*-Activation as opposed to *cis*-activation by oxoanions is also observed in special cases. S-Bonded sulphite ion is a good example of a *trans*-labilizing group, and some recent further examples are reported for cobalt(III) complexes of the type *trans*-$[CoA_4(X)SO_3]^{n+}$ (A = NH_3 or A_2 = en; X = H_2O or SO_3^{2-})[18–20] and *trans*-$[Co(dmgH)_2(SO_3)L]$ (dmgH = dimethylglyoximate ion; L = pyridine or α-, β-, or γ-picoline).[21] The *trans* influence of S-bonded sulphite ion is demonstrated in a crystal structure of $[Co(NH_3)_5SO_3]Cl,H_2O$ where the cobalt–nitrogen bond in the *trans* position to the sulphito-ligand is significantly longer (205.5 pm) than the average value of the four in-plane cobalt–nitrogen bond lengths (*ca.* 196 pm).[22] S-Bonded hydrogen sulphite ion is reported to have a reduced *trans*-labilizing effect compared with sulphite ion in cobalt(III) complexes,[23] and this is supported by kinetic studies[5] of *trans*-$[Ru(NH_3)_4X(OH_2)]^{n+}$ (X = SO_2, HSO_3^-, or SO_3^{2-}), where the order of the *trans* effect is $SO_3^{2-} > HSO_3^- > SO_2$.

In recent years interest in the substitution reactions of cobalt(III) complexes has

[14] G. Guastalla and T. W. Swaddle, *Canad. J. Chem.*, 1974, **52**, 527.
[15] G. Guastalla and T. W. Swaddle, *Inorg. Chem.*, 1974, **13**, 61.
[16] S. N. Choi and D. W. Carlyle, *Inorg. Chem.*, 1974, **13**, 1818.
[17] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1971, 1632; *Chem. Comm.*, 1969, 29.
[18] K. L. Scott, R. S. Murray, W. C. E. Higginson, and S.-W. Foong, *J.C.S. Dalton*, 1973, 2335.
[19] M. A. Thacker, K. L. Scott, M. E. Simpson, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 674.
[20] K. L. Scott, *J.C.S. Dalton*, 1974, 1486.
[21] L. N. Istru and G. P. Syrtsova, *Zhur. neorg. Khim.*, 1974, **19**, 1303.
[22] R. C. Elder and M. Trkula, *J. Amer. Chem. Soc.*, 1974, **96**, 2635.
[23] H. Siebert and G. Wittke, *Z. anorg. Chem.*, 1974, **405**, 63.

increased, especially in those cases where the non-leaving groups confer class (*b*) or 'soft' character upon the central cobalt(III) ion {*e.g.* in $[Co(CN)_5X]^{n-}$ or cobaloximes of the type *trans*-$[Co(dmgH)_2XY]^{n-}$, where X and Y are unidentate ligands, the order of lability of halide ions being Cl > Br > I, *i.e.* the opposite order to that found in $[CoA_4XY]^{n+}$ (A = NH_3 or A_2 = en)}. This interest arises partly because of the dominance of the previously unexplored S_N1 limiting or *D* mechanism in their reactions, but also because some of these compounds are models for biochemical systems. Notable are studies related to the cobalamins and vitamin B_{12}. Cobaloximes and other cobalt(III) complexes of dioximato-ligands which are models for the cobalamins continue to be widely studied and this is an area where the recent growth of work has been considerable.[24] This research is discussed mainly in the section dealing with the effect of non-leaving groups on cobalt(III) aquations. The implication of methylcobalamin in the formation of the pernicious poison methylmercury(II) ion[24,25] by methyl-group transfer from cobalt(III) to mercury(II) ion is just one aspect of this work which has been explored recently through the use of model systems.[26] The interaction of organometallic compounds with living organisms has been reviewed,[24] and a further review deals with structural aspects of transition-metal oxime complexes.[27]

Mention has already been made of the way in which ruthenium ions can markedly affect the reactivity of co-ordinated ligands. Another aspect of the reactions of co-ordinated ligands which shows considerable promise concerns those studies in which the metal ion helps to direct the stereochemical course of a reaction as in a template synthesis. Buckingham, Sargeson, and co-workers have made several model studies of this type in recent years using cobalt(III) complexes. In particularly interesting recent examples the stereoselective synthesis of polyamine complexes was achieved by base-catalysed intramolecular condensation between N-co-ordinated amino-acetaldehyde or aminoacetone and a neighbouring co-ordinated amino-group.[28,29] A knowledge of the different rates of proton exchange in polyamine complexes of this type (see, for example, the recent work of Tobe and co-workers[30,31]) which can be accelerated, for example, by a *trans*-halide ion[32] will no doubt lead to many more stereoselective syntheses of this type. The reactivity of amino-acids when co-ordinated to metal ions has been reviewed recently, with special emphasis given to the formation and hydrolysis of esters and peptides, to some reactions of complexes of amino-acids and Schiff bases, to aldol condensations, and to isotopic exchange and racemization at the α-carbon atom.[33]

[24] J. S. Thayer, *J. Organometallic Chem.*, 1974, **76**, 265; D. G. Brown, *Progr. Inorg. Chem.*, 1973, **18**, 177.
[25] H. J. Segall and J. M. Wood, *Nature*, 1974, **248**, 456; D. R. Storm and R. P. Gunsalus, *ibid.*, 1974, **250**, 778.
[26] G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Organometallic Chem.*, 1974, **81**, 107; *J.C.S. Chem. Comm.*, 1973, 413.
[27] A. Chakravorty, *Coordination Chem. Rev.*, 1974, **13**, 1.
[28] B. T. Golding, J. MacB. Harrowfield, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1974, **96**, 3003.
[29] J. D. Bell, A. R. Gainsford, B. T. Golding, A. J. Herlt, and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1974, 980.
[30] G. Marangoni, M. Panayotou, and M. L. Tobe, *J.C.S. Dalton*, 1973, 1989.
[31] E. Ahmed and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 3027.
[32] K. B. Nolan and R. W. Hay, *J.C.S. Dalton*, 1974, 914; 1973, 2503.
[33] A. Pasini and L. Casella, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2133.

An extensive compilation of rate data has appeared for ligand-replacement processes in octahedral complexes of metal ions in oxidation state +3 covering the literature to 1971.[34] In this article a useful critique of the errors associated with estimating activation parameters is given and some values are recalculated. The danger in estimating enthalpies and entropies of activation from data obtained over too narrow a temperature range (< 30 K) is stressed. Further reviews containing sections dealing with aspects of the substitution reactions of inert metal complexes have appeared.[35–39] These include discussions of acid-catalysed hydrolyses,[35] thermodynamic and kinetic studies of metal complexes containing tripodal amines {including $[M(tren)XY]^{n+}$, where M = Co^{III} or Rh^{III} and X and Y are unidentate ligands},[36] and the mechanistic assignment of rate laws for acid dependencies observed in perchlorate media.[37]

2 Aquation: Cobalt(III) Complexes

Unidentate Leaving Groups.—Two groups have reported recently on the acid hydrolysis of cobalt(III) ammines and related species at elevated temperatures.[40,41] These studies show that for the very inert $[Co(NH_3)_6]^{3+}$ ion the stepwise loss of up to three co-ordinated ammonia molecules occurs before the product of the third step, $[Co(NH_3)_3(OH_2)_3]^{3+}$, undergoes spontaneous reduction to $[Co(H_2O)_6]^{2+}$ with the formation of NH_4^+, N_2, N_2O, and a minor amount of O_2. For the first step, aquation of $[Co(NH_3)_6]^{3+}$, a study at 413.5 K in 0.1M-$HClO_4$ (μ = 1.0 mol l^{-1})[41] gave a first-order rate constant, $k = 7.9 \times 10^{-5}$ s^{-1}, and activation parameters $\Delta H^{\ddagger}$ = 36.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 10.7 cal K^{-1} mol^{-1}. This reaction is acid-independent but subsequent steps show an inverse acid-dependence owing to the deprotonation of a co-ordinated water molecule. For the aquation of the $[Co(NH_3)_5(OH_2)]^{3+}$ ion in excess acid the pseudo-first-order rate constant is given by $k = k_1 + k_2/[H^+]$, and at 413.7 K $k_1 = 12.6 \times 10^{-5}$ s^{-1}, $\Delta H_1^{\ddagger}$ = 41.9 kcal mol^{-1}, $\Delta S_1^{\ddagger}$ = 24 cal K^{-1} mol^{-1}, $k_2 = 6.2 \times 10^{-5}$ l mol^{-1} s^{-1}, $\Delta H_2^{\ddagger}$ = 43.5 kcal mol^{-1}, and $\Delta S_2^{\ddagger}$ = 26.7 cal K^{-1} mol^{-1}.[41] Similar results are reported for the $[Co(NH_3)_4(OH_2)_2]^{3+}$ ions.[40] A mechanism involving OH and NH_2 radicals is proposed for the redox step.[41]

Dimethyl sulphoxide (DMSO) is a much better leaving group than ammonia, and studies of a variety of reactions involving the $[Co(NH_3)_5(DMSO)]^{3+}$ ion support the expected dissociative interchange or I_d mechanism:

$$[Co(NH_3)_5(DMSO)]^{3+} + H_2O \rightleftharpoons [Co(NH_3)_5(OH_2)]^{3+} + DMSO$$

Both the forward[42] and reverse[43] steps of this reaction have been investigated in aqueous or mixed aqueous–organic solvents. For the forward reaction the rates did

[34] J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47.
[35] P. J. Staples, *Coordination Chem. Rev.*, 1973, **11**, 277.
[36] S. G. Zipp, A. P. Zipp, and S. K. Madan, *Coordination Chem. Rev.*, 1974, **14**, 29.
[37] G. Davies, *Coordination Chem. Rev.*, 1974, **14**, 287.
[38] D. Banerjea, *J. Indian Chem. Soc.*, 1974, **51**, 90.
[39] D. W. Watts, 'Physical Chemistry in Organic Solvent Systems', ed. A. K. Covington, Plenum Press, London, 1973, p. 681.
[40] S. Lum, W. D. Stanley, and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1293, 3587.
[41] A. M. Newton and T. W. Swaddle, *Canad. J. Chem.*, 1974, **52**, 2751.
[42] W. L. Reynolds, S. Ašperger, and M. Biruš, *J.C.S. Chem. Comm.*, 1973, 822; *J.C.S. Dalton*, 1974, 716.
[43] W. L. Reynolds, E. S. Barber, and R. Crandall, *Internat. J. Chem. Kinetics*, 1974, **6**, 51.

not correlate with the water activity, the Grunwald–Winstein Y values, or the heat of mixing of DMSO with the solvent components. The activation parameters are reported[42] to be $\Delta H^{\ddagger} = 23.9 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0.36 \pm 2.29$ cal K^{-1} mol^{-1}. At 318.1 K, exchange of solvent DMSO with the $[Co(NH_3)_5(DMSO)]^{3+}$ ion has a rate constant, k, of $(3.6 \pm 0.8) \times 10^{-4}$ s^{-1}, and comparison of k with the rate of anation of $[Co(NH_3)_5(DMSO)]^{3+}$ by nitrate ion and the rate of solvolysis of $[Co(NH_3)_5(ONO_2)]^{2+}$ by DMSO again supports an I_d mechanism.[43] The equilibrium constant for the formation of $[Co(NH_3)_5(ONO_2)]^{2+}$ from $[Co(NH_3)_5(DMSO)]^{3+}$ in DMSO is 0.28 ± 0.11 at 318.1 K. A similar study[44] of the aquation of the $[Co(NH_3)_5Br]^{2+}$ ion in 0.01 M-$HClO_4$ [$k = (3.9 \pm 0.08) \times 10^{-6}$ s^{-1} at 298.1 K, $\mu = 1.0$ mol l^{-1}] and the anation of the $[Co(NH_3)_5(OH_2)]^{3+}$ ion by Br^- gave a kinetically determined equilibrium constant in good agreement with the thermodynamic value ($K = 0.283 \pm 0.030$ l mol^{-1}). An I_d mechanism is again postulated, there being no evidence from the anation studies of a limiting rate at high [Br^-]. Equilibrium ion-pair constants were too small to be determined,[44] but from a further study of the aquation of $[Co(NH_3)_5Br]^{2+}$ in $NaClO_4$ solutions of various ionic strengths ($\mu = 0.026$—0.126 mol l^{-1}) it is reported that increasing μ has a decelerating effect upon the rate.[45] Sulphate ion has again been demonstrated to have a marked accelerating effect upon aquation rates, this time for the $[Co(NH_3)_5Cl]^{2+}$ ion.[46] The following mechanism is proposed in which the ion pair can react either with interchange of Cl^- with SO_4^{2-} ions, or of Cl^- ion with solvent H_2O:

$$[Co(NH_3)_5Cl]^{2+} + SO_4^{2-} \overset{K_{ip}}{\rightleftharpoons} [Co(NH_3)_5Cl],SO_4 \quad (A)$$

$$[Co(NH_3)_5Cl]^{2+} + H_2O \xrightarrow{k_1} [Co(NH_3)_5(OH_2)]^{3+} + Cl^-$$

$$(A) + H_2O \xrightarrow{k_2} [Co(NH_3)_5(OH_2)],SO_4^{+} + Cl^-$$

$$(A) \xrightarrow{k_3} [Co(NH_3)_5(OSO_3)]^{+} + Cl^-$$

Activation parameters associated with the rate constants k_1, k_2, and k_3 are $\Delta H^{\ddagger}(k_1) = 23.4 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger}(k_1) = -6.7 \pm 0.6$ cal K^{-1} mol^{-1}; $\Delta H^{\ddagger}(k_2) = 19.5 \pm 0.04$ kcal mol^{-1}, $\Delta S^{\ddagger}(k_2) = 17.5 \pm 0.13$ cal K^{-1} mol^{-1}; and $\Delta H^{\ddagger}(k_3) = 22.6 \pm 1.2$ kcal mol^{-1}, $\Delta S^{\ddagger}(k_3) = -13.3 \pm 3.9$ cal K^{-1} mol^{-1}. The ion-pair constant (K_{ip}) is characterized by $\Delta H^{\circ} = 4.1$ kcal mol^{-1} and $\Delta S^{\circ} = 6.2$ cal K^{-1} mol^{-1}.

Ion-pairing is largely avoided by studying anionic complexes. For example, anation studies of the $[Co(CN)_5OH_2]^{3-}$ ion show a limiting rate at high anion concentrations in support of a D mechanism, there being no ambiguity from ion-pairing in this system. Studies of other anionic cobalt complexes are relatively rare, but one recent example has appeared;[47] aquation of the $[Co(NH_3)_2(NO_2)_4]^-$ ion with the formation of $[Co(NH_3)_2(OH_2)(NO_2)_3]$ is reported to have $\Delta H^{\ddagger} = 24.1 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -1.1 \pm 0.8$ cal K^{-1} mol^{-1}. Another example of a reaction of an anionic cobalt(III) complex which has been investigated recently is shown in

[44] W. L. Reynolds, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1974, 719.
[45] V. Holba, *Chem. Zvesti*, 1974, **28**, 17.
[46] N. C. Naik and R. K. Nanda, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3793.
[47] J. Zsakó, Cs. Várhelyi, and K. Szasz-Sata, *Acta Chim. Acad. Sci. Hung.*, 1974, **80**, 177.

equation (2) (X = Cl or Br).[48] This reaction involves final chelate ring closure in

$$[Co(edtaH)X]^- \longrightarrow [Co(edta)]^- + X^- + H^+ \quad (2)$$

going from a species in which the edta is quinquedentate (with a dangling, protonated carboxylate arm) to a species in which the edta is fully co-ordinated in a sexidentate complex. At 303.1 K [μ = 0.10 mol l^{-1} ($NaClO_4$)] the rate constants (k_1) were redetermined and found to have the values $10^6k_1 = 3.33 \pm 0.10$ and 3.09 ± 0.10 s^{-1} for X = Cl and Br respectively. When X = Br analysis of the initial reaction rates gave evidence of two species and yielded a second rate constant ($10^6k_2 = 58.3 \pm 5.0$ s^{-1}) for a faster reacting isomer (A) in addition to the slower reacting isomer (B) in the reaction sequence

$$B \xrightarrow{k_1} A \xrightarrow{k_2} \text{product}$$

Clearer evidence for two isomers when X = Br comes from recent ^{13}C n.m.r. studies in which the major component is assigned the unexpected 'axial' structure (Br out of the N—Co—N plane) in contrast to the more usual 'equatorial' configuration.[49]

Further studies which sometimes involve chelate ring closure are reported for the following systems:[50]

$$cis\text{-}[Co(en)_2\{NH_2(CH_2)_nOH\}Br]^{2+} \longrightarrow cis\text{-}[Co(en)_2\{NH_2(CH_2)_nOH\}(OH_2)]^{3+} + Br^- \quad (3)$$

$$cis\text{-}[Co(en)_2\{NH_2(CH_2)_nOH\}Br]^{2+} \longrightarrow [Co(en)_2\{NH_2(CH_2)_nOH\}]^{3+} + Br^- \quad (4)$$

For the reaction involving 2-aminoethanol (n = 2) the chelate-ring-closure reaction (4) occurs and there is no evidence for an aqua-intermediate [reaction (3)], whereas when n = 3 the reaction is slower and the first step involves simple aquation without chelate ring closure. The reactions were studied in mixed aqueous–organic solvents (MeOH, EtOH, Me_2CO, and glycerol) and a linear correlation was observed between the logarithm of the rate constant and the inverse of the dielectric constant. An S_N1 mechanism is proposed, although for the 2-aminoethanol complex the demonstrated absence of an aqua-intermediate is more in line with an S_N2 mechanism. A similar difference in reactivity with increasing chain length is reported for complex ions of the type *cis*-$[Co(en)_2\{NH_2(CH_2)_nCN\}Cl]^{2+}$. When n = 1, an earlier study[51] showed that in neutral or basic solution linkage isomerizations could occur in a reaction of the type

$$cis\text{-}[Cl(en)_2Co(NH_2CH_2CN)]^{2+} \longrightarrow trans\text{-}[Cl(en)_2Co(NCCH_2NH_2)]^{2+} \quad (5)$$

Reaction (5) is postulated to involve a transition state in which the cyanomethylamine forms a five-membered chelate ring. In acidic solution this isomerization process is so retarded that the kinetics of solvolysis can be determined.[51] In an analogous study of the 2-cyanoethylamine complex (n = 2) the linkage isomerization is not observed,[52] presumably because formation of the six-membered chelate

[48] M. L. Morris, M. E. Banasik, and J. Knoeck, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 331; M. L. Morris and D. H. Busch, *J. Phys. Chem.*, 1959, **63**, 340.

[49] O. W. Howarth, P. Moore, and N. Winterton, *J.C.S. Dalton*, 1974, 2271; *Inorg. Nuclear Chem. Letters*, 1974, **10**, 553.

[50] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Zhur. neorg. Khim.*, 1973, **18**, 1854; *Russ. J. Inorg. Chem.*, 1972, **17**, 1008; 1973, **18**, 234.

[51] S. C. Chan and F. K. Chan, *Austral. J. Chem.*, 1970, **23**, 1175.

[52] S. C. Chan and C.-K. Lee, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1896; W.-K. Chau, W.-K. Lee, and C.-K. Poon, *J.C.S. Dalton*, 1974, 2419.

ring is not so favourable. A comparison of the activation parameters for aquation and base hydrolysis of these two complexes and the analogous *cis*-$[Co(en)_2(NH_2CH_2CH_2Me)Cl]^{2+}$ ion is shown in Table 1. The inductive effect of the cyano-group is

Table 1 *Activation parameters for the acid* (k_{aq}) *and base* (k_{OH}) *hydrolysis of* cis-$[Co(en)_2LCl]^{2+}$ (*from ref.* 52)

L	$\Delta H^{\ddagger}_{aq}{}^{a}$/ kJ mol^{-1}	$\Delta S^{\ddagger}_{aq}{}^{a}$/ J K^{-1} mol^{-1}	$\Delta H^{\ddagger}_{OH}{}^{b}$/ kJ mol^{-1}	$\Delta S^{\ddagger}_{OH}{}^{b}$/ J K^{-1} mol^{-1}
NH_2CH_2CN	125	+38		
$NH_2CH_2CH_2CN$	110±5	−3±4	98±5	104±4
$NH_2CH_2CH_2Me$	96±5	−46±4	98±5	104±4

[a] Acid hydrolysis. [b] Base hydrolysis.

seen to strengthen the cobalt–chloride bond in the cyanomethylamine complex as reflected in an increase in the enthalpy of activation for aquation by 15 kJ mol^{-1} when compared with the 2-cyanoethylamine analogue. The latter has very similar kinetic parameters to the n-propylamine complex, and so the increase in chain length from $n = 1$ to $n = 2$ in *cis*-$[Co(en)_2\{NH_2(CH_2)_nCN\}Cl]^{2+}$ is sufficient to remove the inductive influence of the cyano-group at the cobalt(III) centre.

Several other examples involving the aquation of unidentate ligands in complexes of the type $[Co(en)_2LX]^{n+}$ or $[CoA_4LX]^{n+}$ [A_4 = $(dmgH)_2$ or other planar quadridentate N-donor ligand; L and X are unidentate ligands] will be found in later sections dealing with the effects of non-leaving groups, solvent effects, and acid and base catalysis.

Finally, the Hammett equation has been shown to apply to the aquation of cobalt(III) complexes, and the results comply with a dissociative mechanism.[52] Only one group has suggested an associative mechanism for the solvolysis of the $[Co(NH_3)_5Cl]^{2+}$ ion in mixed aqueous–organic solvents, basing their argument on the variation of the rate constant with the water activity, and on a linear plot of log (rate constant) against log (equilibrium constant) with a slope of 0.17.[53] The weight of evidence is clearly against this conclusion. Good agreement is reported between theoretically calculated and observed values of volumes of activation ($\Delta V^{\ddagger}$) for reactions of the type $[ML_5X]^{2+} + H_2O \rightarrow [ML_5(OH_2)]^{3+} + X^-$ (M = Cr, X = Cl, Br, NO_3, NCS, or H_2O).[54] As pointed out in the introduction[12] measurements of this parameter give a much clearer indication of mechanism for reactions of this type.

Multidentate Leaving Groups.—Very few reports have appeared for this class of reaction. Dicarboxylato-complexes of the type $[Co(ox)_3]^{3-}$ or $[Co(mal)_3]^{3-}$ (ox = oxalate ion, mal = malonate ion) continue to receive attention. Acid-catalysed decomposition of these complex ions is believed to occur concurrently with redox reactions involving the formation of organic radicals, *e.g.* $[Co(ox)_3]^{3-} \rightarrow Co^{2+}(aq) + ox^{-\bullet} + 2ox^{2-}$. Ignoring a previous study of $[Co(mal)_3]^{3-}$ in which an analogous

[53] E. M. Strel'tsova, G. A. Krestov, I. Senyagina, and V. S. Gorshenina, *Chem. Abs.*, 1974, **79**, 97 475a.
[54] E. D. German and R. R. Dogonadze, *Chem. Abs.*, 1974, **79**, 141 425b.

redox mechanism is favoured,[55] new results are reported and the observed rate law,

$$-d[Co(mal)_3^{3-}]/dt = \{k_1[H^+] + k_2[H^+]^2\}[Co(mal)_3^{3-}]$$

is interpreted in terms of a hydrolytic mechanism:[56]

$$[Co(mal)_3]^{3-} + H_3O^+ \rightleftharpoons [Co(mal)_2(O_2CCH_2CO_2H)(OH_2)]^{2-} \quad \text{(rapid)}$$

$$[Co(mal)_2(O_2CCH_2CO_2H)(OH_2)]^{2-} + H_2O \longrightarrow [Co(mal)_2(OH_2)_2]^- + \text{mal } H^-$$

$$[Co(mal)_2(O_2CCH_2CO_2H)(OH_2)]^{2-} + H_3O^+ \longrightarrow [Co(mal)_2(OH_2)_2]^- + \text{mal } H_2$$

In this scheme acid-catalysed ring-opening is rapid, and the rate-determining steps are associated with hydrolysis (with or without acid catalysis) of an intermediate in which the protonated malonate ion is acting as a unidentate ligand. At 298.0 K and $\mu = 1.0$ mol l^{-1}, $k_1 = 6.30 \times 10^{-2}$ l mol^{-1} s^{-1} and $k_2 = 0.245$ l^2 mol^{-2} s^{-1}, and composite activation parameters associated with the values of k_1 and k_2 are $\Delta H^*(k_1) = 23.5$ kcal mol^{-1}, $\Delta H^*(k_2) = 16.7$ kcal mol^{-1}, $\Delta S^*(k_1) = 14.8$ cal K^{-1} mol^{-1}, and $\Delta S^*(k_2) = 5.2$ cal K^{-1} mol^{-1}. The observed rate law is analogous to that found for $[Cr(mal)_3]^{3-}$, but the cobalt(III) results do not allow a clear-cut distinction to be made between the hydrolytic and redox mechanisms. The final product is, of course, $[Co(H_2O)_6]^{2+}$.

A study of micellar catalysis of the redox decomposition of the $[Co(ox)_3]^{3-}$ ion has also appeared,[57] but this will be discussed in the section dealing with catalysed aquation.

Effects of Non-leaving Ligands.—Mention was made in the introduction to the large *trans* effect of S-bonded sulphite ion. Sulphito-complexes of cobalt(III) are analogous to $[Co(ox)_3]^{3-}$ and similar ions discussed in the previous section in that they sometimes react with redox decomposition to cobalt(II) species. In a recent example, the rate-determining step in the redox decomposition of the *trans*-$[Co(NH_3)_4(OH_2)(SO_3)]^+$ ion was found to be the *trans*→*cis* isomerization process.[19] The *cis*-isomer rapidly aquates with loss of the ammonia molecule in the *trans* position to the sulphite ion to give *cis*-$[Co(NH_3)_3(OH_2)_2(SO_3)]^+$ and this ion in turn undergoes an internal redox reaction in which the HSO_3 radical is postulated to be formed along with cobalt(II) ions. The reaction rate increases in the presence of oxygen but is independent of $[H^+]$ in the range 0.01—1.0 mol l^{-1}. These results are in line with studies of the redox decomposition of $[Co(NH_3)_3(OH_2)_3]^{3+}$ ion noted earlier,[40,41] and it is apparent that the oxidizing ability of the cobalt(III) ion increases considerably as the co-ordinated ammonia molecules are replaced by aqua-ligands. Even though sulphite ion is a good reducing agent it is still possible to add two sulphito-ligands to cobalt(III) as shown by the recent synthesis of the *cis*- and *trans*-$[Co(NH_3)_4(SO_3)_2]^-$ ions.[20] The *trans* effect of the S-bonded sulphite ion is again demonstrated by a study of the redox decomposition of these complexes in perchloric acid solution; the immediate products of the reactions are *trans*-$[Co(NH_3)_4(OH_2)(SO_3)]^+$ and $[Co(NH_3)_2(OH_2)_2(SO_3)_2]^-$ from the *trans*- and *cis*-isomers respectively. A study of the redox decomposition of the *cis*-isomer under air-free conditions gave an observed rate constant[20] $k = k_1 + k_2[H^+]$ in the acid range 0.02—0.20 mol l^{-1} $[H^+]$. At 293.1 K and $\mu = 1.0$ mol l^{-1} ($LiClO_4$), $k_2 = 1.39 \times 10^{-2}$ l mol^{-1} s^{-1}, with k_1 only

[55] Ref. 1, p. 170.
[56] Y. Sulfab and M. S. Al-Obadie, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2067.
[57] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J.C.S. Dalton*, 1974, 625.

contributing *ca.* 3% to k at $[H^+] = 0.10$ mol l^{-1}. A study of the *trans* effect of sulphite ion in complex ions of the type *trans*-$[Co(dmgH)_2(SO_3)L]^-$ (dmgH = dimethylglyoximate ion; L = NH_3, $PhNH_2$, *p*-anisidine, pyridine, or α-, β-, or γ-picoline) has also appeared,[21] and for the pyridines the relative rates are py > β- > α- > γ-picoline, in line with their pK_a differences and the postulated *D* mechanism. Methyl and amido-groups are also observed to have a large *trans* effect in complexes of the type $[Co(A_4)LX]^{n+}$ (A_4 = quadridentate nitrogen ligand, L = Me or NH_2) and these results are discussed in the section dealing with base hydrolysis.

Following earlier kinetic studies of the isomerization and acid- and base-catalysed hydrolysis of the [Co(*RR*- and *SS*-Hdtu)NCS]$^{2+}$ ions[58] an analogous study has now appeared for the [Co(*RR*-Hdtu)N_3]$^{2+}$ ion (Hdtu = tetren = 1,11-diamino-3,6,9-triazaundecane).[59] The reaction is complicated by protonation of the azido-ligand and by conjugate base formation with loss of a proton from the amine ligand:

$$[Co(Hdtu)N_3]^{2+} + H^+ \overset{K_1}{\rightleftharpoons} [Co(Hdtu)(N_3H)]^{3+} \quad (6)$$

$$[Co(Hdtu)N_3]^{2+} \overset{K_2}{\rightleftharpoons} [Co(dtu)N_3]^+ + H^+ \quad (7)$$

$$[Co(Hdtu)N_3]^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(Hdtu)OH_2]^{3+} + N_3^- \quad (8)$$

$$[Co(Hdtu)(N_3H)]^{3+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(Hdtu)OH_2]^{3+} + HN_3 \quad (9)$$

$$[Co(dtu)N_3]^+ + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(dtu)OH_2]^{2+} + N_3^- \quad (10)$$

$$[Co(Hdtu)OH_2]^{3+} \overset{K_3}{\rightleftharpoons} [Co(dtu)OH_2]^{2+} + H^+ \quad (11)$$

The rates are generally lower than for the corresponding ammine or ethylenediamine complexes (Table 2) and this can be best ascribed to a solvent effect in which the large organic ligand tends to break up the solvation shell of the complex whilst the complex at the same time makes even greater demands on solvation in proceeding to the transition state. Recent studies of the enhanced stabilities of nickel(II) complexes with cyclic amines[60] support this idea of low solvation for complexes of large macrocyclic ligands. Another factor which can be invoked to account for the enhanced stability of such complexes is the nephelauxetic effect (*d*-orbital expansion) produced by the large organic amine.[58,59]

Table 2 *Rates and activation parameters at* 298.1 K *for reactions* (6)—(11) (*ref.* 59)

Extrapolated constant	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$k_1 = (1.1 \pm 0.3) \times 10^{-10}$ s^{-1}	34.0±0.6	10±2
$k_2K_1 = (1.5 \pm 0.6) \times 10^{-9}$ mol l^{-1} s^{-1}	35±2	17±6
$k_3K_2 = (3.2 \pm 0.9) \times 10^{-12}$ mol l^{-1} s^{-1}	32±2	−5±5
$k_{-3}K_3 = 50 \pm 4^a$	4.4±1	39±4
$k_{-1} = 37 \pm 3^a$		

[a] At 353.1 K.

[58] A. A. El-Awady and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3627; A. A. El-Awady, *J.C.S. Dalton*, 1972, 1463.
[59] A. A. El-Awady, *J.C.S. Dalton*, 1974, 1264.
[60] F. P. Hinz and D. W. Margerum, *J. Amer. Chem. Soc.*, 1974, **96**, 4993; *Inorg. Chem.*, 1974, **13**, 2941.

As in previous volumes, the remainder of this section will be subdivided into parts dealing first with the $[Co(en)_2LX]^{2+}$ ions, then the $[CoL_4X_2]^{n+}$ complexes, and finally dioximato-complexes.

$[Co(en)_2LX]^{2+}$ *Complexes.* In complexes of this type L and X are unidentate ligands, L is a non-leaving group, and X, the leaving group, is often a halide ion. The *cis*-isomer usually aquates faster than the *trans*-isomer, and in general only the reaction of the former species proceeds with retention of configuration. Recent studies have concentrated upon *cis*-complexes of the type $[Co(en)_2(amine)X]^{2+}$, which all appear to aquate without stereochemical change, and these results are collected in Table 3.

Table 3 *Kinetic parameters for the aquation of complexes of the type* cis-$[Co(en)_2LX]^{2+}$

L	X	10^6k/s^{-1} (*temperature*/K)	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}	*Ref.*
Pr^nNH_2	Cl	29.1 (333.4)	102	−25	61
Bu^nNH_2	Cl	32.0 (333.4)	96	−45	61
n-$C_5H_{11}NH_2$	Cl	30.7 (333.4)	85	−77	61
n-$C_xH_{2x+1}NH_2$ (x = 6—12)	Cl	30.7—38.1 (333.4)	86	−71 to −73	61
$MeNHNH_2$	Cl	29.3 (333.2)	87	−70	62
$PhNH_2$	Cl		108	−6.3	63
PhNH	Cl		88	−47	63
m-$MeC_6H_4NH_2$	Cl	19.0 (324.0)	107		64
m-MeC_6H_4NH	Cl	11.2 (324.0)	85		64
n-$C_xH_{2x+1}NH_2$ (x = 1, 2, or 4)	Br		*ca.* 103	−17 to −22	65[a]
$PhNH_2$	Br		121		66[a]
py	Br		112		66[a]
NH_3	C_2O_4H	18.2 (343.1)	113	−2.4	67

[a] In aqueous organic solvents.

A study of the series of complex ions *cis*-$[Co(en)_2(n\text{-}C_xH_{2x+1}NH_2)Cl]^{2+}$ (x = 4—12) follows an earlier investigation of complexes of the type *cis*-$[Co(en)_2\{NH_2(CH_2)_n\text{-}OH\}Cl]^{2+}$ (n = 2—6).[61,68] As in previous experiments the variation in rate with increasing chain length of the non-leaving groups is only marginal, although there is a noticeable decrease in the enthalpy of activation as x increases from 3 to 6. This enthalpy decrease is compensated for by the change in $\Delta S^{\ddagger}$ so that the rate constants vary little. An explanation similar to that given for the results in Table 1 can be invoked.

A study of the reaction of *trans*-$[Co(en)_2Cl_2]^+$ with methylhydrazine in concentrated solutions has led to the synthesis of the *cis*-$[Co(en)_2(NH_2NHMe)Cl]^{2+}$ ion. An

[61] S. C. Chan and C.-K. Lee, *Z. anorg. Chem.*, 1974, **404**, 87.
[62] S. C. Chan and C.-K. Lee, *Austral. J. Chem.*, 1973, **26**, 1923.
[63] J. Zsakó, Cs. Várhelyi, and E. J. Maxim, *Rev. Chim. minérale*, 1973, **10**, 681.
[64] Cs. Várhelyi, J. Zsakó, and A. Ionut, *Monatsh*, 1973, **104**, 1231.
[65] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Zhur. neorg. Khim.*, 1973, **18**, 1590.
[66] V. V. Udovenko and L. G. Reiter, *Zhur. neorg. Khim.*, 1973, **18**, 2450.
[67] A. C. Dash and R. K. Nanda, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2071.
[68] S. C. Chan and O. W. Lau, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2361.

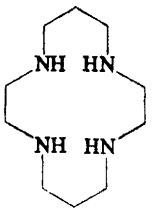
analogous study of the reaction of *trans*-$[Co(en)_2Cl_2]^+$ with hydrazine resulted in reduction to cobalt(II) species, whereas for reaction with 1,1-dimethylhydrazine disproportionation to the $[Co(en)_3]^{3+}$ ion is reported to occur.[62] When *cis*-$[Co(en)_2(NH_2NHMe)Cl]^{2+}$ is dissolved in aqueous solution, an intramolecular redox reaction occurs with the stoicheiometric formation of one mole of dinitrogen and one mole of methylamine. At 293.8 K a specific rate constant of 13.6×10^{-5} s^{-1} is reported for this redox process ($\Delta H^{\ddagger} = 50$ kJ mol^{-1}, $\Delta S^{\ddagger} = 149$ J K^{-1} mol^{-1}).[62] Acidification of the *cis*-$[Co(en)_2(NH_2NHMe)Cl]^{2+}$ ion with $HClO_4$ (>0.4 mol l^{-1}) prevents this redox process even though in 0.5 mol l^{-1} $[H^+]$ only 5% formation of *cis*-$[Co(en)_2(NH_2\overset{+}{N}H_2Me)Cl]^{3+}$ is observed.[62] The results obtained for the rate of chloride-ion release at $[H^+] = 0.5$ mol l^{-1} are shown in Table 3.

The complex ions *cis*-$[Co(en)_2LCl]^{2+}$ with L = aniline[63] or *m*-toluidine[64] have both been shown readily to lose a proton to form their respective conjugate bases (L = $PhNH^-$ or *m*-$MeC_6H_4NH^-$), and rate data for chloride-ion aquation are reported for all four species (Table 3). Above pH 3 significant concentrations of these conjugate bases are present since the equilibrium formation constants are *ca.* 10^{-3}. The enhanced reactivity of the conjugate bases is in line with the now well established S_N1cb mechanism for base hydrolysis.

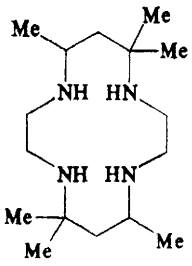
A study[67] of the acid-catalysed hydrolysis of the *cis*-$[Co(en)_2(NH_3)(C_2O_4H)]^{2+}$ ion in excess acid (0.02—1.0 mol l^{-1} $[H^+]$) led to the observed pseudo-first-order rate constant $k = (k_1 + k_2[H^+])/(1 + K_1/[H^+])$. At 343 K, the acid dissociation constant for the unidentate, monoprotonated oxalato-ligand is $K_1 = (3.0 \pm 0.5) \times 10^{-2}$ mol l^{-1}, and $k_2 = (31.4 \pm 2.2) \times 10^{-6}$ s^{-1} ($\Delta H^{\ddagger} = 24.0 \pm 1.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9.7 \pm 5$ cal K^{-1} mol^{-1}); rate parameters associated with k_1 are collected in Table 3. This reaction and reactions of analogous complexes are also catalysed by metal ions, and these will be discussed in the section concerned with catalysed aquations.

A study of the aquation of the *cis*-$[Co(en)_2LBr]^{2+}$ ion (L = py or $PhNH_2$) is reported to involve the slow loss of L following the more rapid aquation of the bromide ion.[66]

$[CoL_4X_2]^+$ *Complexes.* Included in this section are those studies in which $L_4 = (NH_3)_4$ and open-chain or cyclic quadridentate amines such as trien ($NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$) and cyclam (1). For convenience the multidentate ligands will be referred to by their trivial names and some of their structures are summarized here [(1)—(6)]. A review dealing with complexes of the tripodal amine ligands [*e.g.* tren, $N(CH_2CH_2NH_2)_3$], including those of cobalt(III), was referred to



(1)



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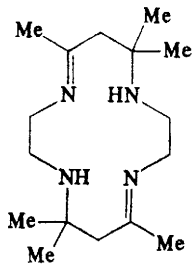
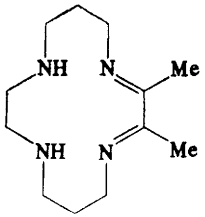


(3)



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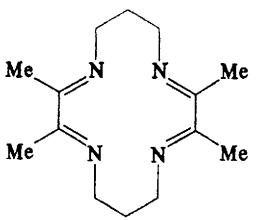
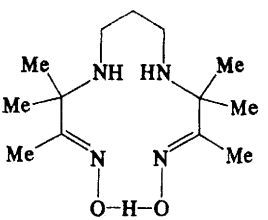


(5)



(6)

earlier.[36] A study of the acid hydrolysis of carbonate complexes of the type α-*cis*- and β-*cis*-$[Co(L)CO_3]^+$ [L = edda[69] or $NH_2CH_2CH_2N(Me)CH_2CH_2N(Me)CH_2CH_2NH_2$ (dmtr)[70]] follows the expected rate law (12):

$$-d[Co(L)(CO_3)^+]/dt = \{k_0 + k_1[H^+]\}[Co(L)(CO_3)^+] \quad (12)$$

Rate data associated with the two rate constants k_0 and k_1 are collected in Table 4.

Table 4 *Rate data at* 298.1 K [μ = 1.0 mol l^{-1} (ClO_4^-)] *for the acid hydrolysis of* α-cis- *and* β-cis-$[Co(L)CO_3]^+$ (*from refs.* 69 *and* 70)

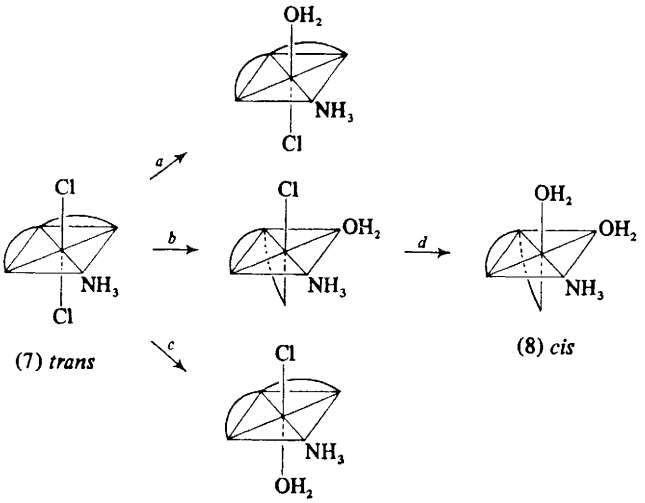
Isomer	L	10^5k_0/ s^{-1}	$\Delta H^{\ddagger}(k_0)$/ kJ mol^{-1}	$\Delta S^{\ddagger}(k_0)$/ J K^{-1} mol^{-1}	k_1/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}(k_1)$/ kJ mol^{-1}	$\Delta S^{\ddagger}(k_1)$/ J K^{-1} mol^{-1}
α-*cis*	edda[a]	217	87±13	0±50	82.6	69±4	23±13
β-*cis*	edda	38.0	89±13	10±50	3.04	73±4	10±13
α-*cis*	dmtr[b]	102			1.8×10^{-2}		
β-*cis*	dmtr	3.6			5.6×10^{-4}		

[a] edda = $[O_2CCH_2NHCH_2CH_2NHCH_2CO_2]^{2-}$.
[b] dmtr = $NH_2CH_2CH_2N(Me)CH_2CH_2N(Me)CH_2CH_2NH_2$.

The results reported for L = dmtr[70] extend a previously reported correlation[71] between the values of k_1 and the 'average pK_a' of the amine ligands (L). As the average basicity of related amines (L) increases, so the cobalt–oxygen bond is strengthened and values of k_1 decrease. The rate constants reported for the complexes of edda are more than ten times as great as those observed for analogous trien and dmtr complexes, the rate difference arising from more favourable entropies of activation. This rate difference is interpreted in terms of charge and solvation effects.[69] The question of whether these reactions proceed by Co—O or C—O bond fission has not been resolved by tracer studies, but a comparison of the values of k_0 for the dmtr complexes in Table 4 with those of earlier studies leads to the conclusion that a switch in mechanism has occurred from Co—O bond rupture in the earlier examples[71] to C—O bond fission in the present cases.[70] The difference in reactivity between the α- and β-isomers parallels analogous studies of trien and tren complexes and can be attributed to the greater carbonate ring strain imposed by the conformations of the amine chelate rings in the *trans* position to the carbonate ring.[70]

[69] P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, 1974, **8**, 313, 307.
[70] D. J. Francis and G. H. Searle, *Austral. J. Chem.*, 1974, **27**, 269.
[71] D. J. Francis and R. B. Jordan, *Inorg. Chem.*, 1972, **11**, 461.

A study of the kinetics and steric course of the acid hydrolysis of *mer*- or *trans*-$[Co(dien)(NH_3)Cl_2]^+$ (7) (dien = $NH_2CH_2CH_2NHCH_2CH_2NH_2$) indicates the stereochemical scheme shown in Scheme 1.[72] At 298.1 K in 0.3M-H^+, the composite



Scheme 1

rate parameters for release of chloride ion from pathways *a*, *b*, and *c* are reported to be: $10^4k = 5.21\ s^{-1}$, $\Delta H^{\ddagger} = 96.7\ kJ\ mol^{-1}$, and $\Delta S^{\ddagger} = +7.9\ J\ K^{-1}\ mol^{-1}$ This reaction is estimated to proceed with $(50 \pm 10)\%$ stereochemical change. Release of the second chloride ion from the *cis*-isomer (pathway *d*) in 1M-HNO_3 at 298.1 K is characterized by $10^5k = 7.89 \pm 0.28\ s^{-1}$, $\Delta H^{\ddagger} = 96.3 \pm 2.1\ kJ\ mol^{-1}$, and $\Delta S^{\ddagger} = -8.2 \pm 4.2\ J\ K^{-1}\ mol^{-1}$. The same product (*cis*-diaqua-complex[8]) is obtained by isomerization of the *trans*-isomer in acidic solution. At 298.1 K the half-life for this isomerization process is *ca.* 30 min. *trans*-$[Co(dien)(NH_3)(H_2O)_2]^{3+}$ [stereochemistry the same as in (7)] is obtained by base hydrolysis of (7) followed by acidification.[72]

The apparently abnormal behaviour of the *trans*-$[Co(cyclam)(NH_3)Cl]^{2+}$ ion, which was previously reported[73] to be hydrolysed in acid with loss of ammonia rather than chloride ion, has now been reinvestigated.[74] The rate of loss of chloride ion ($k = 7.3 \times 10^{-8}\ s^{-1}$ at 298.1 K) was measured by adding thiocyanate ion to give *trans*-$[Co(cyclam)(NH_3)(NCS)]^{2+}$, and this rate was found to be much greater than the rate of loss of the co-ordinated ammonia ($k = 4.2 \times 10^{-11}\ s^{-1}$). However, the equilibrium constant for reaction (13) is $2 \times 10^{-4}\ mol\ l^{-1}$ at 344.6 K, and so

$$trans\text{-}[Co(cyclam)(NH_3)Cl]^{2+} + H_2O \rightleftharpoons trans\text{-}[Co(cyclam)(NH_3)(OH_2)]^{3+} + Cl^- \quad (13)$$

although the rate of loss of chloride ion is greater than the rate of loss of ammonia, the former reaction is thermodynamically unfavoured.

[72] M. C. Couldwell and D. A. House, *Inorg. Chem.*, 1974, **12**, 2949.
[73] K. S. Mok and C.-K. Poon, *Chem. Comm.*, 1971, 1358.
[74] W.-K. Lee and C.-K. Poon, *Inorg. Chem.*, 1973, **12**, 2016.

More data have appeared (Tables 5 and 6) for the kinetics of the acid and base hydrolyses of other complexes of the type *trans*-$[CoL_4XY]^{n+}$ in which it is possible to

Table 5 *References to studies of the aquation of complex ions of the type* trans-$[Co(L_4)AX]^{n+}$ (X = *leaving ion*)

L_4	A	X	*Ref.*
cyclam (1)	NH_3	Cl	73, 74
cyclam	N_3, NCS	Cl	75, 76
$(NH_3)_4$	N_3	Cl	75, 76
cyclam	CN	Br	75
$(NH_3)_4$	CN	Br	75
tet-*b* (2)	NO_2, N_3, NCS, CN	Cl	76, 81
edda	Cl, H_2O	Cl	77
edda, dmtr[a]	H_2O	CO_3	Table 4
ete[b]	Cl	Cl	78
(3)	N_3, NCS	Cl, Br	81
(4)	Cl, Br, NH_3	Cl, Br, NH_3	82
(5)	Cl, Br, NH_3	Cl, Br, NH_3	82
(6)	NO_2	NO_2	83

[a] See Table 4 for definition of these ligands. [b] ete = $NH_2CH_2CH_2S(CH_2)_3SCH_2CH_2NH_2$.

Table 6 *Comparison of rate constants* (k_X) *at* 298.1 K (*unless specified*) *for the aquation of the* trans-$[Co(L)(A)X]^{n+}$ *ions* (*data from refs.* 76, 81, *and* 82)

L	A	k_{Cl}/s^{-1}	k_{Br}/s^{-1}	k_{NH_3}/s^{-1} [a]	k_{Br}/k_{Cl}
(1)	Cl	1.1×10^{-6}		4.2×10^{-11} [b]	
	Br		2.2×10^{-5}		
	NCS	1.1×10^{-9}			
	NO_2	4.3×10^{-5}			
	N_3	3.6×10^{-6}			
	CN	4.8×10^{-7}			
	NH_3	7.3×10^{-8} [b]			
(2)	Cl	9.3×10^{-4}			
	Br		3.8×10^{-2}		
	NCS	7.0×10^{-7}	6.1×10^{-6}		8.7
	NO_2	4.1×10^{-2}			
	N_3	6.5×10^{-3}	7.1×10^{-2}		10.9
	CN	3.4×10^{-4}			
	NH_3			5×10^{-6}	
(3)	Cl	3.6×10^{-2}			
	Br		5.1×10^{-2}		
	NCS	1.4×10^{-6}	3.0×10^{-6}		2.1
	N_3	2.1×10^{-2}	5.5×10^{-2}		2.6
	NH_3			3×10^{-6}	
(4)	Cl	2.3×10^{-4}			
	Br		7.8×10^{-2}		
	NH_3			*ca.* 9×10^{-7}	
(5)	Cl	2.1×10^{-3}			
	Br		0.12		
	NH_3			8×10^{-7}	
$(dmgH^-)_2$ [d]	Cl	2.7×10^{-4}			
	Br		3.8×10^{-4}		
	I	6.0×10^{-5}	7.2×10^{-5}		1.2[c]
	NO_2	1.0×10^{-4}	1.2×10^{-4}		1.2[c]

[a] At 341.6 K. [b] Ref. 74. [c] k_I/k_{Br} = 0.059. [d] Dimethylglyoximate ion.

assess the effect of changing L_4 along the series $(NH_3)_4$, $(en)_2$, and cyclam.[74–76] In general the rates of acid hydrolysis decrease, and the rates of base hydrolysis increase along the series. This variation correlates with the nephelauxetic effect (*d*-orbital expansion) at the cobalt(III) ion which is more pronounced for a cyclic amine such as cyclam.[74–76] The larger organic amine ligands are also expected to affect the hydrolysis rates by having a marked influence upon the complex-ion solvation shell as discussed previously.[58–60] Another factor which has a considerable effect upon the rates of these reactions is clearly demonstrated by comparing the results for the *trans*-$[Co(L)ACl]^+$ ions where L = cyclam (1) or tet-*b* (2) and A = N_3, NCS, NO_2, or CN.[76] At 298 K the complexes of tet-*b* aquate at a rate *ca.* 10^3 times as great as the analogous cyclam complexes (Table 6) and this can be attributed to steric acceleration in the very crowded complexes of tet-*b*. The electronic influence of the nonlabile *trans*-ligand A is independent of this steric effect as shown by a linear Hammett plot with unit gradient (over 5 decades) of the two sets of results for L = (1) and (2) in Table 6.[76] Charge has surprisingly little effect upon the rates of aquation of the anionic complexes *α-cis-* and *β-cis*-$[Co(edda)Cl_2]^-$, which are observed to aquate (with the stepwise loss of both chloride ions) at rates very similar to those of the analogous $[Co(trien)Cl_2]^+$ ions.[77] The aquation of the intermediate [Co(edda)-(OH_2)Cl] complexes is subject to the usual base catalysis at intermediate pH's owing to the ready formation of the $[Co(edda)(OH)Cl]^-$ ion.

An interesting comparison has been made between the rates of the spontaneous and mercury(II)- and base-catalysed aquations of the *trans*-$[Co(ete)Cl_2]^+$ and *trans*-$[Co(2,3,2\text{-tet})Cl_2]^+$ ions.[78] The quadridentate ligand ete $[NH_2CH_2CH_2S(CH_2)_3SCH_2CH_2NH_2]$ has a geometry corresponding to that of 2,3,2-tet except that sulphur atoms replace the NH groups of the latter. Only one isomer of $[Co(ete)Cl_2]^+$ has so far been synthesized and this is tentatively assigned the *trans*-(*RS*)-configuration. It may be that inversion at sulphur can occur in the complex without the need for bond rupture and this would account for the isolation of only one isomer.[78] Spontaneous aquation of this complex occurs with 100% isomerization to the *cis*-$[Co(ete)(OH_2)Cl]^{2+}$ ion, and the rate parameters (at 298.1 K, 10^6k = 4.1 s^{-1}, $\Delta H^{\ddagger}$ = 26.1 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = +4 cal K^{-1} mol^{-1}) are not very different from those reported for the first step in the aquation of the *trans*-$[Co(2,3,2\text{-tet})Cl_2]^+$ ion. The mechanism of this isomerization could not be unequivocally established since *trans*-$[Co(ete)(OH_2)Cl]^{2+}$ (generated by acidifying the first product of base hydrolysis) isomerizes to the *cis*-isomer at a much greater rate than that of the hydrolysis of *trans*-$[Co(ete)Cl_2]^+$. {For the isomerization of *trans*-$[Co(ete)(OH_2)Cl]^{2+}$, 10^4k = 1.12 s^{-1} at 293.6 K, $\Delta H^{\ddagger}$ = 23.0 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = +1 cal K^{-1} mol^{-1}.} The faster mercury(II)-catalysed aquation of *trans*-$[Co(ete)Cl_2]^+$ proceeds with retention of configuration as expected. Base hydrolysis is significantly slower than for the corresponding 2,3,2-tet complex, in line with the absence of the secondary amine groups which are known to be primarily involved in conjugate-base formation from the $[Co(2,3,2\text{-tet})Cl_2]^+$ ion.

[75] C.-K. Poon and H.-W. Tong, *J.C.S. Dalton*, 1974, 1.
[76] W.-K. Chau, W.-K. Lee, and C.-K. Poon, *J.C.S. Dalton*, 1974, 2419.
[77] P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, 1974, **8**, 307.
[78] M. L. Tobe and M. L. Tucker, *Inorg. Chem.*, 1974, **12**, 2994.

Although only the *trans*-isomer of $[Co(ete)Cl_2]^+$ has been synthesized[78,79] an analogous study of complexes of the quadridentate arsenic ligand tetars $\{[Me_2As(CH_2)_3As(Ph)CH_2]_2\}$ has led to the synthesis and characterization of the *α-cis-*, *β-cis-*, and *trans*-$[Co(tetars)Cl_2]^+$ ions of racemic tetars.[80] Their topological equilibria were investigated and a rate constant (at 292.5 K, $10^4k = 1.05\ s^{-1}$) was reported for the *β-cis-* to *trans*-complex rearrangement in anhydrous methanol. These reactions are apparently not catalysed by redox processes as are those of many other arsenic–cobalt(III) species, and very little solvolysis occurs. A hitherto unknown method of inverting co-ordinated arsenic atoms is reported.[80]

Recently a number of studies have appeared for systems of the type $[Co(L)(A)X]^{n+}$ in which L is a cyclic quadridentate amine ligand [*e.g.* (3)—(6)] in which the degree of unsaturation varies. These systems are intermediate between those of saturated cyclic amines already discussed [*e.g.* L = (1) or (2), Table 5] and the dioximato-complexes which appear in the next part of this section. They are especially interesting since it is known that cobalt(III) complexes of saturated amines such as (1) and (2) show class (*a*) or 'hard' behaviour [*e.g.* for analogous complexes the rate of aquation of Cl^- (k_{Cl}) is lower than for Br^- (k_{Br})], whereas cobaloximes are examples of class (*b*) or 'soft' metal complexes (*e.g.* $k_{Br}/k_{Cl} = 1.2$ and $k_I/k_{Br} = 0.059$; see Table 6). In those complex ions of the type *trans*-$[Co(L)(A)X]^+$ which do not contain methyl groups of L in close proximity to the axial ligand (X) there is a marked increase in axial ligand lability with increasing unsaturation of the cyclic amine (L). An increase in rate of the order of 10^3—10^4 seems characteristic of replacing a cyclic tetra-amine (1) with a tetraimine (5).[82] The increase in lability is of the same magnitude irrespective of the *trans* effect of the ligand A.[81] When methyl groups are constrained to be near to the axial ligand (X) there is a further substantial increase in lability for the imine complexes[82] as well as the amine complexes discussed earlier.[76] The complexes of the tetraimine (5) are more labile than their dimethylglyoxime analogues and comparable in reactivity to the very labile cobalt(III) porphyrins.[83,84] $[Co(L)X_2]^+$ ions [L = (5)] are also more stable when X = Br than when X = Cl, and this increased 'soft' character is further supported by the synthesis of a stable complex when X = I.[82] The analogous iodo-complexes when L is a saturated amine are unstable because of the ready oxidation of the iodide ion by the cobalt(III) amine.

A crystal structure is reported for $[Co(L)(NO_2)_2]$ [L = (6)] in which the nitro-groups are shown to be at different distances from the cobalt(III) ion.[85] The cobalt(III) ion is slightly displaced out of the plane of the di-imine ligand and the two Co—NO_2 bond distances are 198.4 and 193.7 pm. This ground-state difference is reflected in the kinetic non-equivalence of the ligands X in *trans*-$[Co(L)X_2]$ [L = (6); X = NO_2, N_3, or Cl].[86] These reactions, which proceed by a *D* mechanism, are discussed further in the sections dealing with formation reactions and ligand exchange.

[79] B. Bosnich, W. R. Keen, and A. T. Phillip, *Inorg. Chem.*, 1969, **8**, 2567.
[80] B. Bosnich, W. G. Jackson, and S. B. Wild, *J. Amer. Chem. Soc.*, 1973, **95**, 8269.
[81] W.-K. Lee and C.-K. Poon, *J.C.S. Dalton*, 1974, 2423.
[82] R. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Amer. Chem. Soc.*, 1973, **95**, 6987.
[83] R. F. Pasternack and M. A. Cobb, *J. Inorg. Nuclear Chem.*, 1973, **35**, 4327.
[84] R. F. Pasternack and M. A. Cobb, *Biochem. Biophys. Res. Comm.*, 1973, **51**, 507.
[85] R. K. Murmann and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 2625.
[86] H. Goff, S. Kidwell, J. Lauher, and R. K. Murmann, *Inorg. Chem.*, 1973, **12**, 2631.

Dioximato-complexes. Studies of dioximato-complexes continue to be extensive probably because of their close similarity to the cobalamins and vitamin B_{12}. Dissociative (often *D*) mechanisms are most commonly observed for the aquation reactions as well as for formations and for ligand exchange. Since these reactions are so similar most of the results will be collected together in this section. References to kinetic studies of aquation,[21,87–92] ligand-exchange, and anation reactions[93–98] of neutral and anionic complexes of the type *trans*-[Co(dioxime)$_2$AX] {dioxime = [HON=C(R^1)C(R^2)=NO]$^-$ where R^1 and R^2 are alkyl groups} are collected in Table 7.

The class (*b*) or 'soft' character of dimethylglyoxime complexes is illustrated by aquation studies of *trans*-H[Co(dmgH)$_2$(N$_3$)X] (X = Cl, Br, or I). These reactions are reported to be independent of pH in the range pH = 1—5. At 308.1 K, 10^5k/s^{-1} = 60.1, 28.8, and 0.73, $\Delta H^{\ddagger}$/kcal mol^{-1} = 25.5, 26.3, and 27.2, and $\Delta S^{\ddagger}$/cal K^{-1} mol^{-1} = 9.3, 10.5, and 6.3 for X = Cl, Br, and I respectively.[87] For *trans*-[Co(dioxime)$_2$X$_2$]$^-$ ions (X = Cl or Br) increasing the size of the substituent alkyl groups on the dioxime backbone has only a small effect upon the aquation of X,[88,90] but increasing [H$^+$] is reported to reduce the rate of reaction owing to protonation of the anionic complex.[88] Dissociative mechanisms are proposed on the basis of solvent effects for a number of systems.[90–92] Sulphite ion has been investigated as a *trans*-labilizing group in *trans*-[Co(dmgH)$_2$(SO$_3$)L]$^-$ (L = amines), and for L = pyridines the order of reactivity is py > 3-Me- > 2-Me- > 4-Me-py as expected on the basis of their pK_a's.[21]

A *D* mechanism has been firmly established for the anation by Br$^-$, NCS$^-$, and NCO$^-$ of *trans*-[Co(dmgH)$_2$A(DMSO)] (A = NO$_2$ or Me).[93] The reactions were studied in DMSO and rates were in agreement with the solvent-exchange rate established by ^{1}H n.m.r. measurements. The marked *trans* effect of the methyl group is shown by the much higher rates when A = Me compared with those when A = NO$_2$. Other alkyl groups are known to have a large *trans*-labilizing influence. For example, reactions (14) (M = Fe^{II}, Co^{III}, Fe^{III}, or Cr^{III}) are sufficiently rapid for the stopped-flow method to be needed. For reaction (14) a *D* mechanism was not observed in all cases; instead an outer-sphere association followed by a rate-determining loss of H$_2$O occurs.[94] This study is analogous to the recently reported

$$[Co(dmgH)_2(Et)OH_2] + [M(CN)_6]^{n-} \longrightarrow [(Et)(dmg)_2CoNCM(CN)_5]^{n-} + H_2O \quad (14)$$

results[18] for the reaction between *trans*-[Co(en)$_2$(SO$_3$)OH$_2$]$^+$ and [M(CN)$_6$]$^{n-}$ or [Fe(CN)$_5$NO]$^{2-}$, where a *D* mechanism is again not certain. A comparison of the *trans* effect of different alkyl groups (R) has been made in *trans*-[RCo(dmgH)$_2$-

[87] Z. Finta and Cs. Várhelyi, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2199.
[88] Cs. Várhelyi, Z. Finta, A. Benko, and A. Binder, *Monatsh.*, 1974, **105**, 490.
[89] V. R. Vijayaraghavan and M. Santappa, *J. Inorg. Nuclear Chem.*, 1974, **36**, 163.
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[91] N. M. Samus, A. V. Ablov, and G. A. Konunova, *Zhur. neorg. Khim.*, 1973, **18**, 2651.
[92] A. V. Ablov, A. A. Popova, and N. M. Samus, *Zhur. neorg. Khim.*, 1973, **18**, 1994.
[93] S. T. D. Lo and D. W. Watts, *Inorg. Chim. Acta*, 1974, **9**, 217, 221.
[94] J. H. Espenson and R. Russell, *Inorg. Chem.*, 1974, **13**, 7.
[95] W. C. Trogler, R. C. Stewart, and L. G. Marzilli, *J. Amer. Chem. Soc.*, 1974, **96**, 3697.
[96] R. J. Guschl, R. S. Stewart, and T. L. Brown, *Inorg. Chem.*, 1974, **13**, 417.
[97] B. A. Bovykin, *Zhur. neorg. Khim.*, 1973, **18**, 3006; 1974, **19**, 778.
[98] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1974, **19**, 421.

Table 7 *Kinetic studies of aquation and formation of neutral and anionic dioximato-complexes,* trans-$[Co(dioxime)_2AX]$ (dioxime = $[HON{=}C(R^1)C(R^2){=}NO]^-$; A *is the non-leaving group*)

R^1	R^2	A	X	*Conditions/remarks*	*Ref.*
Me	Me	N_3	Cl, Br, I	Independent of pH in the range pH 1—5; $\Delta H^{\ddagger}$ = 25.5, 26.3, and 27.2 kcal mol^{-1} for X = Cl, Br, and I respectively	87
Me	Pr^i	Cl, Br	Cl, Br	Rate decreases with increasing $[H^+]$; pH 4—5; μ = 0.1 mol l^{-1}	88
Me	Me	py, 4-Me-py	Cl, Br	$8 < pH < 13$; μ = 0.1 mol l^{-1}; aqueous organic solvents	89
Me	Me, Et, Pr^n, Bu^n	Cl, H_2O	Cl	Rate decreases as size of R^2 increases (dichloro-complexes)	90
Me	Me	amines	Cl, Br	45—70 °C; pH 4; μ = 0.1 mol l^{-1}; $\Delta H^{\ddagger}$ 90—124 kJ mol^{-1}; rates increase with increase in pH (pH 3—6.5)	91
Me	Me	NCO	Cl, Br	20—40 °C; μ = 1.0 mol l^{-1}; pH 5.5—6.5; aqueous organic solvents	92
Me	Me	SO_3	py, 2-Me-, 3-Me-, 4-Me-py	Rates increase in the order py > 2-Me- > 3-Me- > 4-Me-py	21
Me	Me	NO_2, Me	DMSO	Anation by Br^-, NCS^- (A = NO_2) and Br^-, NCS^-, NCO^- (A = Me); *D* mechanism	93
Me	Me	Et	H_2O	Anation by $[M(CN)_6]^{n-}$ ($M = Fe^{II}$, Co^{III}, Fe^{III}, Cr^{III}); not always by a *D* mechanism	94
Me	Me	RR′PO (R, R′ = MeO or Ph)	neutral N- or P-donor	*D* Mechanism	95
Me	Me	alkyls (see text)	$P(OMe)_3$	Solvents of different dielectric constant (*e.g.* PhMe, $PhNO_2$); high temperatures (≥ 100 °C)	96
Me	Me	NO_2	tu	Aqueous–organic solvents	97
Me	Me	tu	NCS	$\Delta H^{\ddagger}$ 17—18 kcal mol^{-1} in various solvents	98

$P(OMe)_3$].[96] At 383 K the relative rates of loss of the ligand $P(OMe)_3$ decrease by a factor of *ca.* 200 with changes in R in the order $CH_2SiMe_3 > Me > CH_2F > CHF_2 > CH_2Cl > CF_3 \approx CH_2Cl_2 \approx CH_2Br > CHBr_2$. Variations in the dielectric constant of the solvent in going from toluene to nitrobenzene affect the rate by a factor of *ca.* 2, but deuteriation of the O—H—O bridges in the planar dimethylglyoxime ligands has no observable rate effect. Ligands of the type RR'PO (R and R' are MeO or Ph) are also observed to have quite a substantial *trans* effect in cobaloximes of the type *trans*-[(RR'PO)Co(dmgH)$_2$L] (L = neutral N- or P-donor ligand).[95] A *D* mechanism is again observed, and competition ratios for ligands attacking the five-co-ordinate intermediate (formed by loss of L) are close to unity in most cases.

Studies of substitution reactions of *trans*-[Co(dmgH)$_2$(tu)X] (X = NO_2 or SCN) have been made which show that reaction with thiourea when X = SCN leads to the loss of thiocyanate ion, whereas when X = NO_2 it is the co-ordinated thiourea which is more readily displaced.[97,98] The formation of *trans*-[Co(dmgH)$_2$(tu)$_2$]$^+$ from *trans*-[Co(dmgH)(tu)SCN] and thiourea is characterized by $\Delta H^{\ddagger} = 17.3$—18.0 kcal mol^{-1} and $\Delta S^{\ddagger} = -24$ to -18 cal K^{-1} mol^{-1} in a range of aqueous–organic solvents.

Bridged Dicobalt Complexes.—A study of the acid-catalysed bridge cleavage of the doubly bridged $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(NH_3)_4]^{4+}$ ion (9) in the presence of bromide ion is postulated to involve the intermediate formation of a singly bridged species $[(H_2O)(NH_3)_4Co\text{-}\mu\text{-}(OH)\text{-}Co(NH_3)_4Br]^{4+}$ (10), which then anates and finally ring closes again to give the doubly bridged ion $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,Br)\text{-}Co(NH_3)_4]^{4+}$ (11).[99]

$$\underset{(9)}{[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(NH_3)_4]^{4+}} + H^+ + Br^- \overset{K_A}{\rightleftharpoons} \underset{(10)}{[(H_2O)(NH_3)_4Co\text{-}\mu\text{-}(NH_2)\text{-}Co(NH_3)_4Br]^{4+}}$$

$$\underset{(10)}{[(H_2O)(NH\ )_4\text{-}Co\text{-}\mu\text{-}(NH_2)\text{-}Co(NH_3)_4Br]^{4+}} \overset{K_B}{\rightleftharpoons} \underset{(11)}{[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,Br)\text{-}Co(NH_3)_4]^{4+}}$$

In the presence of excess H^+ and Br^- ions, pseudo-first-order rate constants (k) for the equilibration of (9) and (11) are given by

$$k = k_1[H^+][Br^-] + k_2[Br^-] + k_b \qquad (15)$$

In equation (15) k_1 and k_2 are rate constants for the cleavage of the hydroxo-bridged species (9) with and without acid catalysis respectively, and k_b is the rate constant for the back reaction. At 298.1 K, $10^4k_1 = 4.33 \pm 0.17$ l^2 mol^{-2} s^{-1}, $\Delta H^{\ddagger}(k_1) = 17.3 \pm 0.8$ kcal mol^{-1}, and $\Delta S^{\ddagger}(k_1) = 16.2 \pm 2.6$ cal K^{-1} mol^{-1}; $10^4k_2 = 1.4 \pm 0.2$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger}(k_2) = 25.7 \pm 1.8$ kcal mol^{-1}, and $\Delta S^{\ddagger}(k_2) = 10.8 \pm 5.7$ cal K^{-1} mol^{-1}, and the product of the equilibrium constants, K_AK_B, is *ca.* 1.1 l^2 mol^{-2}. At bromide concentrations above 1.7 mol l^{-1} a further reaction occurs to give the $[Br(NH_3)_4Co\text{-}\mu\text{-}(NH_2)\text{-}Co(NH_3)_4Br]^{3+}$ ion, probably by bromide-ion anation of the intermediate (10). At 298.1 K, the equilibrium constant associated with the formation of this ion is *ca.* 0.03 l mol^{-1}, and the rate constant for its dissociation at 274.6 K is greater than 2×10^{-2} s^{-1} [μ = 2.0 mol l^{-1} ($NaClO_4$)].[99]

[99] S.-W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1974, 1453.

This study is typical of several hydroxo-bridge cleavage reactions made in recent years in the presence of co-ordinating anions (X^{n-}) for which the rate equation (15) applies. In a recent communication[100] values of k_1 [equation (15), $Br^- = X^{n-}$] and associated activation parameters have been summarized for various anions (X^{n-}) and these results are collected in Table 8. Although these data are believed to refer to

Table 8 *Kinetic parameters*[a] *at* 298.1 K *for hydroxo-bridge cleavage reactions of the* $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(NH_3)_4]^{4+}$ *ion* (μ = 2.0 mol l^{-1})

X^{n-}	$10^4k_1/l^2$ mol^{-2} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
SeO_4^{2-}	130	18.2±0.3	−6.3±0.9
SO_4^{2-}	215	17.7±0.05	−6.6±0.15
$H_2PO_4^-$	11.8	19.5±0.7	−6.5±2.3
$HSeO_4^-$	*ca.* 2		
HSO_4^-	1.5	17.9±0.25	−16.1±0.8
Br^-	4.3	17.3±0.8	−16.2±2.6
Cl^-	9.6	16.2±0.5	−18.1±1.8
NO_3^-	4.2	13.7±0.6	−28.4±2.0
NCS^-	4.8	17.5±0.4	−14.7±1.4
H_3PO_4	0.85	14.3±0.8	−29.2±2.8
HOAc	0.065	14.3±0.6	−34.4±1.9
H_2O	0.79[b]	12.5±1.1	−35.3±3.6

[a] Data from Ref. 100. [b] Units are l mol^{-1} s^{-1}.

the formation of a species of type (10) (Br = X), the final product is never of this type but always involves further substitution of the aqua-ligand by the co-ordinating anion X^{n-}. At an ionic strength of 2 mol l^{-1}, the equilibrium constant for the protonation of (9) is less than 0.07 l mol^{-1} at 298.1 K and, as can be seen from the data in Table 8, values of k_1 vary with the charge on the anion X^{n-}. At 298 K, values of $10^4k_1/l^2$ mol^{-2} s^{-1} are in the ranges 130—215, 1.5—11.8, and 0.06—0.90 for n = 2, 1, and 0 respectively. An S_N2 mechanism can be ruled out for these reactions since the ratio of the rate constants for the substitution by thiocyanate and chloride ions, k_{NCS}/k_{Cl}, is 0.5. This ratio should be compared with much larger values of k_{NCS}/k_{Cl} for the anation of other ions where S_N2 mechanisms are now thought to apply (see introduction and reference 12). Thus, for anations of $[M(H_2O)_6]^{3+}$ ions values of k_{NCS}/k_{Cl} are 60 (M = Cr), >36 (M = V), and 59 (M = Mo). For the bridged dicobalt complexes an S_N1 mechanism is believed to apply in accord with other substitutions at cobalt(III).

A further study of the acid-catalysed cleavage of the singly bridged dicobalt(III) ion $[(NH_3)_5Co\text{-}\mu\text{-}(OH)\text{-}Co(NH_3)_5]^{3+}$ has been made[101] in an attempt to find evidence for the elusive five-co-ordinate intermediate ion $[Co(NH_3)_5]^{3+}$. The reaction was investigated as a function of $[H^+]$ (10^{-4}—1.0 mol l^{-1}) and added anion concentration ($[Y^-]$, Y = Cl or $MeSO_3$), and the observed rate constant (k) was fitted to an equation of the type

$$k = (k_0 + k_1[H^+] + k_2[H^+][Y^-] + k_3[H^+][Y^-]^2)(1 + K_Y[Y^-])^{-1} \quad (16)$$

Equation (16) is interpreted as involving ion aggregation as well as protonation of the

[100] R. S. Taylor and A. G. Sykes, *Inorg. Chem.*, 1974, **13**, 2524.
[101] D. A. Buckingham, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, 1974, **13**, 2165.

hydroxo-bridge, and although the rate data and results of competition studies are consistent with a dissociative mechanism, the ion-pairing hinders further interpretation.[101]

Two studies have appeared dealing with the kinetics of hydroxo-bridge-cleavage reactions of triply bridged complex ions of the type $[(N_3)Co\text{-}\mu\text{-}(OH)_3\text{-}Co(N_3)]^{3+}$ [(N_3) = $(NH_3)_3$, dien, or *cis,cis*-1,3,5-triaminocyclohexane][102,103] and $[(NH_3)_3Co\text{-}\mu\text{-}\{NH_2,(OH)_2\}\text{-}Co(NH_3)_3]^{3+}$. Some of the constants obtained for reactions (17)—(21) at an ionic strength of 1.0 mol l^{-1} (ClO_4^- medium) and 298.1 K are shown in

$$[(N_3)Co\text{-}\mu\text{-}(OH)_3\text{-}Co(N_3)]^{3+} + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(N_3)Co\text{-}\mu\text{-}\{H_2O,(OH)_2\}\text{-}Co(N_3)]^{4+} \quad (17)$$

$$[(N_3)Co\text{-}\mu\text{-}\{H_2O,(OH)_2\}\text{-}Co(N_3)]^{4+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(H_2O)(N_3)Co\text{-}\mu\text{-}(OH)_2\text{-}Co(N_3)(OH_2)]^{4+} \quad (18)$$

$$[(H_2O)(N_3)Co\text{-}\mu\text{-}(OH)_2\text{-}Co(N_3)(OH_2)]^{4+} + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [(H_2O)_2(N_3)Co\text{-}\mu\text{-}(OH)\text{-}Co(N_3)(OH_2)_2]^{5+} \quad (19)$$

$$[(H_2O)_2(N_3)Co\text{-}\mu\text{-}(OH)\text{-}Co(N_3)(OH_2)_2]^{5+} \overset{K}{\rightleftharpoons} H^+ + [(H_2O)(HO)(N_3)Co\text{-}\mu\text{-}(OH)\text{-}Co(N_3)(OH_2)_2]^{4+} \quad (20)$$

$$[(H_2O)(HO)(N_3)Co\text{-}\mu\text{-}(OH)\text{-}Co(N_3)(OH_2)_2]^{4+} \underset{(2H^+)}{\overset{k_4}{\rightleftharpoons}} 2[(N_3)Co(OH_2)_3]^{3+} \quad (21)$$

Table 9. The results obtained by the two research groups[102,103] for first bridge-cleavage reactions of the $[(NH_3)_3Co\text{-}\mu\text{-}(OH)_3\text{-}Co(NH_3)_3]^{3+}$ ion are in reasonable agreement, and the observed rate constant (k) in excess [H^+] (0.01—0.5 mol l^{-1}) for reactions (17) and (18) is given[103] by $k = \{(k_2k_1/k_{-1})[H^+]/(1 + k_1/k_{-1}[H^+])\} + k_{-2}$. The equilibrium constant for protonation of the complex [reaction (17)] is[103]

Table 9 *Rate data at* 293.1 K *(unless specified otherwise) and ionic strength* 1.0 mol l^{-1} (ClO_4^- *medium) for acid hydrolysis of* $[(N_3)Co\text{-}\mu\text{-}(OH)_3\text{-}Co(N_3)]^{3+}$ *and* $[(NH_3)_3Co\text{-}\mu\text{-}\{NH_2,(OH)_2\}\text{-}Co(NH_3)_3]^{3+}$ *ions [reactions* (17)—(21)]

$[(N_3)Co\text{-}\mu\text{-}(OH)_3\text{-}Co(N_3)]^{3+}$ (N_3)	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	pK_1 [a]	k_2/s^{-1}	10^3k_{-2}/s^{-1}	10^5k_3/ l mol^{-1} s^{-1}	$k_{-3}K/k_4$
$(NH_3)_3$ [b]	3.0	1.1	0.4	0.094		3.89	0.416
$(NH_3)_3$ [c]				0.186[d]	6.62[e]		
dien[b]	11.4	10.7	0.0	0.119	*ca.* 0.4	1.2	0.28
tach[b,f]	260	12.5	1.3	0.14	*ca.* 40		

For $[(NH_3)_3Co\text{-}\mu\text{-}\{NH_2,(OH)_2\}\text{-}Co(NH_3)_3]^{3+}$ at 298.1 K, k_2k_1/k_{-1} = 1.01 ± 0.02 l mol^{-1} s^{-1} ($\Delta H^\ddagger$ = 12.4 ± 0.5 kcal mol^{-1}, $\Delta S^\ddagger$ = −17.1 ± 1.7 cal K^{-1} mol^{-1}) and 10^2k_{-2} = 1.96 ± 0.4 s^{-1} ($\Delta H^\ddagger$ = 28.9 ± 1.0 kcal mol^{-1}, $\Delta S^\ddagger$ = 30.6 ± 3.4 cal K^{-1} mol^{-1}); $k_1/k_{-1} < 0.05$ l mol^{-1}.

[a] $K_1 = k_{-1}/k_1$. [b] Data from ref. 102 at μ = 1.0 mol l^{-1} (ClO_4^-); further data are given at μ = 0.5 (ClO_4^-) and 1.0 mol l^{-1} (Cl^-). [c] Data from ref. 103 at 298.1 K. [d] $\Delta H^\ddagger$ = 23.4 ± 2.7 kcal mol^{-1}; $\Delta S^\ddagger$ = 16.6 ± 8.9 cal K^{-1} mol^{-1}. [e] $\Delta H^\ddagger$ = 22.8 ± 1.4 kcal mol^{-1}; $\Delta S^\ddagger$ = 7.6 ± 4.4 cal K^{-1} mol^{-1}. [f] tach = *cis,cis*-1,3,5-triaminocyclohexane.

[102] H. C. Kaehler, G. Geier, and G. Schwarzenbach, *Helv. Chim. Acta*, 1974, **51**, 802.
[103] J. D. Edwards, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1974, 2198.

(k_1/k_{-1} = 1.51 ± 0.18 l mol^{-1}, ΔH° = −9.7 ± 3.7 kcal mol^{-1}, and ΔS° = 31.2 ± 12.2 cal K^{-1} mol^{-1}. For the $[(NH_3)_3Co\text{-}\mu\text{-}\{NH_2,(OH)_2\}\text{-}Co(NH_3)_3]^{3+}$ ion opening of the first hydroxo-bridge has a simpler rate dependence of the type $k = (k_2k_1/k_{-1})[H^+] + k_{-2}$, owing to a less favourable protonation equilibrium constant ($k_1/k_{-1} < 0.05$ l mol^{-1}).[103] The rate constants (k_1) associated with first protonation of a hydroxo-bridge [reaction (17)] are surprisingly small [at 293 K and pH 0, half-lives are 0.2, 0.03, and 0.025 s for (N_3) = $(NH_3)_3$, dien, and *cis,cis*-tach respectively], although the overall reactions (17) and (18) are unusually rapid. The second step, reaction (19), is *ca.* 100 times slower than the first, but even so at pH 0 and 293 K the half-lives are in the range 4—9 s for the three complexes studied.[102] The final bridge cleavage is much slower and has a more complex acid dependence ascribed to reactions (20) and (21).

Another triply bridged complex ion $[(NH_3)_3Co\text{-}\mu\text{-}\{SO_3,(OH)_2\}\text{-}Co(NH_3)_3]^{2+}$ has been reported recently but kinetic studies have yet to appear.[104] A kinetic study of this ion would be interesting for comparison with the results above and with the results which demonstrate the strong *trans* effect of sulphite ion in mononuclear cobalt(III) complexes discussed previously.[18-20]

Solvent Variation.—The dubious use of mixed aqueous–organic solvents for obtaining information about the mechanisms of cobalt(III) substitutions continues to be widespread, but for reasons outlined previously[105] too much reliance cannot be put upon some of these results. The problem of ion-pairing is particularly acute for ionic complexes, especially in non-aqueous media where extensive aggregation can occur. Ion-pair constants in the range 20—700 are reported in methanol for interactions between nucleophiles such as NO_2^-, N_3^-, and NCS^- ions and the complex ion *trans*-$[Co(en)_2(L)Cl]^+$ at low ionic strength (*ca.* 0.05 mol l^{-1}).[106] Replacement of the chloride ion by these nucleophiles in methanol was studied as a function of L (L = NO_2, N_3, CN, Cl, or NCS), the rate variation being about the same as that found in aqueous solution. Replacement of Cl^- ion by OMe^- ion is faster when L = CN^- than when L = NO_2^- (rate constants at 283.1 K are 0.83 and 0.18 l mol^{-1} s^{-1} respectively). When L = CN^- ion the replacement of Cl^- by NO_2^- ion occurs with retention of configuration, an uncommon result for these *trans*-complexes.[106] Studies of the aquation of the ions *trans*-$[Co(en)_2(NO_2)Cl]^+$ and *trans*-$[Co(en)_2Cl_2]^+$ in mixed aqueous–organic solvents (up to 10% v/v MeOH, EtOH, dioxan, or acetone in water) show a linear correlation of the Grunwald–Winstein Y values with the logarithm of the rate constant for aquation. The slopes of these plots have values of 0.32 and 0.09 for the dichloro- and chloronitro-complexes respectively, and this is said to indicate a smaller extent of charge separation in the transition state for the chloronitro-complex compared with the dichloro-complex.[107] A dissociative (I_d) mechanism is postulated in line with studies in aqueous media. Similar correlations with Grunwald–Winstein Y values are reported for the aquation of the *trans*-$[Co(dap)_2Cl_2]^+$ ion (dap = 1,3-diaminopropane), slopes of 0.36, 0.34, and 0.17 being recorded for methanol–, ethanol–, and acetone–water mixtures respectively.[108]

[104] V. H. Siebert and G. Wittke, *Z. anorg. Chem.*, 1974, **406**, 282.
[105] Ref. 1, pp. 182—183.
[106] Z. Bradić, M. Biruš, D. Pavlović, M. Pribanić, and S. Ašperger, *J.C.S. Dalton*, 1973, 2514.
[107] M. Pribanić, M. Biruš, D. Pavlović, and S. Ašperger, *J.C.S. Dalton*, 1973, 2518.
[108] G. Thomas and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1974, 1688.

A study of the aquation of the $[Co(NH_3)_5(DMSO)]^{3+}$ ion in mixed aqueous–organic solvents which involves loss of an uncharged ligand does not show any correlation with solvent parameters, including the Grunwald–Winstein Y values, the water activity, or the heats of mixing of DMSO with solvent components.[42] Nevertheless an I_d mechanism is proposed and the activation parameters are $\Delta H^{\ddagger} = 23.9 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0.36 \pm 2.29$ cal K^{-1} mol^{-1}.

A number of other mixed-solvent studies have appeared for the aquation of *cis*-$[Co(en)_2(amine)Br]^{2+}$ ions[65, 66, 109] (amine = RNH_2, where R = H, Me, Et, Bu^n, Ph, or $PhCH_2$, or amine = py). An S_N1 mechanism is usually proposed but when amine = py or $PhNH_2$, S_N2 mechanisms are reported.[66] These reactions are also observed to involve slow loss of the amine after the more rapid bromide-ion aquation. In another study ready formation of conjugate-base complexes is reported when L = $PhNH_2$ (Table 3).[63]

References to studies of *trans*-$[Co(dioxime)_2(A)X]$ complexes (A and X are unidentate ligands) in non-aqueous media will be found in Table 7.

An article dealing with the influence of solvent on chemical reactivity has appeared.[110]

Catalysed Aquation.—Acid catalysis occurs whenever the leaving group is the anion of a weak base (*e.g.* F^-, N_3^-, CN^-, and many oxoanions) or for multidentate leaving groups which often protonate when only partially chelated. Examples appear in earlier sections and will not be considered specifically here. Catalysis by micelles, by electrophiles other than protons (*e.g.* metal ions or NO^+), or by attack at co-ordinated ligands (*e.g.* oxidation and reduction) will be discussed here. Base hydrolysis, which usually involves conjugate-base formation, is dealt with in a later section.

Catalysis by electrophiles, especially labile metal ions, is analogous to acid catalysis and can occur in nearly all cases where acid catalysis is observed. A major difference between catalysis by protons and by metal ions lies in their different binding abilities. A proton can bond readily to class (*a*) or 'hard' substrates (*e.g.* O-, N-, or F-donors), and because of its small size can penetrate donor sites which larger metal ions find sterically hindered. Metal-ion catalysts fall into two broad categories: class (*a*) or 'hard' metal ions (*e.g.* Be^{2+}, Al^{3+}, or Th^{4+}), which again bind most readily to O-, N-, and F-donor sites, and class (*b*) or 'soft' metal ions (*e.g.* Hg^{2+}), which can catalyse reactions which protons do not accelerate [*e.g.* aquation of Cl^-, Br^-, I^-, and some other class (*b*) donor ligands]. A general rate equation for catalysis by a single electrophile E (E = H^+ or M^{n+}) is given by

$$-\mathrm{d[complex]}/\mathrm{d}t = \{k_0 + k_E K_E[E]/(1 + K_E[E])\}[\mathrm{complex}] \qquad (22)$$

In equation (22) k_0 is the rate constant for the uncatalysed aquation, k_E the rate constant for dissociation of the complex–metal ion adduct, and K_E the equilibrium constant for the binding of the electrophile to the complex. Limiting cases occur in which K_E is either large or small, and equation (22) then reduces to give observed rate constants $k = (k_0 + k_E)$ or $(k_0 + k_E K_E[E])$ respectively.

Hydrolysis of the $[Co(en)F_2]^+$ ion shows the expected catalysis by Be^{2+}, Al^{3+}, Sc^{3+}, and Th^{4+} ions, the rate constants increasing with the increasing charge on the metal

[109] V. V. Udovenko, L. G. Reiter, and E. P. Stepanov, *Zhur. neorg. Khim.*, 1974, **19**, 1009.
[110] M. J. R. Dack, *J. Chem. Educ.*, 1974, **51**, 231.

ion.[111] Following a determination of values of K_E [equation (22)] for the adducts $[(NH_3)_5CoC_2O_4M]^{n+}$ (M = bivalent or tervalent metal ion)[112] in which the oxalate ion is acting as a unidentate ligand, the rates of acid hydrolysis have been measured and the relative catalytic activities found to parallel the thermodynamic stabilities of the dinuclear species:[113] $Mn^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$; and $In^{III} < Al^{III} \leqslant Ga^{III} < Fe^{III}$. A similar study of the salicylatopenta-amminecobalt(III) ion was reported earlier and the observed rate constant k found to vary with the metal-ion concentration ($[M^{3+}]$) and the acidity as follows:[114]

$$k = k_0 + k_1[H^+] + (k_E K_E[M^{3+}]/[H^+])(1 + K_E[M^{3+}]/[H^+])^{-1} \quad (23)$$

Equation (23) is analogous to (22), the extra term $k_1[H^+]$ arising from the normal acid catalysis of a carboxylato-complex and the inverse acid terms arising from the equilibrium

$$[Co(NH_3)_5(O_2CC_6H_4OH)]^{2+} + M^{3+} \rightleftharpoons [Co(NH_3)_5(O_2CC_6H_4OM)]^{4+} + H^+$$

Values of $10^5 k_E/s^{-1}$ of (2.0 ± 0.2), (1.1 ± 0.5), and (0.67 ± 0.16) again parallel values of K_E [(2.2 ± 0.5), (0.85 ± 0.42), and (0.16 ± 0.11) for Fe^{III}, Ga^{III}, and Al^{III} ions respectively]. Activation parameters associated with the values of k_0, k_1, and k_E are reported and Co—O bond fission is postulated.[114]

Long-lived and very stable dinuclear intermediates have also been observed during the reduction of the $[Co(NH_3)_5(ntaH_2)]^{2+}$ ion (nta^{3-} = O-bonded nitrilotriacetate ion) by Fe^{II} ion; at 298.1 K and μ = 1.0 mol l^{-1} ($NaClO_4$) log K_E values of 4.4, 6.06, 7.26, 7.57, 8.53, 10.6, and 11.4 are also reported for formation of complexes with the metal ions Ca^{II}, Fe^{II}, Co^{II}, Zn^{II}, Ni^{II}, Cu^{II}, and Fe^{III} respectively.[115] The rates of aquation of these dinuclear intermediates are very low and only approximate rates were obtained.

Halide-ion aquation is well known to be catalysed by the addition of mercury(II) ion, and this can sometimes be used to direct the stereochemical course of a reaction. Thus, the spontaneous aquation of the *trans*-$[Co(ete)Cl_2]^+$ ion gives *β-cis*-$[Co(ete)Cl(OH_2)]^{2+}$, whereas S_E2 catalysis by mercury(II) gives the *trans*-$[Co(ete)Cl(OH_2)]^{2+}$ ion which then isomerizes to the *β-cis*-isomer.[78] The latter isomerization is much faster than the rate of spontaneous aquation and so the stereochemical course of the uncatalysed reaction is uncertain.

Some further studies of the mercury(II)-ion-induced reactions of complexes of the type *cis*-$[Co(en)_2(L)X]^{2+}$ are reported (X = Cl or Br).[32] When L is NH_2CH_2CN (co-ordinated at the NH_2 group) the product of the reaction is the $[Co(en)_2(NH_2CH_2CONH_2)]^{3+}$ ion containing chelated glycine amide. The postulated mechanism involves the replacement of ligand X by H_2O, followed by deprotonation and nucleophilic attack by the co-ordinated OH^- at the carbon atom of the nitrile group. Base hydrolysis of this complex involves a different, but analogous, mechanism in which nucleophilic attack at the nitrile again occurs, but this time it is a deprotonated NH_2 group of one of the 1,2-diaminoethane rings which reacts. Reaction of mercury(II)

[111] I. V. Kozhevnikov, E. S. Rudakov, T. V. Vasserman, and V. A. Bigeeva, *Zhur. neorg. Khim.*, 1973, **18**, 3344.
[112] R. K. Nanda and A. C. Dash, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1595.
[113] A. C. Dash and R. K. Nanda, *Inorg. Chem.*, 1974, **13**, 655.
[114] A. C. Dash and R. K. Nanda, *Inorg. Chem.*, 1973, **12**, 2024.
[115] R. D. Cannon and J. Gardiner, *Inorg. Chem.*, 1974, **13**, 390.

ion with *cis*-$[Co(en)_2(L)X]^{2+}$ ions shows an interesting difference in reactivity when L is $NH_2CH_2CH_2OCOMe$ or $NH_2CH_2CH_2OH$ (both co-ordinated at the NH_2 group). The reactions of the former complexes are slower than those of the latter as shown by the following rate constants: when L = $NH_2CH_2CH_2OCOMe$, k_{Hg}/l mol^{-1} min^{-1} = 0.48 and 68±2 for X = Cl and Br respectively ([H^+] = 0.57 mol l^{-1}), whereas when L = $NH_2CH_2CH_2OH$, k_{Hg}/l mol^{-1} min^{-1} = 3.52 and 400±25 for X = Cl and Br respectively. Neighbouring-group participation in the 2-aminoethanol derivative is postulated to account for this rate difference. The OH group of the 2-aminoethanol is postulated to stabilize the five-co-ordinate intermediate.[32] Removal of the halide ion (X) with mercury(II) from *cis*-$[Co(en)_2X(NH_2CH_2CO_2Et)]^{2+}$ results in chelation and then hydrolysis of the amino-acid ester. The reported effect of perchlorate ion on this reaction and the supposed formation of some *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CO_2Et)]^{3+}$ ion has been shown to be incorrect.[116, 117]

Some further observations are reported and a case is made for the formation of a common five-co-ordinate intermediate during the Hg^{II} and NO^+-promoted aquations of $[Co(en)_2XY]^{n+}$ ions.[118] Two previous reviews have dealt with this subject recently.[119, 120] In the present study the steric course of the Hg^{II}-catalysed aquation of *cis*-$[Co(en)_2Br_2]^+$ and *cis*- and *trans*-$[Co(en)_2(OH_2)X]^{2+}$ ions (X = Cl or Br) and the NO^+-catalysed dissociation of *trans*-$[Co(en)_2XN_3]^{n+}$ ions (X = H_2O, Cl, or Br) was accurately determined at 296 K, including a reinvestigation of some earlier studies. The stereochemical course of these reactions is very dependent on temperature. For example, *cis*-$[Co(en)_2Br_2]^+$ was earlier reported to aquate spontaneously with 73% retention of configuration.[121] At 296 K, the Hg^{II}-catalysed aquation proceeds with only 58% retention of configuration, but at 333 K the steric courses for the spontaneous and induced aquations are identical. Comparison of results for different leaving ions leads the author to infer a common five-co-ordinate intermediate for these reactions.[118] Competition ratios are the same for the neutral molecules DMSO and DMF capturing the postulated $[Co(NH_3)_5]^{3+}$ ion derived from the nitrosation of the $[Co(NH_3)_5N_3]^{2+}$ and $[Co(NH_2)_5(O_2CNH_2)]^{2+}$ ions.[101] The possibility that the same intermediate might be formed during the bridge cleavage of the $[(NH_3)_5Co\text{-}\mu\text{-}(OH)\text{-}Co(NH_3)_5]^{5+}$ ion could not be resolved because of the complication of ion-pairing. However, with a few minor exceptions the results of the bridge-cleavage experiments support and complement the results of Sykes and co-workers on the same system. One difference is that in the presence of thiocyanate ion bridge cleavage is believed to involve the formation of the labile S-bonded thiocyanate complex.[101] Acid hydrolysis and nitrosation of the $[Co(NH_3)_5(NCO)]^{2+}$ ion is reported to involve $[Co(NH_3)_5(NHCO_2H)]^{2+}$ and $[Co(NH_3)_5]^{3+}$ ions as intermediates. The acid-hydrolysis experiments are an extension of an earlier study of the cobalt(III) complex,[122] and a mechanism very similar to that postulated for the analogous rhodium-

[116] D. A. Buckingham and M. Wein, *Inorg. Chem.*, 1974, **13**, 3027.
[117] K. Nomiya and H. Kobayashi, *Inorg. Chem.*, 1974, **13**, 409.
[118] W. G. Jackson, *Inorg. Chim. Acta*, 1974, **10**, 51.
[119] J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta, Rev.*, 1971, **5**, 7.
[120] A. M. Sargeson, *Pure Appl. Chem.*, 1973, **33**, 527.
[121] C. G. Barraclough, R. W. Boschen, W. W. Fee, W. G. Jackson, and P. T. McTigue, *Inorg. Chem.*, 1971, **10**, 1994.
[122] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1970, **9**, 1567.

(III) complex[123] is preferred. These reactions are postulated to involve linkage isomerization of $[Co(NH_3)_5(NHCO_2H)]^{2+}$ to $[Co(NH_3)_5(OCONH_2)]^{2+}$ ion:[124]

$$[(NH_3)_5Co(NCO)]^{2+} + H^+ \overset{K_1}{\rightleftharpoons} [(NH_3)_5Co(NCOH)]^{3+}$$

$$[(NH_3)_5Co(NCOH)]^{3+} + H_2O \xrightarrow{k_1} [(NH_3)_5Co(NH_2CO_2H)]^{3+}$$

$$[(NH_3)_5Co(NH_2CO_2H)]^{3+} \overset{K_2}{\rightleftharpoons} [(NH_3)_5Co(NHCO_2H)]^{2+} + H^+$$

$$[(NH_3)_5Co(NH_2CO_2H)]^{2+} + H_2O \xrightarrow{k_2'} [(NH_3)_5Co(OCONH_2)]^{2+} + H^+$$

$$[(NH_3)_5Co(NH_2CO_2H)] + H_2O \xrightarrow{k_2''} [(NH_3)_5Co(OH_2)]^{3+} + NH_3 + CO_2$$

$$[(NH_3)_5Co(NHCO_2H)]^{2+} \xrightarrow{k_3} [(NH_3)_5Co(NH_2)]^{2+} + CO_2$$

$$[(NH_3)_5Co(NH_2)]^{2+} + H^+ \xrightarrow{\text{fast}} [Co(NH_3)_6]^{3+}$$

Values of the equilibrium constants are $K_1 < 0.05$ and, at $\mu = 3$ mol l^{-1}, $K_2 < 0.424$ mol l^{-1} (the value found at $\mu = 1.0$ mol l^{-1}). The rate constant $k_2 = k_2' + k_2'' = 0.011 \pm 0.005$ s^{-1} at 298.1 K. Nitrosation is believed to involve the following reaction ($k_{NO} \approx 6 \times 10^7$ l mol^{-1} s^{-1}):

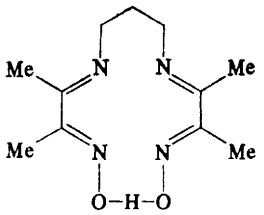
$$[(NH_3)_5Co(NHCO_2H)]^{2+} + NO^+ \xrightarrow{k_{NO}} [(NH_3)_5Co\{NH(NO)CO_2H\}]^{3+}$$

$$[(NH_3)_5Co\{NH(NO)CO_2H\}]^{3+} \xrightarrow{\text{rapid}} [Co(NH_3)_5]^{3+} + N_2 + CO_2 + H_2O$$

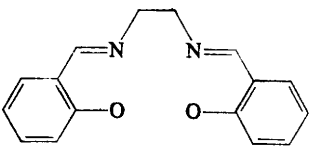
$$[Co(NH_3)_5]^{3+} + Y \longrightarrow [Co(NH_3)_5Y]^{n+} \quad (Y = H_2O \text{ or } Cl^-)$$

Competition ratios for the $[Co(NH_3)_5]^{3+}$ ion are the same as those from the earlier study of the nitrosation of the $[Co(NH_3)_5N_3]^{2+}$ ion in an aqueous chloride medium. This five-co-ordinate intermediate has a very low discriminating ability for different nucleophiles and, therefore, has a very different character from well established intermediates such as the $[Co(CN)_5]^{2-}$ ion.

Kinetic studies of the transfer of co-ordinated carbanions from cobalt(III) to mercury(II) are reported for two families of model vitamin B_{12} compounds.[125] Previous studies in this area have indicated a single-step mechanism, with occasional complications such as the complexing of the benzimidazole of cobalamins by the mercury(II) ion, and the protonation of cobaloximes. In the recent study with complexes of the type *trans*-$[RCo(L)OH_2]$ [L^- = (12); L^{2-} = salen = (13)],



(12)



(13)

[123] P. C. Ford, *Inorg. Chem.*, 1971, **10**, 2153.
[124] D. A. Buckingham, D. J. Francis, and A. M. Sargeson, *Inorg. Chem.*, 1974, **13**, 2630.
[125] G. Tauzher, R. Dreos, G. Costa, and M. Green, *J. Organometallic Chem.*, 1974, **81**, 107; *J.C.S. Chem. Comm.*, 1973, 413.

evidence is presented for a two-step mechanism involving the formation of a mercury(II) adduct followed by alkyl- or aryl-group transfer from cobalt(III) to mercury(II). The adduct presumably involves co-ordination between mercury(II) and an oxygen atom of L remote from the transferred group. Denoting the complexes as RM the proposed mechanism when L = (12) is

$$RM + Hg^{2+} \overset{K_3}{\rightleftharpoons} RMHg^{2+} \quad (24)$$

$$RMHg^{2+} + H_2O \xrightarrow{k_4} MOH_2 + RHg^{+} \quad (25)$$

$$-d[RM]/dt = k_4K_3[RM][Hg^{2+}]/\{1 + K_3[Hg^{2+}]\}$$

A slightly different rate law indicating competition of H^+ and Hg^{2+} for RM is observed when L = (13):

$$-d[RM]/dt = k_4K_3[RM][Hg^{2+}]/\{1 + K_2[H^+] + K_3[Hg^{2+}]\}$$

Values of the rate constants (k_4) and adduct formation constants (K_3) are collected in Table 10. Transmethylation occurs much more readily than transfer of other alkyl groups in the corrinoid and cobaloxime systems.

Table 10 *Rate constants* k_4/s^{-1} *and equilibrium constants* $K_3/l\ mol^{-1}$ *at* 298.1 K *associated with reactions* (24) *and* (25) *(data from ref.* 125)

L	R	$10^2k_4/s^{-1}$	$10^2K_3/l\ mol^{-1}\ s^{-1}$
(12)	Me	133±11	118±11
(12)	Et	0.422±0.033	138±13
(12)	Pr^n	0.400±0.085	73±17
(12)	$PhCH_2$	0.159±0.029	241±49
(12)	Ph	131±22	291±45
(12)	Me (BF_2 derivative)	0.0218±0.0010	319±21
(13)	Me	8370±260	37 600±4200
(13)	Et	24.0±1.9	35 100±8000

Inversion of configuration at the α-carbon atom has been established by deuterium-decoupled ^1H n.m.r. measurements in the conversion of *erythro*-(Bu^{t}CHDCHD)-Co(dmgH)$_2$(py)] into *threo*-(Bu^{t}CHDCHD)HgCl].[126] The relative rates of dealkylation of several cobaloximes by mercury(II) ion parallel some of the results shown in Table 10:[126] Me ≫ Et, $Pr^n > CH_2CHMe_2 > CH_2CMe_3 > CH_2CH_2CMe_3 \gg Pr^i$.

Methyl-group transfer of a different kind has been observed in the reaction of methylcobalamin with the $[PdCl_4]^{2-}$ ion.[127] Although a fast reaction occurs to give a palladium(II) complex in which methylcobalamin is co-ordinated to the 5,6-dimethylbenzimazole nitrogen, this complex is inactive towards methyl-group transfer. However, a much slower direct reaction occurs to give Pd metal, MeCl, and aqua- and chloro-cobalamins.[127]

Reaction (26) is catalysed by the addition of [L′Co^{II}(dmgH)$_2$]:

$$trans\text{-}[LCo^{III}(dmgH)_2X] + L' \longrightarrow trans\text{-}[L'Co^{III}(dmgH)_2X] + L \quad (26)$$

[126] H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *J. Amer. Chem. Soc.*, 1974, **96**, 2378.

[127] W. M. Scovell, *J. Amer. Chem. Soc.*, 1974, **96**, 3451.

A mechanism involving slow, inner-sphere electron transfer between the cobaloximes and cobalt(II) catalyst is postulated.[128] When L = 4-cyanopyridine (4-CN-py) and X is S-bonded thiocyanate ion, adjacent attack occurs with a sulphur-bridged transition state of the type $[(4\text{-CN-py})(dmgH)_2CoS(CN)Co(dmgH)_2L]$.

In addition to studies of metal-ion-catalysed reactions of cobalt(III) some recent studies are reported for the catalysis of ligand exchange and redox reactions by surfactants.[129,130] Rate constants for the formation and dissociation of glycine, imidazole, and NaN_3 adducts of Vitamin B_{12a} were determined in aqueous micellar hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (NaLS), and in dodecylammonium propionate (DAP)- and sodium di-(2-ethylhexyl)-sulphosuccinate (Aerosol-OT)-solubilized H_2O in benzene.[129] The effects in aqueous micelles are relatively small, but for the reactions in the polar cavities of surfactants in benzene a marked rate enhancement is observed for the reactions with glycine, whereas for the reaction with sodium azide in DAP the rate constants are much smaller than those in water. Studies of aquation and electron-transfer reactions of $[M(ox)_3]^{3-}$ (M = Co^{III} or Cr^{III}) and *cis*-$[Co(en)_2(N_3)_2]^+$ ions have also been made in the presence of reversed micelles (DAP and octylammonium tetradecanoate) in benzene. Aquations at constant [surfactant] increase linearly in rate with increasing concentration of solubilized water, whereas at constant $[H_2O]$ increasing surfactant concentration produces an exponential rate decrease. For the oxalato-complexes rate enhancements of the order of 10^3—10^6 are possible. The results are discussed in terms of favourable substrate orientation in the polar cavities of the alkylammonium carboxylate aggregates formed by these surfactants in benzene, where hydrogen-bonding helps H^+ transfer and enhanced water activity accelerates synchronous metal–oxygen bond breaking and nucleophilic attack by water. The micelles have no effect on the electron-transfer processes.

A few studies have appeared dealing with substitutions brought about by oxidation and reduction of co-ordinated ligands. Mention has already been made in this section of the reactions of co-ordinated azides, amides, and isocyanates with NO^+. The reverse process (attack at co-ordinated NO^+) is postulated to have a reactivity pattern which correlates with the i.r. N—O stretching frequencies.[131] Co-ordinated NO^+ behaves as an electrophile if the N—O stretching frequency is less than 1886 cm^{-1} and the force constant is less than 13.8 mdyn $Å^{-1}$. A study of the rate of reaction of *cis*- and *trans*-$[Co(en)_2(NO_2)_2]^+$ ions with hydrazoic acid has also appeared:[132]

$$[Co(en)_2(NO_2)_2]^+ + 2HN_3 + 2H^+ \longrightarrow [Co(en)_2(OH_2)_2]^{3+} + 2N_2 + 2N_2O$$

These reactions were followed between 274 and 288 K by gas-evolution experiments in azide buffers. The reactions are claimed to be independent of pH with a first-order dependence on [complex] and $[HN_3]$. Two stages were observed for each complex, the first stage being *ca.* five times as fast as the second stage, and the *cis*-complexes reacting *ca.* three times as fast as the *trans*-isomers.

[128] L. G. Marzilli, R. C. Stewart, L. A. Epps, and J. B. Allen, *J. Amer. Chem. Soc.*, 1973, **95**, 5796.
[129] J. H. Fendler, F. Nome, and H. C. Van Woert, *J. Amer. Chem. Soc.*, 1974, **96**, 6745.
[130] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J.C.S. Dalton*, 1974, 625.
[131] F. Bottomley, V. F. Brooks, and S. G. Clarkson, *J.C.S. Chem. Comm.*, 1973, 919; F. Bottomley, S. G. Clarkson, and S.-B. Tong, *J.C.S. Dalton*, 1974, 2344.
[132] V. F. Seel and D. Meyer, *Z. anorg. Chem.*, 1974, **408**, 283.

A stopped-flow investigation of the kinetics of the oxidative substitution of the $[Co(NH_3)_5Br]^{2+}$ ion by Cl_2, HOCl, and HOBr has appeared.[133] In excess HOBr, a third-order rate law is observed:

$$\text{Rate} = k_1[\text{HOBr}][H^+][Co(NH_3)_5Br^{2+}]$$

At 298.1 K and $\mu = 1.0$ mol l^{-1}, $k_1 = 3.2 \pm 0.2$ l^2 mol^{-2} s^{-1}, $\Delta H^* = 9.4 \pm 1.5$ kcal mol^{-1}, and $\Delta S^* = -25 \pm 5$ cal K^{-1} mol^{-1}. With HOCl two pathways are indicated with a modified rate law:

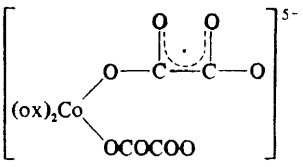
$$\text{Rate} = (k_0 + k_1[H^+])[\text{HOCl}][Co(NH_3)_5Br^{2+}]$$

$k_0 = (4 \pm 1)$ l mol^{-1} s^{-1} and $k_1 = (100 \pm 7)$ l^2 mol^{-2} s^{-1} and the activation parameters associated with k_1 are $\Delta H^* = 3.8 \pm 1$ kcal mol^{-1} and $\Delta S^* = -37 \pm 5$ cal K^{-1} mol^{-1}. The reaction with Cl_2 is much more complex with a rate law

$$\text{Rate} = k_2[Cl_2][Co(NH_3)_5Br^{2+}]$$

where it is proposed that $k_2 = \{A + B[Cl^-] + C[Cl^-]^2 + D[Cl^-]^3\}/\{1 + E[Cl^-] + F[Cl^-]^2\}$. To complicate matters further the effect of added sulphate ion was investigated!

Photochemistry.—Flash photolytic reduction of the $[Co(ox)_3]^{3-}$ ion to cobalt(II) species in aqueous solution goes *via* an intermediate (A) (λ_{max} *ca.* 360 nm) which is in equilibrium with a small amount of a second intermediate (B).[134] These intermediates arise from ligand-to-metal charge transfer followed by rapid spin relaxation of the resulting cobalt(II) centre. (A) is considered to be the $[(ox)_2Co^{II}(C_2O_4^-)]^{3-}$ ion in which cobalt(II) is co-ordinated to a bidentate oxalate radical ion, whereas (B) is postulated to be the $[(ox)_2Co^{II}(C_2O_4^-)(OH_2)]^{3-}$ ion, in which the oxalato-radical ion is a unidentate ligand. (A) decays fairly slowly, the rate being slightly dependent on pH; at 296 K and pH 6, the observed rate constant $k = 58$ s^{-1}, whereas below pH 1 $k = 82$ s^{-1}. (B) has a pK_a of *ca.* 2.5. The formation of more complex species of the type (14) is also postulated.



(14)

A number of studies have appeared dealing with the effect of solvent viscosity upon the charge-transfer-to-metal (CTTM) excitation of cobalt(III) complexes.[135–137] Irradiation of $[Co(NH_3)_5X]^{2+}$ ions (X = Cl, Br, N_3, or NCS) at 400 nm $\geq \lambda \geq$ 214 nm indicates that the solvent plays a more active role in CTTM photochemistry of transition-metal complexes than previously suspected.[135] Photolysis of $[Co(NH_3)_5X]^{2+}$ ions (X = NO_2 or N_3) in polymer solutions indicates that the

[133] J. M. Malin, H. E. Toma, and E. Giesbrecht, *Inorg. Chim. Acta*, 1973, **7**, 423.
[134] N. S. Rowan, M. Z. Hoffman, and R. M. Milburn, *J. Amer. Chem. Soc.*, 1974, **96**, 6060.
[135] J. F. Endicott and G. F. Ferraudi, *J. Amer. Chem. Soc.*, 1974, **96**, 3681.
[136] P. Natarajan, *J.C.S. Chem. Comm.*, 1975, 26.
[137] F. Scandola, C. Bartocci, and M. A. Scandola, *J. Amer. Chem. Soc.*, 1973, **95**, 7900.

viscosity of the medium has no significant effect on product yields, but the solvent structure does determine the product distribution of the photoredox reactions.[136] An earlier study of the viscosity dependence of the $[Co(NH_3)_5(NO_2)]^{2+}$ ion CTTM photochemistry gave evidence for a radical cage recombination reaction.[137]

A transient species has been detected in a 77 K, 365 nm solid-state photochemical study of the nitro→nitrito linkage isomerization of $[Co(NH_3)_5(NO_2)]Cl_2$. This transient is postulated to involve a bidentate nitro-group in which a nitrogen and oxygen atom of the nitrite ion are co-ordinated to the cobalt(III).[138]

In recent years efforts have been directed towards examining the applicability of Adamson's photochemical rules[139] to cobalt(III) systems. These empirical rules were developed largely from studies of chromium(III) ammines and are useful for predicting the stereochemical direction of a photochemical reaction of an octahedral chromium(III) complex. Excitation of aqueous acidic solutions of cobalt(III) complexes in the visible region (*d–d* bands) does give rise to photoaquation but the quantum yields are usually very low. Nevertheless, the stereochemical courses of the systems studied so far are largely in agreement with Adamson's rules. Recent examples include the complexes *α-cis-* and *β-cis*-$[Co(trien)ClX]^{n+}$ and $[Co(tren)ClX]^{n+}$ (X = Cl or H_2O).[140] Irradiation of the *β-cis*-trien complexes in the first or second ligand-field (*d–d*) band gives rise to photoaquation or photoisomerization with quantum yields in the range 10^{-2}—10^{-3}, while the *α-cis*-trien complexes have quantum yields of less than 10^{-5}. Photoirradiation of $[Co(tren)Cl_2]^+$ at 514.5 nm produces $[Co(tren)(OH_2)Cl]^{2+}$ with a quantum yield of 1.5×10^{-2}, but the product is photoinert. Similarly, ligand-field photolysis of the *cis*-$[Co(en)_2Cl_2]^+$ ion in acidic solution proceeds with a quantum yield of 2.4×10^{-3} to give 70—75% *trans-* and 25—30% *cis*-$[Co(en)_2(OH_2)Cl]^{2+}$.[141] This result should be contrasted with the spontaneous thermal aquation of the *cis*-$[Co(en)_2Cl_2]^+$ ion which proceeds with 100% retention of configuration. *cis*→*trans* Photoisomerization of the *cis*-$[Co(en)_2(OH_2)Cl]^{2+}$ ion has a quantum yield of 4.2×10^{-3}, whereas the *trans*-isomer is photoinert. These photochemical results can be explained using Adamson's rules by predicting that labilization of one end of a 1,2-diaminoethane (en) ligand will occur on the weakest ligand-field axis (bearing in mind that chloride ion is lower than water in the spectrochemical series). This dangling (unidentate) 1,2-diaminoethane then ring-closes to an adjacent octahedral position rather than total loss of 1,2-diaminoethane occurring. The only surprising feature of this postulated mechanism is that at the high acidities used protonation of the one-ended 1,2-diaminoethane would be expected to occur with some total loss of ligand.[141] Photolysis studies are also reported by Adamson's group for the ions $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5(OH_2)]^{3+}$, $[Co(NH_3)_5X]^{2+}$ (X = F or Cl), *trans*-$[Co(en)_2Cl_2]^+$, and *trans*-$[Co(cyclam)Cl_2]^+$.[142] Ligand-field excitation gives quantum yields for loss of ammonia from the acido-ammines which are much larger than for loss of halide ions, and for the chelate complexes only chloride-ion aquation occurs. The *trans*-$[Co(en)_2Cl_2]^+$ ion photo-

[138] D. A. Johnson and K. A. Pashman, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 23.
[139] A. W. Adamson, *J. Phys. Chem.*, 1967, **71**, 798.
[140] P. S. Sheridan and A. W. Adamson, *Inorg. Chem.*, 1974, **13**, 2482.
[141] P. S. Sheridan and A. W. Adamson, *J. Amer. Chem. Soc.*, 1974, **96**, 3032.
[142] R. A. Pribush, C.-K. Poon, C. M. Bruce, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1974, **96**, 3027.

aquates with 72% retention of configuration whereas photoaquation of the cyclam complex is 100% stereoretentive. Qualitatively the behaviour is again similar to that of chromium(III) complexes but there are differences in detail. For example, the stereochemistry of the products indicates important differences in excited-state reaction mechanisms.

A ligand-field interpretation of the quantum yields of photosubstitution reactions of d^6 metal complexes has appeared.[143] Similarly, a molecular orbital approach, based on the relative changes in metal–ligand overlap populations between ground and excited states, has been described to determine the relative ligand photolabilizations in the excited states of co-ordination compounds.[144] The results complement the predictions of Adamson's qualitative rules.

It has been suggested that the low quantum yields and relative photoinertness of cobalt(III) ammines when excited at the wavelengths of *d–d* transitions may be the result of an exceptionally efficient non-radiative electronic relaxation of the ligand-field excited states,[145] although this hypothesis has been questioned recently.[146] A photoredox process has now been discovered in the 337 nm pulsed laser photolysis of the $[Co(NH_3)_6]^{3+}$ ion which appears to involve two consecutive single-photon absorptions. This biphotonic process is believed to involve the generation of a photo-active charge-transfer state from absorption by a ligand-field excited state (Scheme 2).[147] *LF and *CT respectively represent excited ligand-field and charge-

$$^1A_{1g} + h\nu \longrightarrow {}^1T_{2g}$$

$$^1T_{2g} \longrightarrow {}^1A_{2g}$$

$$^1T_{2g} \longrightarrow {}^*\mathrm{LF}$$

$$^*\mathrm{LF}\ (\text{or } {}^1T_{2g}) \xrightarrow{H^+} [Co(NH_3)_5(OH_2)]^{3+} + NH_4^+$$

$$^*\mathrm{LF} + h\nu \longrightarrow {}^*\mathrm{CT}$$

$$^*\mathrm{CT} \xrightarrow{(H^+)} [Co(H_2O)_6]^{2+} + 5NH_4^+ + \cdot NH_3^+$$

$$^*\mathrm{CT} \longrightarrow {}^1A_{1g}$$

Scheme 2

transfer states of the $[Co(NH_3)_6]^{3+}$ ion. The results show that the photoaquation and photoredox processes are uncoupled, with the quantum yield for photoaquation *ca.* 5×10^{-3} and the ratio of the quantum yields for aquation and redox processes greater than 10^2. *LF is postulated to have a finite, if short, lifetime of *ca.* 10^{-8} s.

An interesting difference is recognized between the charge-transfer photochemical reactions of azido-complexes of cobalt(III) and rhodium(III). These reactions have

[143] M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, 1974, **13**, 2489.
[144] J. I. Zink, *J. Amer. Chem. Soc.*, 1974, **96**, 4464.
[145] P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, 1973, **95**, 2470.
[146] N. A. P. Kane-Maguire and C. H. Langford, *J.C.S. Chem. Comm.*, 1973, 351.
[147] K. M. Cunningham and J. F. Endicott, *J.C.S. Chem. Comm.*, 1974, 1024.

been reinvestigated recently[7] and found to be more complex than originally postulated.[6] Although photolysis of azido-cobalt(III) complexes produces cobalt(II) and azido-radical ions, the analogous rhodium(III) reactions are postulated to involve intermediate nitrene formation. In the recent study evidence is presented for dimer formation, $[\{Rh(NH_3)_5N\}_2]^{4+}$ from the initially produced nitrene, $[Rh(NH_3)_5N]^{2+}$. These results are discussed further in a later section.

3 Aquation: Chromium(III) Complexes

The case has been made for largely associative (I_a) substitution reactions at chromium(III) centres.[12] For aquations of related chromium(III) complexes plots of log(rate constant) against log(equilibrium constant) are linear, but whereas this plot has a slope of unity for cobalt(III) complexes, where I_d mechanisms apply, the analogous plots for chromium(III) have slopes significantly less than unity (typically 0.5). Furthermore, and again in contrast to cobalt(III) systems, values of the volumes of activation and entropies of activation are often large and negative for chromium(III) substitutions. A recent example comes from a study of the kinetics of exchange of DMSO with the $[Cr(DMSO)_6]^{3+}$ ion, for which the rate constant for exchange of all six solvent molecules is 5.5×10^{-5} s^{-1} at 348.1 K, and $\Delta H^{\ddagger} = 23.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = -11.8$ cal K^{-1} mol^{-1}, and $\Delta V^{\ddagger} = -11.3$ cm^3 mol^{-1} at 298.1 K. The large negative values of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ support an I_a mechanism.[148] It is now thought that dissociative mechanisms may only be important for chromium(III) complexes in the presence of *trans*-labilizing groups (*e.g.* methyl carbanion).

Recently *cis*-activation has been recognized as playing an important part in chromium(III) substitutions whenever potentially chelating co-ordinated oxoanions are present (*e.g.* NO_3^-, SO_3^{2-}, AcO^-, SO_4^{2-}).[14-16] This makes it important that the correct counterion is chosen in studies of substitution reactions of cationic complexes. For example, replacing nitrate ion by perchlorate ion makes a significant difference to the rates of acid hydrolysis of some chromium(III) ammines.[15]

Another feature of chromium(III) substitutions which distinguishes them from analogous cobalt(III) reactions is the dominance of stereoretentive pathways. *trans*-Complexes of cobalt(III), in particular, often undergo stereochemical change, but this is rarely the case for chromium(III). Despite these characteristics which distinguish chromium(III) and cobalt(III) substitutions, there are still many features which make the chemistries of these two metal ions comparable. For example, the relative labilities of analogous complexes is similar, and acid- and base-catalysed reactions often occur for related compounds. These similarities will be apparent in the following sections.

Unidentate Leaving Groups.—*Ammonia Loss.* A number of new studies have appeared recently dealing with the acid hydrolysis of chromium(III) ammines.[15,149] Unfortunately the rates reported previously by Bjerrum and Jorgensen in 1958 were too large because of the use of a nitrate medium, which is believed to produce a *cis*-activation by the co-ordinated nitrate ion as discussed in the introduction to this section.[15] In a perchlorate medium the rates of the isomerization reactions are usually insignificant compared with the rates of acid hydrolysis. In 0.5—1.0M-H^+ the rate constants for

[148] D. L. Carle and T. W. Swaddle, *Canad. J. Chem.*, 1973, **51**, 3795.
[149] L. Monsted and O. Monsted, *Acta Chem. Scand.*, 1974, **A28**, 569; 1973, **27**, 2121.

aquation are acid-independent and values are noticeably smaller than those reported in the earlier study where a nitrate medium was used. The reactions proceed with retention of configuration, and with a few exceptions the results from two different groups in perchlorate media (Table 11) are in reasonable agreement. Approximate

Table 11 *Rate constants (k) and activation parameters for the acid hydrolysis of chromium(III) ammines (μ = 1.0 mol l^{-1} in perchlorate medium)*

No.	*Complex ion*	$10^6k/s^{-1}$ (*temperature*/°C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
1	$[Cr(NH_3)_6]^{3+}$	47.5 (70)	27.0[h]		149[i]
		78 (75)	24.6	−6.9	15[j]
2	$[Cr(NH_3)_5(OH_2)]^{3+}$	47.2 (70)[a]	26.5		149
		77 (75)	24.6	−7.0	15
3	*trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	44.4 (70)[b]	25.7		149
		75 (75)	25.0	−5.9	15
4	*cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	24.2 (70)[c]	25.1		149
		50 (75)	26.7	−1.8	15
5	*mer*-$[Cr(NH_3)_3(OH_2)_3]^{3+}$	23.5 (70)[d]	25.4		149
		26 (75)			15
6	*fac*-$[Cr(NH_3)_3(OH_2)_3]^{3+}$	7.6 (70)[e]	27.0		149
7	*trans*-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	17.5 (70)[f]	25.7		149
		7.1 (75)			15
8	*cis*-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	3.4 (70)[g]	26.4		149
9	$[Cr(H_2O)_5(NH_3)]^{3+}$	1.1 (70)	28.0		149
		1.1 (75)	30.3	+1.0	15

[a] Product is *4*; a negligible amount of *3* is formed. [b] Product is *5*; rate constants at 70 °C for reactions to give *4* and *6* are 10^6k = 4.2 and 0.8 s^{-1} respectively. [c] Product is *6*; rate constants at 70 °C for reactions to give *3* and *5* are 10^6k = 0.0 and 3.3 s^{-1} respectively. [d] Product is *8*; rate constants at 70 °C for reactions to give *6* and *7* are 10^6k = 1.1 and 0.5 s^{-1} respectively. [e] Product is *8*; rate constants at 70 °C for reactions to give *5* and *7* are 10^6k = 0.3 and 0.03 s^{-1} respectively. [f] Rate constant for isomerization to *cis*-isomer *8* is 10^6k = 5.25 s^{-1}. [g] Rate constant for isomerization to *trans*-isomer *7* is negligible. [h] $\Delta H^{\ddagger}$ at 298 K was calculated from the quoted activation energy by subtracting 0.6 kcal mol^{-1}. [i] 0.5—1.0M-$HClO_4$; μ = 1.0 mol l^{-1}. [j] 1.0M-$HClO_4$.

kinetic data for the base-hydrolysis reactions are also reported.[15] Although isomerization reactions usually have rates much lower than those for aquation, for the complex ion *cis*-$[Cr(NH_3)_2(OH_2)_4]^{3+}$ isomerization to the *trans*-isomer contributes *ca.* 20% to its rate of disappearance.[149]

$[Cr(H_2O)_5L]^{n+}$ *Complexes.* Aquation of complexes of this type (L = unidentate ligand) usually proceeds with a generalized rate law of the type

$$-\mathrm{d[complex]}/\mathrm{d}t = (k_{-1}/[H^+] + k_0 + k_1[H^+] + k_2[H^+]^2)[\mathrm{complex}] \quad (27)$$

Terms involving k_1 and k_2 arise only in those cases where L is readily protonated (*e.g.* L = F^-, N_3^-, or CN^- gives rise to a term involving k_1 and L = ONO^- gives rise to terms involving both k_1 and k_2). Rate constants k_0 and k_{-1} are usually associated with the spontaneous uncatalysed aquations of $[Cr(H_2O)_5L]^{n+}$ and $[Cr(H_2O)_4(OH)L]^{(n-1)+}$ respectively. When L is a basic ligand ($pK_a > 2$), the term involving the rate constant k_0 is usually ascribed to the loss of the protonated ligand (HL^+) with the concomitant formation of $[Cr(H_2O)_5(OH)]^{2+}$ in aqueous media:

$$[Cr(H_2O)_5L]^{n+} + H_2O \xrightarrow{k_0} [Cr(H_2O)_5(OH)]^{n-1} + HL^+ \quad (28)$$

$$[Cr(H_2O)_5L]^{n+} + H_2O \xrightarrow{k_0} [Cr(H_2O)_6]^{3+} \quad HL \quad (29)$$

Reaction (28) is postulated to be important when L has a $pK_a > 2$, whereas reaction (29) occurs when L has a $pK_a < 0$.[150]

The complex ion $[Cr(H_2O)_5(SCH_2CH_2NH_3)]^{3+}$ has been separated by ion-exchange methods following the inner-sphere reaction between $[Cr(H_2O)_6]^{2+}$ and $[Co(en)_2(NH_2CH_2CH_2S)]^{2+}$ ions.[150] Aquation in excess acid involves terms in k_0 and k_1 [equation (27)]. The k_0 term is associated with loss of the protonated ligand [reaction (28)]. Rate data are collected in Table 12.

Complexes in which L is a substituted pyridine have been prepared by reducing the corresponding pyridine adducts of diperoxychromium(VI) with acidic ferrous perchlorate followed by the usual ion-exchange separation.[151] Acid aquation of these complexes involves terms in k_{-1} and k_0 [equation (27)]. The recent rate data are collected in Table 12; $\log k_0$ and $\log k_{-1}$ vary linearly with the pK_a of the pyridines.

The interesting complex ion $[Cr(H_2O)_5CF_3]^{2+}$ has been investigated in acidic solutions and the rate of the very slow hydrolysis measured.[152] The reaction is:

$$[Cr(H_2O)_5CF_3]^{2+} + H_3O^+ \longrightarrow [Cr(H_2O)_6]^{3+} + HF + CO \qquad (30)$$

The initial rates involve terms in k_0 and k_1 [equation (27)], the rate constants being *ca.* 10^5 times smaller than for the previously investigated $[Cr(H_2O)_5CH_3]^{2+}$ ion. As the reaction proceeds the rate is accelerated by the formation of the $[Cr(H_2O)_4(CF_3)F]^+$ ion and data shown in Table 12 refer to initial rate measurements. Reaction (30) is explained by a mechanism in which the chromium–carbon and carbon–fluorine bonds are broken in a concerted manner.

Unusual dinuclear complexes are often formed by the oxidation of the $[Cr(H_2O)_6]^{2+}$ ion with an inert metal complex. The species $[(H_2O)_5Cr^{III}(\text{isonicotinamide})Ru^{II}(NH_3)_5]^{5+}$ is formed in this way, in which the isonicotinamide bridges between the two metal ions, being co-ordinated to ruthenium(II) at the heterocyclic pyridine nitrogen atom and to chromium(III) at the carbonyl oxygen atom. The kinetics of the decomposition of this dinuclear species have been investigated in the presence of an acidic aqueous chromium(II) catalyst.[153] The observed rate constant, k, is given by

$$k = k_0 + k_{-1}/[H^+] + k_{-2}[Cr^{II}]/[H^+]$$

Catalysis by chromium(II) involves the formation of a $Cr^{III}—OH—Cr^{II}$ hydroxo-bridged species. Some preliminary data are also reported for the analogous nicotinamide system.[153] A similar study involves the decomposition of a uranium(V)–chromium(III) dinuclear complex in the presence of excess chromium(II).[154] Approximate rate data for the uncatalysed reactions are shown in Table 12.

Other Complexes. Two new complex ions, *cis*-$[Cr(ox)_2(N_3)_2]^{3-}$ and *cis*-$[Cr(ox)_2(N_3)OH_2]^{2-}$, have been characterized and their acid-catalysed aquation reactions established to occur with retention of configuration.[155] For the diazido-complex at high acidities only the term involving k_1 [equation (27)] is important, and at 308.1 K, $k_1 = 0.29\ l\ mol^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 20.5 \pm 0.7$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 5.8 \pm 2.3$ cal K^{-1} mol^{-1}. For the azido-aqua-complex between pH 5 and 0.5 mol l^{-1} [H$^+$] terms

[150] L. E. Asher and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 1774.
[151] A. Bakac, R. Marcec, and M. Orhanovic, *Inorg. Chem.*, 1974, **13**, 57.
[152] S. K. Malik, W. Schmidt, and L. O. Spreer, *Inorg. Chem.*, 1974, **13**, 2986; S. K. Malik, *Diss. Abs. Internat.* (*B*), 1973, **34**, 1416.
[153] R. W. Craft and R. G. Gaunder, *Inorg. Chem.*, 1974, **13**, 1005.
[154] A. Ekstrom, *Inorg. Chem.*, 1973, **12**, 2455.
[155] K. R. Ashley and R. S. Lamba, *Inorg. Chem.*, 1974, **13**, 2117.

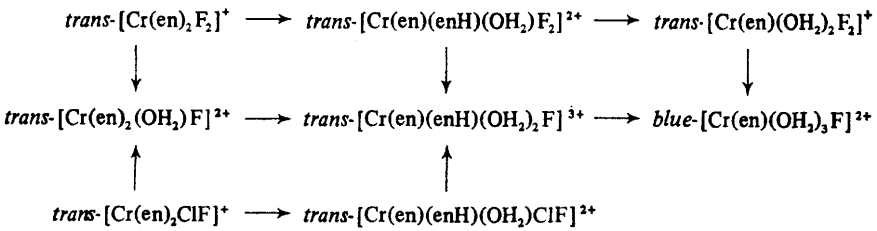
Table 12 *Rate data at* 298.1 K *for the acid hydrolysis of* $[Cr(H_2O)_5L]^{n+}$ *complexes* [*equation* (27)]

L	10^9k_{-1}/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}(k_{-1})$/ kcal mol^{-1}	$\Delta S^{\ddagger}(k_{-1})$/ cal K^{-1} mol^{-1}	10^7k_0/ s^{-1}	$\Delta H^{\ddagger}(k_0)$/ kcal mol^{-1}	$\Delta S^{\ddagger}(k_0)$/ cal K^{-1} mol^{-1}	10^5k_1/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}(k_1)$/ kcal mol^{-1}	$\Delta S^{\ddagger}(k_1)$/ cal K^{-1} mol^{-1}	*Ref.*
$SCH_2CH_2NH_3^{+a}$				450	27.6	14.0	13.1	20.6	−7.1	150
3-Chloropyridine	1.6	33.5	13.7	1.6	26.3	−1.6				151
3-Cyanopyridine	11	31.7	11.3	13	23.9	−5.2				151
CF_3				0.33			8.6×10^{-3}			152
NH_3				11[b]	28.0, 30.3	+1.0				15, 149
Ru^{II}(isonicotinamide)	280			30.7[d]						153
$U^{V}O_2^{+}$				8.3×10^5 [c]	12.8	−21.2				154

[a] μ = 2.0 mol l^{-1} ($LiClO_4$). [b] At 343.1 K, μ = 1.0 mol l^{-1}. [c] At 303.1 K, μ = 3.0 mol l^{-1}. [d] μ = 1.0 mol l^{-1}; at μ = 0.4 mol l^{-1}, 10^7k_0 = 17 s^{-1} and 10^9k_{-1} = 272 l mol^{-1} s^{-1}.

involving k_0 and k_1 [equation (27)] dominate, and the rate constants at 308.1 K are characterized by $10^5k_0 = 7.5\ s^{-1}$, $\Delta H^{\ddagger}(k_0) = 18.4 \pm 1.6$ kcal mol^{-1}, $\Delta S^{\ddagger}(k_0) = 18 \pm 5$ cal K^{-1} mol^{-1}, $10^2k_1 = 4.78$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger}(k_1) = 17.8 \pm 0.4$ kcal mol^{-1}, and $\Delta S^{\ddagger}(k_1) = -7.0 \pm 1.4$ cal K^{-1} mol^{-1}. Protonation is postulated to occur at the co-ordinated azido-groups.

A comparison has been made between the acid hydrolysis of *trans*-$[Cr(tmd)_2FX]^+$ (tmd = 1,3-diaminopropane, X = F, Cl, or Br) and *trans*-$[Cr(en)_2FX]^+$ ions (X = F or Cl).[156] The 1,2-diaminoethane complexes are much more susceptible to opening of the chelate rings (Cr—N bond rupture) than is the case for tmd complexes. Rate data for the pathways shown in Scheme 3 are given at various acidities



Scheme 3

in the original paper (enH represents a dangling monoprotonated unidentate 1,2-diaminoethane).[156] Loss of fluoride ion shows the usual acid catalysis with rate data which are very similar for en and tmd complexes (Table 13). The isomerization and further loss of fluoride ion from the *trans*-$[Cr(tmd)_2(OH_2)F]^{2+}$ ion are much slower and only estimates of the rates were obtained.

Table 13 *Comparison of rate data for the acid hydrolysis of* trans-$[Cr(AA)_2FX]^+$ *complexes* (X = *leaving ion*)

AA	X	$10^4k_0/s^{-1}$ (μ/mol l^{-1}; *temp.*/°C)	$\Delta H^{\ddagger}(k_0)$/ kcal mol^{-1}	$\Delta S^{\ddagger}(k_0)$/ cal K^{-1} mol^{-1}
tmd[b]	F	2.6 (2.0; 50)[a]	25.8	+6.2
tmd	Cl	13 (2.0; 50)	18.0	−14
tmd	Br	110 (1.0; 50)	16.4	−17
en	F	3.5 (6.0; 50)[a]	(28)	
en	Cl	< 7 (0.15; 50)		
		0.62 (0.01; 25)[c]		
		2.59 (0.01; 36)[c]		

[a] Refers to k_1/l mol^{-1} s^{-1}. [b] tmd = 1,3-diaminopropane. [c] Ref. 175; other data from ref. 156.

The aquation of the *trans*-$[Cr(en)_2(NCS)_2]^+$ ion in perchloric acid ($2—20 \times 10^{-3}$ mol l^{-1}) and sodium nitrate (μ = 1.0 mol l^{-1}) is reported to proceed in two stages and it is claimed that the first stage is much slower than the second:[157]

$$trans\text{-}[Cr(en)_2(NCS)_2]^+ + H_2O \xrightarrow[k_1]{\text{slow}} trans\text{-}[Cr(en)_2(OH_2)(NCS)]^{2+} + NCS^- \quad (31)$$

$$trans\text{-}[Cr(en)_2(OH)_2(NCS)]^{2+} + H_2O \xrightarrow{\text{rapid}} trans\text{-}[Cr(en)_2(OH_2)_2]^{3+} + NCS^- \quad (32)$$

[156] J. M. De Jovine, W. R. Mason, and J. W. Vaughn, *Inorg. Chem.*, 1974, **13**, 66.
[157] C. Várhelyi, I. Zsakó, and G. Simo, *Chem. Abs.*, 1973, **79**, 108 536z.

This report is opposite to expectations since reaction (32) could be predicted to proceed at a lower rate than reaction (31) because of the differences in overall charge which affect the ease of metal–ligand bond cleavage. The authors also observed an inverse acid-dependence of the observed rate constant k:

$$k = k_1 + K(k_2 - k_1)/\{[H^+] + K\}$$

k_1 is ascribed to reaction (31), and k_2 is assigned to the aquation (in acidic media!) of the conjugate-base complex $[Cr(en)(en-H)(NCS)_2]$. The equilibrium constant (K) for formation of this conjugate base is unbelievably large: $10^3K = 2.18$—1.96 mol l^{-1} between 338 and 353 K. $10^5k_1 = 2.0\ s^{-1}$ and $10^5k_2 = 19.5\ s^{-1}$ at 338 K, and the respective activation parameters are reported to be $\Delta H^*(k_1) = 29.6 \pm 0.7$ kcal mol^{-1}, $\Delta H^*(k_2) = 24.3 \pm 1.2$ kcal mol^{-1}, $\Delta S^*(k_1) = 7.3 \pm 2.2$ cal K^{-1} mol^{-1}, and $\Delta S^*(k_2) = -4.0 \pm 3.1$ cal K^{-1} mol^{-1}. It should be pointed out that these studies were carried out in a 1.0M nitrate medium, and in view of the marked accelerating effect of nitrate ion upon the rate of aquation of chromium(III) ammines[14–16] it will be necessary to reinvestigate these results in the absence of interfering anions. Also, the possible opening of the 1,2-diaminoethane chelate rings should not be overlooked.

As part of a photochemical study of the *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$ ion, data have been reported for the thermal aquation of the first chloride ion.[158] At 320.9 K, $10^5k = 6.9\ s^{-1}$, $\Delta H^* = 24.8 \pm 0.5$ kcal mol^{-1}, and $\Delta S^* = 1 \pm 1$ cal K^{-1} mol^{-1}.

Following studies of the aquation of $[Cr(H_2O)_5(pyX)]^{3+}$ ions (pyX = pyridine or substituted pyridine),[151] the complex ions *cis*- and *trans*-$[Cr(H_2O)_4(py)_2]^{3+}$ and $[Cr(H_2O)_3(py)_3]^{3+}$ have been prepared and the rate of loss of the first pyridine from each ion has been reported.[159] At 363.1 K, $10^4k = 1.78$ and $5.88\ s^{-1}$ for the *trans*- and *cis*-$[Cr(H_2O)_4(py)_2]^{3+}$ ions respectively, and at 358.1 K $10^4k = 3.62\ s^{-1}$ for $[Cr(H_2O)_3(py)_3]^{3+}$ in 1M-$HClO_4$.

A thesis has appeared concerned with the kinetics of *cis*- and *trans*-water exchange reactions in some aquachromium(III) complexes.[160]

Multidentate Leaving Groups.—Earlier kinetic investigations of the $[Cr(OH_2)_4(SCH_2CO_2)]^+$, $[Co(en)_2(SCH_2CO_2)]^+$, and $[Co(en)_2(SCH_2NH_2)]^{2+}$ ions have been followed[161] by studies of the acid hydrolysis of the analogous complexes $[Cr(en)_2(SCH_2CO_2)]^+$ and $[Cr(en)_2(SCH_2NH_2)]^{2+}$. The reactions are formulated as an approach to equilibrium between chelated and unidentate thiolato-ligands with predominantly chromium–sulphur bond fission, *e.g.*

$$\begin{array}{ccc} [Cr(en)_2(SCH_2CO_2)]^+ + H_2O & \rightleftharpoons & [Cr(en)_2(OH_2)(O_2CCH_2S)]^+ \\ \Big\downarrow\uparrow H^+ & & \Big\downarrow\uparrow H^+ \\ [Cr(en)_2(HSCH_2CO_2)]^{2+} + H_2O & \rightleftharpoons & [Cr(en)_2(OH_2)(O_2CCH_2SH)]^{2+} \end{array}$$

The acid-catalysed pathway predominates, the rates of chromium–sulphur bond fission being more than 10^4 times as great as those found for the analogous breaking of cobalt–sulphur bonds. This rate difference is partly attributed to the different basicities of the co-ordinated sulphur atoms in complexes of cobalt(III) and chro-

[158] C. Kutal and A. W. Adamson, *Inorg. Chem.*, 1973, **12**, 1990.
[159] A. Bakac and M. Orhanovic, *Z. Naturforsch.*, 1974, **29b**, 134.
[160] R. A. Keen, *Diss. Abs. Internat. (B)*, 1973, **34**, 1415.
[161] C. J. Weschler and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 2682.

mium(III). For the acid-independent reactions competitive breaking of chromium–nitrogen bonds occurs at the ethylenediamine–chromium(III) rings.

Data have been reported for the stepwise aquation of the tris(ethanolamine)-chromium(III) ion.[162] The three first-order steps have decreasing rate constants and activation energies of 67.5, 67.0, and 65.6 kJ mol^{-1}.

Acid hydrolysis of the $[Cr(acac)_2(OH_2)_2]^+$ ion in perchloric acid at $\mu = 1.0$ mol l^{-1} and 70—90 °C has a rate law of the type

$$-d[complex]/dt = (k_0 + k_1[H^+])[complex] \quad (33)$$

Rate-determining chelate-ring-opening is postulated with activation parameters associated with k_0 and k_1 as follows: $\Delta H^{\ddagger} = 19.3$ and 26.4 kcal mol^{-1} and $\Delta S^{\ddagger} = 2.51$ and -2.6 cal K^{-1} mol^{-1} respectively. A rate law similar to equation (33) is reported for the equilibration of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ ion with its *trans*-isomer, where $k_0 = k'_0 + k'_{-0}$ and $k_1 = k'_1 + k'_{-1}$. A mechanism involving chelate-ring-opening (with and without acid catalysis) is postulated, k'_0, k'_1, and k'_{-0}, k'_{-1} referring to the forward and reverse reactions respectively.[163]

Effects of Non-leaving Ligands.—Very little work is reported in this area although the results in Table 13 (discussed previously) allow a comparison between 1,3-diaminopropane and 1,2-diaminoethane as non-leaving groups (L) in $[Cr(L)_2FX]^+$ (X = F or Cl) ions. The rate differences are only marginal, the main distinction between these two classes of compound being the greater tendency for 1,2-diaminoethane chelate ring-opening.[156]

The aquation of the *trans*-$[Cr(2,3,2\text{-tet})Cl_2]^+$ ion[158] (at 320.9 K, $10^5k = 6.9$ s^{-1}, $\Delta H^{\ddagger} = 24.8$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 1$ cal K^{-1} mol^{-1}) is slower than that of the related complexes *trans*-$[Cr(AA)_2Cl_2]^+$ (AA = en or pn), in line with similar studies of cobalt(III) complexes.

cis-Activation by oxoanions (*e.g.* NO_3^-, SO_3^{2-}, AcO^-, or ox^{2-}) co-ordinated to chromium(III) has been increasingly recognized in recent years and was discussed in the introduction to this chapter. A recent example is reported from a study of the aquation and base hydrolysis of the $[Cr(NH_3)_5(ONO_2)]^{2+}$ ion.[14] In acid solution aquation yields only 33% $[Cr(NH_3)_5(OH_2)]^{3+}$, the other major products being *cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ and $[Cr(NH_3)_3(OH_2)_3]^{3+}$ ions. At pH 6 the initial products are $[Cr(NH_3)_5(OH)]^{2+}$ and *cis*-$[Cr(NH_3)_4(OH)(ONO_2)]^+$ ions, the rate constant for loss of $[Cr(NH_3)_5(ONO_2)]^{2+}$ being $10^3k = 2.4$ s^{-1} at 298.1 K ($\Delta H^{\ddagger} = 20.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.1$ cal K^{-1} mol^{-1}). Base hydrolysis only gives the $[Cr(NH_3)_5(OH)]^{2+}$ ion ($10^2k_{OH} = 1.1$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 25.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 17.0$ cal K^{-1} mol^{-1}). Formation of $[Cr(NH_3)_3(OH_2)_3]^{3+}$ in the acid-catalysed reaction is believed to involve transient chelation of the co-ordinated nitrate ion at the expense of a *cis*-ligand. A discussion of analogous mechanisms for other oxoanions is given in this paper.[14] Related catalysis by oxoanions[16] is discussed in the section concerned with catalysis.

Bridged Dichromium Complexes.—Recent studies of bridge-cleavage reactions of hydroxo-bridged complexes of the types *cis*-$[(NH_3)_5Cr\text{-}\mu\text{-}(OH)\text{-}Cr(NH_3)_4X]^{4+}$ (X = F or NCS)[164] and *cis*-$[(NH_3)_5Cr\text{-}\mu\text{-}(OH)\text{-}Cr(NH_3)_4OH_2]^{5+}$ (ref. 165) are in line

[162] A. A. Koroleva, N. P. Kumantsova, and E. G. Timofeeva, *Chem. Abs.*, 1974, **80**, 125 338z.
[163] M. W. Rophael and M. A. Malati, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1355.
[164] H. N. Po, Y.-H. Chung, and S. R. Davis, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2849.
[165] H. N. Po and H. Enomoto, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2581.

with earlier studies by Hoppenjans and Hunt (1968—69). These reactions are different from those of the analogous cobalt(III) complexes because no acid catalysis is observed even at high acidities. This can be attributed to the lower basicity of the linear Cr—OH—Cr bridge in the chromium(III) complexes. Rate data for the recently studied reactions were given in Volume 3.[166]

A study of the formation of the *cis*-$[(NH_3)_5Cr\text{-}\mu\text{-}(OH)\text{-}Cr(NH_3)_4NCS]^{4+}$ from the reaction between excess thiocyanate ion and the *cis*-aqua-*erythro*-ion gives an observed pseudo-first-order rate constant, $k = k_a + k_b[NCS^-]$; $10^5k_a = 3.44\ s^{-1}$ and $10^5k_b = 10.1\ l\ mol^{-1}\ s^{-1}$ at 298.1 K. The two-term rate law is interpreted as involving S_N1(lim) and S_N1(ip) mechanisms.[167] Representing *cis*-$[(NH_3)_5Cr\text{-}\mu\text{-}(OH)\text{-}Cr(NH_3)_4OH_2]^{5+}$ as ROH_2^{5+}, the proposed mechanism is

$$\left.\begin{aligned} ROH_2^{5+} &\rightleftharpoons R^{5+} + OH_2 \\ R^{5+} + NCS^- &\longrightarrow RNCS^{4+} \end{aligned}\right\} S_N1(\text{lim})\ \text{mechanism}$$

$$\left.\begin{aligned} ROH_2^{5+} + NCS^- &\rightleftharpoons (ROH_2^{5+},NCS^-)\ (\text{ion pair}) \\ (ROH_2^{5+},NCS^-) &\longrightarrow RNCS^{4+} + H_2O \end{aligned}\right\} S_N1(\text{IP})$$

Non-aqueous Solvents.—Mention has already been made of the evidence for an associative (I_a) mechanism for the exchange of DMSO with the $[Cr(DMSO)_6]^{3+}$ ion.[148] Both the entropy and volume of activation are large and negative. A recent study of the exchange process by n.m.r. in DMSO–$MeNO_2$ mixed solvents (nitromethane is an inert, non-co-ordinating diluent which is known to have very little rate effect) shows that the exchange rate is approximately constant above 0.2 mole fraction of DMSO, but drops off sharply below this concentration.[169] On the other hand the fraction of DMSO molecules in the solvation shell of the $[Cr(DMSO)_6]^{3+}$ ion decreases immediately with the decrease in the DMSO mole fraction. This difference in concentration effects is postulated to arise from a unique outer-sphere solvation site which preferentially binds DMSO molecules and preferentially participates in the exchange reaction.

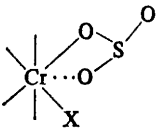
Catalysis.—Acid- and base-catalysed reactions have already been mentioned [equation (27)] and will not be dealt with further in this section. *cis*-Activation by co-ordinated oxoanions has also been discussed in the section dealing with the effects of non-leaving groups. Addition of sulphite, acetate, and nitrate ions to $[Cr(H_2O)_5X]^{2+}$ complexes (X = F, N_3, or AcO) is also reported to accelerate the rate of aquation by the facile formation of oxoanion complexes.[16] Rate data are reported for sulphite labilizations of the acetato- and azido-complexes and the nitrate labilizations of acetato- and fluoro-complexes. The catalysed reactions are characterized by a rate law of the type

$$-d[Cr(H_2O)_5X^{2+}]/dt = k[H^+][\text{oxoanion}][Cr(H_2O)_5X^{2+}] \qquad (34)$$

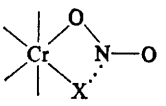
In the case of sulphite ion as a catalyst equation (34) is equivalent to attack by HSO_3^-. This process is readily understood since formation of O-bonded sulphito-

[166] Ref. 1, p. 200.
[167] H. N. Po, Y.-H. Chung, S. R. Davis, and H. Enomoto, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1349.
[168] C. H. Langford, R. Scharfe, and R. Jackson, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1033.
[169] T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, 1966, **5**, 1100; R. J. Balahura and R. B. Jordan, *ibid.*, 1970, **9**, 2639.

complexes is analogous to the formation of nitrito-complexes[17] and is known to be very rapid since chromium–oxygen bond cleavage is not necessary. However, the mechanism for the catalysis by sulphite ion[16] is probably not the same as that proposed for nitrite ion[17] involving a transition state of type (15) rather than type (16).



(15)



(16)

Chelation by the O-bonded sulphite ion is postulated to involve the formation of a seven-co-ordinate intermediate (or transition state) which readily loses the *cis*-ligand (X^-). Catalysis by nitrate ion is also found to obey equation (34) and a mechanism for the loss of X^- analogous to that described above is favoured.[15,16] The facile formation of nitrato-complexes and subsequent rapid loss of X^- is postulated to occur by the following mechanism (X = OAc):

$$[Cr(H_2O)_5X]^{2+} + H^+ \overset{\text{rapid}}{\rightleftharpoons} cis\text{-}[Cr(H_2O)_4(H_3O)X]^{3+} \quad (35)$$

$$cis\text{-}[Cr(H_2O)_4(H_3O)X]^{3+} + NO_3^- \longrightarrow cis\text{-}[Cr(H_2O)_4(ONO_2)X]^+ + H^+ \quad (36)$$

$$cis\text{-}[Cr(H_2O)_4(ONO_2)X]^+ \overset{\text{rapid}}{\longrightarrow} [Cr(H_2O)_5ONO_2]^{2+} + X^- \quad (37)$$

Reaction (35) involves protonation of a co-ordinated water molecule, for which there is prior evidence.[169] This reaction and the subsequent formation of the *cis*-nitrato-complex [reaction (36)] are easier when X^- is acetate ion because of the *cis*-activation of the co-ordinated acetato-group. When X^- is fluoride ion catalysis by nitrate ion is less pronounced and the $[Cr(H_2O)_5ONO_2]^{2+}$ ion is not a product. Although the mechanism depicted by equations (35)—(37) is still favoured when X = F {involving the *cis*-$[Cr(H_2O)_4(ONO_2)F]^+$ ion which loses both NO_3^- and F^- rapidly} one cannot rule out the possibility that other mechanisms may be involved. It is also possible that reaction (35) involves the protonation of the more basic ligand, X.

The bromine-catalysed removal of alkyl, halogenoalkyl, and 4-pyridinomethyl groups (R) from $[Cr(H_2O)_5R]^{2+}$ ions in perchloric acid is consistent with an S_E2 mechanism with postulated stereochemical inversion at the co-ordinated carbon atom:[170]

$$[Cr(H_2O)_5R]^{2+} + Br_2 \longrightarrow [Cr(H_2O)_6]^{3+} + Br^- + RBr \quad (38)$$

This reaction does not lead to any formation of the $[Cr(H_2O)_5Br]^{2+}$ ion, in line with attack at the α-carbon atom. This mechanism is formally analogous to S_E2 attack by mercury(II) ion at alkylcobaloximes.[126]

Catalysis by reversed micelles was also discussed previously in connection with substitution reactions at cobalt(III).[129,130] In a similar study rate constants for the *trans*→*cis* isomerization of the $[Cr(ox)_2(OH_2)_2]^-$ ion in the polar cavities of reversed alkylammonium carboxylate micelles in benzene are up to 63 times as large as values found in pure water.[171] At constant water activity increasing the concentration of

[170] J. H. Espenson and D. A. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 1008.
[171] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1974, **96**, 370.

surfactant increases the rate to a maximum after which the rate remains constant. Similarly, at constant concentration of surfactant, at the plateau region, increasing the water concentration increases the rate of reaction to a maximum value after which the rate remains constant. These results are interpreted in terms of solubilization of the substrate in the polar cavity of the reversed micelle where isomerization involves water in a rate-determining step. A linear free-energy relationship was observed between the logarithm of the rate constants for isomerization and the pK_a differences between amines and carboxylic acids for two series of alkylammonium carboxylate surfactants.

Photochemistry.—Chromium(III) continues to be one of the most popular metal ions for studies of photochemical reactions. Adamson's rules[139] are widely applicable to photosubstitution reactions of chromium(III) for which there is theoretical support.[143,144]

In recent years there has been increasing evidence that for chromium(III) complexes photoaquation reactions following *d–d* irradiation involve stereochemical change. This is in marked contrast to the thermal aquations which nearly always proceed with retention of configuration. Further evidence in support of this generalization comes from a study of the photolysis of a mixture of *cis*- and *trans*-$[Cr(NH_3)_4(^{15}NH_3)Cl]^{2+}$ ions.[172] The $^{15}N/^{14}N$ ratio of the photoaquated ammonia was measured by ^1H n.m.r. Photolysis at 503 nm ($^4T_{2g} \leftarrow {}^4A_{2g}$) results in at least 75% loss of ammonia in a *trans* position to the chloride ion (*i.e.* on the weak average ligand-field axis as predicted by Adamson's rules). However, the product is the *cis*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$ ion and so the photoaquation upon *d–d* irradiation must involve stereochemical change. Photolysis at 254 nm in the charge-transfer region results in the loss of only 40—50% of the ammonia in a *trans* position to the chloride ion as expected.

Quantum yields for the photoaquation of the $[Cr(NH_3)_5Cl]^{2+}$ and $[Cr(RNH_2)_5Cl]^{2+}$ ions (R = Me, Et, or Pr^n) have been remeasured and the value found for loss of chloride ion is an order of magnitude smaller than originally reported.[173] The

$$[Cr(RNH_2)_5Cl]^{2+} + H_3O^+ \xrightarrow{h\nu} \textit{cis}\text{-}[Cr(RNH_2)_4(OH_2)Cl]^{2+} + RNH_3^+ \quad (39)$$

$$[Cr(RNH_2)_5Cl]^{2+} + H_2O \xrightarrow{h\nu} [Cr(RNH_2)_5OH_2]^{3+} + Cl^- \quad (40)$$

$$[Cr(RNH_2)_4(OH_2)Cl]^{2+} + H_2O \xrightarrow{\text{thermal}} [Cr(RNH_2)_4(OH_2)_2]^{3+} + Cl^- \quad (41)$$

problem is that although reaction (39) dominates over reaction (40), the thermal reaction (41) is faster than reaction (40), and so the quantum yield for loss of chloride ion is inaccurate unless allowance is made for this.

The mechanism for the photoaquation of *trans*-$[Cr(A_4)Cl_2]^+$ ions involves the formation of a *trans*-product when A_4 is cyclam (1), but a *cis*-product when A_4 is 2,3,2-tet. The *cis*-$[Cr(cyclam)Cl_2]^+$ ion is analogous to the *trans*-isomer in photoaquating with retention of configuration.[174] These results are to be expected for the complexes of the sterically constrained cyclam ligand. The mechanism most consistent with all the data involves *trans* attack by the incoming solvent molecule with

[172] E. Zinato, P. Riccieri, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1974, **96**, 375.
[173] C. F. C. Wong and A. D. Kirk, *Canad. J. Chem.*, 1974, **52**, 3384.
[174] C. Kutal and A. W. Adamson, *Inorg. Chem.*, 1973, **12**, 1990.

some degree of bond-making involved in the rate-determining step.[174] For *trans*-$[Cr(A_4)Cl_2]^+$ ions [A_4 = $(NH_3)_4$, $(en)_2$, 2,3,2-tet, or cyclam] there is a correlation between the quantum yields and the rate constants for thermal aquation.

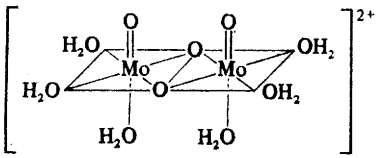
A study of the thermal and photochemical aquation of the *trans*-$[Cr(en)_2ClF]^+$ ion is reported.[175] The results of the thermal aquation are in line with those of another group[156] discussed previously (Table 13), involving the formation of some $[Cr(en)(enH)(OH_2)FCl]^{2+}$ as well as *trans*-$[Cr(en)_2(OH_2)F]^{2+}$ ion in acidic solution. The results of the photoaquation involve loss of chloride ion to give mainly *cis*-$[Cr(en)_2(OH_2)F]^{2+}$ ion, reportedly in violation of Adamson's second rule.[139] Some *trans*-$[Cr(en)_2(OH_2)F]^{2+}$ ion and unidentate 1,2-diaminoethane complex are also formed. The ease with which ligands are lost upon photoaquation is observed to decrease in the order $NH_3 > H_2O > Cl^- \approx NCS^- > F^-$ (and $NH_3 > Br^- > F^-$), whereas a simple interpretation of Adamson's second rule would predict $NH_3 > NCS > H_2O > F^- > Cl^- > Br^-$ as the expected order.[175]

Emission from irradiated $[Cr(bipy)_3]^{3+}$ ion in DMSO solution is assigned as fluorescence from $^4T_2$ to $^4A_2$ states.[176] This is claimed as the first example reported of fluorescence from a chromium(III) complex. Room-temperature emission from aqueous solutions of $[Cr(phen)_3]^{3+}$ and $[Cr(bipy)_3]^{3+}$ ions following *d–d* irradiation gives rise to two phosphorescence bands assigned as arising from the ^2E and $^2T_2$ states, the latter an example of delayed phosphorescence.

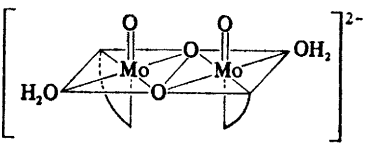
4 Aquation: Other Complexes

***d*¹: Molybdenum(V).**—The di-μ-oxo-bis[oxo(triaqua)molybdenum(v)] ion {$[Mo_2O_4]^{2+}$ (17)} complexes rapidly ($t_{1/2} < 1$ min at 273 K) with oxalate ion ($0.1 < [H^+] < 1.0$ mol l^{-1}) to give complex (18) in which each molybdenum(v) is co-ordinated to one oxalato- and one aqua-ligand.[10,177] Reaction of (17) with iminodiacetate ion at $[H^+] > 0.1$ mol l^{-1} produces very little complex formation, and it was found that the rate of dissociation of the 1 : 1 complex is given by

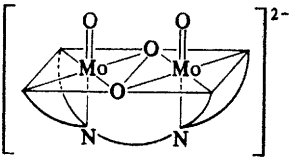
$$-\mathrm{d[complex]}/\mathrm{d}t = k_b[H^+]^2$$



(17)



(18)



(19)

[175] G. Wirth and R. G. Linck, *J. Amer. Chem. Soc.*, 1973, **95**, 5913.
[176] N. A. P. Kane-Maguire, J. Conway, and C. H. Langford, *J.C.S. Chem. Comm.*, 1974, 801.
[177] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1974, 1468.

At 273.1 K and with $0.5 < [H^+] < 1.0$ mol l^{-1}, $10^2k_b = 2.4$ l^2 mol^{-2} s^{-1}. Reaction of ethylenedinitrilotetra-acetic acid (edta) with (17) at $0.5 < [H^+] < 2.0$ mol l^{-1} gives (19), the rate constant for equilibration (k_{eq}) being given by $k_{eq} = k_f[edta] + k_b$. At 298.1 K, $\mu = 2.0$ mol l^{-1} and $[H^+] = 1.0$ mol l^{-1}, $k_f = 0.18$ l mol^{-1} s^{-1}, and $10^3k_b = 2.0$ s^{-1}. Variation of k_f and k_b with $[H^+]$ is complex: the dissociation rate constant $k_b = k_b^1[H^+]^4/\{1 + k_b^2[H^+]^3\}$ and k_f is inversely dependent on $[H^+]$. A chelate-ring-closure mechanism is proposed for the formation reaction following rapid attack by a nitrogen atom of the edta at a *trans* position to one of the Mo=O groups. These oxo-molybdenum groups are expected to exert a strong *trans* effect as observed in the VO^{2+} ion. Although closure of one of the glycinate arms of edta is favoured, bridging across by the second nitrogen atom of the ethylenediamine backbone of edta cannot be ruled out as the rate-determining step.[177] Reaction of the $[HMoO_4]^-$ ion [d^0, molybdenum(VI)] with $[edtaH_2]^{2-}$ is much more rapid than with the molybdenum(V) dimer, requiring the use of relaxation methods.[178]

Three studies have appeared dealing with the di-μ-oxo-bis[oxo-(L-cysteinato)-molybdenum(V)] ion $[Mo_2O_4(cysteine)_2]^{2-}$, which it is claimed may have relevance as a model for molybdenum-containing enzymes.[179-181] Reaction with cysteine in the pH range 8—10 results in cleavage of one oxo-bridge, giving a mixture of mono-oxo-bridged dimers.[179] In the absence of free cysteine the reaction is slow, a second-order rate law being observed (first-order in complex and free cysteine). The second-order rate constant (k_2) decreases with increasing pH, and at pH 9.2 (borate buffer), $\mu = 2.0$ mol l^{-1}, and 303 K, $10^2k_2 = 3.75 \pm 0.16$ l mol^{-1} s^{-1}. Products were identified by e.s.r. and visible spectroscopy.[179] In a similar kinetic study over the pH range 7.5—11.0 catalysis by *N*-acetylcysteine, glutathione, thioglycollic acid, β-mercaptopropionic acid, and histamine is reported, and the product is believed to be μ-oxo-bis[oxodihydroxy-(L-cysteinato)molybdenum(V)] ion.[181]

The di-μ-sulphido-bis[oxotriaquamolybdenum(V)] ion [structure (17) with oxo-bridges replaced by sulphido-bridges] is reported to be very stable even in strong acid solutions,[182] unlike (17) which dissociates into paramagnetic monomeric species.[183]

d^2: Molybdenum(IV).—Several reports have appeared dealing with the existence and properties of molybdenum(IV) in aqueous solutions.[11] Kinetic studies, however, have been concentrated upon photolytic investigations of cyanides of molybdenum(IV). Photolysis of the $[Mo(CN)_8]^{4-}$ ion in liquid ammonia[184] and in 0.1M-NaOH[185] have been reported. The mechanism proposed for the latter study agrees with the results of Samotus (1971) in which a relatively short-lived intermediate $[Mo(CN)_7OH]^{4-}$ and a longer-lived intermediate $[Mo(CN)_6]^{2-}$ were observed.[185] The complex ions $[Mo(CN)_7OH]^{4-}$ and $[MoO(OH)(CN)_4]^{3-}$, relevant to the photochemistry of the $[Mo(CN)_8]^{4-}$ ion, have now been characterized.[186]

[178] D. S. Honig and K. Kustin, *J. Amer. Chem. Soc.*, 1973, **95**, 5525.
[179] R. Stephenson and F. A. Schultz, *Inorg. Chem.*, 1973, **12**, 1762.
[180] A. Kay and P. C. H. Mitchell, *J.C.S. Dalton*, 1973, 1388.
[181] P. Kroneck and T. J. Spence, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3391.
[182] B. Spivack and Z. Dori, *J.C.S. Chem. Comm.*, 1973, 909.
[183] C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 831.
[184] R. D. Archer and D. A. Drum, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1979.
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[186] R. P. Mitra and H. Mohan, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3739.

***d*³: Molybdenum(III).**—A study of the rates of formation of the $[Mo(H_2O)_5X]^{2+}$ ions (X = Cl or NCS)[10] also gave data for the reverse (dissociation) reactions. For the chloro-complex the equilibrium constant (K_{eq}) at 298.1 K is only 10.8 l mol^{-1} and so the observed rate constant (k) for the formation process in the presence of excess chloride ion includes the rate constant (k_b) for the back reaction:

$$k = k_f[Cl^-] + k_b \quad (42)$$

at 298.1 K, $10^4 k_b = 4.26 \pm 0.12$ s^{-1}, $\Delta H^{\ddagger} = 12.9 \pm 0.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -30.7 \pm 2.1$ cal K^{-1} mol^{-1}. Therefore, the molybdenum(III) ion is much more labile than the analogous chromium(III) ion ($3d^3$). For the complex ion $[Cr(H_2O)_5Cl]^{2+}$ the corresponding rate data at 298.1 K are[187] $10^2 k_b = 2.8$ s^{-1}, $\Delta H^{\ddagger} = 25$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -7$ cal K^{-1} mol^{-1}. The $[Mo(H_2O)_5NCS]^{2+}$ ion is much more stable than the chloro-complex and so the value of k_b was not obtained from measurements of k [equation (42), replace Cl by NCS]. Nevertheless an approximate value of k_b can be calculated from the relationship $K_{eq} = k_f/k_b$. This gives k_b as *ca.* 2.7×10^{-6} s^{-1} at 298.1 K for $[Mo(H_2O)_5NCS]^{2+}$, compared with a value of 1.0×10^{-7} s^{-1} for the $[Cr(H_2O)_5NCS]^{2+}$ ion.[187] The greater lability of molybdenum(III) compared with chromium(III) complexes probably arises from the increased size of the molybdenum-(III) ion and the greater associative character of the substitution reactions. The rate data for the formation reactions also indicate S_N2 behaviour and these results are discussed in a later section.

***d*³: Rhenium(IV).**—The mechanism of the base hydrolysis of the $[ReCl_6]^{2-}$ ion has been reinvestigated, but no rate data are reported.[188] A review of the chemistry of rhenium has appeared.[189]

***d*⁴: Ruthenium(IV).**—The μ-nitrido-bis[aquatetrachlororuthenate(IV)] ion, $[(H_2O)Cl_4RuNRuCl_4(OH_2)]^{3-}$, is reported to aquate in acidic solution with loss of three chloride ions over a period of four hours. Rate constants for each of the three steps were determined at 298.1 K by three methods and the reported values are 0.01, 0.025, and 0.009 min^{-1} respectively.[190]

Rate data are reported for the aquation of the $[Ru_2OCl_{10}]^{4-}$ and $[RuCl_6]^{2-}$ ions at 25, 50, and 75 °C in hydrochloric acid. The mononuclear species reacts faster than the oxo-bridged dimer.[191]

***d*⁴: Osmium(IV).**—Iodide ion is known to exert to strong *trans* effect in many complexes such as those of platinum(II), platinum(IV), rhodium(III), iridium(III), and chromium(III). The activation energy for the loss of chloride ion is reported to be lowered by *ca.* 5 kcal mol^{-1} if a *trans*-iodide ion is present in complex ions of the type $[Os^{IV}Cl_nI_{6-n}]^{2-}$. The 18 possible stereospecific ligand-substitution reactions (n = 0—6) were investigated as a function of the ligand concentration, pH, ionic strength, and temperature. The complexes are more inert the greater the number of co-ordinated chloride ions present.[192]

[187] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, New York, 1967, 2nd Edn., p. 164.
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[192] W. Preetz and H. J. Walter, *Z. anorg. Chem.*, 1973, **402**, 169.

d^5: Iron(III).—Substitution reactions of low-spin iron(III) complex ions of the type $[Fe(CN)_5X]^{2-}$ (X = NH_3 or H_2O) in which the ligand X is replaced by nucleophiles Y {Y = N_3^-, NCS^-, OH^-, or $[Co(CN)_6]^{3-}$} are reported to be catalysed by the iron(II) complex ions $[Fe(CN)_5X]^{3-}$. At iron(II) concentrations greater than *ca.* 1% of the total iron species the rate-determining step of these reactions is substitution of $[Fe(CN)_5X]^{3-}$ by Y.[193] These results place in doubt earlier studies of these reactions in which reduction to iron(II) was not recognized. For example, in the recent study of the reaction of the $[Fe(CN)_5OH_2]^{2-}$ ion with thiocyanate ion reduction to the iron(II) complex is now indicated.[193]

High-spin oxo-bridged dimers of iron(III) of the type $[(LL)_2(H_2O)Fe—O—Fe(LL)_2(OH_2)]^{4+}$ contain a linear Fe—O—Fe bridge. A kinetic study of the acid-catalysed bridge-cleavage reactions is reported when LL = 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen).[194] When LL = bipy, acid-catalysed Fe—O—Fe bridge cleavage and bipyridyl chelate ring-opening are invoked to account for the observed rate law. When LL = phen a similar mechanism is proposed but, as expected, chelate ring-opening is not followed by protonation of the one-ended phen species. A limiting rate is observed for both complexes at high acidity (*ca.* 0.4M-H^+ for the phen complex and 0.8M-H^+ for the bipy complex). At 296 K, the first-order rate constant for the dissociation of the protonated species $[(phen)_2(H_2O)Fe—OH—Fe(phen)_2OH_2]^{5+}$ is *ca.* 7.6×10^{-4} s^{-1}, the equilibrium protonation constant being 3.6 l mol^{-1}. Assuming that this rate constant for bridge cleavage also applies to the bipy complex, the rate of bipy chelate ring-opening is estimated from the limiting acid rate to be 6.99×10^{-3} s^{-1} at 296 K. The acid-independent rate constants for loss of bipy and phen are 2.95×10^{-3} s^{-1} ($\Delta H^{\ddagger}$ = 14±2 kcal mol^{-1}) and 9×10^{-4} s^{-1} ($\Delta H^{\ddagger}$ = 16±2 kcal mol^{-1}) respectively. A review of oxo-bridged dinuclear iron(III) complexes has appeared recently.[195]

d^5: Ruthenium(III).—A comparison has been made between the equilibrium formation constants (K_{eq}) and the rate constants for the spontaneous aquation (k_0) of carboxylato-ruthenium(III) complexes of the type $[Ru(NH_3)_5O_2CR]^{2+}$ (R = CF_3, $ClCH_2$, Cl_2CH, Cl_3C, $BrCH_2$, or ICH_2).[196] The results are collected in Table 14. The generalized rate law for these reactions is

$$-\text{d[complex]}/\text{d}t = (k_0 + k_1[H^+])[\text{complex}] \qquad (43)$$

Acid catalysis is unimportant when R = Cl_2CH or Cl_3C. A plot of log k_0 against log K_{eq} is linear with a slope of 1.0, in agreement with an $S_N1(I_d)$ mechanism. S_N2 behaviour is proposed for the acid-catalysed reactions.[196]

Table 14 *Comparison of equilibrium formation constants* (K_{eq}) *and rate constants* [k_0, *equation* (43)] *for the spontaneous aquation of the* $[Ru(NH_3)_5O_2CR]^{2+}$ *ions at* 333 K (*data from ref.* 196)

R	CF_3	$ClCH_2$	Cl_2CH	Cl_3C	$BrCH_2$	ICH_2
$10^5k_0/s^{-1}$	10	7.5	19.1	49.0	6.8	6.7
10^3K_{eq}/l mol^{-1}	5.2	3.6	9.0	23	3.5	3.3

[193] A. D. James, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 1273; J. H. Espenson and S. G. Wolenuck, *Inorg. Chem.*, 1972, **11**, 2034.
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Exchange of labelled bromide ion with the *cis*-$[Ru(NH_3)_4Br_2]^+$ ion is postulated to proceed *via* aquation:[197]

$$cis\text{-}[Ru(NH_3)_4Br_2]^+ + H_2O \longrightarrow cis\text{-}[Ru(NH_3)_4(OH_2)Br]^{2+} \quad (44)$$

$$cis\text{-}[Ru(NH_3)_4(OH_2)Br]^{2+} + {}^*Br \xrightarrow{\text{fast}} cis\text{-}[Ru(NH_3)_4{}^*BrBr]^+ + H_2O \quad (45)$$

The electronic spectrum does not change during the course of the reaction and so reaction (45) must be rapid compared with reaction (44). The process was studied in 1.5% aqueous methanol and an S_N1 mechanism is proposed. Irradiation of *cis*-$[Ru(NH_3)_4X_2]^+$ ions with visible light in the region 330—492 nm produces no photoaquation when X = Cl, but when X = Br or I photoaquation to $[Ru(NH_3)_4(OH_2)X]^{2+}$ ions occurs.[198] Quantum yields are very low and wavelength-dependent; typical values are 2.7×10^{-3} for X = Br at 382 nm and 8.2×10^{-3} for X = I at 408 nm.

Complex ions of the type $[Ru(NH_3)_5(\text{guanine})]^{n+}$ (n = 2 or 3) have been prepared and it has been shown that the rate of the acid-catalysed hydrolysis of the sugar–purine bond in ruthenium(III) nucleosides is much lower than for the free nucleosides.[5]

d^6: Rhodium(III).—Following earlier experiments the mechanism of the mercury(II)-catalysed aquation of $[Rh(NH_3)_5X]^{2+}$ ions (X = Cl, Br, or I) has been further elucidated.[199] Evidence for the formation of intermediates of the type $[Rh(NH_3)_5XHg]^{4+}$ is presented, the relative rates of formation and dissociation of these dinuclear species being $1 : 200 : 1.3 \times 10^6$ and $1 : 0.5 : 6.6 \times 10^{-3}$ for X = Cl, Br, and I respectively. Owing to the large equilibrium formation constant when X = I a limiting rate is observed at high concentrations of mercury(II) ion. At lower mercury(II)-ion concentrations the usual second-order rate law is observed, the relative rates of the catalysed reactions being $1 : 31 : 1.1 \times 10^4$ compared with relative values of 1 : 0.93 : 0.22 for the uncatalysed aquations when X = Cl, Br, and I respectively. Activation parameters are reported from studies over a commendably wide temperature range of 18—70 °C. It is claimed that the rhodium(III) ion may have a $t_{2g}^5 e_g^{*1}$ configuration in the mercury(II) adducts.[199]

Rate data are reported for the acid-catalysed aquation of the $[M(NH_3)_5CO_3]^+$ ions (M = Rh^{III} or Ir^{III}), as well as the rates of formation of these carbonato-complexes from $[M(NH_3)_5OH]^{2+}$ and carbon dioxide.[200] At 298.1 K and μ = 0.5 mol l^{-1}, the aquation rate constants are 1.13 and 1.45 s^{-1} and the formation rate constants 470 and 590 l mol s^{-1} for the rhodium(III) and iridium(III) complexes respectively. The close similarity of these rate constants for both metal ions indicates carbon–oxygen bond fission for the aquation reactions.

The three isomers α-*cis*-, β-*cis*-, and *trans*-$[Rh(trien)Cl_2]^+$ have been prepared and characterized.[201] Photoaquations of the α-*cis*- and β-*cis*-isomers are in accord with

[197] A. Ohyoshi, T. Shinohara, Y. Hosoyamada, T. Yamada, and H. Hiroshima, *Bull. Chem. Soc. Japan*, 1973, **46**, 2133.
[198] A. Ohyoshi, N. Takebayashi, Y. Hiroshima, K. Yoshikuni, and K. Tsuji, *Bull. Chem. Soc. Japan*, 1974, **47**, 1414.
[199] A. B. Venediktov and A. V. Bulyaev, *Chem. Abs.*, 1973, **79**, 46 129y; 1973, **79**, 118 790s.
[200] D. A. Palmer and G. M. Harris, *Inorg. Chem.*, 1974, **13**, 965.
[201] P. M. Gidney, R. D. Gillard, B. T. Heaton, P. S. Sheridan, and D. H. Vaughn, *J.C.S. Dalton*, 1973, 1462.

Adamson's rules, and there is no significant chelate ring-opening for the α-*cis*-form. Kinetics of the substitution of both chloride ions in the α-*cis*-$[Rh(trien)Cl_2]^+$ ion by Y^- (Y = Br, I, N_3, or NCS) were determined and two stages were observed. Both stages were independent of $[Y^-]$ and the rate-determining step in each case is aquation to give the $[Rh(trien)(OH_2)X]^{2+}$ ions which then rapidly anate. The mechanism for each stage is, therefore, analogous to that shown in equations (44) and (45). The relative *cis* effects for these substitution reactions are reported to be $Cl^- > N_3^- > I^- > Br^- \gg NCS^-$, but activation parameters were not determined and this order only refers to results at one temperature.

A dissociative mechanism is proposed for the loss of chloride ion from *mer*-$[RhL^1L^2Cl_3]$ resulting in chelate ring closure:[202]

$$mer\text{-}[RhL^1L^2Cl_3] \rightleftharpoons trans\text{-}[RhL^1{}_2Cl_2]^+ + Cl^- \qquad (46)$$

[L^1 and L^2 are chelated (N- and As-donor) and unidentate (As-donor only) (*o*-dimethylaminophenyl)dimethylarsine respectively]. The rate of the forward reaction is reported to depend on the electrolyte concentration ($NaClO_4$, Et_4NClO_4, and $LiNO_3$ were used) and to increase sharply with the solvent polarity. The activation parameters are said to support the proposed dissociative mechanism. An S_N1(ip) mechanism is suggested for the reverse reaction. Activation parameters for both forward and reverse reactions were obtained in methanol, ethanol, propan-1-ol, and propan-2-ol.

Although studies of cobaloximes have been extensive in recent years, the analogous rhodoximes have been studied relatively little. Dissociative mechanisms are proposed for the loss of chloride ion from *trans*-$[Rh(dmgH)_2(SO_3)Cl]^{2-}$, *trans*-$[Rh(dmgH)_2(NO_2)Cl]^-$, and *trans*-[Rh(α-benzyldioxime)$_2$$(NO_2)Cl]^-$ ions based on studies in mixed aqueous–alcoholic solvents.[203,204] Sulphite ion exerts a strong *trans* effect as in the analogous cobalt(III) complexes,[203] and the complexes of α-benzyldioxime aquate at a greater rate than those of dimethylglyoxime, in line with a dissociative mechanism.[204]

An S_N1ca mechanism is proposed for the acid-catalysed hydrolysis of [Rh(biguanide)$_3$] [equations (47)—(49)].[205] Activation parameters for this reaction are

$$[Rh(big)_3]^{3+} + H^+ \overset{fast}{\rightleftharpoons} \left[(big)_2Rh \begin{array}{l} \diagup NH{=}C(NH_2)(\overset{+}{N}H_3) \\ \diagdown NH{=}C(NH_2)(NH) \end{array} \right]^{4+} \qquad (47)$$

$$[Rh(big)_2(bigH)]^{4+} + H_2O \xrightarrow{slow} [(big)_2Rh\{NH{=}C(NH_2)NHC(\overset{+}{N}H_3){=}NH\}(OH_2)]^{4+} \qquad (48)$$

$$[Rh(big)_2(bigH)(OH_2)]^{4+} + H_2O \longrightarrow [Rh(big)_2(OH_2)_2]^{3+} + bigH^+ \qquad (49)$$

[202] A. Peloso and L. Volponi, *J.C.S. Dalton*, 1974, 278.
[203] G. P. Syrtsova and T. S. Bolgar, *Zhur. neorg. Khim.*, 1973, **18**, 2706.
[204] G. P. Syrtsova and T. S. Bolgar, *Zhur. neorg. Khim.*, 1973, **18**, 2156.
[205] D. Banerjea and B. Chattopadhyay, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2351.

Table 15 *Comparison of activation parameters for the reactions*

$$[M(big)_3]^{3+} + 2H_3O^+ \rightarrow [M(big)_2(OH_2)_2]^{3+} + bigH_2^{2+}$$

M	Cr	Co	Rh
ΔH^*/kcal mol^{-1}	10.1	11.1	21.4
ΔS^*/cal K^{-1} mol^{-1}	−30.2	−31.5	−15.7

compared with those for the analogous cobalt(III) and chromium(III) complexes in Table 15.

Several interesting studies have appeared recently dealing with azido-complexes of rhodium(III) and iridium(III). The thermal studies in acidic solutions have been interpreted in terms of intermediate nitrene complex formation.[206] Further insight into these reactive intermediates has come from photochemical studies, and their reactions are more complex than originally proposed. Charge-transfer photochemical studies of azido-complexes of cobalt(III) and rhodium(III) show that, whereas for cobalt(III) a photoredox reaction occurs to give cobalt(II) and $N_3\cdot$, for $[Rh(NH_3)_5N_3]^{2+}$ nitrene complexes are formed.[7] The reactions were studied by flash photolysis, and for the rhodium(III) complex there is evidence of dimer formation:

$$[Rh(NH_3)_5N_3]^{2+} \xrightarrow{h\nu} [Rh(NH_3)_5N]^{2+} + N_2$$
$$H^+ + [Rh(NH_3)_5N]^{2+} \rightleftharpoons [Rh(NH_3)_5NH]^{3+}$$
$$2[Rh(NH_3)_5NH]^{3+} \rightleftharpoons [\{Rh(NH_3)_5N\}_2H]^{5+} + H^+$$
$$[\{Rh(NH_3)_5N\}_2H]^{5+} \rightleftharpoons [\{Rh(NH_3)_5N\}_2]^{4+} + H^+$$

The dimers $[\{Rh(NH_3)_5N\}_2H]^{5+}$ and $[\{Rh(NH_3)_5N\}_2]^{4+}$ are characterized by peak maxima at 510 and 470 nm respectively, and the rate constants at 298 K for dimer formation and dissociation are 1.2×10^9 l mol^{-1} s^{-1} and 2×10^3 s^{-1} respectively.[7] Photolysis of the $[Rh(NH_3)_5N_3]^{2+}$ ion in 1M-HCl gives $[Rh(NH_3)_5NH_2Cl]^{3+}$ and $[Rh(NH_3)_5OH_2]^{3+}$ ions as products.[6] The quantum yields are wavelength-dependent, the formation of the $[Rh(NH_3)_5NH_2Cl]^{3+}$ ion being favoured at longer wavelengths. Rhodium(II) intermediates were also postulated in this study.[6] Irradiation of the $[Rh(NH_3)_5N_3]^{2+}$ ion in glasses at 77 K gives evidence of a further intermediate,[6] unlike those observed in the study by flash photolysis.[7]

***d*^{6}: Iridium(III).**—Photochemical studies analogous to those described above have also appeared for the $[Ir(NH_3)_5N_3]^{2+}$ ion.[6] In this case the quantum yields are again wavelength-dependent and appreciable for excitation in the ligand-field bands. An unidentified intermediate is also observed upon irradiating the complex in a glass at 77 K, or upon flash photolysis in aqueous solution. This intermediate is postulated to arise from a reaction between the nitrene complex, $[Ir(NH_3)_5N]^{2+}$, and the solvent water. In perchlorate, chloride,[7] and sulphite[207] media the observed reactions of the nitrene are

$$[Ir(NH_3)_5N]^{2+} + 2H^+ + Cl^- \longrightarrow [Ir(NH_3)_5(NH_2Cl)]^{3+}$$
$$[Ir(NH_3)_5N]^{2+} + H^+ + ClO_4^- \longrightarrow [Ir(NH_3)_5(NHOClO_3)]^{2+}$$
$$[Ir(NH_3)_5(NHOClO_3)]^{2+} + H_2O \longrightarrow [Ir(NH_3)_5(NH_2OH)]^{3+} + ClO_4^-$$
$$[Ir(NH_3)_5N]^{2+} + HSO_3^- + H^+ \longrightarrow [Ir(NH_3)_5(NH_2SO_3)]^{2+}$$

The last reaction has also been studied for the ruthenium(III) complex.[207]

[206] L. A. P. Kane-McGuire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1970, **92**, 5865; B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *ibid.*, 1972, **94**, 3786.

[207] R. T. Weaver and F. Basolo, *Inorg. Chem.*, 1974, **13**, 1535.

Studies of the luminescence of the photoinert ion *cis*-$[Ir(phen)_2Cl_2]^+$ in deaerated DMF in the presence of naphthalene gives evidence for the formation of an exciplex between an excited state (most probably the emitting one) of the complex and ground-state naphthalene.[208]

A study of the kinetics of aquation of the $[IrCl_6]^{3-}$ ion at pH 1 in 3M-LiCl and 3M-LiCl–KCl shows that formation of the ion pair $K^+,[IrCl_6]^{3-}$ results in a slowing of the aquation reaction.[209] Ion-pairing with barium ions, however, lowers the activation for aquation by 3.6 kcal mol^{-1} to 23 kcal mol^{-1}. The enthalpy and entropy of formation of the barium ion pair are reported to be 4.9 kcal mol^{-1} and -5.7 cal K^{-1} mol^{-1} respectively.[210]

***d*⁶: Iron(II).**—An analogy can be drawn between the substitution reactions of $[M(CN)_5X]^{n-}$ ions when M is cobalt(III) and iron(II). The cobalt(III) complexes are well established to react by a *D* mechanism and show class (*b*) or 'soft' character. The $[Fe(CN)_5(DMSO)]^{3-}$ ion has been synthesized and shown by ^1H n.m.r. and i.r. studies to contain an S-bonded DMSO molecule characteristic of a class (*b*) metal ion.[211] The reaction between $[Fe(CN)_5DMSO]^{3-}$ ion and *N*-methylpyrazinium ion in aqueous solution is postulated to proceed by a *D* mechanism, a limiting rate being observed at high concentrations of *N*-methylpyrazinium ion. The limiting first-order rate constant at 298.1 K for loss of DMSO from $[Fe(CN)_5DMSO]^{3-}$ is estimated from these studies to be $(7.5 \pm 0.1) \times 10^{-3}$ s^{-1} ($\Delta H^{\ddagger} = 26.0 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 11 \pm 2$ cal K^{-1} mol^{-1}).[211] The rate of formation of the $[Fe(CN)_5DMSO]^{3-}$ ion from $[Fe(CN)_5OH_2]^{3-}$ was also measured: at 298.1 K the formation rate constant, k_f, is $(2.4 \pm 0.1) \times 10^2$ l mol^{-1} s^{-1} ($\Delta H^{\ddagger} = 15.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 4 \pm 2$ cal K^{-1} mol^{-1}) and the equilibrium formation constant for the $[Fe(CN)_5DMSO]^{3-}$ ion is $(3.3 \pm 0.5) \times 10^6$ l mol^{-1}. It is unfortunate that in this work substitution of the co-ordinated DMSO was accomplished with a positively charged (*N*-methylpyrazinium) ligand. One of the virtues of studying anionic complexes is to avoid complexities arising from ion-pair formation. It is to be hoped, therefore, that further studies with anionic ligands will confirm the proposed *D* mechanism. It should be noted that reaction of the $[Fe(CN)_5OH_2]^{3-}$ ion with uncharged nitrogen heterocyclic bases shows no sign of reaching a limiting rate at high base concentrations, although a *D* mechanism is still favoured.[212] A *D* mechanism is established for the reaction of the $[Fe(CN)_5SO_3]^{5-}$ ion with cyanide ion,[213] the five-co-ordinate intermediate ion, $[Fe(CN)_5]^{3-}$, showing a discrimination factor of 8.76 for CN^- over SO_3^{2-} at 316 K, pH 10.8, and $\mu = 1.0$ mol l^{-1}.

Further studies have appeared dealing with the acid hydrolysis and cyanide-ion-induced dissociations of low-spin iron(II) complexes of the type $[Fe(LL)_3]^{2+}$ [LL = phen, bipy, or *N*-(2-pyridylmethylene)aniline][214] and $[Fe(terpy)_2]^{2+}$.[214,215] A correlation is observed between the rate parameters and the wavelength of maximum

[208] R. Ballardini, G. Varoni, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, 1974, **96**, 7123.
[209] I. Lakatos-Varsanyi, A. N. Kochetkova, E. G. Tsventarnyi, and V. I. Kravtsov, *Zhur. neorg. Khim.*, 1973, **18**, 3014; *Magyar Kém. Folyóirat*, 1973, **79**, 361.
[210] A. N. Kochetkova, E. G. Tsventarnyi, and V. I. Kravtsov, *Zhur. neorg. Khim.*, 1973, **18**, 1998.
[211] H. E. Toma, J. M. Malin, and E. Giesbricht, *Inorg. Chem.*, 1973, **12**, 2084.
[212] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2080, 1039.
[213] Z. Bradić, D. Pavlović, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1974, 344.
[214] J. Burgess and M. V. Twigg, *J.C.S. Dalton*, 1974, 2032.
[215] M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 17.

Table 16 *Kinetic parameters at* 298.1 K *for fission of the first iron–nitrogen bond of low-spin iron*(II) *complexes, and values of* λ_{max}, *the wavelength of maximum absorbance of the lowest-energy charge-transfer band for each complex* (*refs.* 214 *and* 215)

Complex	λ_{max}/nm	10^4k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Fe(phen)_3]^{2+}$	510	0.73	29.4±0.2	21.1±0.6
$[Fe(bipy)_3]^{2+}$	525	7.8	26.1±0.1	14.8±0.3
$[Fe(terpy)_2]^{2+}$	552	52	24.2±0.2	12.3±0.6
$[Fe(pma)_3]^{2+}$ [a]	574	930	22.1±0.6	10.7±2.0

[a] pma = *N*-(2-pyridylmethylene)aniline.

absorbance of the lowest-energy charge-transfer band for each complex (Table 16). For the reaction of the $[Fe(terpy)_2]^{2+}$ ion with cyanide ion the rate law is:

$$-\text{d[complex]/d}t = \{k_1 + k_2[CN^-]\}[\text{complex}]$$

At 308.1 K, μ = 0.1 mol l^{-1} (KCl), 10^4k_1 = 0.8±0.1 s^{-1}, and k_2 = 0.019 l mol^{-1} s^{-1} ($\Delta H^{\ddagger}$ = 21.7±0.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 4±2 cal K^{-1} mol^{-1}). At very high cyanide-ion concentrations terms in the rate law involving $[CN^-]^2$ are indicated. The primary product of this reaction is the $[Fe(terpy)(CN)_3]^-$ ion, which has a very solvent-dependent charge-transfer spectrum (λ_{max} correlates with Reichardt's E_T values).[214] An associative mechanism is proposed for the reaction with cyanide ion. The spin change which accompanies the acid-hydrolysis reactions is believed to occur at the breakage of the first iron–nitrogen bond.[215] The effect of added salts on the rate of aquation of the $[Fe(5\text{-}NO_2\text{-}phen)_3]^{2+}$ ion has also been investigated.[216] The presence of $[n\text{-}Bu_4N]I$ increases the rate, whereas KBr, $[Et_4N]Br$, and CsBr bring about a rate decrease. The data are analysed in terms of salt effects upon the initial and transition states. Use is made of the effect of the added salts upon the solubility of the ligand in water, and also of other parameters which describe cation–cation interactions in mixed-salt solutions.

Catalysis of the aquation of nitroprusside ion by azide ion at pH 6 has been investigated, and from tracer studies the observed initial reaction is

$$[Fe(CN)_5(N^*O)]^{2-} + {}^*NNN^- + H_2O \xrightarrow{\text{pH 6}} [Fe(CN)_5(OH_2)]^{3-} + N_2 + {}^*NN^*O$$

The $[Fe(CN)_5OH_2]^{3-}$ ion (λ_{max} = 455 nm, ε_M = 460 l mol^{-1} cm^{-1}) then dimerizes to $[Fe_2(CN)_{10}]^{6-}$ (λ_{max} = 395 nm, ε_M = 940 l mol^{-1} cm^{-1}). The initial reaction proceeds *via* an intermediate (A):[217]

$$[Fe(CN)_5(NO)]^{2-} + N_3^- + H_2O \xrightarrow{k_{1a}} (A) \xrightarrow{k_{1b}} [Fe(CN)_5(OH_2)]^{3-} + N_2 + N_2O$$

At 296 K and pH 6, k_{1a} is *ca.* 0.2 l mol^{-1} s^{-1} and k_{1b} *ca.* 0.2 s^{-1}. In the presence of excess azide ion the dimer reacts to give the $[Fe(CN)_5N_3]^{4-}$ ion (λ_{max} = 440 nm, ε_M = 1400 l mol^{-1} cm^{-1}). Reaction of nitroprusside ion with hydroxylamine in basic solution was also investigated and a further intermediate (B) (λ_{max} = 445 nm,

[216] M. J. Blandamer, J. Burgess, and S. H. Morris, *J.C.S. Dalton*, 1974, 1717.
[217] S. K. Wolfe, C. Andrade, and J. H. Swinehart, *Inorg. Chem.*, 1974, **13**, 2567.

$\varepsilon_M = 800\ l\ mol^{-1}\ cm^{-1}$) observed:

$$[Fe(CN)_5(NO)]^{2-} + {}^{+}NH_2{}^{*}OH + OH^- \longrightarrow (B) \longrightarrow [Fe(CN)_5(OH_2)]^{3-} + N{}^{+}N{}^{*}O + H_2O$$

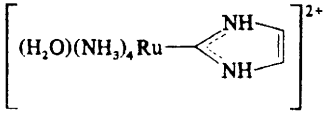
$$d[B]/dt = k[Fe(CN)_5(NO)^{2-}][NH_2OH][OH^-]$$

At 298.1 K, $10^{-5}k = 4.5\ l^2\ mol^{-2}\ s^{-1}$ and $E_a = 0.5 \pm 1.0$ kcal mol^{-1}. It is possible that (B) is the $[Fe(CN)_5(N_2O)]^{3-}$ ion. These studies are complicated by the atmospheric oxidation of iron(II) to iron(III). For example, at 298.1 K,

$$d[Fe(CN)_5N_3]^{3-}/dt = (3.0 \pm 0.7) \times 10^2[Fe(CN)_5N_3{}^{4-}][O_2]$$

Cyano-complexes of iron(II) are also reported to catalyse substitution reactions of cyano-complexes of iron(III).[192] Photosubstitution of $[Fe(CN)_5(NO)]^{2-}$ ion by thiocyanate ion and thiourea is also believed to involve oxidation of iron(II) to iron(III).[218] One of the products of the two-electron reduction of nitroprusside ion is reported[219] to be an isocyano-complex ion $[Fe(CN)_4(NC)(NO)]^{4-}$.

***d*^{6}: Ruthenium(II).**—The ruthenium complexes $[Ru(NH_3)_5L]^{n+}$ ($n = 2$ or 3; L = imidazole, 1-methyl-, 4-methyl-, or 4,5-dimethyl-imidazole, or benzimidazole) have been prepared and characterized.[3] Below pH 2 the ruthenium(II) complexes are unstable and dissociate to mixtures of products containing mainly the $[Ru(NH_3)_5(OH_2)]^{2+}$ ion (73% at $[H^+] = 0.025$ mol l^{-1}; 84% at $[H^+] = 0.1$ mol l^{-1}). For the imidazole complex a novel C-bonded imidazole ylide derivative (20) is also obtained in low yield (2—4%).



(20)

The rate law for the acid hydrolysis of the $[Ru(NH_3)_5(pyrazine)]^{2+}$ ion is

$$-d[complex]/dt = (k_0 + k_1[H^+])[complex] \quad (50)$$

In equation (50) k_0 is negligible when the observed rate constants are corrected for the side reactions. Values of k_1 are compared for L = imidazole, ammonia, and pyridine in Table 17. The equilibrium formation constants (K_{eq}) increase with the increasing π-acceptor capacity of the nitrogen bases, but values of k_1 vary in the

Table 17 *Comparison of acid-catalysed rate constants* k_1 [*equation* (50)] *for the aquation of* $[Ru(NH_3)_5L]^{2+}$ *ions at* 298.1 K

L	*Ionic strength*/ mol l^{-1}	10^5k_1/l mol^{-1} s^{-1}	$10^{-4}K_{eq}$/l mol^{-1} [a]	$\varepsilon°$/V[b]
Imidazole	1.0	3380	280	0.11
	0.1	1180		
NH_3	0.5	21[c]	3.5	
Pyridine	0.5	5.42	2400	0.305

[a] Equilibrium formation constant. [b] $Ru^{II} \rightleftharpoons Ru^{III}$. [c] Corrected by a statistical factor of 6.

[218] P. A. Stoeri and D. X. West, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2347, 3883.
[219] J. Masek and E. Maslova, *Coll. Czech. Chem. Comm.*, 1974, **39**, 2141.

order imidazole > NH_3 > pyridine. The +2 oxidation state is less stabilized by imidazole (E° = 0.11 V) than by pyridine (E° = 0.305 V). Acid catalysis is associated with protonation of the t_{2g}^6 electrons in these ruthenium(II) complexes to give a ruthenium(III) hydride.

Hydrolysis of $[Ru(NO)X_5]^{2-}$ ions (X = Cl, Br, or I) proceeds by a multistep mechanism, the first step of which is very slow and characterized by activation energies of 23 ± 3, 21 ± 3, and 15 ± 3 kcal mol^{-1} for X = Cl, Br, and I respectively.[220] A thesis dealing with the hydrolysis of bromo-complexes of nitrosylruthenium has also appeared.[221]

d^6: Platinum(IV).—The complex ions *trans*-$[Pt(en)(Br)_2(NO_2)_2]$ and *trans*-$[Pt(NH_3)_4X_2]^{2+}$ (X = Cl or Br) are very inert, the latter not even aquating in the presence of 10^{-2}M mercuric nitrate. Although *trans*-$[Pt(en)(Br)_2(NO_2)_2]$ does not aquate spontaneously, mercury(II) ion brings about hydrolysis, the reaction being further catalysed in the usual way by a platinum(II) complex, $[Pt(en)(NO_2)_2]$:

$$trans\text{-}[Pt(en)(Br)_2(NO_2)_2] + H_2O \xrightarrow[Pt^{II}]{Hg^{II}} trans\text{-}[Pt(en)(Br)(OH)(NO_2)_2] + H^+ + NO_2^-$$

$$-d[complex]/dt = k[Hg^{II}][Pt(en)(NO_2)_2][Pt(en)(Br)_2(NO_2)_2]$$

At 298.1 K, $10^{-5}k = 1.7$ l^2 mol^{-2} s^{-1}, $\Delta H^{\ddagger} = 2.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -26.5$ cal K^{-1} mol^{-1}. A transition state of the type $[Hg—Br—Pt^{IV}(en)(NO_2)_2—Br—Pt^{II}(en)_2—OH_2]$ is envisaged to account for the third-order rate law.[222]

Some rate data are also reported for the aquation of the *trans*-$[Pt(en)_2(NO_2)_2]^{2+}$ ion which are said to give information about the *trans* effect of the nitro-groups.[223]

5 Base Hydrolysis

In this section specific base-catalysed hydrolysis, which often involves deprotonation of a co-ordinated ammonia or amine, will be discussed but some references will also be made to attack by hydroxide ion at other co-ordinated ligands (*e.g.* nitriles).

Cobalt(III) Complexes.—The S_N1cb mechanism originally proposed by Garrick in 1937 is now widely accepted as the most likely mechanism for the base hydrolysis of cobalt(III) complexes. The use of ^{59}Co n.m.r. shows some promise for determination of the pK_a's of co-ordinated amines. An equilibrium constant of 0.39 ± 0.05 l mol^{-1} has been established in this way for reaction (51).[224]

$$[Co(en)_3]^{3+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(en)_2(en-H)]^{2+} + H_2O \qquad (51)$$

The anomalously fast base hydrolysis of the *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(ddn)Cl_2]^+$ ions (ddn = *R,S*-2,3,2-tet = *R,S*-1,9-diamino-3,7-diazanonane) has been shown to arise mainly from the unusually high lability of their conjugate bases.[225] Using deuteriated complexes the extent of replacement of the labelled amine protons

[220] K. A. Bol'shakov, N. M. Sinitsyn, V. V. Borisov, and L. A. Zvorykina, *Zhur. neorg. Khim.*, 1973, **18**, 2701.
[221] H. J. Greenberg, *Diss. Abs. Internat. (B)*, 1973, **34**, 118.
[222] W. L. Dickinson and R. C. Johnson, *Inorg. Chem.*, 1973, **12**, 2048.
[223] N. Zheligovskaya, N. Kamalov, and V. I. Spitsyn, *Chem. Abs.*, 1974, **81**, 30 160s.
[224] J. Wilinski and R. J. Kurland, *Inorg. Chem.*, 1973, **12**, 2202.
[225] G. Marangoni, M. Panayotou, and M. L. Tobe, *J.C.S. Dalton*, 1973, 1989.

was measured in the substrate and the product by ^{1}H n.m.r. as a function of the extent of reaction. The results confirm a dissociative conjugate-base mechanism, and for the 2,3,2-tet complex it is a secondary amine proton which is lost. The ratio of the rate constants for reprotonation of the conjugate base (k_{-1}) and its unimolecular dissociation (k_2) were measured and found to be $10 > (k_{-1} : k_2) > 4$ and $5 > (k_{-1} : k_2) > 0.5$ for *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(ddn)Cl_2]^+$ ions respectively. A similar study is reported for the *trans*-$[Co\{R,R(S,S)$-2,3,2-tet$\}Cl_2]^+$ ion.[31] In this case the product of the reaction is the *meso*-isomer *trans*-[Co(*RS*-2,3,2-tet)(OH)Cl]$^+$, the amido-conjugate base formed being at least 20 times more likely to dissociate than to be reprotonated. The high lability of the conjugate base is believed to be due to π-donor stabilization of the five-co-ordinate intermediate by the amido-ligand, which becomes planar at this stage. The effect of replacing the secondary NH groups of 2,3,2-tet by S-atoms has been investigated for the complex ion *trans*-$[Co(ete)Cl_2]^+$. The rate of base hydrolysis is less by a factor of 8—20 than for the analogous 2,3,2-tet complex, in line with the absence of secondary amine protons.[78]

In complex ions of the type *trans*-$[Co(L)(NH_3)_2]^{3+}$ [L = cyclam (1) or $(en)_2$] it has been shown that the axial ammine protons undergo faster exchange than the amine protons of L. The rates of exchange of the ammine protons decrease with changes in L in the order cyclam > $(en)_2$ > $(NH_3)_4$, in accordance with the nephelauxetic effect of these ligands.[226] Rate data are also reported for the base hydrolysis of *trans*-$[Co(L)XY]^+$ ion [L = cyclam or $(NH_3)_4$], and these results are summarized in Table 18 together with other recently determined base-hydrolysis results for cobalt(III) amine complexes. The complex ions *cis*-$[Co(en)_2(A)Cl]^{2+}$ (A = aniline or *m*-toluidine) readily form their respective conjugate bases even in acidic solution (K_{eq} *ca.* 10^{-3}), and the activation parameters quoted in these cases refer to the first-order rate constants for the dissociation of the amido-compounds (Table 18). Some data have also been obtained for the base hydrolysis of $[Co(RNH_2)_5Cl]^{2+}$ ions (R = Me, Et, Pr^n, or Bu^n) at pH 9.26 and 12.5 and at 17.5 °C.[227]

Table 18 *Kinetic parameters for the base hydrolysis of cobalt*(III) *complexes*

Complex	k_{OH}/l mol^{-1} s^{-1} (*temperature*/°C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
trans-$[Co(NH_3)_4(CN)Br]^+$	0.99 (0.0)	22.3±0.3	24±4	75
trans-[Co(cyclam)(CN)Br]$^+$	20 (0.0)	20.1±0.4	21±5	75
trans-$[Co(NH_3)_4(N_3)Cl]^+$	6.6×10^{-3} (0.0)	24.0±0.2	20±3	75
trans-[Co(cyclam)(N_3)Cl]$^+$	68 (0.0)	23.5±0.2	36±5	75
trans-[Co(cyclam)(NH_3)Cl]$^{2+}$	400 (25.0)[a]			74
[Co(*RR*-tetren)N_3]$^{2+}$	3.2×10^{-12} (25.0)[b]	32±2[c]	−5±5[c]	59
trans-[Co(ete)Cl_2]$^+$	1.6×10^3 (13.5)[d]			78
cis-[Co(en)$_2$(n-$C_xH_{2x+1}NH_2$)Cl]$^{2+}$		22.9—20.5[e]	−10.7 to −17.4[e]	61
cis-[Co(en)$_2$(MeNHNH$_2$)Cl]$^{2+}$	4.29 (20.4)	23.4	+24	62
cis-[Co(en)$_2$(aniline)Cl]$^{2+}$		21.1[f]	−11.2	63
cis-[Co(en)$_2$(*m*-toluidine)Cl]$^{2+}$		20.4[f]		64

[a] k_{OH} for loss of NH_3 is 1.7 l mol^{-1} s^{-1}. [b] Extrapolated rate constant; tetren = 1,11-diamino-3,6,9-triazaundecane. [c] At 363 K. [d] At 16.8 °C, $k_{OH} = 2.8\times10^3$ l mol^{-1} s^{-1}. [e] As x varies from 4 to 12. [f] Refers to the first-order dissociation of the conjugate base.

[226] C.-K. Poon and H.-W. Tong, *J.C.S. Dalton*, 1974, 930.
[227] R. Mitzner and W. Depkat, *Z. phys. Chem.* (*Leipzig*), 1973, **254**, 189.

Studies of the acid hydrolysis of $[Co(L)(A)X]^{n+}$ ions (Table 6) have also been extended to basic solution.[82] These results allow a comparison to be made of the effect of increasing unsaturation in the cyclic ligands (2)—(5) (p. 140) upon the rates of hydrolysis. The results of the base-hydrolysis experiments are shown in Table 19. It is interesting that for complexes of the unsaturated ligand (5) which

Table 19 *Rate constants for the stepwise base hydrolysis of* trans-$[Co(L)X_2]^{n+}$ *ions at* 298.1 K (*ref.* 82)

L	X	k_{OH}/l mol^{-1} s^{-1} (*first step*)[a]	k_{OH}/l mol^{-1} s^{-1} (*second step*)[a]
(2)	NH_3	$(3.2\pm0.5)\times10^6$	very slow
(3)	NH_3	$(3.2\pm0.3)\times10^6$	0.34 ± 0.03
(4)	NH_3	$(1.1\pm0.1)\times10^3$	0.84 ± 0.04
(4)	Cl	$(8\pm1)\times10^5$	
(4)	Br	$(1.1\pm0.5)\times10^6$	
(5)	NH_3	36 ± 3	fast
(5)	Cl	2.7 ± 0.3	
(5)	Br	$(1.2\pm0.2)\times10^3$	21 ± 5

[a] Refers to stepwise replacement of X by OH^-.

contain no acidic amine protons base hydrolysis is very slow whereas in acidic solution the complexes are even more labile than their cobaloxime analogues. The rates reported for the base hydrolysis of the *trans*-diammine complexes are reported to be about the fastest ever recorded for cobalt(III). The order of the *trans* effect for the isoelectronic anions is $CH_3^- > NH_2^- > OH^-$, in close agreement with the σ-donor ability of the labilizing ligands (*i.e.* the cobalt–ligand σ-bond strength in the *trans* position). Any tendency of these ligands to stabilize the dissociative transition states through π-donor interaction is thought to be relatively small.[82]

Base hydrolysis of the $[Co(NH_3)_5(OH)]^{2+}$ ion is reported to involve ion-pair formation between hydroxide ion and the $[Co(NH_3)_5(OH)]^{2+}$ ion or its conjugate base.[228] The reverse reaction has been studied as well and an I_d mechanism is proposed.[229] The effect of ionic strength upon the base hydrolysis of the $[Co(NH_3)_5Br]^{2+}$ ion is also reported.[45] The rate decreases with increasing ionic strength, and activation parameters extrapolated to zero ionic strength are $\Delta H^{\ddagger} = 25.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 18$ cal K^{-1} mol^{-1}.

Base hydrolysis of the *trans*-$[Co(A_4)(aa)_2]^+$ ions [A_4 = 2,3,2-tet (3,7-diaza-1,9-nonanediamine), 3,2,3-tet (4,7-diaza-1,10-decanediamine), or 5-Me-3,2,3-tet (4,7-diaza-5-methyl-1,10-decanediamine); aa = anions of glycine, alanine, valine, or sarcosine] is reported to occur in two distinct stages:[230]

$$trans\text{-}[Co(A_4)(aa)_2]^+ + OH^- \longrightarrow trans\text{-}[Co(A_4)(aa)OH]^+ + aa^- \quad (52)$$

$$trans\text{-}[Co(A_4)(aa)OH]^+ \longrightarrow uns\text{-}cis\text{-}[Co(A_4)aa]^{2+} + OH^- \quad (53)$$

Reaction (52) involves the loss of one unidentate O-bonded amino-acid anion, and reaction (53) is a process of chelate ring closure and topological shift to give the

[228] E. G. A. M. Bohte and S. Balt, *Rec. Trav. chim.*, 1974, **93**, 178.
[229] S. Balt, *Inorg. Chim. Acta*, 1974, **8**, 159; 1973, **7**, 453.
[230] J. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, 1973, **12**, 2988.

unsymmetrical *cis*-product. Rate constants and activation parameters are reported for both stages. Reaction (52) is postulated to have an I_d mechanism, and the chelate ring closure is interpreted as an example of edge displacement.

The isomeric complexes Δ-$(-)_{589}$-(*RR*)- and -(*RS*)-β_1-[Co(trien)(gly)]I_2 have been synthesized and characterized (including an *X*-ray structure).[231] At 298.1 K and $\mu = 1.0$ mol l^{-1}, the overall rate constant for the base-catalysed mutarotation reaction (54) is $10^{-3}k_{inv} = 1.11 \pm 0.05$ l mol^{-1} s^{-1}. The product of the mutarotation is an equilibrium mixture of the Δ-β_1-(*RS*)- and Δ-β_1-(*RR*)-isomers, the

$$\Delta\text{-}\beta_1\text{-}(RS)\text{-}[Co(trien)(gly)]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \Delta\text{-}\beta_1\text{-}(RR)\text{-}[Co(trien)(gly)]^{2+} \qquad (54)$$

equilibrium constant (K) being 1.22 ± 0.05. Since $K = k_1/k_{-1}$ [reaction (54)], and $k_{inv} = k_1 + k_{-1}$, the individual rate constants are $10^{-2}k_1 = (5.0 \pm 0.3)$ l mol^{-1} s^{-1} and $10^{-2}k_{-1} = (6.1 \pm 0.4)$ l mol^{-1} s^{-1}. Each reaction is first order in [complex] and first order in [OH^-]. A comparison of the rates of mutarotation with the rates of base-catalysed proton exchange at the amine groups was also undertaken. The protons which exchange most rapidly were assigned to the 'planar' NH group of the β-trien ligand. These protons are 10^2 times more labile than the remaining secondary NH proton and the primary NH_2 protons of trien. At 307.4 K, the rate constant for proton exchange is $10^{-8}k_{ex} = 8.2 \pm 0.3$ l mol^{-1} s^{-1}, and hence k_{ex}/k_{inv} is *ca.* 10^6. The results are consistent with a common deprotonated intermediate for the exchange and inversion processes. A knowledge of the relative rates of proton exchange in complexes of this type can be used to advantage in the synthesis of new complexes by intramolecular template reactions, sometimes with stereoselectivity.[28, 29]

Base hydrolysis of the *cis*-[$Co(en)_2X(NH_2CH_2CN)$]$^{2+}$ ions (X = Cl or Br) gives rise to the following reaction:[32]

$$cis\text{-}[Co(en)_2X(NH_2CH_2CN)]^{2+} \xrightarrow{(OH^-)} [Co(en)\{NH_2CH_2C(NH_2)=N(CH_2)_2NH_2\}X]^{2+} \qquad (55)$$

The reaction begins with the rapid deprotonation of the 1,2-diaminoethane NH_2 group in the *trans* position to ligand X (halide ion). The NH^- group which is produced then attacks in the slow step at the carbon atom of the adjacent nitrile group. Rapid hydrolysis then produces the observed product which contains a terdentate amidine ligand. The kinetics of these template reactions were studied and at 298.1 K, $\mu = 1.0$ mol l^{-1}, pH 5.9—7.0, the base-catalysed rate constants were found to be $10^{-4}k_{OH} = 2.57$ and 4.50 l mol^{-1} s^{-1} for X = Cl and Br respectively. Base hydrolysis and mercury(II)-ion-induced loss of ligand X from the product of reaction (55) were also studied. These reactions proceed with retention of configuration, and rate constants at 298.1 K ($\mu = 0.1$ mol l^{-1}) for the base hydrolysis are reported to be 2.44 and 11.8 l mol^{-1} s^{-1} for X = Cl and Br respectively. The mercury(II)-catalysed reactions of the *cis*-[$Co(en)_2X(NH_2CH_2CN)$]$^{2+}$ ions were also investigated, yielding a glycine amide complex ion [$Co(en)_2(NH_2CH_2CONH_2)$]$^{3+}$. The postulated mechanism involves mercury(II)-catalysed replacement of ligand X by solvent water, followed by nucleophilic attack at the carbon atom of the nitrile by the co-ordinated OH group.

[231] D. A. Buckingham, P. J. Creswell, R. J. Dellaca, M. Dwyer, G. J. Gainsford, L. G. Marzilli, I. E. Maxwell, W. T. Robinson, A. M. Sargeson, and K. R. Turnbull, *J. Amer. Chem. Soc.*, 1974, **96**, 1713.

A study of the base hydrolysis of the amino-acid ester complexes *cis*-$[Co(en)_2X(NH_2CH_2CH_2OCOMe)]^{2+}$ (X = Cl or Br) is also reported.[232] The product is the *cis*-$[Co(en)_2OH(NH_2CH_2CH_2OH)]^{2+}$ ion, the reaction occurring in two stages in basic media. The first stage involves loss of the halide ion and is characterized by rate constants $10^{-3}k_{OH}$ = 1.38 and 8.7 l mol^{-1} min^{-1} at 298.1 K (μ = 0.1 mol l^{-1}) for X = Cl and Br respectively. The second stage is slower, involving hydrolysis of the co-ordinated ester ($10^{-3}k$ = 0.144 l mol^{-1} min^{-1}). This co-ordinated ester hydrolysis is eighteen times faster than for the free ester, and twice as fast as for the protonated ester.

Base hydrolysis of co-ordinated acetonitrile in the ion $[Co(NH_3)_5(NCMe)]^{3+}$ [equation (56)] is *ca.* 2×10^6 times as fast as for the unco-ordinated ligand. A second-order rate law is observed (first order in [complex] and [OH^-]) and the second-order rate constant is 3.40 l mol^{-1} s^{-1} at 298.1 K (μ = 1.0 mol l^{-1}).[233] Deuteriation

$$[Co(NH_3)_5(NCMe)]^{3+} + OH^- \longrightarrow [Co(NH_3)_5NHCOMe]^{2+} \qquad (56)$$

experiments at 306 K and pD 9.60 show that the protons of the methyl group exchange at a greater rate ($k = 1.36 \times 10^{-3}$ s^{-1}) than that of the base-hydrolysis reaction ($k = 9.7 \times 10^{-4}$ s^{-1}). Therefore, although reaction (56) is believed to involve attack by OH^- at the nitrile carbon atom, it is also possible that the following mechanism applies:

$$[(NH_3)_5Co{-}N{\equiv}C{-}CH_3]^{3+} + OH^- \longrightarrow [(NH_3)_5Co{-}N{\equiv}C{-}\bar{C}H_2]^{2+}$$

$$[(NH_3)_5Co{-}N{\equiv}C{-}\bar{C}H_2]^{2+} \longrightarrow [(NH_3)_5Co{-}\bar{N}{=}C{=}CH_2]^{2+}$$

$$[(NH_3)_5Co{-}\bar{N}{=}C{=}CH_2]^{2+} + H_2O \longrightarrow [(NH_3)_5CoNHCOCH_3]^{2+}$$

Protonation of the product of this reaction (pK_a 3.02) occurs at the carbonyl oxygen atom rather than at the NH group.[233] Data are also reported for the base hydrolysis of benzonitriles in complex ions of the type $[Co(NH_3)_5(NCC_6H_4R)]^{3+}$ (R = 4-CN, 3-CN, 4-Ac, 3-CHO, or 4-CHO).[234] The results of these studies are compared with analogous results for other metal nitriles in Table 20. Ruthenium(III) is seen to be most effective in catalysing the base hydrolysis of acetonitrile, and this is attributed

Table 20 *Rate constants at* 298.1 K *for the base hydrolysis of* $[M(NH_3)_5NCR]^{3+}$ *ions* (μ = 1.0 mol l^{-1})

$$[M(NH_3)_5NCR]^{3+} + OH^- \rightarrow [M(NH_3)_5NHCOR]^{2+}$$

M	R	k_{OH}/ l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
Co^{III}	Me	3.4			233
Co^{III}	4-CNC_6H_4	369	13.3	−2	234
Co^{III}	3-CNC_6H_4	322	15.6	+5	234
Co^{III}	4-AcC_6H_4	135	12.3	−7	234
Rh^{III}	Me	1.0			9
Ru^{III}	Me	220			9
Ru^{III}	Ph	2000			9
Ru^{II}	Me	$< 6 \times 10^{-5}$			9
Unco-ordinated	MeCN	1.6×10^{-6}			9

[232] K. B. Nolan, B. R. Coles, and R. W. Hay, *J.C.S. Dalton*, 1973, 2503.
[233] D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1973, **95**, 5649.
[234] R. J. Balahura, P. Cock, and W. L. Purcell, *J. Amer. Chem. Soc.*, 1974, **96**, 2739.

to the greater π-accepting ability of this metal ion.[9] Ruthenium(II) is very ineffective as a catalyst, in line with its known π-donor ability. The reactions of 3- and 4-formylbenzonitrile complexes are complicated by the hydration of the formyl group.[234]

The base hydrolysis of O-bonded DMF in the complex ion $[Co(NH_3)_5(DMF)]^{3+}$ involves the following reaction as the major pathway in which attack occurs at the carbonyl group:[235]

$$[(NH_3)_5Co(OCNMe_2)]^{2+} + OH^- \longrightarrow [(NH_3)_5Co(OCHO)]^{2+} + NHMe_2 \quad (57)$$

This reaction is characterized by the activation parameters $\Delta H^{\ddagger} = 13.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 12$ cal K^{-1} mol^{-1}. Base hydrolysis by the S_N1cb pathway to give the $[Co(NH_3)_5OH]^{2+}$ ion as a minor product is found to have a much higher activation energy: $\Delta H^{\ddagger} = 28$ kcal mol^{-1} and $\Delta S^{\ddagger} = +35$ cal K^{-1} mol^{-1}. Co-ordination of DMF to cobalt(III) increases the rate of base hydrolysis by more than a factor of 10^4, largely because of a more favourable entropy of activation.

The aquations of cobaloximes are usually carried out in acidic solution. A few examples have appeared of base-catalysed reactions of *trans*-$[Co(dmgH)_2XY]$ complexes including the systems where X = py or 4-Me-py and Y = Cl or Br,[236] and where X = CN^- and Y = NO_2^-.[237] These reactions involve replacement of Y by OH and are catalysed by deprotonation of the O—H—O bridges of the dimethylglyoxime ligands. For the complex $[Co(dmgH)_2(NCSe)(OH_2)]$ deprotonation of the co-ordinated water molecule occurs as well.[238] Rate data are reported for the ions $[Co(dmg)(dmgH)(OH)(NCSe)]^{2-}$ and $[Co(dmgH)_2(OH)(NCSe)]^-$.

Chromium(III) Complexes.—Aqua-chromium(III) complexes form conjugate bases even at low pH owing to the acidity of the co-ordinated water molecules. Base hydrolysis of such complexes usually results in precipitation of polymeric hydroxo-compounds. A reaction of this type investigated[239] recently is

$$[Cr(en)(ox)(OH_2)_2]^+ + 3OH^- \overset{K}{\rightleftharpoons} \underset{\text{(unidentate oxalate)}}{[Cr(en)(ox)(OH)_3]^{2-}} + 2H_2O$$

$$[Cr(en)(ox)(OH)_3]^{2-} \xrightarrow{k_1} [Cr(en)(OH)_3] + ox^{2-}$$

$$[Cr(en)(OH)_3] + OH^- \xrightarrow{\text{fast}} [Cr(en)(OH)_4]^-$$

$$[Cr(en)(OH)_4]^- \longrightarrow \text{polynuclear species}$$

The first stage is rapid and involves opening of one end of the oxalato-chelate ring. The observed rate constant is given by $k = k_1K[OH^-]/\{1 + K[OH^-]\}$, and for k_1 the Arrhenius parameters are $E_a = 87.6 \pm 0.5$ kJ mol^{-1} and $\log_{10} A = 27.35$.

Base hydrolysis of the $[Cr(en)_2(NCS)_2]^+$ ion is reported to involve the deprotonation of both 1,2-diaminoethane molecules to give the conjugate bases $[Cr(en)(en-H)(NCS)_2]$ and $[Cr(en-H)_2(NCS)_2]^-$. The latter ion undergoes olation and the former species aquates.[240]

[235] D. A. Buckingham, J. MacB. Harrowfield, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1974, **96**, 1726.
[236] V. R. Vijayaraghavan and M. Santappa, *J. Inorg. Nuclear Chem.*, 1974, **36**, 163.
[237] R. Ripan, Z. Finta, and Cs. Várhelyi, *Rev. Roumaine Chim.*, 1974, **19**, 37.
[238] J. Zsakó, Z. Finta, and Cs. Várhelyi, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2839.
[239] M. B. Davies, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3789.
[240] J. Zsakó, Cs. Várhelyi, and F. Manok, *Rev. Roumaine Chim.*, 1973, **18**, 1897.

Whereas acid hydrolysis of the $[Cr(NH_3)_5(ONO_2)]^{2+}$ ion proceeds with loss of co-ordinated ammonia molecules to give mixtures of products owing to the *cis* activation by the nitrate ion, base hydrolysis gives only the $[Cr(NH_3)_5(OH)]^{2+}$ ion. The base hydrolysis proceeds with chromium–oxygen bond cleavage and is characterized by the following rate parameters: at 298.1 K, $10^2k_{OH} = 1.1$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 25.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -2.1$ cal K^{-1} mol^{-1}. Approximate kinetic data for the base hydrolysis of chromium(III) ammines are reported.[15]

6 Formation

In this section substitution reactions involving the formation (often anation) of inert metal complexes are discussed with cations arranged in order of increasing number of *d* electrons. Metal ions with d^0, d^1, d^2, or d^{10} configurations are usually labile and most references to these systems will be found in Chapter 4.

d^0: Titanium(IV).—The formation of the 1 : 1 complex of titanium(IV) with methylthymol blue[241] and ethylene glycol[242] at low pH is reported to follow second-order kinetics in both cases, and the reactions are relatively slow. With methylthymol blue (H_6L) a study in the pH range 1.10—1.85 indicated that a reaction between H_4L^{2-} and TiO^{2+} and $[TiO(OH)]^+$ ions is involved. The activation parameters are $\Delta H^{\ddagger}$ *ca.* 6 kcal mol^{-1} and $\Delta S^{\ddagger}$ *ca.* -35 cal K^{-1} mol^{-1}.

d^1: Molybdenum(V).—Rate data are reported for the formation and dissociation of the edta complex of the molybdenum(v) dimer $[Mo_2O_4]^{2+}$.[177] The structure of the product [(19), p. 171] involves bridging of the edta between the two molybdenum(v) ions. The reaction was studied at $[H^+]$ between 0.5 and 2.0 mol l^{-1}, and at 298.1 K and $\mu = 2.0$ mol l^{-1} ($LiClO_4$) the formation rate constant is 0.18 l mol^{-1} s^{-1}. The acid dependence of the reaction is complex. A rate-determining chelate-ring-closure mechanism is favoured after an initial rapid attack by a nitrogen atom of edta at a *trans* position to one of the Mo=O groups. The water molecule in a *trans* position to Mo=O is expected to be labile. Although closure of one of the glycinate arms of edta is believed to be rate determining, it is also possible that bridging across by the edta is involved in the slow step.[177]

d^3: Chromium(III).—A study has been made of the anation of the $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5(MeOH)]^{3+}$ ions by fluoride and thiocyanate ion in a methanol–water mixture (0.308M-MeOH).[243] The products of the reactions with thiocyanate ion were separated and found to be the $[Cr(H_2O)_5(NCS)]^{2+}$ and the *cis*- and *trans*-$[Cr(H_2O)_4(MeOH)(NCS)]^{2+}$ ions. The rate law for these reactions is

$$\text{Rate} = \{k_1[Cr(H_2O)_6]^{3+} + (k_2 + k_3 + k_4)[Cr(H_2O)_5(MeOH)]^{3+}\}[NCS^-] \quad (58)$$

In equation (58) k_1 and k_2 are associated with the formation of the $[Cr(H_2O)_5(NCS)]^{2+}$ ion and k_3 and k_4 with the formation of *trans*- and *cis*-$[Cr(H_2O)_4(MeOH)(NCS)]^{2+}$ ions respectively. Values of these rate constants at 303.1 K are $10^6k_1 = 2.5$, $10^6k_2 = 1.3$, $10^6k_3 = 0.87$, and $10^6k_4 = 1.9$ l mol^{-1} s^{-1}. The statistically corrected rate constants (*i.e.* observed rate constants divided by the number of reacting sites) are therefore $10^6k_1 = 0.42$, $10^6k_2 = 1.3$, $10^6k_3 = 0.87$, and $10^6k_4 = 0.48$ l mol^{-1}

[241] T. B. Mal'kova and L. A. Fomina, *Russ. J. Inorg. Chem.*, 1974, **19**, 377.
[242] C. Liegeois, *Bull. Soc. chim. France*, 1973, 2177.
[243] R. J. Baltisberger, C. L. Knudson, and M. F. Anderson, *Inorg. Chem.*, 1974, **13**, 2354.

s^{-1} and it can be seen that the replacement of the co-ordinated methanol, and of the water molecule in a *trans* position to it, is most facile. For the reactions with fluoride ion the products were not separated and only the composite rate constants were obtained. Some data for the solvolysis of the various isothiocyanato-complexes are also reported. The formation reactions are discussed in terms of an associative interchange (I_a) mechanism. This mechanism is thought to be most likely for substitution reactions at chromium(III).[12]

The influence of ionic strength (using the theory of Moelwyn-Hughes) upon the activation parameters for the reaction between $[Cr(H_2O)_6]^{3+}$ and thiocyanate ions is also reported.[244] The reaction was studied at ionic strengths in the range 0.014—0.254 mol l^{-1} but only over a 20 K temperature range (313—333 K). An S_N2 mechanism is said to be supported for the anation of the $[Cr(H_2O)_6]^{3+}$ ion on the basis of quantum mechanical calculations![13]

A two-term rate law is observed for the thiocyanate-ion anation of the hydroxo-bridged *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]^{5+}$ ion, the product being the *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(NCS)]^{4+}$ ion:[245]

$$-\mathrm{d[complex]}/\mathrm{d}t = (k_1 + k_2[NCS^-])[\mathrm{complex}] \qquad (59)$$

This rate law is interpreted in terms of S_N1 and $S_N1(ip)$ mechanisms:

$$\begin{array}{ccc} \textit{cis}\text{-}[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]^{5+} & \rightleftharpoons & \textit{cis}\text{-}[(NH_3)_5Cr(OH)Cr(NH_3)_4]^{5+} + H_2O \\ \Big\downarrow\uparrow NCS^- & & \Big\downarrow NCS^- \\ \text{(complex, } NCS^-\text{) ion pair} & \longrightarrow & \textit{cis}\text{-}[(NH_3)_5Cr(OH)Cr(NH_3)_4(NCS)]^{4+} \end{array}$$

At 298.1 K, $10^5k_1 = 3.44\ s^{-1}$ and $10^5k_2 = 10.1\ l\ mol^{-1}\ s^{-1}$.

Following an earlier study of the reaction between $[Cr(NH_3)_5(OH_2)]^{3+}$ and oxalate ions to give the $[Cr(NH_3)_4(ox)]^+$ ion,[246] kinetic data are now reported for the first step in the following reactions:[247]

$$[Cr(en)(OH_2)_4]^{3+} + ox^{2-} \longrightarrow [Cr(en)(ox)(OH_2)_2]^+$$
$$[Cr(en)(ox)(OH_2)_2]^+ + H^+ \longrightarrow [Cr(enH)(ox)(OH_2)_3]^{2+}$$
$$[Cr(enH)(ox)(OH_2)_3]^{2+} + H_2O \longrightarrow [Cr(ox)(OH_2)_4]^+ + enH^+$$
$$[Cr(ox)(OH_2)_4]^+ + ox^{2-} \longrightarrow [Cr(ox)_2(OH_2)_2]^-$$

The same overall reaction also occurs without the intermediate formation of the $[Cr(en)(ox)(OH_2)_2]^+$ ion (this alternative pathway contributes *ca.* 40% at 318—333 K). The rate-determining step in the first stage of both pathways is the formation of a unidentate oxalato-complex, and subsequent oxalato-chelate-ring closure to give the $[Cr(en)(ox)(OH_2)_2]^+$ and $[Cr(enH)(ox)(OH_2)_3]^{2+}$ ions is rapid. The reactions were studied in the range 0.03—0.50M-H^+, and in this acidity range the observed second-order rate constant k varies with $[H^+]$ as follows:

$$1/k = 1/k_1 + [H^+]/k_1K_1$$

k_1 is the rate constant for the reaction of the $[Cr(en)(OH_2)_4]^{3+}$ ion with $[C_2O_4H]^-$, and K_1 is the first acid dissociation constant of oxalic acid. At 323.1 K and $\mu = 1.0$ mol

[244] V. Holba, *Chem. Abs.*, 1974, **80**, 41 260e.
[245] H. N. Po, Y.-H. Chung, S. R. Davis, and H. Enomoto, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1349.
[246] O. Nor and A. G. Sykes, *J.C.S. Dalton*, 1973, 1232.
[247] O. Nor, J. N. Lethbridge, and A. G. Sykes, *J.C.S. Dalton*, 1973, 1758.

l^{-1}, $10^2k_1 = 4.02\ l\ mol^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 23.4 \pm 1.0$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 7.4 \pm 3.1$ cal $K^{-1}\ mol^{-1}$.

The mechanism of the reaction between aqueous chromium(III) and edta (H_4L) is reported to involve the ions $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5(OH)]^{2+}$, $[Cr(H_2O)_4(OH)_2]^{+}$, and H_2L^{2-} or HL^{3-}.[248]

***d*³: Molybdenum(III).**—A comparison of recent results for the anation of the $[Mo(H_2O)_6]^{3+}$ ion[10] with results for analogous studies of other inert metal ions of the type $[M(H_2O)_6]^{3+}$ is made in Table 21. A comparison of the d^3 systems chromium(III) and molybdenum(III) is particularly interesting. Molybdenum(III) is seen to react much more rapidly than chromium(III), the activation energies for formation of the chloro- and isothiocyanato-complexes of molybdenum(III) being 7—9 kcal mol^{-1} lower than for chromium(III). The rate of formation of the $[Mo(H_2O)_5(NCS)]^{2+}$ ion is *ca.* 10^2 lower than originally reported,[249] possibly because of catalysis by traces of the metal ion in some other, more labile, oxidation state. An S_N2 mechanism is proposed for these substitution reactions of molybdenum(III), in line with the conclusions reached recently for chromium(III)[12] and the larger size of the molybdenum(III) ion. The latter factor must also contribute to its greater reactivity. The pseudo-first-order rate constants k for the formation of the $[Mo(H_2O)_5Cl]^{2+}$ ion in the presence of excess chloride ion are given by

$$k = k_f[Cl^-] + k_b$$

Hence values of the formation rate constant k_f and the dissociation rate constant k_b are obtained from the variation of k with $[Cl^-]$, and $K_{eq} = k_f/k_b$. For the $[Mo(H_2O)_5(NCS)]^{2+}$ ion the value of K_{eq} is much larger and so a value of k_b is not obtained from the values of k.

Table 21 *Comparison of rate data at* 298.1 K *for the formation of* $[M(H_2O)_5X]^{2+}$ *ions from* $[M(H_2O)_6]^{3+}$ (M = *tervalent metal ion*, X^- = *anion*); *data from ref.* 10

M	X	K_{eq}/ l mol^{-1} [a]	k/ l $mol^{-1}\ s^{-1}$ [b]	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal $K^{-1}\ mol^{-1}$
Mo^{III}, t_{2g}^3	Cl	10.8	4.6×10^{-3} [c]	23.5	9.6
Mo^{III}, t_{2g}^3	NCS	*ca.* 10^5	0.27[c]	16.3	−6.4
Cr^{III}, t_{2g}^3	Cl	0.11	2.9×10^{-8} [d]	30.3	8.6
Cr^{III}, t_{2g}^3	NCS	136	1.8×10^{-6} [d]	25.1	0.7
V^{III}, t_{2g}^2	Cl		$\leqslant 3$		
Fe^{III}, t_{2g}^3, e_g^*	Cl		9.4		
Co^{III}, t_{2g}^6	Cl		$\leqslant 2$[e]		
Ru^{III}, t_{2g}^5	Cl		*ca.* 10^{-6}		
Rh^{III}, t_{2g}^6	Cl		5.5×10^{-6} [f]		

[a] Equilibrium formation constant. [b] Formation rate constant. [c] In 1 mol l^{-1} lithium toluene-*p*-sulphonate. [d] Calculated values from activation parameters; $\mu = 0.5$—1.0 mol l^{-1}. [e] A fast reaction may be due to some high-spin cobalt(III). [f] At 348.1 K.

[248] B. S. Grigor'ev and Y. Y. Makarov-Zemlyanskii, *Zhur. fiz. Khim.*, 1974, **48**, 1173.
[249] K. Kustin and D. Toppen, *Inorg. Chem.*, 1972, **11**, 2851.

d^4: Rhenium(III).—The reaction of dichloro-μ-tetrapropionato-dirhenium(III) with bromide ion in acetonitrile solution has been investigated:[250]

$$[Re_2(EtCO_2)_4Cl_2] + Br^- \rightleftharpoons [Re_2(EtCO_2)_4ClBr] + Cl^-$$

At 298.1 K the equilibrium constant $K_1 = (1.1 \pm 0.1) \times 10^{-2}$, and the formation rate constant $k_f = A[Br^-]/\{[Cl^-] + B[Br^-]\}$, where $10^5A = 3.4\ s^{-1}$ and $10^2B = 4.1$. This variation of k_f with concentration of halide ions is interpreted in terms of a dissociative mechanism. Representing $[Re_2(EtCO_2)_4Cl_2]$ as Re_2Cl_2, the proposed mechanism is

$$Re_2Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Re_2Cl^+ + Cl^-$$

$$Re_2Cl^+ + Br^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Re_2ClBr$$

Estimated values of the rate constants for the reaction at 298.1 K in acetonitrile are then: $10^4k_1 = 8.1 \pm 0.7\ s^{-1}$, $10^2k_2/k_{-1} = 4.1 \pm 0.6$, and $10^3k_{-2} = 3.0 \pm 0.3\ s^{-1}$. Rhenium(III) is, therefore, behaving as a class (*a*) or 'hard' metal ion ($k_{-2} > k_1$). The reaction is strongly catalysed by traces of neutral donor molecules, including water, and the catalytic rate constants (k_N) show a rough correlation with the basicity of the nucleophile. Values of 10^2k_N/l mol^{-1} s^{-1} are 83, 75, 40, 11, 6.6, 4.3, 0.12, and 5×10^{-2} for the catalysts H_2O, py, urea, DMF, acetamide, THF, and EtCN respectively.

d^5: Manganese(II).—This ion is normally very labile. However, the reaction of 2,2′,2″-terpyridyl (terpy) with a large excess of $[Mn(DMSO)_6]^{2+}$ ion is observed to take minutes to go to completion at room temperature in DMSO solution.[251] The reaction proceeds in two stages, the first stage being very fast and typical of a manganese(II) substitution. The product of the first stage is believed to be a mixture of complex ions in which the terpy is acting as a bidentate ligand to one manganese(II) ion while the third pyridine ring is either unco-ordinated or bound to a second manganese(II) ion (giving a dinuclear complex). The second, slow stage is attributed to final chelate ring closure.

d^5: Iron(III).—Substitution reactions of the low-spin iron(III) complex ions $[Fe(CN)_5X]^{2-}$ (X = NH_3 or H_2O) have been observed to be catalysed by small amounts of the iron(II) complex ions $[Fe(CN)_5X]^{3-}$. Reaction with ligands Y {Y = N_3^-, NCS^-, OH^-, or $[Co(CN)_6]^{3-}$} at iron(II) concentrations greater than *ca.* 1% of the total iron species are believed to proceed entirely *via* the iron(II) complexes.[193] A previous study of the reaction with thiocyanate ion is in doubt owing to the reduction of iron(III) to iron(II) by the thiocyanate ion.[193]

d^5: Ruthenium(III).—An I_d mechanism is suggested for the formation of $[Ru(NH_3)_5(OCOR)]^{2+}$ ions (R = CF_3, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, or CH_2I).[196] The formation rate constants are very similar for these reactions (at 333.1 K, k_f is *ca.* 2×10^{-2} l mol^{-1} s^{-1}) and for the spontaneous aquations a plot of log (rate constant) against log (equilibrium constant) has a slope of 1.0, in support of an I_d mechanism. Rate constants for the anation of the $[Ru(NH_3)_5(OH_2)]^{3+}$ ion have been estimated by an iterative search technique.[196]

[250] T. R. Webb and J. H. Espenson, *J. Amer. Chem. Soc.*, 1974, **96**, 6289.
[251] D. M. W. Buck and P. Moore, *J.C.S. Chem. Comm.*, 1973, 60.

d^6: Iron(II).—An S_N1(lim) (or *D*) mechanism is proposed for formation of iron(II) complexes of the type $[Fe(CN)_5L]^{3-}$ (L = nitrogen heterocyclic base) from the $[Fe(CN)_5(OH_2)]^{3-}$ ion.[212] To avoid polymerization the aqua-complex was generated *in situ* at low dilution from the $[Fe(CN)_5(NH_3)]^{3-}$ ion. A comparison of the rates of formation with the previously reported rates of dissociation is given in Table 22. The

Table 22 *Rate data for the formation and dissociation of the low-spin* $[Fe^{II}(CN)_5L]^{n-}$ *complexes at* 298.1 K (*refs.* 211 *and* 212)

L	$10^{-2}k_f$/ l mol^{-1} s^{-1}	$\Delta H_f^{\ddagger}$/ kcal mol^{-1}	$\Delta S_f^{\ddagger}$/ cal K^{-1} mol^{-1}	10^4k_d/ s^{-1}	$\Delta H_d^{\ddagger}$/ kcal mol^{-1}	$\Delta S_d^{\ddagger}$/ cal K^{-1} mol^{-1}
DMSO	2.40	15.4	4	75	26.5	11
4-Me-py[a]	3.60	15.1	4	11.5	24.0	9
py	3.65	16.1	7	11.0	24.8	11
4-NH_2CO-py[b]	2.96	15.8	6	7.3	26.0	14
pz[c]	3.80	15.4	5	4.2	26.4	14
mpz$^+$ [d]	5.50	16.8	10	2.8	27.5	18

[a] 4-Methylpyridine. [b] Isonicotinamide. [b] 1,4-Pyrazine. [d] *N*-Methyl-1,4-pyrazinium ion.

invariance in the formation rate constants supports a dissociative mechanism but a limiting rate at high ligand concentration was not observed. For the reaction of $[Fe(CN)_5(DMSO)]^{3-}$ ion with *N*-methyl-1,4-pyrazinium cation a limiting rate is reached[211] but in this case ion-pairing is possible. Support for a *D* mechanism comes from a study of the $[Fe(CN)_5(SO_3)]^{5-}$ ion reacting with cyanide ion from which a discriminating factor of 8.76 (k_2/k_{-1}) can be estimated (at 316 K, pH 10.8, k_2/k_{-1} = 1.0) for the reaction of the assumed five-co-ordinate intermediate $[Fe(CN)_5]^{3-}$ with cyanide ion compared with sulphite ion:[213]

$$[Fe(CN)_5(SO_3)]^{5-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + SO_3^{2-}$$

$$[Fe(CN)_5]^{3-} + CN^- \xrightarrow{k_2} [Fe(CN)_6]^{4-}$$

Part of this discrimination factor could be ascribed to differences in charge between sulphite and cyanide ions.

The photocatalysed substitution reactions of nitroprusside ion, $[Fe(CN)_5(NO)]^{2-}$, with thiocyanate ion and thiourea involve oxidation of iron(II) to iron(III).[218] This contrasts with the reduction of cyano-complexes of iron(III) to iron(II) by thiocyanate ion noted in the previous part of this section.[192] For the photocatalysed reactions the following mechanism is proposed:

$$[Fe(CN)_5(NO_2H)] + H^+ \overset{K}{\rightleftharpoons} [Fe(CN)_5(NO)]^{2-} + H_2O$$

$$[Fe(CN)_5(NO_2H)]^{3-} + L \xrightarrow{k_2} [Fe^{II}(CN)_5L]^{3-} + HNO_2$$

$$[Fe^{II}(CN)_5L]^{2-} + H^+ + HNO_2 \xrightarrow{\text{fast}} [Fe^{III}(CN)_5L]^{2-} + NO + H_2O$$

Hydrolysis of nitroprusside ion induced by azide ion or hydroxylamine was discussed in an earlier section.[217] One of the products of the two-electron reduction of nitroprusside ion is reported to be the $[Fe(CN)_4(NC)(NO)]^{4-}$ ion with an N-bonded isocyano-group.[219]

The kinetics of formation of nitrosyl complexes of iron(II) from the reaction between ferricyanide and nitric and nitrous acid in strongly acidic solution have been reported.[252, 253] These reactions involve reduction of iron(III) to iron(II) and oxidation of cyanide ion to cyanate ion. The ferricyanide is attacked by NO_2 which is formed from the following rapid equilibria:

$$H^+ + HNO_2 + NO_3^- \rightleftharpoons H_2O + N_2O_4 \rightleftharpoons 2NO_2$$

A nitrosyl-bridged intermediate, believed to be the *cis*-$[(NC)_5Fe(NO)Fe(NO)(CN)_4]^{3-}$ ion, is formed from the reaction between $[Fe(CN)_6]^{3-}$ and NO_2, and this intermediate slowly reacts to give a product which is postulated to be the $[(NC)_4Fe(NO)_2Fe(CN)_4]^{2-}$ ion containing two bridging nitrosyl groups. A reinvestigation of the formation of the $[Fe(CN)_5(CNSO_3)]^{4-}$ ion from the reduction of ferricyanide by sulphite ion[254] has been shown to arise from the reaction of $[Fe(CN)_6]^{3-}$ with the sulphite radical ion, $SO_3^{-\bullet}$.

***d*⁶: Ruthenium(II).**—A comparison of the *trans* effects of S-bonded sulphur dioxide, hydrogen sulphite, and sulphite ions is possible from studies of the following complex systems:[4]

$$trans\text{-}[Ru(NH_3)_4(SO_2)(OH_2)]^{2+} + H_2O \rightleftharpoons trans\text{-}[Ru(NH_3)_4(HSO_3)(OH_2)]^+ + H^+ \quad (60)$$

$$trans\text{-}[Ru(NH_3)_4(HSO_3)(OH_2)]^+ \rightleftharpoons trans\text{-}[Ru(NH_3)_4(SO_3)(OH_2)] + H^+ \quad (61)$$

For co-ordinated sulphur dioxide the pK_a values representing equilibria (60) and (61) are $pK_1 = 2.15 \pm 0.1$ and $pK_2 = 5.05 \pm 0.1$ respectively ($\mu = 0.1$ mol l^{-1}). At 298.1 K rate constants for the reaction of 1,4-pyrazine with *trans*-$[Ru(NH_3)_4(SO_3)(OH_2)]$, *trans*-$[Ru(NH_3)_4(HSO_3)(OH_2)]^+$, and *trans*-$[Ru(NH_3)_4(SO_2)(OH_2)]^{2+}$ ions are 13.5 ± 0.1, 0.20 ± 0.01, and 0.033 ± 0.004 l mol^{-1} s^{-1} respectively, and hence the relative *trans* effects are $SO_3^{2-} > HSO_3^- > SO_2$. Reaction of pyrazine with *trans*-$[Ru(NH_3)_4(SO_3)(OH_2)]$ is characterized by $\Delta H^{\ddagger} = 16.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0.8$ cal K^{-1} mol^{-1}, compared with values of $\Delta H^{\ddagger} = 17.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6$ cal K^{-1} mol^{-1} for reaction of pyrazine with the $[Ru(NH_3)_5(OH_2)]^{2+}$ ion. Hence the *trans* effect of sulphite ion manifests itself in changes in both the enthalpy and the entropy of activation, although the difference in charge types for these two complexes is expected to have some effect upon the entropy of activation. The rate of reaction of *cis*-$[Ru(NH_3)_4(SO_3)(OH_2)]$ with pyrazine or isonicotinamide is independent of the concentration of the ligands, the rate-determining step being dissociation of the ammonia molecule in the *trans* position to the sulphito-group. At 298.1 K the rate of loss of the co-ordinated ammonia molecule is accelerated by a factor of 6×10^3 by the presence of the *trans*-sulphito-ligand.

The π-donor ability of ruthenium(II) is known to increase the basicity of co-ordinated ligands such as 1,4-pyrazine. This is demonstrated by the ready formation of bridged dinuclear complex ions of the type $[(NH_3)_5Ru\text{-}\mu\text{-}(1,4\text{-pyrazine})\text{-}M(OH_2)_5]^{4+}$. Formation constants of 17, 32, and 3.1 l mol^{-1} are reported for M = Ni^{II}, Cu^{II}, and Zn^{II} respectively. The rate of formation and dissociation of the nickel(II) complex is typical of substitution reactions at nickel(II) ion: $10^{-3}k_f = 1.1 \pm 0.1$ l mol^{-1} s^{-1}

[252] K. M. Davies and G. Stedman, *J.C.S. Dalton*, 1974, 2176.
[253] J. C. Bates, K. M. Davies, and G. Stedman, *J.C.S. Dalton*, 1974, 2182.
[254] R. S. Murray, *J.C.S. Dalton*, 1974, 2381.

($\Delta H_f^{\ddagger} = 10 \pm 1$ kcal mol^{-1}, $\Delta S_f^{\ddagger} = -11 \pm 3$ cal K^{-1} mol^{-1}); $k_d = 66 \pm 5$ s^{-1} ($\Delta H_d^{\ddagger} = 16 \pm 1$ kcal mol^{-1}, $\Delta S_d^{\ddagger} = 4 \pm 3$ cal K^{-1} mol^{-1}).[255]

Rate data for the reaction of the *cis*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$ ion with benzonitrile or 2-aminomethylpyridine and for the reaction of the *trans*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$ ion with pyridine are very similar.[256] Activation parameters are in the ranges $\Delta H^{\ddagger}$ = 14.4—16.7 kcal mol^{-1} and $\Delta S^{\ddagger} = -5$ to -17 cal K^{-1} mol^{-1}. For the two-step reactions the first step is approximately ten times faster than the second step, in line with steric and electronic effects.

The formation of ruthenium complexes is often complicated by the reactivity of the co-ordinated ligands. Thus, reaction of the $[Ru(NH_3)_6]^{3+}$ ion with nitric oxide in aqueous solution at *ca.* pH 7 involves substitution to give the nitrosyl complex ion $[Ru(NH_3)_5(NO)]^{3+}$. However, above pH 8.3 oxidation of a co-ordinated ammonia molecule occurs to give the dinitrogen complex ion, $[Ru(NH_3)_5N_2]^{2+}$. It is possible that the latter reaction involves attack by the nitric oxide at the ruthenium(III) followed by migration of an adjacent ammonia molecule to the co-ordinated NO group.[257] A similar reaction is reported for the formation of the $[Ru(en)_2(N_2)(OH_2)]^{2+}$ ion from the reaction between nitric oxide and $[Ru(en)_3]^{3+}$ in alkaline solution.[258] This reaction results in breakage of a carbon–nitrogen bond of a co-ordinated 1,2-diaminoethane. The remarkable stability of ruthenium(II)–dinitrogen bonds is demonstrated by these reactions.

The reactivity of ruthenium nitrosyls has been investigated for the following reactions (Ar = aromatic group):[259,260]

$$[Ru(bipy)_2(*NO)Cl]^{2+} + ArNH_2 \longrightarrow [Ru(bipy)_2(*NNAr)Cl]^{2+} + H_2O \quad (62)$$

$$[Ru(bipy)_2(NO)Cl]^{2+} + PhNMe_2 \longrightarrow [Cl(bipy)_2Ru{-}N(=O){-}C_6H_4{-}NMe_2] \quad (63)$$

Reaction (62) was established to proceed as shown by ^{15}N labelling,[259] and the ArN_2 group of the products was found to vary in character from arylazo (Ar—N=N$^-$) to diazonium (Ar—N≡N$^+$) groups just as nitrosyls can vary in character from NO$^-$ to NO$^+$. Reaction (63) involves electrophilic attack by the co-ordinated NO group at the activated aromatic ring and occurs for *N*-methyl- and *NN*-dimethyl-aniline.[260]

d^6: Cobalt(III).—Anation of the $[Co(NH_3)_5(OH_2)]^{3+}$ ion by bromide ion shows no saturation effect at bromide-ion concentrations of up to 1.0 mol l^{-1}. The equilibrium constant for formation of the $[Co(NH_3)_5Br]^{2+}$ ion is 0.283 ± 0.30 l mol^{-1}, and at 298.1 K the formation rate constant is $(1.32 \pm 0.06) \times 10^{-6}$ l mol^{-1} s^{-1}. An equilibrium constant for ion-pair formation could not be resolved.[44] In a similar study of the $[Co(NH_3)_5(DMSO)]^{3+}$ ion reacting with nitrate ion an I_d mechanism was established from studies in DMSO–water mixtures, and the DMSO solvent-exchange rate constant is reported to be $(3.6 \pm 0.8) \times 10^{-4}$ s^{-1} at 318.1 K.[43]

[255] M. S. Pereira and J. M. Malin, *Inorg. Chem.*, 1974, **13**, 386.
[256] R. J. Allen and P. C. Ford, *Inorg. Chem.*, 1974, **13**, 237.
[257] S. D. Pell and J. N. Armor, *J. Amer. Chem. Soc.*, 1973, **95**, 7625.
[258] S. D. Pell and J. N. Armor, *J.C.S. Chem. Comm.*, 1974, 259.
[259] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5084.
[260] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1974, **96**, 5605.

An S_N1(ip) mechanism is proposed for the reaction of the $[Co(NH_3)_5(OH_2)]^{3+}$ ion with glycine at pH 2.75—4.00 to give $[Co(NH_3)_5(O_2CCH_2NH_3)]^{3+}$.[261] From studies in the range 323—343 K, activation parameters for this reaction are reported to be $\Delta H^{\ddagger} = 27.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = +5.2$ cal K^{-1} mol^{-1}.

Extensive studies are reported for the formation of the $[Co(NH_3)_5(OH)]^{2+}$ ion from reactions between ammonia and *cis*- and *trans*-$[Co(NH_3)_4(OH_2)_2]^{+}$ and $[Co(NH_3)_4(OH_2)(OH)]^{2+}$ ions.[229] An I_d mechanism is proposed, conjugate-base formation contributing at high pH. Isomerization and substitution by ammonia occur at similar rates. A further study of the tetramerization and isomerization of $[Co(NH_3)_4(OH_2)(OH)]^{2+}$ and $[Co(NH_3)_4(OH)_2]^{+}$ ions has appeared.[262]

Formation of μ-cyano-complexes is reported from the reaction between the *trans*-$Co(en)_2(SO_3)(OH_2)]^{+}$ ion and $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, and $Fe(CN)_5(NO)]^{2-}$ ions,[18] *e.g.*

$$trans\text{-}[Co(en)_2(SO_3)(OH_2)]^{+} + [M(CN)_6]^{n-} \longrightarrow trans\text{-}[(H_2O)(en)_2CoNCM(CN)_5]^{(n-1)-}$$

The strong *trans*-effect of the S-bonded sulphite ion is again apparent, and for the reaction with ferrocyanide ion a first-order reaction is observed even at a 1 : 1 ratio of reactants. Although a *D* mechanism is indicated for the reaction with ferrocyanide ion, the limiting rate at high $[Fe(CN)_6^{4-}]$ is higher than the value reported for the reaction of sulphite ion with the *trans*-$[Co(en)_2(SO_3)(OH_2)]^{+}$ ion.[263]

In an analogous study, formation of *trans*-$[Et(dmgH)_2CoNCM(CN)_5]^{n-}$ ions is reported from the reactions between *trans*-$[EtCo(dmgH)_2(OH_2)]$ and $[M(CN)_6]^{n-}$ ions (M = Fe^{II}, Co^{III}, Fe^{III}, and Cr^{III}). As S_N1(lim) or *D* mechanism is not found in all cases. Sometimes an outer-sphere association followed by a rate-determining loss of water is proposed.[94] A *D* mechanism is reported to apply to anation reactions of *trans*-$[Co(dmgH)_2(NO_2)(DMSO)]$ and *trans*-$[Co(dmgH)_2(Me)(DMSO)]$ and to substitution reactions of other cobaloximes discussed in a previous section (see dioximato-complexes in Section 2).[93, 97, 98]

A crystal structure of the complex *trans*-$[Co(PnAO-H)(NO_2)_2]$ [PnAO − H = (6), p. 141] shows that the nitro-ligands are non-equivalent, the cobalt–NO_2 bond lengths being 198.4 and 193.7 pm.[85] This ground-state difference is reflected in the kinetic non-equivalence of the cobalt–X bonds in *trans*-$[Co(PnAO - H)X_2]$ (X = NO_2, N_3, or Cl).[86] Representing the complexes as RX_2, kinetic data are reported for the reactions $R(NO_2)_2 + N_3^- \rightarrow R(NO_2)(N_3) + NO_2^-$ (*via* aquation), $R(NO_2)(N_3) + N_3^- \rightarrow R(N_3)_2 + NO_2^-$, $R(NO_2)(OH_2)^+ + N_3^- \rightarrow R(NO_2)(N_3) + H_2O$, and $R(NO_2)(OH_2) + NO_2^- \rightarrow R(NO_2)_2 + H_2O$. The reactions proceed by a dissociative mechanism but are abnormally fast. An unexpected dependence on the hydroxide-ion concentration is observed for the anation of the aqua-complex and for isotopic anion-exchange studies, but not for water exchange in the aqua-complex. This is attributed to unidentified conjugate-base formation. Although *trans*-$[Co(tetra\text{-}Me\text{-}en)_2(NO_2)_2]^{+}$ ion is similar in lability to *trans*-$[Co(PnAO - H)(NO_2)_2]$ the pH-dependence of its reactions is different, and the nitro-ligands are kinetically indistinguishable. Anation reactions of the $[R(NO_2)(OH_2)]^{+}$ ion reach a limiting rate

[261] D. Banerjea and J. Roy, *Z. anorg. Chem.*, 1973, **400**, 89.
[262] S. Balt and P. M. Kwantes, *J. Inorg. Nuclear Chem.*, 1973, **35**, 2407.
[263] D. R. Stranks and J. K. Yandell, *Inorg. Chem.*, 1970, **9**, 751.

at high anion concentrations, in agreement with the proposed *D* mechanism:

$$[R(NO_2)(OH_2)]^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [R(NO_2)]^+ + H_2O$$

$$[R(NO_2)]^+ + X^- \xrightarrow{k_3} [R(NO_2)X]$$

For $X^- = N_3^-$ and NO_2^-, $10^2k_1 = 1.17$ and $1.21\ s^{-1}$ respectively at pH 7.5, $\mu = 0.55$ mol l^{-1}, and 308 K. Values of the respective discrimination factors k_2/k_3 are 0.023 and 0.112 mol l^{-1} under the same conditions. The value of k_1 is comparable with the solvent-exchange rate, but unfortunately this had to be determined under different conditions. At 273 K, pH 7.8, and $\mu = 0.24$ mol l^{-1} the rate constant for water exchange is $4.65 \times 10^{-4}\ s^{-1}$.

Studies in methanol are reported for the replacement of chloride ion by the nucleophiles NCS^-, N_3^-, and NO_2^- in *trans*-$[Co(en)_2(L)Cl]^+$ (L = NO_2, N_3, CN, Cl, or NCS).[106] Ion-pair constants in the range 20—700 are reported for these reactions. When L is cyanide ion, the reaction with nitrite ion proceeds with retention of configuration.

A study of reaction (64) between pH 4.5 and 5.2 is reported to proceed with 100% stereochemical change.[264] The change in geometry occurs after the rate-determining

$$\alpha\text{-}cis\text{-}[Co(edda)(OH_2)_2]^+ + ox^{2-} \longrightarrow \beta\text{-}cis\text{-}[Co(edda)(ox)]^- \qquad (64)$$

step, and the proposed mechanism involves the formation of ion pairs between α-*cis*-$[Co(edda)(OH_2)_2]^+$ and $HC_2O_4^-$ or $C_2O_4^{2-}$ ions, and between α-*cis*-$[Co(edda)(OH)(OH_2)]$ and $C_2O_4^{2-}$. At 301 K and $\mu = 0.50$ mol l^{-1}, ion-pair constants for $HC_2O_4^-$ and $C_2O_4^{2-}$ interacting with the α-*cis*-$[Co(edda)(OH_2)_2]^+$ ion are reported to be 41 and 72 respectively, and activation parameters for the formation of the product are $\Delta H^{\ddagger} = 27.6 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.6 \pm 1.1$ cal K^{-1} mol^{-1}.

Formation of the bridged dicobalt(III) complex ions $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,Br)\text{-}Co(NH_3)_4]^{4+}$ and $[(NH_3)_4BrCo\text{-}\mu\text{-}(NH_2)\text{-}Co(NH_3)_4Br]^{3+}$ by acid-catalysed cleavage of the $[(NH_3)_4Co\text{-}\mu\text{-}(OH,NH_2)\text{-}Co(NH_3)_4]^{4+}$ ion was discussed in Section 2.[99]

Anation of the water-soluble porphyrin complex $[Co(P)(OH_2)_2]^{5+}$ [H_2P = 5,10,15,20-tetrakis-(*N*-methylpyridyl)porphine] is very fast for a substitution reaction at cobalt(III).[84] Rate data are also reported for the anation of the $[Co(P)(NCS)(OH_2)]^{4+}$ and $[Co(P)(NCS)(OH)]^{3+}$ ions, and thiocyanate ion is shown to have a strong *trans* effect ($> 10^4$) upon the remaining co-ordinated water molecule. Omitting charges for convenience, rate data for the following reactions were as shown:

$$[Co(P)(OH_2)_2] + NCS \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(P)(OH_2)(SCN)]$$

$$[Co(P)(OH_2)(SCN)] + NCS \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(P)(SCN)_2]$$

At 298.1 K and pH 2, $k_1 = 2.11$ l mol^{-1} s^{-1} ($\Delta H^{\ddagger} = 19.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 10.7$ cal K^{-1} mol^{-1}); $k_2 = 2.8 \times 10^4$ l mol^{-1} s^{-1}; $10^4k_{-1} = 3.13\ s^{-1}$ ($\Delta H^{\ddagger} = 24.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9.7$ cal K^{-1} mol^{-1}); and $k_{-2} = 3.0 \times 10^3\ s^{-1}$.

A few studies have appeared dealing with the formation of cobalt(III) complexes without the cleavage of metal–ligand bonds. These reactions often involve nucleo-

[264] J. A. Weyh, A. K. Newlun, T. J. Baker, and T. K. Shioyam, *Inorg. Chem.*, 1973, **12**, 2374.

philic attack by co-ordinated OH^- or H_2O groups at some other electrophilic centre. Well known examples are described for the formation of carbonato- and nitrito-complexes. A recent example of this type is reported in the formation of arsenato-cobalt(III) complexes of the type $[Co(NH_3)_5(AsO_4H_n)]^{n+}$; this can be regarded as an associative (S_N2) substitution reaction at arsenic(v):[265]

$$d[Co(NH_3)_5(AsO_4H_n)^{n+}]/dt = \{k_{-1}[HAsO_4^{2-}] + k_{-2}[H_2AsO_4^-]\}[Co(NH_3)_5(OH_2)^{3+}]$$

At 295 K and $\mu = 1.0$ mol l^{-1}, $10^2k_{-1} = 11 \pm 1$ l mol^{-1} s^{-1} and $10^4k_2 = 120 \pm 15$ l mol^{-1} s^{-1}. The reverse reaction occurs by As—O bond fission and is characterized by a rate law of the type

$$\text{Rate} = \{K_{a2}k_1 + k_2[H^+] + k_3[H^+]^2\}\{K_{a2} + [H^+]\}^{-1}[\text{total arsenato-complex}]$$

At 295 K, $10^7k_1 = 290 \pm 15$ s^{-1}, $10^6k_2 = 408 \pm 20$ s^{-1}, $10^3k_3 = 670 \pm 34$ l mol^{-1} s^{-1}, and $pK_{a2} = 3.30 \pm 0.05$. Another reaction of this type is involved in the formation of the $[Co(en)_2(acac)]^{2+}$ ion from the reaction between *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ and *cis*-$[Co(en)_2(OH)(OH_2)]^{2+}$ and acetylacetone (acacH).[266] The reaction proceeds with retention of configuration at cobalt(III) and involves nucleophilic attack by the two co-ordinated oxygen atoms at the two carbonyl centres of the acetylacetone. The reaction is complicated by some *cis*→*trans* isomerization of $[Co(en)_2(OH)(OH_2)]^{2+}$ and only the *cis*-isomer is involved in the formation of the $[Co(en)_2(acac)]^{2+}$ ion. Reconversion (*trans*→*cis*) produces more acac complex, and the dynamics of the isomerization process were investigated.

***d*⁶: Rhodium(III).**—Following a recent study of the formation of the $[Co(NH_3)_5(OCO_2)]^+$ ion,[267] data are now reported for the formation and acid hydrolysis of the analogous rhodium(III) and iridium(III) complexes.[200] The proposed mechanism of these reactions can be summarized as follows:

$$\begin{array}{ccc} [M(NH_3)_5(OH)]^{2+} + CO_2 & \underset{k_1}{\overset{k_2}{\rightleftharpoons}} & [M(NH_3)_5(CO_3H)]^{2+} \\ \Big\Vert K_A & \overset{K_1}{\Big\Vert} & \Big\Vert K_C \\ & HCO_3^- & \\ & \overset{K_2}{\Big\Vert} & \\ [M(NH_3)_5(OH_2)]^{3+} + CO_3^{2-} & & [M(NH_3)_5(OCO_2)]^+ \end{array} \qquad (65)$$

In buffered solutions containing excess carbonate ion, the observed rate constant k for the above equilibria is given by the following expression (h = hydrogen-ion concentration, b = total carbonate concentration):

$$k = k_1\{h/(h + K_C)\} + k_2b\{K_A/(h + K_A)\}\{h^2/(h^2 + K_1h + K_1K_2)\}$$

Values of the rate parameters are collected in Table 23. The close agreement of these rate parameters for the three metal ions is a clear indication that metal–ligand bond

[265] T. A. Beech, N. C. Lawrence, and S. F. Lincoln, *Austral. J. Chem.*, 1973, **26**, 1877.
[266] D. A. Buckingham, J. MacB. Harrowfield, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1973, **95**, 7281.
[267] E. Chaffee, T. P. Dasgupta, and G. M. Harris, *J. Amer. Chem. Soc.*, 1973, **95**, 4169.

Table 23 *Rate data at* 298.1 K *and* μ = 0.50 mol l^{-1} *for the formation and acid hydrolysis of* $[M(NH_3)_5(OCO_2)]^+$ *ions [equilibria* (65)]; *data from ref.* 200

M	k_1/ s^{-1}	$\Delta H^*(k_1)$/ kcal mol^{-1}	$\Delta S^*(k_1)$/ cal K^{-1} mol^{-1}	k_2/ l mol^{-1} s^{-1}	$\Delta H^*(k_2)$/ kcal mol^{-1}	$\Delta S^*(k_2)$/ cal K^{-1} mol^{-1}
Co^{III}	1.10	16.8	−2	220	15.3	3.6
Rh^{III}	1.13	17.0	−1	470	17	12
Ir^{III}	1.45	19.0	+6	590		

cleavage is not involved. The small variation in the values of k_2 follows the metal–oxygen bond strengths, which decrease in the order Ir > Rh > Co.

An I_a mechanism is proposed for anation of the $[Rh(NH_3)_5(OH_2)]^{3+}$ ion by azide and acetate ions in weakly acidic media.[268]

Formation of complexes of the type $[Rh(NH_3)_5(NH_2X)]^{3+}$ by trapping the nitrene $[Rh(NH_3)_5N]^{2+}$, generated by the thermal or photochemical dissociation of the $[Rh(NH_3)_5N_3]^{2+}$ ion, with an anion X^{n-} (*e.g.* Cl^- or SO_3^{2-}) was discussed in Section 4. Evidence for the formation of a nitrene dimer was also presented.[6,7]

Replacement of both chloride ions in *α-cis*-$[Rh(trien)Cl_2]^+$ by other anions proceeds in two stages. The rates of these reactions are independent of the concentrations of the added anions, and so a mechanism is proposed in which the rate-determining step for each stage is aquation, followed by rapid anation of the aqua-intermediates,[201] *e.g.*

$$[Rh(trien)Cl_2]^+ + H_2O \xrightarrow{\text{slow}} [Rh(trien)Cl(OH_2)]^{2+} + Cl^-$$

$$[Rh(trien)Cl(OH_2)]^{2+} + Y^- \xrightarrow{\text{fast}} [Rh(trien)ClY]^+ + H_2O$$

The *cis* effect of the non-leaving groups is relatively small and decreases in the order $Cl^- > N_3^- > I^- > Br^- \gg NCS^-$.

Formation of the *trans*-$[RhL^1{}_2Cl_2]^+$ ion from *mer*-$[RhL^1L^2Cl_3]$ by chelate-ring closure [L^1 and L^2 correspond to bidentate and unidentate (As-donor only) (*o*-dimethylaminophenyl)dimethylarsine respectively] shows a dependence on the concentration of added electrolyte ($NaClO_4$, Et_4NClO_4, and $LiNO_3$ were used) and the rate increases sharply with solvent polarity. The reverse reaction shows a linear

$$mer\text{-}[RhL^1L^2Cl_3] \rightleftharpoons trans\text{-}[RhL^1{}_2Cl_2]^+ + Cl^-$$

dependence on [LiCl] when the ionic strength is controlled with $LiNO_3$, but in the absence of $LiNO_3$ the rate varies with $[LiCl]^{1/2}$. An S_N1(ip) mechanism is proposed.[202]

***d*⁶: Iridium(III).**—Rate data for the formation of the $[Ir(NH_3)_5(OCO_2)]^+$ ion are summarized in Table 23 and discussed in the previous section.

Trapping of iridium nitrenes (Section 4) can be used to obtain complexes of the type $[Ir(NH_3)_5(NH_2X)]^{n+}$ (X = anion). Synthesis of the complex ions $[M(NH_3)_5(NH_2SO_3)]^{2+}$ (M = Ru^{II} or Ir^{III}) can be achieved in this way.[207] The iridium(III) complex has a pK_a of 7.1 associated with the following equilibrium:

$$[Ir(NH_3)_5(NH_2SO_3)]^{2+} \rightleftharpoons [Ir(NH_3)_5(NHSO_3)]^+ + H^+$$

The electrophilic behaviour of co-ordinated NO^+ has been investigated in complex

[268] C. Chatterjee and P. Chaudhuri, *Indian J. Chem.*, 1973, **11**, 777.

ions of the type $[IrX_5NO]^-$ (X^- = halide ion). Reactions with a variety of nucleophiles were studied:[131]

$$[IrX_5(NO)]^- + 2OH^- \rightleftharpoons [IrX_5(NO_2)]^{3-} + H_2O \quad (66)$$

$$[IrX_5(NO)]^- + 2NH_2OH \longrightarrow [IrX_5(OH_2)]^{2-} + N_2O + H^+$$

$$[IrX_5(NO)]^- + N_3^- + H_2O \longrightarrow [IrX_5(OH_2)]^{2-} + N_2O + N_2$$

$$[IrX_5(NO)]^- + 2NH_3 \longrightarrow [IrX_5(NH_3)] + N_2 + H_3O^+$$

The $[IrBr_5(NO)]^-$ ion reacts with hydrazine hydrate by an unknown route to give $[IrBr_3(N_2H_4)_3]$. The equilibrium constant for reaction (66) was established.

d^6: Platinum(IV).—Formation of the $[PtI_6]^{2-}$ ion from $[PtBr_6]^{2-}$ and iodide ions is known to occur by reductive elimination followed by oxidative addition (r.e.o.a.).[269] The successive stages in the reaction have been reinvestigated with particular attention to the pH-dependence, and two of the three stages have been reassigned. The overall reaction proceeds as follows:

$$I^- + Br{-}Pt^{IV}{-}Br \longrightarrow IBr + Pt^{II} + Br^- \xrightarrow{I^-} 2Br^- + I{-}Pt^{IV}{-}I$$

The first stage is typical and involves the following reactions:

$$[PtBr_6]^{2-} + I^- \xrightarrow{\text{slow}} IBr + [PtBr_4]^{2-} + Br^-$$

$$[PtBr_4]^{2-} + IBr \xrightarrow[(H_2O)]{\text{fast}} \textit{trans}\text{-}[PtBr_4I(OH_2)]^- + Br^-$$

$$\textit{trans}\text{-}[PtBr_4I(OH_2)]^- \rightleftharpoons \textit{trans}\text{-}[PtBr_4I(OH)]^{2-} + H^+ \quad (pK_a\ 3.7)$$

The activation parameters for this stage are $\Delta H^{\ddagger} = 56.6 \pm 2.9$ kJ mol^{-1} and $\Delta S^{\ddagger} = -44.2 \pm 9.7$ J K^{-1} mol^{-1}.

Miscellaneous Metal Ions.—Mention has been made already of a relatively slow formation reaction for the normally labile manganese(II) ion.[251] Incorporations of the labile bivalent metal ions zinc(II), copper(II), manganese(II), cobalt(II), and nickel(II) into water-soluble porphyrin molecules such as tetrakis-(4-*N*-methylpyridyl)porphine, tetrasulphonated tetraphenylporphine, and uroporphine are also relatively slow reactions.[270] However, by taking into account the porphyrin deformation which is necessary, an I_d mechanism can be fitted to these reactions. The rates of formation and dissociation of nickel(II), copper(II), cobalt(II), and zinc(II) complexes of the sterically hindered ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (Me_4cyclam) are also 10^3—10^4 smaller than is 'normal' for these metal ions.[271]

7 Ligand Exchange and Replacement

Several examples of ligand exchange and replacement were considered in the previous sections and most of these will not be described further in this section.

Solvent Exchange.—Recent results for the exchange of DMSO with complexes of cobalt(III), chromium(III), and iron(II) are summarized in Table 24. Different mechanisms are proposed for all three metal ions, an I_d mechanism being favoured for cobalt(III), an I_a mechanism for chromium(III), and a D mechanism for the $[Fe(CN)_5(DMSO)]^{3-}$ ion. The contrasting values of $\Delta S^{\ddagger}$ for iron(II) and chromium(III)

[269] D. W. Johnson and A. J. Poë, *Canad. J. Chem.*, 1974, **52**, 3083.
[270] P. Hambright and P. B. Chock, *J. Amer. Chem. Soc.*, 1974, **96**, 3123.
[271] L. Hertli and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1328.

Table 24 *Rate constants (k_{ex}) for the exchange of* DMSO *with octahedral complexes*

Complex	*Temperature/* K	k_{ex}/ s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	*Ref.*
$[Co(NH_3)_5(DMSO)]^{3+}$	318.1	3.6×10^{-4}			43
$[Cr(DMSO)_6]^{3+}$	348.1	5.5×10^{-5} [a]	23.1	−11.8	148, 168
$[Fe(CN)_5(DMSO)]^{3-}$	298.1	7.5×10^{-3}	26.0	11	211

[a] Refers to exchange of all six DMSO molecules; $\Delta V^{\ddagger} = -11.3$ cm^3 mol^{-1}.

complexes support the proposed mechanisms, and for chromium(III) the large negative value of $\Delta V^{\ddagger}$ gives further evidence of an associative mechanism.

A thesis is concerned with the kinetics of *cis*- and *trans*-water exchange in some aquachromium(III) complexes.[160]

Ligand Exchange and Replacement: Unidentate by Unidentate.—Earlier studies of ligand exchange in adducts of niobium(v) and tantalum(v) halides of the type $[MCl_5L]$ (L = RCN or $OPCl_3$) indicated a dissociative mechanism.[272] Recent studies of $[TaCl_5(R_2Y)]$ (R = Me or Et; Y = O, S, Se, or Te) in chloroform or CH_2Cl_2 solution show interesting differences with changes in the donor atom Y.[273] The results for the Me_2Y adducts are collected in Table 25. The rate of exchange of the

Table 25 *Activation parameters for the exchange of* Me_2Y *with the adducts* $[TaCl_5(Me_2Y)]$ *in chloroform solution*

Y	$\Delta G^{\ddagger}$(273 K)/ kJ mol^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
O	65.5±0.4	70.4±1.9	+18±6
S	50.5±0.2	25.7±0.8	−91±3
Se	49.8±0.2	25.1±1.3	−92±5
Te[a]	49.4±0.2	24.3±0.9	−92±4

[a] In CH_2Cl_2.

'hard' donor molecule Me_2O is independent of $[Me_2O]$, and a dissociative mechanism is again indicated. However, for the 'soft' donor molecules Me_2S, Me_2Se, and Me_2Te the exchange rate is first order in $[Me_2Y]$ and an I_a mechanism is proposed. The activation parameters clearly support this change in mechanism. Further evidence comes from a study of the Et_2O and Et_2S adducts. The rate of exchange of Et_2O is very similar to that for the exchange of Me_2O, and a first-order rate law is observed. However, Et_2S exchange is an order of magnitude slower than Me_2S exchange, indicating steric crowding in the seven-co-ordinate transition state. Tantalum(v) now joins Ti^{III}, V^{III}, Mo^{III}, Cr^{III}, Rh^{III}, and Ga^{III}, which all undergo associative substitution reactions for their octahedral complexes.

A dissociative mechanism is indicated from n.m.r. line-broadening studies for the exchange of 3,5-lutidine with adducts of the type $[M(CH_2Ph)_4(3,5\text{-lutidine})]$ (M = Zr^{IV} or Hf^{IV}). At 228 K the relaxation times (τ) are $10^3\tau = 72$ s (Hf) and

[272] A. E. Merbach and J. C. Bünzli, *Helv. Chim. Acta*, 1972, **55**, 1903, 2867.
[273] R. Good and A. E. Merbach, *J.C.S. Chem. Comm.*, 1974, 163.

15 s (Zr), and the activation parameters are ΔH^{+}/kcal mol^{-1} = 15.3 and 17.1 and ΔS^{+}/cal K^{-1} mol^{-1} = +13.0 and +23.7 for Hf^{IV} and Zr^{IV} respectively.[274]

Exchange studies using radiotracers have appeared for the systems $[Cr(NCSe)_6]^{3-}$–$Se^{14}CN^-$ (ref. 275) and $[Ru(SCN)_6]^{3-}$–$S^{14}CN^-$ (ref. 276). From studies between 293 and 313 K an activation enthalpy of 27.3 kcal mol^{-1} is reported for the selenocyanate exchange. It is claimed for the exchange with the $[Ru(SCN)_6]^{3-}$ ion that two of the thiocyanate ligands exchange *ca.* 10^2 times as fast as the other four ligands.

The kinetics of the scrambling of cyano- and bromo-ligands has been investigated for the following reaction in water–dioxan mixed solvents:[277]

$$[HgBr_2] + [Hg(CN)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[Hg(CN)Br]$$

$$-d[HgBr_2]/dt = k_1[HgBr_2][Hg(CN)_2] - k_{-1}[Hg(CN)Br]^2$$

Variation of k_1 and k_{-1} with the dioxan concentration showed three maxima and three minima, although the equilibrium constant, $K = k_1/k_{-1}$, did not change significantly. The unusual alternation of the rate constants was attributed to selective solvation of the reactants.

A comparison of the rates of nitrite-ion exchange in cobalt(III) complexes of the type *trans*-$[Co(A_4)(NO_2)_2]^{n+}$ (A_4 = amine ligands) is shown in Table 26. The

Table 26 *Comparison of the rates of nitrite-ion isotopic exchange for cobalt*(III) *complexes at* 298 *K and* pH 6.7 ([complex] = 5×10^{-3} mol l^{-1}; [NO_2^-] = 0.1 mol l^{-1}); *data from ref.* 86

Complex	*Exchange rate constant*/s^{-1}
trans-$[Co(AO)_2(NO_2)_2]$[a]	7.29×10^{-7}
trans-$[Co(dmgH)_2(NO_2)_2]^-$	1.61×10^{-8}
trans-$[Co(en)_2(NO_2)_2]^+$	5.36×10^{-8}
trans-$[Co(tetra\text{-}Me\text{-}en)_2(NO_2)_2]^+$ [b]	5.0×10^{-6}
trans-$[Co(PnAO)(NO_2)_2]$[c]	2.6×10^{-4} and 8.6×10^{-6}

[a] AO = 2-amino-2-methylbutan-3-one oxime anion. [b] tetra-Me-en = 2,3-diamino-2,3-dimethylbutane. [c] PnAO = cyclic quadridentate ligand (6) (p. 141); two exchange rates observed.

complex formed with the cyclic quadridentate amine oxime ligand (6) (p. 140) is unusual in having markedly different exchange rates for the two nitro-groups.[86] This rate difference is reflected in the inequality of the two Co—NO_2 bond lengths (198.4 and 193.7 pm), the cobalt(III) ion being slightly out of the plane of the cyclic amine oxime.[86] A *D* mechanism is proposed for the reaction of this complex as shown by the results of anation studies discussed previously (Section 6). A number of exchange reactions of cobaloximes were described in earlier sections including those of *trans*-$[(RR'PO)Co(dmgH)_2L]$ (R and R′ are MeO or Ph; L is the exchanging neutral P- or As-donor ligand),[95] *trans*-$[RCo(dmgH)_2\{P(OMe)_3\}]$ [$P(OMe)_3$ exchange; R = Me, CH_2SiMe_3, or halogeno-alkyl groups],[96] and *trans*-$[Co(dmgH)_2(tu)(SCN)]$ (replacement of NCS^- by tu).[97, 98] Halide-ion exchange and replacement was also discussed

[274] J. L. Felten and W. P. Anderson, *Inorg. Chem.*, 1973, **12**, 2334.
[275] S. Wajda, U. Sikorowicz, and A. Zarzeczny, *Chem. Abs.*, 1974, **81**, 30 165x.
[276] S. Wajda and K. Rachlewicz, *Nukleonika*, 1973, **18**, 407.
[277] M. T. Beck, E. S. Porzsolt, and J. Ling, *Magyar Kém. Folyóirat*, 1974, **80**, 143.

in earlier sections for the systems *cis*-$[Ru(NH_3)_4Br_2]^{+}$–*Br^-,[197] $[Re_2(EtCO_2)_4Cl_2]$ + Br^-,[250] and $[PtBr_6]^{2-}$ + I^-.[269] The photocatalysed exchange of NO with thiocyanate ion and thiourea in $[Fe(CN)_5(NO)]^{2-}$ involves oxidation of iron(II) to iron(III).[218]

Ligand Replacement: Multidentate by Unidentate.—The cyanide-ion-induced dissociations of $[Fe(LL)_3]^{2+}$ and $[Fe(terpy)_2]^{2+}$ ions [LL = phen, bipy, or *N*-(2-pyridylmethylene)aniline] were described in Section 4.[214,215] Cyanide ion has a marked stabilizing effect upon the rate of dissociation of $[Ni(gga)X]^{n-}$ and $[Ni(ggg)]^-$ ions (gga = $NH_2CH_2CONCH_2CONH$, X = CN^- or H_2O; ggg = triglycinate ion with one proton ionized from each peptide nitrogen atom). The observed rate law is:

$$-\mathrm{d[complex]}/\mathrm{d}t = \{k_0 + k_1[H^+]\}[\mathrm{complex}]$$

For the $[Ni(gga)X]^{n-}$ ions, when X = H_2O, an earlier study at 298.1 K and pH 9 gave $k_0 = 3.1\ s^{-1}$, whereas when X = CN^-, $k_0 = 8.0 \times 10^{-5}\ s^{-1}$ and $k_1 = 4.3 \times 10^3\ l\ mol^{-1}\ s^{-1}$ [μ = 0.1 mol l^{-1} ($NaClO_4$)].[278] For the $[Ni(ggg)]^-$ ion $k_1 = 2.0 \times 10^5\ l\ mol^{-1}\ s^{-1}$, and for reaction with cyanide ion $[Ni(ggg)CN]^{2-}$ is again more inert than the reactant, whereas the $[Ni(ggg)(CN)_2]^{3-}$ ion is more labile.[279]

Ligand Replacement: Unidentate by Multidentate.—Reactions of the cobaltinitrite ion with amino-acid anions (L^-) have been investigated:[280]

$$[Co(NO_2)_6]^{3-} + L^- \longrightarrow [Co(NO_2)_4L]^{2-} + 2NO_2^-$$

The reactions were studied between pH 6.40 and 8.72 and the rate was found to be independent of the concentration of the amino-acid ion. Reactions with glycine, α- and β-alanine, α-aminobutyric acid, α-aminoisobutyric acid, valine, and norvaline were studied and the first-order rate constants are all very similar. Activation energies for the reactions with glycinate, β-alinate, and valinate ions are *ca.* 37.5 kcal mol^{-1}.

Ligand Replacement: Multidentate by Multidentate.—A review of multidentate ligand exchange reactions and their application to analytical chemistry has appeared for systems involving egta and 4-(2-pyridylazo)resorcinol.[281]

Reactions of zinc(II) and cobalt(II) complexes of ida^{2-}, $Hida^-$, nta^{3-}, Eten, and dien with $cydta^{4-}$ and $Hcydta^{3-}$ have been studied.[282] The steric effect of the cyclohexane ring in cydta on the rate of substitution is discussed. Other reports of the replacement of one multidentate ligand by another have appeared for the systems[283] Ni(Hida) + dtpa, Ni(edta-OH) + dtpa, and Co(gedta) + (edta-OH) [Hida = *N*-(2-hydroxyethyl)iminodiacetate, (edta-OH) = *N*-(2-hydroxyethyl)ethylenediamine-*NN'N'*-triacetate, gedta = 2,2'-ethylenedioxybis(ethylamine)-*NNN'N'*-tetra-acetate). Similar studies of aminopolycarboxylate replacement have appeared for zinc(II), lead(II), and cadmium(II).[284]

[278] G. K. Pagenkopf, *Inorg. Chem.*, 1974, **13**, 1591.
[279] V. T. Brice and G. K. Pagenkopf, *J.C.S. Chem. Comm.*, 1974, 75.
[280] M. B. Celap, T. J. Janjic, and P. N. Radivojsa, *Rev. Chim. minérale*, 1973, **10**, 607.
[281] S. Funahashi and M. Tanaka, *Chem. Abs.*, 1974, **80**, 33 411g.
[282] M. Kodama and K. Hagiya, *Bull. Chem. Soc. Japan*, 1973, **46**, 3151.
[283] M. Kodama, *Bull. Chem. Soc. Japan*, 1974, **47**, 2200.
[284] M. Kodama, K. Namekawa, and T. Horiuchi, *Bull. Chem. Soc. Japan*, 1974, **47**, 1430, 2011.

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 ion (or the exchange with a labelled metal ion) are listed in Table 27. These reactions often proceed by dissociation, with or without acid catalysis and with the possible formation of dinuclear species.

Table 27 *Kinetic studies of the displacement and exchange of cations from multidentate ligand complexes*

Complex	*Displacing or exchanging cation*	*Ref.*
$[Tb(edta)]^-$	$^{160}Tb^{III}$	285
$[M(edta)]^-$	$*M^{3+}$ (rare earth)	286, 287
$[M(cydta)]^-$ (M = Ce^{III}, Eu^{III}, Tb^{III})	Er^{III}	288
$[Eu(edta)]^-$	Cm^{III}, Bk^{III}, Cf^{III}	289
$[Pb(Y^{n-})]^{(2-n)+}$ [a]	Ga^{III}	290
$[Fe(Y)]$ [b]	Ga^{III}	291
$[Cu(ttha)]^{4-}$	Ni^{II}	292
$[Ni(L)]^{2+}$ [c]	Cu^{II}	293

[a] Y^{n-} = $edta^{4-}$, $cydta^{4-}$, $dtpa^{5-}$. [b] Y^{n-} = [*N*-(hydroxyethyl)ethylenediamine-*NN'N'*-triacetate]$^{3-}$ or $dtpa^{5-}$. [c] L = *NN'*-bis-(2-picolyl)ethylenediamine.
For other ligand abbreviations see the list at the start of this volume.

For the exchange of $^{160}Tb^{3+}$ with $[Tb(edta)]^-$ in 0.025 mol l^{-1} ammonium acetate the observed rate constant, k, is given by the following expression, with the k_1 term dominant:[285, 286]

$$k = k_1[H^+] + k_2[H^+]^2 + k_3[H^+][Tb^{3+}]$$

A similar study of the exchange of Ce^{III} with its polyaminecarboxylate complexes involves the formation of a more labile chloro-complex in a chloride medium.[287] Negative volumes of activation are reported for the displacement of Ce^{III}, Eu^{III}, and Tb^{III} from their cydta complexes by Er^{III}, but the mechanistic significance of these results is uncertain.[288] Reaction of $[Eu(edta)]^-$ with the actinides Cm^{III}, Bk^{III}, and Cf^{III} involves acid-catalysed dissociation and the formation of dinuclear intermediates.[289] Transfer of the ligand *N*-(hydroxyethyl)ethylenediaminetriacetate from its lead(II) and iron(III) complexes to gallium(III) proceeds by a simple dissociative mechanism, whereas for edta, cydta, and dtpa dinuclear intermediates are involved.[290, 291] Dinuclear intermediates of nickel(II) and copper(II) are also reported with the multidentate ligands ttha and *NN'*-bis-(2-picolyl)ethylenediamine.[292, 293]

[285] R. E. Jervis and K. Neelakantan, *Canad. J. Chem.*, 1974, **52**, 1086.
[286] K. Neelakantan and R. E. Jervis, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 67.
[287] C. I. Balcombe and B. Wiseall, *J. Inorg. Nuclear Chem.*, 1974, **36**, 881.
[288] E. Brücher and J. Kelm, *J. Coordination Chem.*, 1974, **4**, 133.
[289] K. R. Williams and G. R. Choppin, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1849.
[290] T. Nozaki, K. Kasuga, and N. Suemitsu, *Nippon Kagaku Kaishi*, 1974, 485.
[291] T. Nozaki and K. Kasuga, *Chem. Abs.*, 1973, **80**, 41 267n.
[292] M. S. Haque and M. Kopanica, *Bull. Chem. Soc. Japan*, 1973, **46**, 3072.
[293] R. K. Steinhaus and C. L. Barsuhn, *Inorg. Chem.*, 1974, **13**, 2922.

9 Isomerization and Racemization

General.—Racemizations of tris-chelate complexes are usually envisaged as proceeding by ring-opening or by various kinds of intramolecular twist mechanism. A third possibility has been examined theoretically in which entry, or partial entry, of a unidentate solvent molecule is involved, with the formation of a seven-co-ordinate complex with a much lower activation energy for intramolecular rearrangement.[294] It is concluded that 'the mechanism of racemization may change from a triple twist process to a double-opposed-initiated twist process (with one chelate ring not twisting) as the co-ordinating ability of the solvent increases'. It is pointed out that the two types of process are experimentally distinguishable if asymmetric chelating agents are involved.

The use of n.m.r. line-broadening for dynamic studies of racemization processes has been of prime importance in recent years. A useful book has appeared concerned with the chemical applications of n.m.r. in paramagnetic molecules which deals in part with this subject.[295]

Cobalt(III) Complexes.—At 303.1 K the rate constant for the *trans*→*cis* isomerization of the $[Co(en)_2(OCOCH_2CO_2H)(OH_2)]^{2+}$ ion is $10^6k = 28.0\ s^{-1}$, the activation energy being 27.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ 9.5 cal K^{-1} mol^{-1}. The isomerization is postulated to occur by elimination of the co-ordinated water molecule to give a trigonal-bipyramidal transition state.[296] Replacing the hydrogen malonate ion by the less basic benzoate ion increases the reaction rate from $10^6k = 220\ s^{-1}$ to $10^6k = 384\ s^{-1}$ at 318.1 K and pH 1.5.

The α- and β-isomers of $[Co(edda)(tmd)]^+$ have been prepared and the kinetics of equilibration measured in carbonate buffers. Reactions in both directions show the expected first-order rate law.[297] The α-*cis*-, β-*cis*-, and *trans*-$[Co(R,S\text{-tetars})Cl_2]^+$ ions of racemic tetars, $[Me_2As(CH_2)_3As(Ph)CH_2]_2$, have also been prepared and their topological equilibria investigated. Conversion of β-*cis*-$[Co(R,S\text{-tetars})Cl_2]ClO_4$ into the *trans*-isomer was investigated in dry methanol and at 302.5 K the rate constant is reported to be $10^4k = 1.05 \pm 0.02\ s^{-1}$. Solvolysis of these complexes is very slow, and unlike many other arsenic-ligand compounds catalysis is not observed. A hitherto unknown method of inverting co-ordinated arsenic atoms is reported.[80]

The kinetics of isomerization of $[Co(NH_3)_4(OH_2)_2]^{3+}$ and $[Co(en)_2(OH_2)(OH)]^{2+}$ ions have been measured as a part of the studies of other reactions of these two ions. The kinetics of tetramerization and isomerization of the $[Co(NH_3)_4(OH_2)(OH)]^{2+}$ and $[Co(NH_3)_4(OH)_2]^+$ ions have been investigated by stopped-flow and pH-stat experiments.[262] The *cis*–*trans* isomerization of $[Co(en)_2(OH_2)(OH)]^{2+}$ ions was measured as part of a study of the reaction of the *cis*-isomer with acetylacetone.[266] At 298.1 K and $\mu = 0.25$ mol l^{-1} the rate constants for the *trans*→*cis* and *cis*→*trans* rearrangements are 4×10^{-3} and $1 \times 10^{-3}\ s^{-1}$ respectively. The kinetics of isomerization of *cis*- and *trans*-$[Co(en)_2(NO_2)_2]^+$ have also been reported.[132]

Basic oxyanions (*e.g.* phosphate, selenite, sulphate) have a profound effect upon

[294] D. L. Kepert, *Inorg. Chem.*, 1974, **13**, 2758.
[295] 'Chemical Applications of NMR in Paramagnetic Molecules', ed. G. N. La Mar, W. D. Horrocks, and R. H. Holm, Academic Press, New York, 1973.
[296] V. Carunchio, G. G. Strazza, and T. Prosperi, *Gazzetta*, 1974, **104**, 903.
[297] K. Kuroda, *Chem. Letters*, 1974, 17.

the distribution of the three geometric isomers of the $[Co(dien)_2]^{3+}$ ion.[298] A comparison has been made between the thermodynamic data and the predictions made from energy-minimized conformational analyses of different topological forms of the complex.

The dynamic stereochemistry of β-diketone complexes of cobalt(III) of the type *cis*- and *trans*-$[Co(acac)_2(py)X]$ (X = N_3, NO_2, CN, or NCO) has been investigated in $CDCl_3$ in the range 302—333 K by ^1H n.m.r.[299] The results are shown in Table 28.

Table 28 *Rate data for the* trans–cis *isomerization of* $[Co(acac)_2(py)X]$ *in* $CDCl_3$

X	10^5k/s^{-1} (302 K)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
N_3	19.2±1.3	26.7±2.7	13.1±9.1
NCO	1.75±0.20	33.2±2.9	29.8±9.9
NO_2	0.106±0.005	38.8±1.0	42.9±3.4
CN	no exchange		

Several dissociative mechanisms involving trigonal-bipyramidal intermediates are postulated, the trend in reaction rates being related to the ability of X^- to stabilize the intermediate formed by a process of π-donation. Twist mechanisms can be ruled out because of the large entropies of activation. The S-bonded thiocyanato-complex *trans*-$[Co(acac)_2(SCN)py]$ was also synthesized by the following reaction:[300]

$$[Co_2(acac)_4(OH)_2] + 2KSCN + 2py \xrightarrow{2\,HOAc} 2trans\text{-}[Co(acac)_2(SCN)py] + 2KOAc + 2H_2O$$

Linkage isomerization to the N-bonded isothiocyanato-complex *trans*-$[Co(acac)_2(NCS)py]$ was observed to have a half-life of *ca.* 4 h in chloroform solution. In the solid state linkage isomerization at 341 K has a half-life of *ca.* 12 h, and this is followed by geometric isomerization with a half-life of *ca.* 2 days. The latter process is suspected to be catalysed by cobalt(II).

The novel synthesis of optically active tris-dithiocarbamato-complexes of the type $[Co(RR\text{-}dtc)_3]$ (R = NN-bonded alkyl groups) is described from the reactions between optically active K[Co(edta)] or K[Co(pdta)] and the sodium salt of the appropriate dithiocarbamate.[301] Preliminary results are reported for the optical inversion (racemization) of the $(+)_{546}$-$[Co(R\text{-}dtc)_3]$ complex (R = pyrrolidyl) determined by polarimetry in chloroform solution. At 298.1 K, 10^5k = 0.01 s^{-1}, $\Delta H^{\ddagger}$ = 23.4±2.1 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −0.8±7.0 cal K^{-1} mol^{-1}.

A number of studies in which stereochemical changes occur have been described in previous sections. The steric course of the acid hydrolysis of the *trans*-$[Co(dien)(NH_3)Cl_2]^+$ ion was outlined in Section 2.[72] Reaction of α-*cis*-$[Co(edda)(OH_2)_2]^+$ with oxalate ion to give 100% β-*cis*-$[Co(edda)(ox)]^-$ was described in Section 6.[264] The rate-determining step in the redox decomposition of the *trans*-$[Co(NH_3)_4(OH_2)(SO_3)]^+$ ion involves isomerization to the *cis*-complex, which then rapidly loses an

[298] R. F. Keene and G. H. Searle, *Inorg. Chem.*, 1974, **13**, 2173.
[299] D. R. Herrington and L. J. Boucher, *Inorg. Chem.*, 1973, **12**, 2378.
[300] L. J. Boucher, D. R. Herrington, and C. G. Coe, *Inorg. Chem.*, 1974, **13**, 2290.
[301] L. R. Gahan, J. G. Hughes, and M. J. O'Connor, *J. Amer. Chem. Soc.*, 1974, **96**, 2271.

ammonia molecule in the position *trans* to the S-bonded sulphite ion.[19] The use of ^{13}C n.m.r. to identify two geometric isomers of $[Co(edta)Br]^{2-}$ has also been mentioned previously.[49] The steric course of the Hg^{2+}- and NO^{+}-promoted aquations of $[Co(en)_2XY]$ (X, Y = halide or azide) was discussed in Section 2.[119] The rate of *trans*→*cis* isomerization of $[Co(ete)Cl(OH_2)]^{2+}$ is fifty times greater than the rate of aquation of *trans*-$[Co(ete)Cl_2]^{+}$.[78] The ions *α-cis*- and *β-cis*-$[Co(edda)Cl_2]^{-}$ aquate with retention of configuration.[69] The kinetics of mutarotation (k_{inv}) of Δ-$(-)_{589}$-(*RR*)- and (*RS*)-β_1-$[Co(trien)(gly)]^{2+}$ were compared with the rate of base-catalysed proton exchange (k_{ex}), and k_{inv}/k_{ex} is *ca.* 10^6.[231]

Chromium(III) Complexes.—The *cis*→*trans* isomerization of $[Cr(tfac)_3]$ (tfac = 1,1,1-trifluoropentane-2,4-dione) has been studied in the gas phase using gas chromatography.[302] The results are very similar to those of earlier studies in solution, indicating that the solvent may not play as important a mechanistic role as previously thought. Activation parameters for the *cis*→*trans* and *trans*→*cis* isomerizations are respectively $\Delta H^{\ddagger} = 28.2 \pm 1.1$ and 24.6 ± 1.1 kcal mol^{-1}, and $\Delta S^{\ddagger} = -5.5 \pm 3.0$ and -17.0 ± 5.7 cal K^{-1} mol^{-1}. The equilibrium constant ([*trans*-isomer]/[*cis*-isomer] = 3.56) is temperature-independent between 391.9 and 421.9 K and slightly larger than the value predicted from the random statistical distribution. These reactions proceed by a trigonal-twist mechanism.

The stereochemical rigidity of NN-disubstituted dithiocarbamate complexes, $[Cr(R^1R^2\text{-dtc})_3]$, has been established by ^1H n.m.r. in chloroform solution at temperatures up to 357 K.[303] The relative rates of rearrangement by a trigonal-twist mechanism (resulting in optical inversion) have been established for a series of tervalent metal ions and the order is Ga, In, V > Mn > Cr. These results are discussed further in the next section.

The kinetics of the *cis–trans* equilibration of the $[Cr(ox)_2(OH_2)_2]^{-}$ ion have been measured; the reaction proceeds by an acid-catalysed ring-opening mechanism.[163] The accelerating effect of micelles on the rate of this reaction in benzene solution has been discussed previously (Section 3).[171]

cis–trans-Isomerization contributes less than 20% to the disappearance of *cis*-$[Cr(NH_3)_2(H_2O)_4]^{3+}$ in 1M perchloric acid.[149] The dynamics and stereochemical course of the complete aquation of the $[Cr(NH_3)_6]^{3+}$ ion are now well established.[148,149] The stereochemical course of the thermal[156] and photochemical[175] aquation of *trans*-$[Cr(en)_2FX]^{+}$ and *trans*-$[Cr(tmd)FX]^{+}$ ions has been discussed in Section 3.

Intramolecular Rearrangements of Tris-chelate Complexes.—Recently there has been considerable attention paid to the stereochemical non-rigidity of tris-chelate complexes and a number of reviews have dealt with the subject.[304] Studies of NN-disubstituted dithiocarbamato-complexes of the type $[M(R^1R^2\text{-dtc})_3]$ (R^1, R^2 = alkyl or aryl) have been extended and the results for intramolecular metal-centre inversion (probably by the Bailar trigonal-twist mechanism) are summarized for ruthenium(III) complexes in Table 29. The low values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are surprising for ruthenium(III) since previous studies indicated that tris-chelates of this

[302] C. Kutal and R. E. Sievers, *Inorg. Chem.*, 1974, **13**, 897.
[303] L. Que, jun. and L. H. Pignolet, *Inorg. Chem.*, 1974, **13**, 351.
[304] L. H. Pignolet and G. N. La Mar, ref. 295, Ch. 8; N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, 1972, **17**, 391; J. J. Fortman and R. E. Sievers, *Coordination Chem. Rev.*, 1971, **6**, 331.

Table 29 *Activation parameters for intramolecular metal-centred inversion of* $[Ru(R^1R^2\text{-dtc})_3]$ *complexes* (R^1R^2-dtc = NN-*disubstituted alkyl or aryl dithiocarbamate*)

R^1	R^2	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1} (*temperature*/°C)
Et	Et[a]	10.3±1	−8±5	12.8±0.2 (22)
Bn	Bn[b]	11.6±1	−7±5	13.8±0.2 (42)
Me	Bn[c]	11.1[c]		13.3±0.2 (15)
Me	Ph[c]	10.1[c]		12.1±0.2 (9)

[a] In CD_2Cl_2. [b] Bn = benzyl. [c] Values estimated from $\Delta G^{\ddagger}$ assuming $\Delta S^{\ddagger} = -7.5$ cal K^{-1} mol^{-1}.

metal ion (*e.g.* with $MeCOCH_2COCF_3$) are rigid on the n.m.r. time-scale. At higher temperatures complexes of the unsymmetrically substituted ligands also show ligand-centred geometrical isomerizations assigned to S_2C—N bond rotation. The free energies of activation for metal-centred inversion and ligand-centred isomerization are *ca.* 13 and 15.6 kcal mol^{-1} respectively.[305] It is the bite angle (α) which is believed to be of prime importance in determining the solid-state geometry of these complexes,[305] and an approximate correlation of this parameter with the activation enthalpies for the metal-centred inversions is shown for several metal ions[303,305] in Table 30. A similar comparison can be made with the twist and pitch angles and, as

Table 30 *Comparison of the activation enthalpies for metal-centred inversion by the Bailar trigonal-twist mechanism with the bite* (α), *twist* (ϕ), *and pitch* (ψ) *angles of* NN-*disubstituted tris(dithiocarbamate) metal complexes*

	$\Delta H^{\ddagger}$/ kcal mol^{-1}	α/°	ϕ/°	ψ/°
[In(pyr-dtc)$_3$][a]	$\ll$8.6	69.4	32.8	25.3
[Fe(pyr-dtc)$_3$]	7.6	74.4	37.4	26.5
[Fe(MePh-dtc)$_3$]	8.7	75.1	40.7	28.9
[Ru(EtEt-dtc)$_3$]	10.3	73.0	38.1	27.8
[Mn(EtEt-dtc)$_3$]	11.0	72.8	40.2	29.9
[Co(EtEt-dtc)$_3$]	23.6	76.2	43.7	30.7

[a] pyr = pyrrolidyl.

expected, the more the ground-state geometry is twisted towards the trigonal-prismatic transition state, the lower is the activation energy of the process. The rates of metal-centred inversion of analogous $[M(dtc)_3]$ complexes vary in the order high-spin Fe^{II}, V^{III}, Ga^{II}, In^{III} > high-spin $Fe^{III} \gtrsim$ low-spin Fe^{III}, $Fe^{IV} > Mn^{III} > Ru^{III} \gg Co^{III} > Rh^{III}$, with Cr^{III} faster than Ru^{III}. Low-spin Fe^{II} complexes have also been shown to be much more rigid than the high-spin Fe^{II} complexes.[305]

Miscellaneous.—Twisting as opposed to bond-rupture modes of activation are favoured for metal-centred rearrangements of several zirconium β-diketonates (dik) of the type $[(h^5\text{-}C_5H_5)Zr(dik)_2Cl]$, $[(h^5\text{-}C_5H_5)Zr(dik)_3]$, and a new cationic species $[(h^5\text{-}C_5H_5)Zr(dik)_2]^+$. The methyl ^1H n.m.r. line-broadening patterns associated with

[305] D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, 1974, **13**, 2045.

ligand interchange were analysed for [(h^5-C_5H_5)Zr(L)Cl] [L = acac$^-$ or (Bu^tCOCH-$COBu^t$)$^-$], and although the twisting process is non-random no single-step facial twist mechanism operates. Instead a combination of facial- and digonal-twist mechanisms is favoured.[306]

The kinetics of the *cis*-Δ–*cis*-Λ inversion of ruthenium(II) dimethylphosphinodithioato-complexes of the type *cis*-[$Ru(S_2PMe_2)(PR_3)_2$] (R = Me, Ph, OMe, or OPh) have been measured by ^1H n.m.r. lineshape analysis.[307] The proposed mechanism involves solvent-assisted cleavage of a ruthenium–sulphur bond in a *trans* position to a phosphine. For the analogous *NN*-dimethyldithiocarbamato-complexes *cis*-[$Ru(S_2CNMe_2)_2(PR_3)_2$] the temperature-dependent ^1H n.m.r. spectra indicate a different mechanism involving restricted rotation about the carbon–nitrogen bonds. The same conclusion was reached for the tris-chelates of ruthenium(III) discussed in the previous section, except that the metal-centred inversion was also measurable in those cases at lower temperatures.[305] A comparison of the results for the two types of ruthenium(II) complex[307] is given in Table 31.

Table 31 *Rates and activation parameters for the interchange of methyl groups in* cis-[$Ru(S_2PMe_2)_2L_2$] *and* cis-[$Ru(S_2CNMe_2)_2L_2$] *at* 298 K (cis-Δ ⇌ cis-Λ *inversion*)

L	*Solvent*	log (k/s^{-1})	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
(*a*) *cis*-[$Ru(S_2PMe_2)_2L_2$]				
PPh_3	$CDCl_3$	3.53±0.02	47.1±1	−19±3
$PMePh_2$	$CDCl_3$	2.78±0.02	58.0±2	3±7
$P(OMe)_3$	$CDCl_3$	2.23±0.34	65.3±2	17±13
PMe_2Ph	$CDCl_3$	1.61±0.12	59.6±2	−15±4
PMe_2Ph	PhCl	1.01±0.01	67.2±1	0±4
PMe_2Ph	PhH	0.04±0.12	123.5±4	170±11
$P(OPh)_3$	$CDCl_3$	0.41±0.01[a]	71.2±2	2±8
		1.69±0.05[a]	44.8±4	−62±15
(PPh_3){$P(OPh)_3$}	CH_2Cl_2	1.62±0.03	40.0±3	−80±9
(PPh_3)(CO)	PhCl	−1.90±0.08	119±2	119±7
(*b*) *cis*-[$Ru(S_2CNMe_2)_2L_2$]				
PMe_2Ph	$CDCl_3$	0.71±0.01	91.5±2	75±7
PPh_3	$CDCl_3$	0.22±0.02	103±2	105±6
$P(OPh)_3$	$CDCl_3$	0.01±0.02	77±3	12±9
(PPh_3){$P(OPh)_3$}	$CDCl_3$	0.23±0.01[a]	107±2	120±5
		0.15±0.05[a]	55±3	−60±11

[a] From different resonances.

The stereochemical non-rigidity of eight-co-ordinate metal complexes has been demonstrated by ^1H and ^{13}C n.m.r. for the systems [$M(S_2CNEt_2)_4$] (M = Ti, Zr, or Hf^{IV}) and [$M(CN)_8$]$^{4-}$ (M = Mo or W). The dithiocarbamato-complexes were investigated at temperatures down to 133 K in CS_2–CD_2Cl_2 solution, and the [$Pr^n{}_4N$]$_4$[$M(CN)_8$] salts at temperatures down to 113 K in $CHClF_2$–CH_2Cl_2 as

[306] T. J. Pinnavaia, J. J. Howe, and R. E. Teets, *Inorg. Chem.*, 1974, **13**, 1074.
[307] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 739, 754.

solvent. The single ^{13}C line at very low temperatures for the $[M(CN)_8]^{4-}$ ions indicates a very low energy barrier for the internal rearrangements. Possible mechanisms for this process are discussed. The polytopal form of the $[W(CN)_8]^{4-}$ ion (but not the molybdenum analogue) is observed to change in going from the potassium to the tetra-n-propylammonium salt.[308]

Electrolytic oxidation and reduction of four diastereoisomers of tris-[{(+)-3-acetylcamphorato}ruthenium(III)] to corresponding ruthenium(IV) and ruthenium(II) species has been carried out and the circular dichroism and absorption spectra are reported.[309] The ruthenium diastereoisomers isomerize in solution at 443 K, and the isomer abundances and rates of 12 isomerizations for the four diastereoisomers have been measured using high-pressure liquid chromatography.

10 Co-ordination Numbers Greater than Six

Apart from the lanthanide and actinide exchange reactions described in Sections 7 and 8, the photochemical investigations of the cyano-complexes of molybdenum(IV) mentioned in Section 4,[184-186] and the n.m.r. investigations outlined above,[308] no further kinetic studies of metal ions with high co-ordination numbers have appeared.

[308] E. L. Muetterties, *Inorg. Chem.*, 1973, **12**, 1963.
[309] G. W. Everett, jun. and R. R. Horn, *J. Amer. Chem. Soc.*, 1974, **96**, 2087.

4
Labile Metal Complexes

BY D. N. HAGUE

1 Complex Formation involving Unsubstituted Metal Ions: Unidentate Ligands and Solvent Exchange

The application of ultrasonic absorption to the kinetics of complex formation has been reviewed.[1] This technique, which is particularly interesting from an historical standpoint, may frequently be used to determine the characteristic time of each elementary step in the overall formation of the complex.

Main-group Ions.—Ultrasonic absorption has been used[2] with aqueous solutions of calcium acetate at concentrations of 0.14—1.09 mol l^{-1} over the temperature range 2.5—45.5 °C. At low concentrations a single relaxation was observed, while at high concentrations two effects were seen. On the basis of these measurements and analogous studies with Mg^{2+}, Ba^{2+}, and Ni^{2+} it is concluded that the relaxations are due to the substitution of one or two water molecules by acetate in the inner co-ordination sphere of the Ca^{2+} ion. The rate constant for substitution of the first water molecule is quoted as being in the range $6—9 \times 10^8$ s^{-1}.

The n.m.r. technique has been used to measure the kinetics of solvent exchange at the beryllium[3] and magnesium[4] ions in trimethyl phosphate (tmp). In both cases, a temperature range could be found over which the ^1H signal of tmp in the first co-ordination sphere of the metal appears as a doublet downfield from the doublet signal of tmp in the bulk solvent. With Be^{2+}, the co-ordination number was found to be four and the rate law

$$\text{Rate} = 4k_{ex}[Be\{(MeO)_3PO\}_4^{2+}]$$

with $k_{ex}(298\ K) = 3.6\ s^{-1}$, $\Delta H^{\ddagger} = 56.9$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -43.9$ J K^{-1} mol^{-1}. The rate law is consistent with either a dissociative tmp exchange mechanism or with exchange occurring in $[Be\{(MeO)_3PO\}_4]^{2+}$ exclusively solvated by tmp through either an associative or a dissociative process, but the authors favour the former. With Mg^{2+}, the co-ordination number was six and the following rate law was determined:

$$\text{Rate} = 6k_{ex}[Mg\{(MeO)_3PO\}_6^{2+}]$$

The observed parameters were $k_{ex}(193\ K) = 3.2\ s^{-1}$, $\Delta H^{\ddagger} = 70.7$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 135$ J K^{-1} mol^{-1}. It is concluded that a dissociative mechanism is indicated here also and the authors compare their rate data with those for other magnesium systems in the light of the Frank–Wen model for metal solvation.

[1] N. Purdie and M. M. Farrow, *Coordination Chem. Rev.*, 1973, **11**, 189.
[2] G. Atkinson, M. M. Emara, and R. Fernández-Prini, *J. Phys. Chem.*, 1974, **78**, 1913.
[3] J. Crea and S. F. Lincoln, *J.C.S. Dalton*, 1973, 2075.
[4] J. Crea, S. F. Lincoln, and R. J. West, *Austral. J. Chem.*, 1973, **26**, 1227.

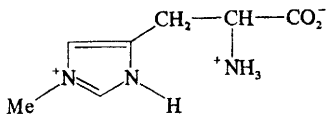
Nickel(II).—As an extension of their earlier work with histidine and related ligands, Letter and Jordan[5] have measured the kinetics of the reaction of Ni^{2+} with *N*-methylimidazole derivatives (1) and (2). In the latter case, both the protonated cation and the neutral molecule react (Table 1) but with (1) only reaction of the neutral form was detected. This system was different from that of histidine (previously studied) in that it did not show a second slow reaction. This is consistent with the previous assignment of the second reaction to the co-ordination of a second metal ion at the pyrrole nitrogen of the co-ordinated imidazole part of histidine. A two-step reaction was observed in the case of (2), where it was suggested that the ligand acts as two complexing units (the first step being attributed to complexing of the imidazole part of the molecule and the second involving co-ordination of a second nickel to the glycine part) rather than chelating, as does histidine. The expected parallel between ligand charge and rate constant is, on the whole, observed (Table 1).

The effect of charge on the incoming ligand is a topic which is considered in some detail by Lin and Rorabacher.[6] They have studied the reaction of solvated nickel(II) with the cationic ligand (3) as a function of solvent dielectric constant in methanol–

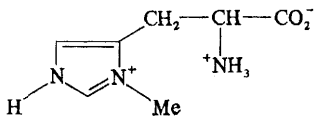
Table 1 *Rate constants for complex formation with nickel*(II) *in water*

Ligand	*Rate constant*/ $l\ mol^{-1}\ s^{-1}$	*Temp.*/ °C	*Ionic strength*/ $mol\ l^{-1}$	*Ref.*
N-Methylimidazole $MeHL^+$	2.3×10^2	23.7	0.10	5
N-Methylimidazole MeL	4.5×10^3	23.7	0.10	5
(1) MeHL	2.1×10^3	23.7	0.10	5
(2) MeH_2L^+	$\sim4.8\times10^2$	23.7	0.10	5
(2) MeHL	1.8×10^3	23.7	0.10	5
(2) $MeLNi^+$	5.5×10^2	23.7	0.10	5
(3)	4.8×10^2	25.0	0.2	6
o-Phthalate	6.3×10^5	25.0	→0	7
en	3.5×10^5	25.0	0.1	27
enH^+	1.8×10^2	25.0	0.1	27
NN-diMeen	3.2×10^4	25.0	0.1	28
NN-diMeenH^+	69	25.0	0.1	28
NN'-diMeen	4.3×10^4	25.0	0.1	28
NN'-diMeenH^+	29	25.0	0.1	28
triMeen	2.9×10^3	25.0	0.1	28
triMeenH^+	9.6	25.0	0.1	28
Anthranilate	2.3×10^3	25	0.10	29
Salicylate	5.3×10^3	25	0.10	29
5-Sulphosalicylate	4.7×10^3	25	0.10	29
Lactate	2.6×10^4	25	→0	31
Glycollate	2.6×10^4	25	→0	30
$H_{-2}(5)^-$	2.2×10^3	25	0.1	32
$Phthalate^{2-}$	2.6×10^5	25	0.10	33
H $Phthalate^-$	3.4×10^4	25	0.10	33
$Ethylmalonate^{2-}$	7.6×10^4	25	0.10	33
H $Ethylmalonate^-$	4.9×10^3	25	0.10	33
$Benzylmalonate^{2-}$	9.4×10^4	25	0.10	33
H $Benzylmalonate^-$	4.5×10^3	25	0.10	33

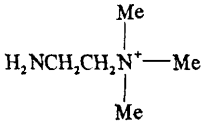
[5] J. E. Letter and R. B. Jordan, *Inorg. Chem.*, 1974, **13**, 1152.
[6] C. T. Lin and D. B. Rorabacher, *Inorg. Chem.*, 1973, **12**, 2402.



(1)



(2)



(3)

water mixtures containing 0—90% (by weight) of methanol. Assuming the normal dissociative-interchange mechanism, the value of 6.5 Å is estimated for the value of the charge centre-to-centre distance between the metal and ligand in the 'effective' ion pairs (those leading to complex formation). This is taken with a previously calculated value of 4 Å for the reactive site centre-to-centre distance, along with estimated steric factors, and used to evaluate a 'reactive' ion-pair formation constant for charged bidentate ligands. The relevance of their results to complex formation with the zwitterionic forms of amino-acids is also considered.

The thermodynamic and kinetic parameters for the formation of the nickel(II) complex of *o*-phthalate suggest[7] that the anion acts as a unidentate rather than a bidentate ligand.

The kinetics of the formation and dissociation of the thiocyanate complexes of Ni^{2+} in the solvents H_2O, DMSO, DMF, methanol, and acetonitrile have been investigated[8] by various relaxation techniques. In all solvents except water, two temperature- and concentration-dependent relaxation times were observed; they were attributed to the mono- and bis-complexes and the corresponding rate constants and activation parameters were evaluated. It is suggested that the rate and equilibrium constants can be correlated with the 'donicity' scale for the solvents introduced by Gutmann (see below).[9] The normal dissociative-interchange (I_d) mechanism is invoked for the formation of nickel monothiocyanate in DMSO[10] and of nickel nitrate, toluene-4-sulphonate, and trifluoroacetate in acetonitrile.[11]

Transition Metals M^{2+} (except Ni^{2+}).—Ultrasonic relaxation data on $Cu(ClO_4)_2$ in methanol at 25 °C are consistent[10] with an I_d mechanism. Representing the formation of the mono-complex by equation (1) (where S = MeOH),

$$[CuS_6]^{2+} + ClO_4^- \underset{k_{10}}{\overset{k_{01}}{\rightleftharpoons}} [CuS_6]^{2+},ClO_4^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [CuS_5ClO_4]^+ \qquad (1)$$

the values of k_{01}, k_{10}, and k_{12} are, respectively, 6.0×10^{10} l mol^{-1} s^{-1}, 5.1×10^8 s^{-1}, and 1.1×10^8 s^{-1}. The corresponding value of the exchange rate constant is quoted[12] as 7.4×10^7 s^{-1}.

Metals of Valency Three and Higher.—A comprehensive list of the rate parameters for ligand-replacement processes in octahedral complexes of metals in oxidation state three has appeared.[13]

Of all the first-row transition-metal ions, Fe^{III} has been one of the most difficult to

[7] S. Harada, H. Tanabe, and T. Yasunaga, *Bull. Chem. Soc. Japan*, 1973, **46**, 2450.
[8] F. Dickert, H. Hoffmann, and T. Janjic, *Ber. Bunsengesellschaft phys. Chem.*, 1974, **78**, 712.
[9] V. Gutmann, 'Coordination Chemistry in Non-aqueous Solutions', Springer-Verlag, Vienna, 1968, p. 19.
[10] J. Williams, S. Petrucci, B. Sesta, and M. Battistini, *Inorg. Chem.*, 1974, **13**, 1968.
[11] H. Hoffmann, T. Janjic, and R. Sperati, *Ber. Bunsengesellschaft phys. Chem.*, 1974, **78**, 223.
[12] R. Poupko and Z. Luz, *J. Chem. Phys.*, 1972, **57**, 3311.
[13] J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47.

study kinetically. The free metal ion readily hydrolyses, even in moderately acidic solutions, to $FeOH^{2+}$ (which can dimerize), and the incoming ligand can therefore react with either the free ion or the hydrolysed ion, or both. If, in addition, the ligand itself can exist in unprotonated and protonated forms the number of possible mechanistic pathways rapidly increases and it becomes increasingly difficult to assign rate constants unequivocally. Unless the ligand is 'simple' (*e.g.* Cl^- or Br^-, which only attack in the anionic form, or SCN^- or SO_4^{2-}, which can react either in the singly protonated or in unprotonated forms) it is necessary to choose between possible alternatives by examining the 'reasonableness' of the rate constants obtained. Gouger and Stuehr[14] have measured the rate constants for the formation of the complexes with phenol and *o*-aminophenol and have compared their results with previous measurements involving a wide variety of ligands in an attempt to resolve questions of this 'proton ambiguity'.

Table 2 *Summary*[a] *of rate constants* (l mol^{-1} s^{-1}) *for* Fe^{3+} + L (k_1) *and* $FeOH^{2+}$ + HL (k_5)

Ligand	k_1	k_5	*Ionic strength*/ mol l^{-1}
Cl^-	9.4		1.0
	19		1.0
Br^-	50		1.0
	20		1.7
$[Fe(CN)_6]^{3-}$	1750		0.5
SCN^-	127		0.4
$H_2PO_2^-$	270	2.1×10^4	1.0
SO_4^{2-}	(6.4×10^3)	1.4×10^5	0.5
	1×10^3	3×10^4	
	$(3.5—4.6)\times10^3$	5×10^4	0.5
F^-	(4×10^3)	3.1×10^3	0.5
$CH_2ClCO_2^-$	(4.9×10^3)	6.8×10^3	1.0
N_3^-	(1.6×10^5)	6.8×10^3	1.0
		7.4×10^3	0.1
	(1.4×10^5)	6.1×10^3	1.0
$MeCO_2^-$	(3.4×10^5)	5.3×10^3	1.0
$EtCO_2^-$	(4.2×10^5)	5.1×10^3	1.0
CrO_4^{2-}	(5×10^7)	9.2×10^3	1.0
PhO^-	*b*	7.2×10^2	0.1
$C_6H_4(NH_2)O^-$	*b*	1.1×10^3	0.1
5-Sulphosalicylate^{3-}	*b*	1.2×10^4	1.0
Salicylate^{2-}	*b*	1.4×10^4	1.0

[a] Data from ref. 14. [b] Values, if computed, would exceed the diffusion-controlled limit.

Table 2 summarizes much of the known data on Fe^{3+} + L (k_1) and $FeOH^{2+}$ + HL (k_5). (In cases where both k_1 and k_5 are given, the values of the former are given in parentheses to emphasize the fact that both sets of numbers cannot simultaneously be correct.) Gouger and Stuehr point out that, if pathway 1 were accepted for the ambiguous systems, it would be necessary to assume that the mechanism switches, at some limit of ligand basicity, to pathway 5 since otherwise the computed value of k_1

[14] S. Gouger and J. Stuehr, *Inorg. Chem.*, 1974, **13**, 379.

would be larger than the diffusion-controlled value of *ca.* 10^{10} l mol^{-1} s^{-1}. For this and other reasons (including the fact that the spread of values of k_5 is considerably less than that of values of k_1), it is concluded that pathway 5 is the more reasonable in cases where the 'proton ambiguity' exists. Likewise, Tamura[15] has suggested that this is the only significant pathway in the reaction of iron(III) with *m*-nitrophenol (formation and dissociation rate constants at 25 °C and ionic strength 0.10 mol l^{-1} being, respectively, 5.9×10^2 l mol^{-1} s^{-1} and 1.8×10^2 s^{-1}).

The kinetics of complexation of silver(III) by periodate and tellurate ions have been measured[16] by the stopped-flow method. Both reactions result in a rate law attributable to stepwise formation of the bis-complex:

$$[Ag(OH)_4]^- + H_2XO_6^{3-} \xrightarrow{k_1} [Ag(OH)_2(H_2XO_6)]^{2-} + 2OH^-$$

$$[Ag(OH)_2(H_2XO_6)]^{2-} + H_2XO_6^{3-} \xrightarrow{k_2} [Ag(H_2XO_6)_2]^{3-} + 2OH^-$$

Values of the second-order rate constants k_1 and k_2 (25 °C) are 4.5×10^4 and 9.3×10^3 l mol^{-1} s^{-1} for X = I and 2.7×10^3 and 1.0×10^4 l mol^{-1} s^{-1} for X = Te. Activation parameters are consistent with the associative-type mechanisms common to other square-planar low-spin d^8 metal ions.

The results of three ultrasonic investigations on lanthanide salts have been reported. The studies on erbium(III) perchlorate in aqueous methanol suggest[17] that inner-sphere perchlorate complexes occur at water mole fractions of less than 0.9. On that basis, the rate constant for the formation of the inner-sphere complex from the outer-sphere complex at 25 °C is 1.2×10^8 s^{-1}. The case of erbium(III) nitrate in aqueous methanol is more complicated and it is suggested[18] that the mechanism involves the existence of two forms of the solvated lanthanide ion, differing in co-ordination number, in equilibrium with the outer- and inner-sphere complexes. The results for aqueous yttrium nitrate, on the other hand, represent a simplification over those of previous ultrasonic studies on the lanthanides. The authors reject[19] the normal multistep mechanism in favour of a single diffusion-controlled process. Unfortunately, the computed value for the formation rate constant k_f of 1.0×10^8 l mol^{-1} s^{-1} is at least two orders of magnitude lower than the value calculated on the Debye–Smoluchowski approach, but the discrepancy is attributed to steric effects.

Table 3 *Activation parameters*[a] *for ligand-exchange reactions for* $TaCl_5,Me_2Y$ *in chloroform*

Ligand	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$ (0 °C)/kJ mol^{-1}
Me_2O	70.4	18	65.5
Me_2S	25.7	−91	50.5
Me_2Se	25.1	−92	49.8
Me_2Te[b]	24.3	−92	49.4

[a] Data from ref. 20. [b] In dichloromethane.

[15] K. Tamura, *Bull. Chem. Soc. Japan*, 1973, **46**, 1581.
[16] L. J. Kirschenbaum, J. H. Ambrus, and G. Atkinson, *Inorg. Chem.*, 1973, **12**, 2832.
[17] H. B. Silber, *J. Phys. Chem.*, 1974, **78**, 1940.
[18] J. Reidler and H. B. Silber, *J. Inorg. Nuclear Chem.*, 1974, **36**, 175.
[19] H. Wang and P. Hemmes, *J. Phys. Chem.*, 1974, **78**, 261.
[20] R. Good and A. E. Merbach, *J.C.S. Chem. Comm.*, 1974, 163.

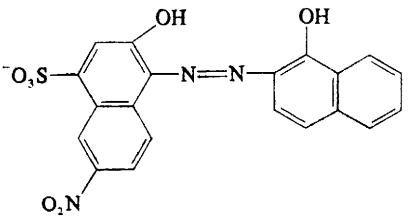
In dichloromethane and in chloroform, the dimeric tantalum(v) chloride reacts quantitatively with Lewis bases to form monomeric, non-electrolyte adducts with 1 : 1 stoicheiometry. The n.m.r. method has been used[20] to measure the kinetics of the reaction with Me_2Y (Y = O, S, Se, or Te). In the case of Me_2O the mechanism appears to be dissociative, but for the other bases an associative mechanism is postulated on the basis of their adherence to a second-order rate law, the activation parameters (Table 3), and steric effects.

2 Complex Formation involving Unsubstituted Metal Ions: Multidentate Ligands

Main-group Ions.—The formation of complexes between the alkali metals and large ring systems such as the crown polyethers is considered in Part III.

Further kinetic data have been reported for the formation of di- and tri-phosphate complexes of magnesium. To explain the results with pyrophosphate, it was necessary to consider[21] three parallel substitution pathways involving the species $P_2O_7^{4-}$, $HP_2O_7^{3-}$, and $H_2P_2O_7^{2-}$. No evidence for a significant acceleration of water loss was found with these highly charged ligands and it was concluded that an S_N1 mechanism adequately describes the substitution process. Results with ATP^{4-}, ADP^{3-}, and CDP^{3-} are also consistent[22] with an S_N1 mechanism. In this case the authors measured the activation parameters and, after making various assumptions regarding the enthalpy of formation of the outer-sphere complex, calculated $\Delta H^{\ddagger}$ for the ligand penetration step. This they found to be *ca.* 10 kcal mol^{-1} in the case of Mg^{2+} and point out that $\Delta H^{\ddagger}$ values can be more reliable than rate constants in indicating the type of mechanism since the latter may be distorted by steric or statistical factors (which, of course, will be reflected in the entropies of activation).

The kinetics of the reaction between Mg^{2+} and Eriochrome-Black-T (4) have been



(4)

investigated[23] in the presence of 12% ethanol. The reaction was found to proceed by two parallel paths, one involving the tervalent unprotonated ligand (D^{3-}) and the other its monoprotonated form (HD^{2-}). The rate constant for the unprotonated ligand (*ca.* 1.5×10^6 l mol^{-1} s^{-1} at 23.3 °C) is 'normal' whereas that for the protonated form (*ca.* 10^3 l mol^{-1} s^{-1}) is lower than 'normal'. Moreover, it is different under different conditions, and the authors suggest that this discrepancy may be explained, at least partially, on the assumption that the intermediate MgHD loses its proton not only to H_2O but also to other bases present in the solution.

[21] R. C. Patel and R. S. Taylor, *J. Phys. Chem.*, 1973, 77, 2318.
[22] J. L. Banyasz and J. E. Stuehr, *J. Amer. Chem. Soc.*, 1973, 95, 7226.
[23] R. Koren, B. Perlmutter-Hayman, and R. Shinar, *Internat. J. Chem. Kinetics*, 1974, 6, 39.

Conventional d.c. polarography[24] and n.m.r. spectroscopy[25] have been used to measure the rates of dissociation of several aminopolycarboxylate complexes of lead(II).

Nickel(II).—The rate constants have been measured[26] for complex formation and dissociation with neutral and anionic ligands in the presence of polyelectrolytes [sodium polystyrene sulphonate, sodium poly(ethylene sulphonate), and poly-(ethylenimine) hydrochloride]. In the reaction with the murexide anion, the formation rate constant k_f was decreased by the presence of either anionic or cationic polyelectrolyte, whereas the dissociation rate constant k_d remained unchanged. With the neutral ligands (phen, bipy, and pada), however, the polyelectrolytes with hydrophobic residues enhanced k_f (the value of k_d again being unchanged). It appears that the increase in k_f is associated with a reduction in the activation enthalpy (*e.g.* 13.5 kcal mol^{-1} for bipy with no added polyelectrolyte but 11.2 kcal mol^{-1} with 1.5×10^{-3} equiv l^{-1} of sodium polystyrene sulphonate). The authors discuss their results in terms of the formation of polyelectrolyte–metal complexes but it is quite clear that the presence of 'innocent' species can have large effects on the kinetics of metal complex formation – even with neutral ligands which apparently follow the 'normal' mechanism.

Rorabacher and co-workers[27] have studied the reaction between Ni^{2+} and ethylenediamine in some detail; they find the following rate law:

$$d[Ni(en)^{2+}]/dt = k_1[Ni^{2+}][en] + k_2[Ni^{2+}][enH^+] - k_{-1}[Ni(en)^{2+}] - k_{-2}[H^+][Ni(en)^{2+}].$$

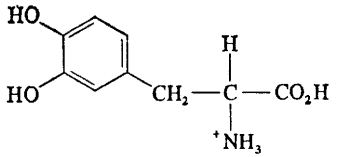
They discuss the difficulties inherent in the application of the temperature-jump technique to this system and resolve the disagreement between *T*-jump and stopped-flow results. The formation rate constant for unprotonated en (Table 1) is about 200 times larger than would be anticipated on the basis of a normal dissociative mechanism while that for enH^+ is approximately one-third too low. In attributing this enhancement to outer-sphere *intermolecular* hydrogen-bonding between a donor atom of the ligand and a co-ordinated water molecule in terms of the internal conjugate-base (ICB) effect, the authors imply that the principal accelerating factor is an increase in the outer-sphere equilibrium constant K_{os} (as the result of a decrease in the rate at which the two reactants can diffuse apart). In the case of enH^+, an apparent retardation in the rate of formation of the complex is attributed to the influence of *intramolecular* hydrogen-bonding in decreasing the fraction of the ligand in the outer-sphere complex which is in a reactive conformation.

The relative importance of steric and ICB effects in nickel(II) complex formation has been investigated further by Turan,[28] who used *NN*-dimethylethylenediamine (*NN*-diMeen), *NN'*-dimethylethylenediamine (*NN'*-diMeen), and *NNN'*-trimethylethylenediamine (triMeen) as incoming ligands. The results (Table 1) are compared with those for other polyamines and use is made in the analysis of the 'organic substituent function' E_S, defined as $\log(k/k_0)$, where k and k_0 are rate constants representing, respectively, the substituted and reference ligands. It is pointed out

[24] M. Kodama, K. Namekawa, and T. Horiuchi, *Bull. Chem. Soc. Japan*, 1974, **47**, 2011.
[25] B. J. Fuhr and D. L. Rabenstein, *Inorg. Chem.*, 1973, **12**, 1868.
[26] S. Kunugi and N. Ise, *Z. phys. Chem. (Frankfurt)*, 1974, **92**, 69.
[27] R. W. Taylor, H. K. Stepien, and D. B. Rorabacher, *Inorg. Chem.*, 1974, **13**, 1282.
[28] T. S. Turan, *Inorg. Chem.*, 1974, **13**, 1584.

that the modest steric effects associated with *N*-methyl substitution in en may be used to advantage in isolating ICB from steric factors and it appears that, in higher-order substitution, large steric constraints may obscure subtle features of reaction mechanisms. A linear relationship is obtained between the 'ICB effect' and the pK_a of the incoming ligand and it is concluded that, with ligands exerting moderate steric influence on k_f, the dissociation rate constants also seem to reflect the steric constraints. However, the exact role played by the dissociation steps is complex and no generalizations are yet possible.

Several further reports have appeared of values of k_f which are less than 'normal'. With the 5-sulphosalicylate anion (Table 1) it is suggested[29] that the comparatively low value can be rationalized in terms of charge delocalization, while with glycollate it is thought[30] that ring closure is responsible. The fact that k_f for lactate[31] is identical with that for glycollate suggests[30] either that the methyl group in lactate has no effect or that any steric effect is balanced by some other factor. The values of k_d are similar but not identical (for glycollate $k_d = 2.6 \times 10^2\ s^{-1}$; for lactate $k_d = 1.7 \times 10^2\ s^{-1}$). The steric factor has been invoked[32] in the case of the biologically important ligand L-dopa (5).

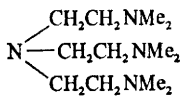


(5)

The kinetics of the reaction between Ni^{2+} and phthalic acid have been measured over a range of pH values and it is suggested[33] that the metal ion reacts with both the di- and mono-anionic forms of the dicarboxylic acid (the acid acting as a bidentate ligand). As an extension of this work, the reaction with ethyl- and benzyl-malonic acids has also been studied.[34] Again, parallel paths involving deprotonated and monoprotonated forms of the ligand were found, and the fact that the rate constants for formation of the unidentate intermediates are markedly smaller than those for phthalic acid (but are similar for all the malonic acid derivatives studied so far) is ascribed to the different flexibility and structure of the two types of ligand. The dissociation rate constants provide further evidence that the opening of the seven-membered ring (phthalate: $k = 1.3 \times 10^4\ s^{-1}$) is faster than that of the six-membered rings (monosubstituted malonates: $k \simeq 3 \times 10^3\ s^{-1}$). Moreover, although the differences for the latter ligands are small (less than a factor of two) it seems that there is some dependence of the ring-opening rate on the length and size of the substituent group.

[29] J. Williams and S. Petrucci, *J. Amer. Chem. Soc.*, 1973, **95**, 7619.
[30] S. Harada, Y. Okuue, H. Kan, and T. Yasunaga, *Bull. Chem. Soc. Japan*, 1974, **47**, 769.
[31] S. Harada, H. Tanabe, and T.Yasunaga, *Bull. Chem. Soc. Japan*, 1973, **46**, 3125.
[32] M. L. Barr, K. Kustin, and S. T. Liu, *Inorg. Chem.*, 1973, **12**, 1486.
[33] F. P. Cavasino, E. Di Dio, and G. Locanto, *J.C.S. Dalton*, 1973, 2419.
[34] G. Calvaruso, F. P. Cavasino, and E. Di Dio, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2061.

From an analysis of the polarographic behaviour of [Ni(edda)] it has been concluded[35] that the mechanism of formation of this complex involves the hydrolysed form of the metal and the protonated form of the acid. The rate constant for $Ni(OH)^+ + Hedda^-$ was estimated to be 6.9×10^3 l mol^{-1} s^{-1}. Since this is numerically close to the water-exchange rate constant at Ni^{2+}_{aq}, and the outer-sphere formation constant is expected to be *ca.* 1 l mol^{-1}, the author suggests[35] that the 'normal' mechanism applies in this case. Measurement of the dissociation rate of the nickel complex of (6) has also been used[36] to estimate k_f; the results are discussed



(6)

below, together with those for the analogous complexes of cobalt(II) and copper(II). Similarly, complex formation with three macrocyclic ligands is discussed in the next section.

The debate continues over the mechanism of complex formation between Ni^{2+} and bipy in non-aqueous solvents. In ethanol, the values of k_f (6.6×10^3 l mol^{-1} s^{-1} at 25 °C), $\Delta H_f^{\ddagger}$ (10.1 kcal mol^{-1}), and $\Delta S_f^{\ddagger}$ (-7.3 cal K^{-1} mol^{-1}) are all close to the corresponding values for solvent exchange, and it is concluded[37] that a dissociative-interchange mechanism applies. However, the difference in the values for the kinetic parameters of this reaction and those previously reported for phen (3.1×10^4 l mol^{-1} s^{-1}, 15.9 kcal mol^{-1}, and 15.4 cal K^{-1} mol^{-1}, respectively) imply a degree of ligand specificity for the reactions in ethanol which is considerably larger than that found in reaction in water and in methanol. Moreover, a common I_d mechanism with first-bond formation being rate determining is not applicable to both reactions.

Further support is provided[38] for rate-limiting ring closure for the bipy reaction in DMSO, a conclusion which is borne out by subsequent work[39] on several bidentate substituted pyridines. Although the rate constants for 2-(aminomethyl)-, 2-(2-aminoethyl)-, 2-(aminomethyl)-6-methyl-, and 2-[(methylamino)methyl]-pyridine are close to the value reported for solvent exchange between the $[Ni(DMSO)_6]^{2+}$ ion and bulk DMSO at 298 K, because of the wide variation in the activation parameters ($\Delta H^{\ddagger}$ in the range 8.8—14.5 kcal mol^{-1}; $\Delta S^{\ddagger}$ between -14 and $+7$ cal K^{-1} mol^{-1}) the agreement is not so good at elevated temperatures. However, the values of k_f (in the range $2.1—5.4 \times 10^3$ l mol^{-1} s^{-1} at 298 K) are all considerably larger than that for bipy (69 l mol^{-1} s^{-1}). The authors invoke steric hindrance in the case of bipy (and terpy which, likewise, has a low k_f) but keep an open mind as to whether this is exerted during the formation of the first metal–ligand bond or during the subsequent chelate-ring closure(s). As they point out, such steric effects for bipy and terpy appear to be of no importance in aqueous solution, but in DMSO the O-co-ordinated tetrahedral solvent molecules are much bulkier and steric hindrance is much more likely.

[35] M. Kodama, *Bull. Chem. Soc. Japan*, 1974, **47**, 2490.
[36] S. F. Lincoln and C. D. Hubbard, *J.C.S. Dalton*, 1974, 2513.
[37] M. L. Sanduja and W. M. Smith, *Canad. J. Chem.*, 1973, **51**, 3975.
[38] P. Moore and D. M. W. Buck, *J.C.S. Dalton*, 1973, 1602.
[39] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1974, 2082.

The reaction between nickel(II) and pada has been studied in pyridine and pyridine–nitromethane mixtures,[40] in t-butyl alcohol–water mixtures,[41] and in glycerol at different pressures.[42]

Transition Metals M^{2+} (except Ni^{2+}).—The kinetics of the reaction of pada with cobalt(II), nickel(II), copper(II), and zinc(II) in glycerol have been measured[42] (Table 4). The formation rate constants k_f for all four metals at 20 °C and 1 bar

Table 4 *Kinetic parameters*[a] *for the reaction of* pada *with metals in glycerol*

Metal	k_f/l mol^{-1} s^{-1} (*at* 1 bar, 20 °C)	$\Delta H_f^{\ddagger}$/kcal mol^{-1} (*at* 1 bar)	$\Delta V^{\ddagger}$/cm^3 mol^{-1} (*at* 20 °C)
Co^{II}	5.5×10^3	16.2	+9.6
Ni^{II}	5×10^3		
Cu^{II}	*ca.* 1×10^4		
Zn^{II}	1.98×10^4	17.3	+12.2

[a] Data from ref. 42.

differ only by a factor of 4, in striking contrast to the values in water which cover a range of more than 10^4. This suggests that some property of the solvent, rather than of the cation, is limiting the rate but, interestingly, the value for a diffusion-controlled reaction in glycerol is calculated to be 10^6—10^7 l mol^{-1} s^{-1}. However, the values of $\Delta H_f^{\ddagger}$ for Co^{2+} and Zn^{2+} are close to the diffusion-controlled value of 16.6 kcal mol^{-1}, suggesting that the difference between the observed k_f and the diffusion-controlled value must be attributed to $\Delta S^{\ddagger}$. The value of $\Delta V^{\ddagger}$ is close to the diffusion-controlled value for Zn^{2+} but rather lower for Co^{2+}. The authors propose the following scheme, which can account for all the measured parameters. The reactant molecules first come together in an encounter complex, within which displacement of the hydroxy-groups of co-ordinated glycerol by the bidentate ligand molecule LL subsequently occurs. Glycerol (G) is presumably a terdentate ligand, forming complexes G_2M^{2+}, so the scheme can be written (omitting charges):

$$G_2M + LL \underset{k_{21}}{\overset{k_D}{\rightleftharpoons}} (G_2M,LL) \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} G_2MLL \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} G_2M\begin{matrix}L\\ \diagup\\ \diagdown\\ L\end{matrix}$$

Application of the steady-state approximation gives

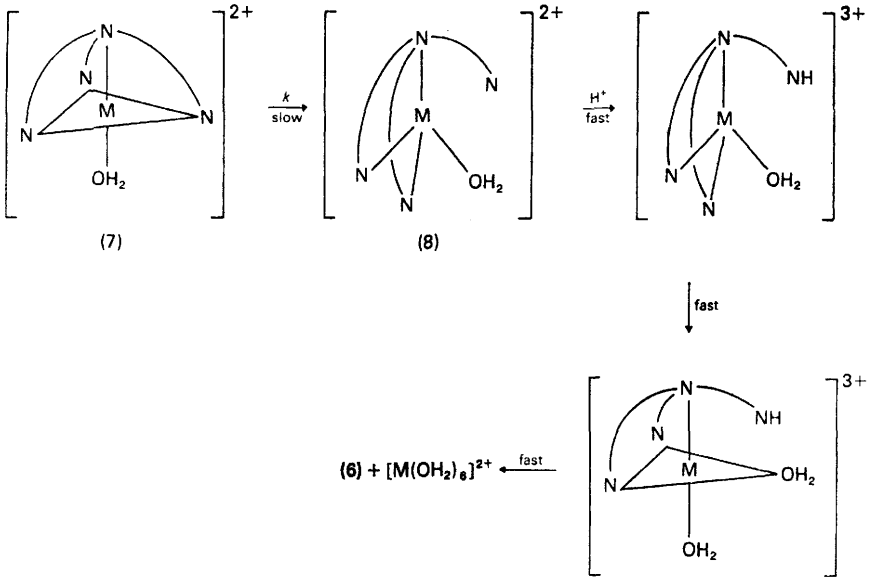
$$k_f = k_D(k_{23}/k_{21})(k_{34}/k_{32})$$

and the low observed value of k_f would imply that $(k_{23}/k_{21})(k_{34}/k_{32})$ is *ca.* 10^{-2}—10^{-3} and varies little from one cation to another. This can readily be understood in terms of steric factors [leading to low (k_{23}/k_{21})] which vary little from metal to metal, since all are of approximately the same size, and hindrance to ring closure [leading to low (k_{34}/k_{32})].

In a stopped-flow study of the dissociation of the (five-co-ordinate) cobalt(II) complex of ligand (6) and its nickel(II) and copper(II) analogues in aqueous-acidic

[40] H. L. Fritz and J. H. Swinehart, *Inorg. Chem.*, 1973, **12**, 1259.
[41] E. F. Caldin and P. Godfrey, *J.C.S. Faraday I*, 1974, **70**, 2260.
[42] E. F. Caldin and M. W. Grant, *J.C.S. Faraday I*, 1973, **69**, 1648.

2.0M perchlorate, a single process, attributed[36] to the dissociation of the first amine group, was observed for all three complexes (see Scheme 1). Interestingly, the order



Scheme 1

of lability (at 298 K) of the five-co-ordinate species $[M(6)H_2O]^{2+}$ ($Cu^{2+} > Ni^{2+} > Co^{2+}$; see Table 5) contrasts with that observed in six-co-ordinate systems ($Cu^{2+} >$

Table 5 *Activation parameters*[a] *for the dissociation of* $[M(6)H_2O]^{2+}$

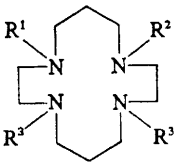
M	k (293 K)/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Co	0.97	61.9	−33.5
Ni	7.87	58.9	−26.4
Cu	28.0	81.1	59.9

[a] Data, from ref. 36, refer to 1.0M perchloric acid at 2.0 mol l^{-1} ionic strength ($NaClO_4$).

$Co^{2+} > Ni^{2+}$). Similarly, the relatively high value of $\Delta H^{\ddagger}$ for the copper(II) compound contrasts with values for the six-co-ordinate state in which $\Delta H^{\ddagger}$ is expected to vary as $Cu^{2+} < Co^{2+} < Ni^{2+}$. These differences must be largely attributed to the change from six- to five-co-ordination and the consequent modification of the *d*-orbital energies, and also to variations in metal–ligand distances within the $[M(6)H_2O]^{2+}$ series which, by analogy with $[M(6)Br]^{2+}$ (the *X*-ray structures of which have been determined), is assumed to possess trigonal-bipyramidal geometry. If dissociation of the first amine group [(7)→(8)] proceeds through an approximately tetrahedral transition state, the appropriate crystal-field activation energies (c.f.a.e.) are, respectively, 0.10, 2.70, and 5.30 Dq for high-spin cobalt(II), nickel(II), and copper(II). As the authors point out, the uncertainties involved in crystal-field

calculations must make c.f.a.e. values somewhat speculative, but it is noteworthy that the highest c.f.a.e. is that of copper(II), which also exhibits the largest value of ΔH^{+}. An alternative mechanism to that represented in Scheme 1 is an associative mechanism in which a second water molecule is co-ordinated to give a five-co-ordinate product [species (8) with an additional water molecule] from a six-co-ordinate transition state. It is not, unfortunately, possible to decide between these two mechanisms on the basis of the present data; perhaps such a distinction will become possible when further work has been done with complexes of this type.

There have been further reports on the kinetics of complex formation and dissociation with macrocyclic ligands. The rate constants k_f for Ni^{2+} and Cu^{2+} complexes of (9a—d) are lower[43] (Table 6) than for the open-chain amines, for which water



(9) a; $R^1 = R^2 = R^3 = H$
b; R^1 = Me, $R^2 = R^3 = H$
c; $R^1 = R^2$ = Me; $R^3 = H$
d; $R^1 = R^2 = R^3$ = Me

Table 6 *Kinetic parameters*[a] *for complex formation of* Ni^{2+} *and* Cu^{2+} *with macrocyclic ligands*

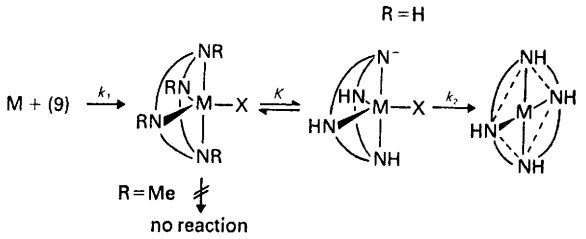
Reaction	k_f/l mol^{-1} s^{-1}	ΔH^{+}/kcal mol^{-1}
Ni^{2+} + (9a)	7.4	18.1
Ni^{2+} + (9b)	55	19.7
Ni^{2+} + (9c)	10	18.5
Ni^{2+} + (9d)	1.4	17.8
Cu^{2+} + (9a)	2.6×10^{5}	
Cu^{2+} + (9b)	1.2×10^{7}	18.8
Cu^{2+} + (9c)	2.8×10^{6}	18.6
Cu^{2+} + (9d)	2.9×10^{5}	19.0

[a] Data from ref. 43.

substitution is the rate-determining step. Moreover, one might expect that successive methylation of (9) would lead to gradual reduction in k_f until, when all four nitrogens have been methylated (9d), an abrupt drop would occur. This is not found. Thus, either (*a*) steric effects are not important in first-bond formation with these macrocycles because the ring already induces such a high steric hindrance that any further change can little affect the reactivity, (*b*) the expected decrease in complexation rates from (9a) to (9d) is compensated by some other effect (for example, a different conformation of the ligand), or (*c*) the rate-determining step for the macrocycles is not the same as for the open-chain amines. The authors[43] favour the last explanation

[43] R. Buxtorf and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1035.

and propose the scheme shown in Scheme 2 involving a five-co-ordinate intermediate. In an extension[44] of the work with (9d) to cobalt(II) and zinc(II), the values



Scheme 2

of k_f, although a factor of 10^3—10^4 less than the 'normal' values for each metal, were found to follow the same order as that of the water-exchange rate constants ($Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$), thus providing further evidence that a step other than water exchange plays an important role in the rate-determining process.

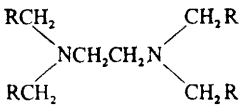
In a polarographic study, the rates of dissociation of some aminopolycarboxylato-zinc(II), -cadmium(II), and -lead(II) complexes have been measured,[24] and n.m.r. has been used[25] in an analogous study on the same metals. The kinetics of the dissociation of the cobalt(II) complex of ethylenediamine monoacetate have also been measured polarographically,[35] and the rate constants for the formation of the cobalt(II) complexes of anthranilate,[29] salicylate,[29] 5-sulphosalicylate,[29] and ligand (5)[32] have been compared with those of the respective nickel(II) analogues.

There appears to have been a concerted attempt to understand the mechanism of complex formation at aquocopper(II). For ligand substitution at this ion both dissociative and associative mechanisms have been proposed. Although the bulk of evidence has suggested that the normal dissociative mechanism applies, ligand-dependent rate constants have been reported for both unidentate and bidentate ligands. Moreover, the considerable uncertainty in the rate constant for water exchange (values ranging from 2×10^8 to 8×10^9 s^{-1} having been reported) has made the comparison between observed and calculated ($= K_{os}k_{ex}$) values of k_f an even more hazardous procedure than it usually is. As an alternative approach, both Moss, Lin, and Rorabacher[45] and Roche and Wilkins[46] have compared the rate constants for the formation of copper(II) complexes with those for the analogous complexes of nickel(II). Because the two metal ions are of the same charge and approximate size, it is assumed that electrostatic and steric factors will be the same in the two cases, leading to identical values of K_{os}. Thus, since a dissociative mechanism is accepted for most Ni^{II} substitution reactions, a constant ratio of the rate constants for the two metals may be interpreted as strong evidence for a dissociative mechanism for Cu^{II} as well. In Table 7 are listed the relevant rate constants (l mol^{-1} s^{-1}) for copper(II) (k_{Cu}) and nickel (k_{Ni}) and the ratio of the two. It will be seen that in most cases the value of log (k_{Cu}/k_{Ni}) falls in the range 4.5—5.0, which can therefore be termed 'normal', supporting the conclusion that complex formation at copper(II) is generally dissociative in character. Values outside this range must now be rationalized in terms of a

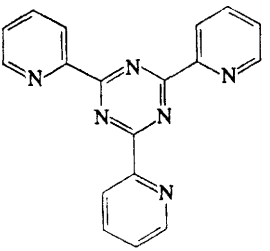
[44] L. Hertli and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1328.
[45] D. B. Moss, C. T. Lin, and D. B. Rorabacher, *J. Amer. Chem. Soc.*, 1973, **95**, 5179.
[46] T. S. Roche and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1974, **96**, 5082.

Table 7 *Comparative rate constants*[a] *(in* $l\ mol^{-1}\ s^{-1}$*) for ligand substitution on* Ni^{II} *and* Cu^{II}

Ligand	$\log k_{Ni}$	$\log k_{Cu}$	$\log (k_{Cu}/k_{Ni})$	*Ref.*
H_2O	4.5[b]	~9.2[b,c]	~4.7*	45
NH_3	3.7	8.3	4.6*	45
en	5.6	9.6	4.0	45
enH^+	2.3	5.2	2.9	45
(10a)	2.6	8.2	5.6	45
$(10a)H^+$	−0.7	3.0	3.7	45
$trienH_2^{2+}$	1.9	6.9	5.0*	45
$trienH_3^{3+}$	~1.0	4.2	~3.2	45
$tetrenH_2^{2+}$	3.0	7.6	4.6*	45
$tetrenH_3^{3+}$	0.5	5.0	4.5*	45
TEA	2.5	7.5	5.0*	45
(10b)	2.4	7.5	5.1	45
$(10b)H^+$	0.9	4.7	3.8	45
$(10c)H^+$	0.4	4.7	4.3	45
imid	3.8	8.8	4.0	46
phen	3.5	7.8	4.3*	46
$phenH^+$	0.5	<2.7	<2.2	46
bipy	3.3	7.7	4.4*	46
$bipyH^+$	1.4	5.4	4.0	46
$(11)H^+$	3.2	7.4	4.2*	46
$(11)H_2^{2+}$	~1.0	<3.0	<2.0	46
ida^{2-}	4.9	9.5	4.4*	46
$Hida^-$	−1.1	4.1	5.2	46
$(12)H^+$	1.5	3.9	2.4	46
$terpyH^+$	2.0	5.9	3.9	46
$terpyH_2^{2+}$	~−0.3	<2.7	<3.0	46



(10) a; R = H
b; R = CH_2OH
c; R = CH(Me)OH



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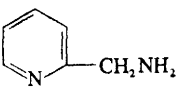


(12)

[a] Data refer to 25 °C and, in most cases, I = 0.1 mol l^{-1}. [b] First-order rate constant (s^{-1}).
[c] Estimated from ligand-substitution rates.
* Regarded as 'normal' (see text).

special mechanism either for the nickel(II) complex or for the copper(II) complex (or both).

In the first place, the ratio for the ethylenediamine rate constants is a little low. The anomalously large rate constant for the reaction of this ligand with Ni^{2+} has already been attributed to the operation of an internal conjugate-base (ICB) mechanism (see above), and it may be argued[45] that the same explanation holds with copper but that in this case the diffusion-controlled limit (estimated to be *ca.* 6×10^9 l $mol^{-1}\ s^{-1}$ for a neutral ligand) has been reached before the 'full' enhancement in k_f has been

experienced. Consistent with this interpretation is the observation that log (k_{Cu}/k_{Ni}) for (10a) is abnormally large. This ligand is rather more basic than en (pK_a = 9.1 compared with 10.0 for en) so that the ICB rate enhancement should be diminished; thus, the diffusion limit is not exceeded in its reaction with Cu^{2+}. [A strict interpretation of the ratio of these formation rate constants as reflecting a greater ICB effect for Cu^{2+} than Ni^{2+} is cautioned against,[45] however, since it has recently been concluded that with Ni^{2+} + (10a) the rate-determining step may be second-bond formation.]

In the case of many of the protonated ligands [*e.g.* enH^+, $(10a)H^+$, and $trienH_3^{3+}$] it is necessary for a proton to be lost before the (first) chelate ring can be formed. The low ratios probably reflect reduced rate constants for Cu^{II} resulting from a shift in the rate-determining step to the point of the proton loss preceding second-bond formation.

A particularly important feature in determining the high lability of copper(II) is the operation of the Jahn–Teller effect. Thus, the first donor atom is seen to bond at an axial position in the inner sphere and this is followed by rapid inversion of the inner sphere, in which the axial bonds are contracted while the bonds along an equatorial axis are lengthened in a concerted process, thereby defining a new equatorial plane containing the ligand donor atom (Figure 1). If this were not the case, second-bond formation between Cu^{II} and a multidentate ligand would require the direct loss of an equatorial water molecule, a process which is presumably rather slow (a value of

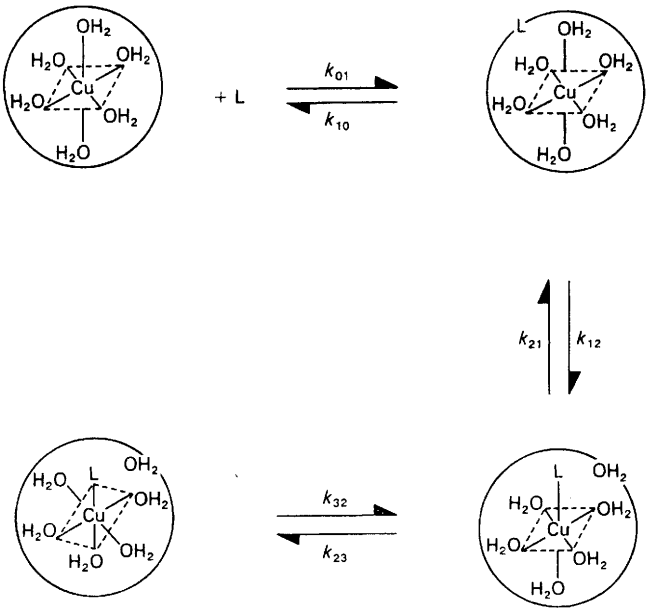


Figure 1 *Schematic representation of the dissociative mechanism for ligand substitution on* $[Cu(H_2O)_6]^{2+}$ *with subsequent Jahn–Teller inversion. The large circle represents the next layer of solvent molecules surrounding the inner coordination sphere*

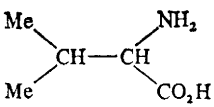
10^4 s^{-1} has been estimated). Several of the results quoted in Table 7 have a bearing on the operation of this effect.

For the polyamine reactions, the initial bond formed involves a donor atom (amine nitrogen) which binds more strongly than the water molecule replaced in the substitution process – making the subsequent inversion a thermodynamically favoured process. For the poly(amino-alcohol) ligands, however, studies on nickel(II) have established that the tertiary nitrogen donor atoms are too sterically hindered to permit direct bonding to the metal ion. Thus, the reaction mechanisms for these ligands with Ni^{II} involve first-bond formation with an alcoholic oxygen donor atom followed by nitrogen bond formation as the rate-determining step. The steric requirements for these ligands suggest that the same mechanism holds for Cu^{II}. Now there is evidence to suggest that an alcoholic oxygen forms a weaker bond to Cu^{II} than does a water oxygen, so it must be concluded that, in the reactions of this metal with the poly(amino-alcohols), the Jahn–Teller inversion must be unfavourable from a thermodynamic point of view. Yet, as already mentioned, the only alternative route to second-bond formation would appear to involve the direct loss of an equatorial water molecule. It is therefore, at first sight a little surprising that the rate-constant ratios for reaction with TEA and with (10b) are 'normal' or slightly higher. Thus, the Jahn–Teller inversion must be a rapid process – indeed, as will be seen, it is possible to put fairly narrow limits on its half-time. [It might be pointed out that the possibility that slow inversion may be occurring with TEA and (10b), compensated by an ICB effect, could be ruled out on the basis of recent evidence that the latter is not normally a significant factor with these ligands.]

In a previous report,[47] based on e.s.r. measurements, it had been found that the dynamic Jahn–Teller effect is inhibited for copper(II) when the inner co-ordination sphere is inhomogeneous. Moreover, such inhomogeneities occur when ethanol is added to aqueous Cu^{II} solutions. Thus, in order to reconcile the kinetics with these e.s.r. findings (which refer to a time-scale of 10^{-11}—10^{-10} s), it must be assumed that the inversion time for the kinetic intermediate is in the range 10^{-10}—10^{-8} s. The implied decrease in the k_{23}/k_{32} ratio (Figure 1) would then presumably be compensated by the increase in the k_{12}/k_{21} ratio (alcohol *vs.* water) for Cu^{II} relative to Ni^{II}.

As with the highly protonated polyamines, the monoprotonated forms of (10b) and (10c) exhibit low rate-constant ratios, suggesting that proton loss is the rate-determining step. Unlike the protonated polyamines, however, the formation of the first chelate ring in $(10b)H^+$ and $(10c)H^+$ does not *require* proton loss. Perhaps this means that, in the reaction of Cu^{2+} with these ligands, the rate-determining step is shifted to a point following the closure of the first chelate ring – an apparently rare occurrence in the formation of metal complexes.

The kinetics of mono- and bis-complex formation of Cu^{2+} with (13) and (14) have



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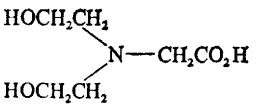


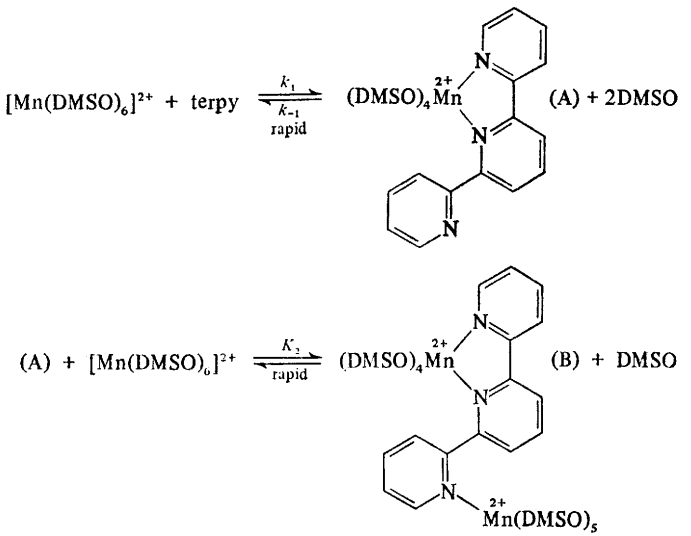
(14)

[47] M. Noack, G. F. Kokoszka, and G. Gordon, *J. Chem. Phys.*, 1971, **54**, 1342.

been measured; they can be rationalized[48] in terms of steric effects which are more pronounced for bis-complex formation, particularly when bulky groups are co-ordinated to the amino nitrogen. The kinetics of the Cu^{II}–adenine interaction have also been studied by stopped-flow and temperature-jump methods, and it is suggested[49] that the major contribution to the observed effects comes from formation of the bis-complex.

Measurements of the spin–lattice relaxation rates of the ^{31}P nucleus in manganese(II) + ATP solutions have been used to determine the dissociation rate constant of the Mn^{II}–ATP complex; it is given[50] as $1.5 \times 10^5\ s^{-1}$ at 25 °C. (Incidentally, a detailed consideration of the results in terms of the dipolar interaction between the electron and nuclear spins leads to the conclusion that the α-P atom is further from the manganese ion than the β- or γ-P atoms, which are equidistant. This contrasts with the situation in Mn^{II}–TP where the three P atoms are equidistant from the metal. The matter is considered in greater detail in Part III.)

The reaction between manganese(II) and terpy in DMSO has been shown[51] to occur in two stages; the rapid formation of a dinuclear intermediate is followed by a very slow reaction, which is attributed to final chelate-ring closure. The proposed mechanism is shown in Scheme 3. Analysis of the rate behaviour yielded the following rate constants: $k_1 = 1.64 \times 10^3\ l\ mol^{-1}\ s^{-1}$ and $k_{-1} = 46.1\ s^{-1}$ (both at 292.1 K); $k_3 = 2.58 \times 10^{-3}\ s^{-1}$ (at 314.1 K).



Scheme 3

[48] J. W. Brubaker, A. F. Pearlmutter, J. E. Stuehr, and T. V. Vu, *Inorg. Chem.*, 1974, **13**, 559.
[49] G. Boivin and M. Zador, *Canad. J. Chem.*, 1973, **51**, 3322.
[50] F. F. Brown, I. D. Campbell, R. Henson, C. W. J. Hirst, and R. E. Richards, *European J. Biochem.*, 1973, **38**, 54.
[51] D. M. W. Buck and P. Moore, *J.C.S. Chem. Comm.*, 1974, 60.

Metals of Valency Three and Higher.—The kinetics of complex formation of iron(III) with various aminopolycarboxylates[52,53] and catechol[54] have been reported (see Table 8). After considering the pH dependence of the observed rate constants,

Table 8 *Rate constants*[a] *and activation parameters for the formation of* Fe^{III} *chelates*

Reaction	k/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	*Ref.*
$[FeOH]^{2+}$(aq) + H_2ida	2.5×10^3	6.1	−23	52
$[FeOH]^{2+}$(aq) + $Hida^-$	8.8×10^3	4.9	−22	52
$[FeOH]^{2+}$(aq) + H_3nta	1.5×10^4	9.9	−5	52
$[FeOH]^{2+}$(aq) + H_2nta^-	5.6×10^4	6.3	−16	52
$[FeOH]^{2+}$(aq) + H_4edta	3.0×10^4	7.3	−15	53
$[FeOH]^{2+}$(aq) + H_3edta^-	1.1×10^5	5.7	−15	53
$[FeOH]^{2+}$(aq) + H_5dtpa	5.3×10^4			53
$[FeOH]^{2+}$(aq) + H_4dtpa^-	1.6×10^5			53
$[FeOH]^{2+}$(aq) + catechol	3.1×10^3	9.6	−11	54

[a] Data refer to 25 °C.

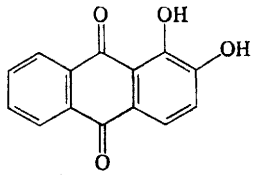
the authors conclude that in all cases the metal reacts in its monohydroxo-form (*cf.* the discussion in Section 1 on the 'proton ambiguity'). It is noteworthy that the rate constants for the undissociated acids increase in the order $H_2ida < H_3nta < H_4edta < H_5dtpa$ (and those for the mono-anions follow a similar order), which corresponds to the increase in the number of chelate rings formed. This is the opposite order to that which might be expected if ring closure contributed to the rate-determining process. The authors are unable to rationalize it unequivocally but point out that two possible explanations are reasonable. In the first, it is noted that the reacting ligands are, in effect, zwitterions, so that when outer-sphere complex formation occurs it will be between the ion $[Fe(H_2O)_5(OH)]^{2+}$ and carboxylato-groups; thus, the ligand will bear, with respect to the metal, an overall negative charge which will increase on going from H_2ida ($Hida^-$) to H_5dtpa (H_4dtpa^-) and this will be associated with a gradually increasing value of K_{os} and therefore k_f. The other possibility is a statistical one: on going down the series the number of carboxylato-groups available for forming the first metal–ligand bond increases, so the probability of occurrence of reaction is accordingly increased. As the authors point out,[52–54] the results are in all cases consistent with the assumption that the rate of formation of the complex is 'normal' {*i.e.* the rate-determining step is displacement of the first water molecule from $[Fe(H_2O)_5(OH)]^{2+}$}, although the activation enthalpy does appear to be somewhat dependent on the nature of the entering species.

Farrow and Purdie have recently attempted[55] to correlate rate data for metal complex formation obtained by transient relaxation methods with those obtained by the ultrasound-absorption technique. Sound-absorption measurements on aqueous samarium(III) sulphate solutions were made as a function of the ionic strength (maintained with $NaClO_4$) and there was found to be essentially no change in the kinetics of the rate-determining step. In the sound-absorption spectrum of Sm^{III}

[52] E. Mentasti, E. Pellizzetti, and G. Saini, *Gazzetta*, 1974, **104**, 201.
[53] E. Mentasti, E. Pellizzetti, and G. Saini, *J.C.S. Dalton*, 1974, 1944.
[54] E. Mentasti and E. Pellizzetti, *J.C.S. Dalton*, 1973, 2605.
[55] M. M. Farrow and N. Purdie, *Inorg. Chem.*, 1974, **13**, 2111.

malonate an additional relaxation was observed at lower frequencies, which was attributed to a rate-determining ring-closure step. On a complete steady-state kinetic analysis of the multistep complex-formation mechanism there was fair agreement between the calculated overall k_f and the value obtained experimentally by transient methods. Similarly, the agreement between the rate constants for formation of the murexide complex of samarium(III) as determined by the dissociation-field effect (*E*-jump) and temperature-jump methods was satisfactory.[56]

Complex formation of vanadate ions by edta and (15) has been studied[57] by the



(15)

stopped-flow technique. The results for both reactions were found to be consistent with the same simple scheme, shown in Scheme 4 [where HA represents the monoprotonated form of edta (a trianion) or (15) (a monoanion)]. The rate constants for

$$\begin{array}{ccc} [VO_2(OH)_3]^{2-} + HA^- & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & [\text{complex: } CH_{-1}] \\ \Big\Downarrow \text{fast} & & \Big\Downarrow \text{fast} \\ [VO_2(OH)_2]^- + HA^- & \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} & [\text{complex: C}] \end{array}$$

Scheme 4

complex formation are essentially independent of the nature of the incoming ligand and agree with the previously determined rate constant for vanadate dimerization from $[VO_2(OH)_2]^-$ and $[VO_2(OH)_3]^{2-}$ (3.1×10^4 l mol^{-1} s^{-1}). k_2 for Hedta^{3-} is 2.4×10^3 and for H_{-1} (15)$^-$ is 1.2×10^3 l mol^{-1} s^{-1}; k_5 for Hedta^{3-} is 2.3×10^4 and for H_{-1}(15)$^-$ is 2.3×10^4 l mol^{-1} s^{-1}.

Aqueous molybdate–edta solutions have been studied[58] by temperature jump in the pH range 7.25—8.25 at 25 °C and ionic strength 0.1 mol l^{-1}. The rate constant for the reaction

$$[HMoO_4]^- + H_2Y^{2-} \longrightarrow [MoO_3YH]^{3-} + H_2O$$

where H_2Y^{2-} is the deprotonated form of edta, is 2.26×10^5 l mol^{-1} s^{-1}. Upper limits could be determined for the rate constants of the reactions

$$[MoO_3Y]^{4-} + [HMoO_4]^- \longrightarrow [O_3MoYMoO_3]^{4-} + OH^-$$

and

$$[MoO_3YH]^{3-} + [MoO_4]^{2-} \longrightarrow [O_3MoYMoO_3]^{4-} + OH^-$$

[56] M. M. Farrow, N. Purdie, and E. M. Eyring, *Inorg. Chem.*, 1974, **13**, 2024.
[57] K. Kustin and D. L. Toppen, *J. Amer. Chem. Soc.*, 1973, **95**, 3564.
[58] D. S. Honig and K. Kustin, *J. Amer. Chem. Soc.*, 1973, **95**, 5525.

They are, respectively, 3.26×10^4 and 1.03×10^1 l mol^{-1} s^{-1}. Comparison of these results with those of previous studies with 8-hydroxyquinoline and catechol suggests[58] that the mechanism of complex formation at molybdate is associative.

The kinetics of the decomposition of pentamolybdodiphosphates and heptamolybdates in alkaline solution have been measured,[59] and the molybdate studies with catechol and some of its derivatives have been extended to tungstate.[60]

3 The Effect of Bound Ligands

Gutmann and Schmid have reviewed[61] what they term the 'empirical approach to ligand effects on the kinetics of substitution and redox reactions'. This is an attempt to give a unified and general description of the effect of a change in the co-ordination sphere of the metal on its reactions and it makes use of what has been termed the 'donicity' of each ligand involved. The donicity, or 'donor number' is a measure of the ability of the ligand to function as an electron-pair donor towards antimony(v) chloride and is represented as $-\Delta H$ for this particular reaction in dilute solution in 1,2-dichloroethane. The concept is qualitative in nature and does not, unfortunately, allow quantitative predictions. However, it does disclose a number of semiquantitative relationships and the authors suggest that it may serve as a useful guide for predicting changes in rates associated with changes of ligands, solvents, or solvent composition.

Reactions in Water.—Tanaka has developed[62] his idea of using mechanistic considerations as the basis for predictions of the stability constants of mixed-ligand ternary complexes to copper(II).

The kinetics of formation of ternary complexes between nickel(II) species and the dianion from 5-nitrosalicylic acid (nsa^{2-}) have been measured.[63] In Figure 2 the rate constants (suitably adjusted to take account of the reduced number of water molecules available for replacement in the substituted-nickel species) are compared with those obtained with NH_3 and pada as incoming ligands, together with the few known rate constants for water exchange. The general increase in k_f^S found with NH_3, pada, and H_2O as the number of bound aliphatic nitrogen atoms increases is, as expected, found also with nsa^{2-}. The other principal feature of Figure 2 is that, for a given complex NiL, k_f^S for the charged nsa^{2-} is always larger than for the neutral NH_3 and pada ligands. The ratio of k_f^S for nsa^{2-} and the neutral ligands varies from 15 to 70 for the cationic [NiL] species whereas it is generally less than 10 for the neutral and anionic [NiL] species, being smallest (*ca.* 3) for $[Ni(nta)]^-$. {The larger difference between k_f for nsa^{2-} and pada with the complexes $[Ni(trien)]^{2+}$ and $[Ni(tren)]^{2+}$ is probably associated with the contribution of ring closure to the rate-determining step for the latter incoming ligand.} This result confirms the indications of similar studies with the d^0 and high-spin d^5 metal ions Mg^{2+} and Mn^{2+} where, however, the data are less complete. Thus, the complex-formation rate data for these ternary complexes can be rationalized in terms of the normal dissociative model only if the *local* charge density on the metal ion is considered rather than the *overall* charge on

[59] R. Mellström and N. Ingri, *Acta Chem. Scand.*, 1974, **A28**, 203.
[60] K. Kustin and S. T. Liu, *Inorg. Chem.*, 1973, **12**, 2362.
[61] V. Gutmann and R. Schmid, *Coordination Chem. Rev.*, 1974, **12**, 263.
[62] M. Tanaka, *J. Inorg. Nuclear Chem.*, 1974, **36**, 151.
[63] D. N. Hague and K. Kinley, *J.C.S. Dalton*, 1974, 249.

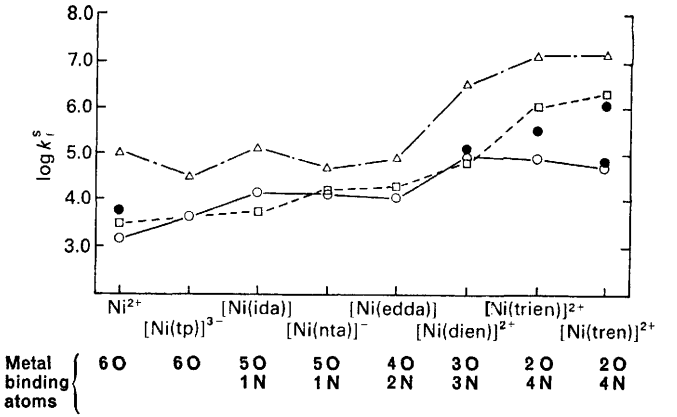


Figure 2 *Statistically adjusted rate constant* (log k_f^s) *for reaction of nickel*(II) *species with charged and neutral ligands:* nsa (△), pada (○), NH_3 (□), *and* H_2O (●). *In the case of water exchange, the first-order rate constants have been converted into second-order rate constants by treating the solvent as a reagent of concentration* 55.5 mol l^{-1} *to permit direct comparison with the other rate constants*
(Reproduced from *J.C.S. Dalton*, 1974, 249)

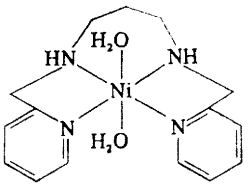
the substituted metal ion. In particular, the net charge on the metal species should not be used to calculate the formation constant of the outer-sphere complex from the Fuoss equation; the metal species still behaves as a positive centre even though it may carry a formal negative charge.

Stability and rate constants have been determined[64] for the substitution of one or both of the water molecules in (16) by ammonia, ethylamine, glycine, or *dl*-alanine. The measured stability constants for ternary complex formation with NH_3 (175) and $EtNH_2$ (58) are considerably smaller than those for glycine (710) and *dl*-alanine (820), suggesting that the α-amino-acids achieve bidentate co-ordination by the displacement of a terminal chelate arm of the quadridentate ligand or a rearrangement of the ligand so that *cis* co-ordination positions are available. The larger rate constant for NH_3 ($k_f = 7.0 \times 10^3$) than for $EtNH_2$ (1.5×10^3 l mol^{-1} s^{-1}) indicates considerable S_N2 character for these reactions and the much longer relaxation times observed for glycine or *dl*-alanine addition are interpreted in terms of a chelation step which is hindered by a structural reorganization of the co-ordination sphere of the metal.

In a temperature-jump study using a pulsed neodymium laser, Creutz and Sutin[65] were able to study the interconversion between the low-spin planar ($^1A_{1g}$) and high-spin octahedral ($^3A_{2g}$) forms of the nickel(II) complex of (17). The relaxation time was 0.30 μs at 23 °C and was, as expected, independent of the concentration of the complex.

The significant effect[26] exerted by certain polyelectrolytes on the kinetics of formation of nickel(II) complexes, even with neutral ligands, has already been

[64] D. T. Farrar, J. E. Stuehr, A. Moradi-Araghi, F. L. Urbach, and T. G. Campbell, *Inorg. Chem.*, 1973, **12**, 1847.
[65] C. Creutz and N. Sutin, *J. Amer. Chem. Soc.*, 1973, **95**, 7177.



(16)

$NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$

(17)

reported. It is suggested[26] that the interaction between the hydrophobic residues on the polyelectrolytes (present in the inner sphere of the metal) and the incoming aromatic ligands phen, bipy, and pada leads to enhanced values of k_f. Similar enhancements have been reported[66] when the bound ligand is a comparatively small aromatic or heterocyclic ligand. The results (Table 9) suggest that the rate enhancements are due to ligand association prior to the water-substitution process. In addition, the 'stacking interaction' will assist the substitution process only if the incoming

Table 9 *Formation rate constants*[a] *and rate enhancements due to stacking interactions*

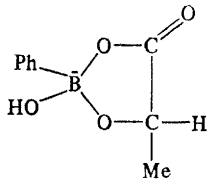
Complex	*Ligand*	k_f/l mol^{-1} s^{-1}	*Rate enhancement*
$[Ni(phen)]^{2+}$	NH_3	1.5×10^3	1.0
	benzylamine	1.53×10^3	1.7
	phen	3×10^3	0.8
	bipy	3.70×10^4	23
	Me_2bipy	1.58×10^5	52
	pada	9.64×10^4	70
	terpy	1.00×10^5	65
	(11)	1.29×10^5	63
$[Ni(terpy)]^{2+}$	pada	4.45×10^5	190
	bipy	2×10^4	7
	terpy	2.76×10^5	106
$[Ni(bipy)]^{2+}$	terpy	5.60×10^4	23
	pada	5.25×10^4	24
$[Ni(5\text{-Mephen})]^{2+}$	terpy	1.75×10^5	108
$[Ni(3,4,7,8\text{-Me}_4\text{phen})]^{2+}$	terpy	1.12×10^6	543
	pada	1.38×10^6	744
	(11)	5.8×10^6	2110
$[Ni(phen)]^{2+}$	NH_3	1.01×10^3	—
	terpy	4.83×10^3	*ca.* 4.8
$[Ni(3,4,7,8\text{-Me}_4\text{phen})]^{2+}$	terpy	2.53×10^4	*ca.* 19

[a] Data, from ref. 66, refer to 25 °C and, generally, 0.1 mol l^{-1} ionic strength.

ligand is sufficiently flexible to permit one donor group to become oriented in a position suitable for replacing a co-ordinated water molecule while the rest of the molecule is in a stacked arrangement. As expected, the larger the area of interaction between the stacking molecules the greater is the formation rate constant.

The complex between phenylboronic acid and lactic acid (18) is formed[67] by the reaction of $PhB(OH)_2$ with fully protonated lactic acid (k_f = 140 l mol^{-1} s^{-1} at

[66] G. R. Cayley and D. W. Margerum, *J.C.S. Chem. Comm.*, 1974, 1002.
[67] S. Friedman, B. Pace, and R. Pizer, *J. Amer. Chem. Soc.*, 1974, **96**, 5381.

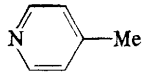
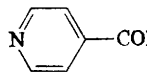
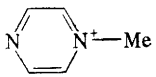


(18)

25 °C) or its anion (k_f = 1500 l mol^{-1} s^{-1}). It is suggested that an interaction of the electron-rich carboxylate anion with the phenyl ring in $PhB(OH)_2$ is the origin of the higher rate constant in the latter case.

The formation of some pentacyanoferrate(II) complexes of aromatic heterocycles has been followed[68] by the stopped-flow method. In the presence of excess ligand, varied over a large range of concentrations, each reaction was found to obey the rate law $d[Fe(CN)_5L^{n-}]/dt = k_f[Fe(CN)_5(H_2O)^{3-}][L]$, and the kinetic parameters (in particular $\Delta S^{\ddagger}$: see Table 10) are interpreted in terms of an S_N1 mechanism. A

Table 10 *Kinetic parameters*[a] *for formation and dissociation of complexes of* $Fe(CN)_5$

Ligand	$10^{-2}k_f$/ l mol^{-1} s^{-1}	$\Delta H_f^{\ddagger}$/ kcal mol^{-1}	$\Delta S_f^{\ddagger}$/ cal K^{-1} mol^{-1}	10^4k_d/ s^{-1}	$\Delta H_d^{\ddagger}$/ kcal mol^{-1}	$\Delta S_d^{\ddagger}$/ cal K^{-1} mol^{-1}
	3.60	15.1	4	11.5	24.0	9
	3.65	16.1	7	11.0	24.8	11
	2.96	15.8	6	7.3	26.0	14
	3.80	15.4	5	4.2	26.4	14
	5.50	16.8	10	2.8	27.5	18

[a] Data, from ref. 68, refer to 25 °C.

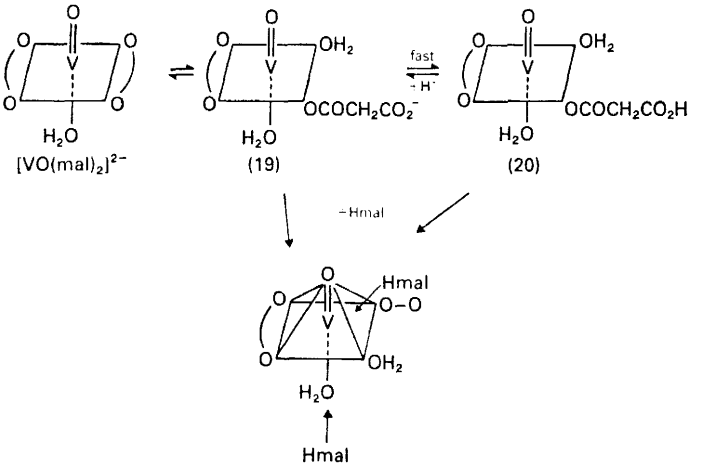
similar mechanism is proposed[69] for the reaction of $[Fe(CN)_5H_2O]^{3-}$ with DMSO. A kinetic study on the formation of a series of ternary complexes between bipy and substituted manganese(II) provides further evidence[70] that the bound ligand generally has little influence with this metal.

The associative character of the substitution reactions of MeHgOH has already

[68] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039, 2080.
[69] H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, 1973, **12**, 2084.
[70] D. N. Hague and S. R. Martin, *J.C.S. Dalton*, 1974, 254.

been noted,[71] but Geier and Erni have recently pointed out,[72] in a preliminary note, that there is a striking analogy between these and proton-transfer reactions regarding the relationship between the rate constants and the pK_a of the incoming ligand.

The kinetics of malonate exchange on $[VO(mal)_2]^{2-}$ are consistent[73] with the mechanism shown in Scheme 5. The first step is the dissociation of one of the chelate rings to form the intermediate (19), in which one of the two malonate ions in equatorial positions is co-ordinated as a unidentate ligand. In acidic solution, (19)



Scheme 5

may become protonated to form (20). Then, (19) and (20) {which are analogous in structure to $[VO(gly)]^+$ and $[VO(Hgly)]^{2+}$, respectively} can accept the attack of $Hmal^-$ from the axial position or the position above the triangular face of the tetragonal pyramid structure, as has been suggested in the chelation of $[VO(gly)]^+$. The activation parameters for the acid-independent and acid-catalysed paths are very close; they are, respectively, $\Delta H^{\ddagger} = 8.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -16.2$ cal K^{-1} mol^{-1} and $\Delta H^{\ddagger} = 8.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -13.5$ cal K^{-1} mol^{-1}.

There have been several reports concerning studies of ligand-exchange reactions involving multidentate ligands, including those detailed in references 74—82.

[71] M. Eigen, G. Geier, and W. Kruse, 'Essays in Coordination Chemistry', *Experientia*, Suppl. IX, Birkhäuser, Basel, 1964, p. 164.
[72] G. Geier and I.W.Erni, *Chimia* (*Switz.*), 1973, **27**, 635.
[73] H. Tomiyasu, S. Ito, and S. Tagami, *Bull. Chem. Soc. Japan*, 1974, **47**, 2843.
[74] H. Hauer, G. R. Dukes, and D. W. Margerum, *J. Amer. Chem. Soc.*, 1973, **95**, 3515; W. C. Crouse and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 1437.
[75] R. K. Steinhaus and R. L. Swann, *Inorg. Chem.*, 1973, **12**, 1855; R. K. Steinhaus and C. L. Barshun, *ibid.*, 1974, **13**, 2922.
[76] E. J. Billo, *Inorg. Chem.*, 1973, **12**, 2783.
[77] M. Kodama and K. Hagiya, *Bull. Chem. Soc. Japan*, 1973, **46**, 3151; M. Kodama, *ibid.*, 1974, **47**, 1430.
[78] M. S. Haque and M. Kopanica, *Bull. Chem. Soc. Japan*, 1973, **46**, 3072.
[79] H. Ogino, T. Watanabe, J. J. Chung, and N. Tanaka, *Bull. Chem. Soc. Japan*, 1973, **46**, 2460.
[80] A. D. Zuberbühler and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1897.
[81] N. R. Larsen and A. Jensen, *Acta Chem. Scand.*, 1974, **A28**, 638.
[82] G. K. Pagenkopf, *Inorg. Chem.*, 1974, **13**, 1591.

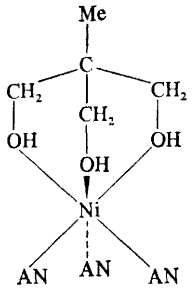
Reactions in Non-aqueous Solvents.—Lincoln and West[83] have determined the kinetic parameters for the exchange of acetonitrile in a series of substituted nickel(II) species which were chosen so that the relative effects of oxygen- and of primary- and tertiary-nitrogen-binding could be assessed. The complexes are shown in structures (21)—(25) (AN = acetonitrile) and the results in Table 11. The 555-fold variation

Table 11 *Kinetic parameters*[a] *for acetonitrile exchange at* Ni^{II}

Complex	*No. of equivalent sites for* AN	$10^{-3}k_{ex}/s^{-1}$	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Ni(AN)_6]^{2+}$	6	2.0	16.4	12.0
(21)	3	1.0	15.9	8.7
(22)	3	555	9.3	−0.9
(23)	2	180	12.0	5.4
(23)	1	<1		
(25)	1	165	10.8	1.4
(25)	1	>2000		
(24)	1	40	12.0	2.8
(24)	1	~2		

[a] Data, from ref. 83, refer to 25 °C.

of acetonitrile lability in the stereochemically similar (21) and (22) is explicable in terms of electron donation to (and consequent reduction of charge on) nickel(II) by the NH_2 co-ordinating groups, which causes a considerable labilization of acetonitrile in contrast to the OH co-ordinating groups which appear to reduce lability {if the data for $[Ni(MeCN)_6]^{2+}$ are taken as a reference}. The parameters characterizing the single observed exchange process in (23) indicate that such labilization is a



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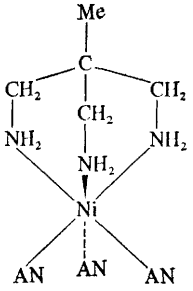

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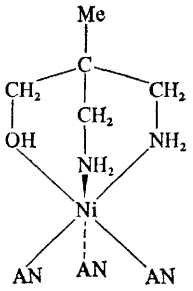

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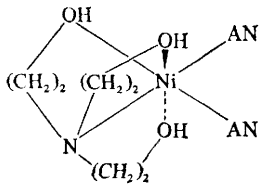

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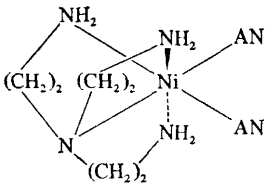


(25)

[83] S. F. Lincoln and R. J. West, *J. Amer. Chem. Soc.*, 1974, **96**, 400.

function of all the co-ordinating groups of the multidentate ligand. In the case of (25) the two distinct exchange processes observed are indicative of a directional character in the labilization induced by the multidentate ligand, and there is substantial evidence that the acetonitrile *trans* to the NH_2 group is the more labile. Similarly, the two exchange processes observed in (24) indicate a directional labilizing influence and, as observed in the terdentate ligand systems, the magnitudes of the exchange parameters are a function of all the co-ordinating groups. The authors conclude that the labilizing effects of the co-ordinating groups (at 25 °C) decrease in the order $-NH_2 > -N\equiv > -OH \approx -NCMe$.

Structural interconversions of dichloro-1,1,7,7-tetraethyldiethylenetriaminenickel(II) ($NiLCl_2$) in acetonitrile have been studied[84] by relaxation methods in which the equilibria were suddenly perturbed by an electric-field jump or by means of a pulse of radiation from a *Q*-switched neodymium laser. The results are interpreted in terms of the mechanism

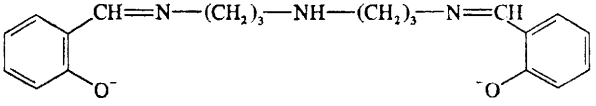
$$[NiLCl_2] \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [NiLCl]^+ \| Cl^- \overset{k_{23}}{\underset{k_{32}}{\rightleftharpoons}} [NiLCl]^+ + Cl^-$$

where the intermediate is an outer-sphere complex. Values for the rate constants k_{21} and k_{32} were estimated to be 7×10^5 s^{-1} and 2×10^9 l mol^{-1} s^{-1}, respectively, at 20 °C.

The exchange processes involving the five-co-ordinate nickel(II) complex of 2,6-lutidine 1-oxide[85] and the tributylphosphine adduct of bis(diethyldithiophosphato)-nickel(II) in benzene[86] both appear to be dissociative in character.

The kinetic parameters for the exchange of pyridine in *trans*-$[M(acac)_2(py)_2]$ complexes, where M is cobalt(II) [k_{ex}(298 K) = 1.5×10^6 s^{-1}, $\Delta H^{\ddagger}$ = 28 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = -33 J K^{-1} mol^{-1}] or nickel(II) [k_{ex}(298 K) = 9.8×10^4 s^{-1}, $\Delta H^{\ddagger}$ = 42 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = -9 J K^{-1} mol^{-1}] are discussed[87] in terms of a solvent-exchange model involving solvent interactions outside the first co-ordination sphere in the activation process.

Kildahl and Drago[88] have compared the enthalpy of formation of the adduct of 4-methylpyridine (4-Mepy) with the Ni^{II} complex of (26) and the activation enthalpy



(26)

for the exchange reaction, *viz.*

$$[Ni(26)(4\text{-Mepy})] + 4\text{-Mepy}^* \rightleftharpoons [Ni(26)(4\text{-Mepy}^*)] + 4\text{-Mepy}$$

in the solvents methylene chloride and toluene. They found that in both solvents the activation enthalpy is substantially larger than the enthalpy of adduct formation, the difference being 3.0 kcal mol^{-1} in CH_2Cl_2 and 1.4 kcal mol^{-1} in toluene, and conclude that this provides some of the best evidence to date for the existence of a stable

[84] H. Hirohara, K. J. Ivin, J. J. McGarvey, and J. Wilson, *J. Amer. Chem. Soc.*, 1974, **96**, 4435.
[85] P. M. Enriquez and S. S. Zumdahl, *Inorg. Chem.*, 1973, **12**, 2475.
[86] D. A. Sweigart and P. Heidtmann, *J.C.S. Chem. Comm.*, 1973, 556.
[87] S. F. Lincoln, *J.C.S. Dalton*, 1973, 1896.
[88] N. K. Kildahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1973, **95**, 6245.

intermediate in the dissociative pathway. The 1.6 kcal mol^{-1} discrepancy in the differences in the two solvents is discussed in terms of differing degrees of solvent participation in the kinetic process. The first-order exchange rate constants are *ca.* 10^7 s^{-1} at 25 °C.

The rate parameters for the exchange of acetonitrile on the high-spin cobalt(II) analogues of (21) and (24) have been reported,[89] together with those for low-spin $[Co(9a)(MeCN)_n]^{2+}$ (where *n* is considered to be 1 or 2). The rate constants are, respectively, 2.3×10^5 s^{-1} at 298 K, $\geqslant 2 \times 10^6$ s^{-1} at 223 K, and $\geqslant 8 \times 10^6$ s^{-1} at 266 K. $\Delta H^{\ddagger}$ for Co(21) is 40 kJ mol^{-1} and $\Delta S^{\ddagger} \approx 10$ J K^{-1} mol^{-1}. A single acetonitrile exchange process on $[Co(diap)(MeCN)_3]^{2+}$ [diap = 2,2-di(aminomethyl)-propan-1-ol] in acetonitrile solution is observed[90] in the temperature range 221—315.6 K. On the assumption that this process characterizes the two equivalent acetonitrile sites the following parameters have been derived: $k_{ex}(298\ K) = 4.5 \times 10^6$ s^{-1}, $\Delta H^{\ddagger} = 31$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -14$ J K^{-1} mol^{-1}, where the exchange rate is given by $2k_{ex}[Co(diap)(MeCN)_3^{2+}]$.

Clear evidence for the operation of the kinetic *trans* effect has been found[91] in $[Co(MeOH)_5py]^{2+}$ in that the *trans*-site exchange rate constant per co-ordinated methanol molecule (1200 s^{-1} at −30 °C) is 2.5—3.0 times that for the *cis* site (410 s^{-1}). The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are, respectively, 11.9 kcal mol^{-1} and 2.9 cal K^{-1} mol^{-1} for the *cis* site and 11.2 kcal mol^{-1} and 2.9 cal K^{-1} mol^{-1} for the *trans* site.

In a preliminary note, evidence is produced[92] that the acetate ion in the second co-ordination sphere of $[Co(MeOH)_5(O_2CMe)]^+$ appreciably enhances the methanol exchange rate relative to that for the non-ion-paired complex.

Kinetic parameters have been determined[93] for the exchange of acetonitrile on several complexes of copper(II). In $[Cu(MeCN)_6]^{2+}$, k_{ex} is $\geqslant 1.6 \times 10^7$ s^{-1} at 228 K, but the value is very much lower in the Cu^{II} analogues of (25) (5.1×10^3 s^{-1}) and (24) (8.0×10^4 s^{-1}) and in the hexa-*N*-methyl derivative of the analogue of (25) ($< 10^2$ s^{-1}). It is suggested that the reduction in lability on co-ordination of multidentate ligands is due to the elimination of an exchange pathway in which the dynamic Jahn–Teller effect can be invoked. [It should be noted that the co-ordination number of the metal in the copper(II) analogue of (25) and its hexa-*N*-methyl derivative is five rather than six.]

The rates of several substitution reactions at palladium(II) have been measured[94] in methanol. For *trans*-$[PdL_2(NO_2)_2] + Y^- \rightarrow$ *trans*-$[PdL_2(NO_2)Y] + NO_2^-$, where L = PPr^n_3, $AsEt_3$, or piperidine and Y^- = Cl^-, N_3^-, Br^-, I^-, SCN^-, or $(NH_2)_2CS$, a set of nucleophilic reactivity constants $n_{Pd}^0 = \log(k_2[MeOH]/k_1)$ has been calculated, where k_1 and k_2 refer to rate constants for the solvolytic path and for direct nucleophilic attack on the complex *trans*-$[Pd(PPr^n_3)_2(NO_2)_2]$. All the complexes studied obey the linear free-energy relation $\log k_2 = sn_{Pd}^0 + \log k_1$, where *s* is a nucleophilic discrimination factor. The n_{Pd}^0 sequence resembles that already found for platinum(II) complexes.

[89] S. F. Lincoln and R. J. West, *Austral. J. Chem.*, 1974, **27**, 97.
[90] S. F. Lincoln, *Austral. J. Chem.*, 1974, **27**, 899.
[91] K. Plotkin, J. Copes, and J. R. Vriesenga, *Inorg. Chem.*, 1973, **12**, 1494.
[92] J. Kurtz and J. R. Vriesenga, *J.C.S. Chem. Comm.*, 1974, 711.
[93] R. J. West and S. F. Lincoln, *J.C.S. Dalton*, 1974, 281.
[94] M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 490.

5
Solvent Effects

BY J. BURGESS

The aims and coverage of this chapter are similar to those of the analogous chapters in Volumes 1 and 3. Reactions in pure, *i.e.* single, solvents and in mixed solvents are dealt with in the first and second sections. The final section includes references to non-classical effects of electrolytes on rates of reactions in aqueous salt solutions. Within each section two aspects of solvent effects on reactivities are covered. The first is the use of reactivity trends in various solvents or solvent mixtures for the diagnosis of mechanisms of substitution. This remains a popular exercise despite the numerous hazards in interpretation. The second is the understanding of reactivities in terms of the established properties of the solvents and their interactions with the initial and transition states. References which merely state kinetic results in non-aqueous or mixed solvents are in general not included. Insofar as such references concentrate on the compound rather than the solvent they are more appropriately mentioned elsewhere in this Report.

1 Pure Solvents

Substitution and Solvolysis.—*Isotope Effects.* Hydroxylamine-*O*-sulphonate, $H_2NOSO_3^-$, reacts with thiosulphate to give the $H_2NSSO_3^-$ anion and then tetrathionate ($S_4O_6^{2-}$), and with thiourea to give the novel $(H_2N)_2CSNH_2^+$ cation. Both reactions conform to second-order rate laws and have negative activation entropies. This kinetic evidence and product characterization suggest a bimolecular mechanism, of S_N2 attack at the nitrogen atom. The ratios of the rate constants (k_H/k_D) for these reactions in H_2O and in D_2O are 1.12 for thiosulphate and 1.07 for thiourea. The similarity between these values is consistent with a common S_N2 mechanism for the two substitutions.[1] Further reactions of hydroxylamine-*O*-sulphonate, in mixed aqueous media, are mentioned below.

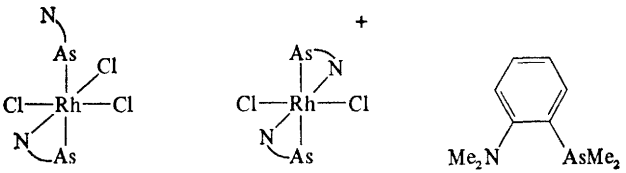
Rate constants for alkaline hydrolysis of adducts R_2NHBH_2CN are 60—70% lower in H_2O than in D_2O. This, and other, evidence is consistent with a mechanism in which there is rapid reversible loss of the proton from the nitrogen followed by rate-determining decomposition of the conjugate base thus produced. If, as seems likely, the second step is dissociative in character, then these reactions are exactly analogous to S_N1cb base hydrolysis of cobalt(III) ammine-halide complexes. Compelling evidence to support the conjugate-base mechanism for base hydrolysis of these R_2NHBH_2CN compounds is provided by the very slow, and hydroxide-concentration-independent, rates of base hydrolysis of R_3NBH_2CN adducts which

[1] P. F. Blanchet and J. H. Krueger, *Inorg. Chem.*, 1974, **13**, 719.

have no acidic proton on the nitrogen (*e.g.* when R_3N = Me_3N or *N*-methylmorpholine). Activation enthalpies for base hydrolysis of morpholine cyanoborane are 21.5 kcal mol^{-1} in H_2O and 19.6 kcal mol^{-1} in D_2O; activation entropies are +9.4 and +3.8 cal deg^{-1} mol^{-1}, respectively.[2]

Non-aqueous Solvents. The electronic effects of ligands L = NO_2, N_3, CN, Cl, or NCS on reactivities of *trans*-$[Co(en)_2LCl]^+$ cations in methanol and in water have been compared. In fact the effects of the named ligands are very similar in the two solvents, on solvolysis, ligand replacement, or base hydrolysis.[3]

The kinetics of both the forward and the back reactions of the equilibrium (1)⇌(2) + Cl^- [the ligand N⌒As is shown separately as (3) for the sake of clarity] have been studied in a range of solvents. The rate constant for (1)→(2) + Cl^- increases sharply as the polarity of the solvent increases, for solvents methanol,



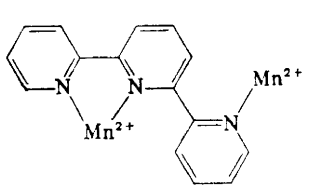
(1) (2) (3)

ethanol, and propan-1- and -2-ol. Such a rate trend is the opposite of that observed in solvolysis of rhodium(III) or cobalt(III) ammine- or amine-halide complexes, and moreover is characterized by an unusually high Grunwald–Winstein *m* value (*cf.* mixed-solvent section below) of +1.3. Rate constants for the reverse reaction, (2) + Cl^-→(1), vary by only a few per cent over the solvent range examined. This small effect is thought to represent a balance between solvent effects on the ionization of the lithium chloride reagent and on the formation constant for the ion-pair intermediate in the proposed $S_N1(ip)$ (I_d) mechanism.[4]

Formation.—The Eigen–Wilkins mechanism for formation reactions of metal complexes in solution involves equilibrium pre-association of the solvento-metal cation and the potential ligand, followed by a rate-determining interchange step in which a molecule of co-ordinated solvent is replaced by the ligand molecule. For the majority of 2+ cations, the interchange step is thought to be dissociative in character, from comparisons of estimated interchange rate constants with experimentally determined rate constants for solvent exchange at the metal ion in question. It is normally tacitly assumed that the rate of solvent exchange with the solvento-cation would be the same, or at least closely similar, in an ion-pair of the type involved as intermediates in the Eigen–Wilkins mechanism for complex formation. The effect of ion-pairing on solvent exchange rates has now been reported for methanol exchange at the $[Co(MeOH)_5(OAc)]^+$ cation. Addition of free acetate enhances methanol exchange rates by a factor of up to about two. This comfortingly modest rate change was monitored by n.m.r. spectroscopy, which also provided evidence of interaction between the added acetate anions and solvating methanol molecules.[5]

[2] C. Weidig, S. S. Uppal, and H. C. Kelly, *Inorg. Chem.*, 1974, **13**, 1763.
[3] Z. Bradić, M. Biruš, D. Pavlović, M. Pribanić, and S. Ašperger, *J.C.S. Dalton*, 1973, 2514.
[4] A. Peloso and L. Volponi, *J.C.S. Dalton*, 1974, 278.
[5] J. Kurtz and J. R. Vriesenga, *J.C.S. Chem. Comm.*, 1974, 711.

2,2′-Bipyridyl has long been a popular ligand for use in kinetic studies of formation reactions. Its kinetic behaviour in complex formation in aqueous solution appears to be normal, involving rate-determining interchange followed by rapid ring closure to give the chelate product. However, evidence is now accumulating that in non-aqueous media the ring-closure step may be rate-limiting. Bennetto and Caldin[6] in 1971 ascribed the anomalously low rate of formation of $[Ni(bipy)]^{2+}$ in DMSO to the particular properties of this solvent and their influence on the Eigen–Wilkins mechanism. But in the same year Dickert and Hoffmann[7] found that the reactions of Ni^{2+} with thiocyanate or chloride in DMSO took place more rapidly, at rates approximating to that for solvent exchange. The Ni^{2+} plus thiocyanate results have recently been confirmed by a pressure-jump study of the kinetics in DMSO.[8] Reactions of Ni^{2+} with bidentate 2-aminopyridines in DMSO have rate constants in the range $2.1—5.4 \times 10^3$ l mol s^{-1} (at 25 °C), which are consistent with the rate-determining ligand interchange of the Eigen–Wilkins mechanism. But rates of reaction with 2,2′-bipyridyl or with 2,2′,2″-terpyridyl are much lower, 0.069 and 0.026 l mol s^{-1} respectively, indicating rate-determining ring closure for these latter two ligands. Presumably the greater steric demands of these ligands make the competition of the second (or third) nitrogen with solvent DMSO much less effective here. Interestingly, the activation parameters for the Ni^{2+} plus 2-aminopyridines reactions in DMSO do not compare comfortably with those for solvent exchange. This may mean that ring closure becomes rate-limiting at some temperatures within the ranges studied.[9] It thus now seems that the balance between rate-determining interchange on loss of the first co-ordinated solvent molecule and rate-determining ring closure is controlled by the nature of the solvent. Earlier discussions of the role of the solvent in determining reactivities for transition-metal cations with 2,2′-bipyridyl or with 2,2′,2″-terpyridyl must therefore, when they assume the Eigen–Wilkins mechanism to operate under all conditions of solvent composition, be read with caution. The reaction of Mn^{2+} with 2,2′,2″-terpyridyl, again in DMSO, occurs in two kinetically distinct steps. The first has a rate constant similar to that for solvent exchange at Mn^{2+} and is thought to produce a dinuclear intermediate (4). The second step is very much slower, having a half-life of several hours. This is thought to be the conversion of (4) into the mononuclear $[Mn(terpy)]^{2+}$ product.[10]



(4)

Early investigators of the kinetics of the reaction of Fe^{3+}_{aq} with thiocyanate ion in aqueous solution were unable to choose between a dissociative and an associative

[6] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2190, 2198.
[7] F. Dickert and H. Hoffmann, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 1320.
[8] J. Williams, S. Petrucci, B. Sesta, and M. Battistini, *Inorg. Chem.*, 1974, **13**, 1968.
[9] D. M. W. Buck and P. Moore, *J.C.S. Dalton*, 1974, 2082.
[10] D. M. W. Buck and P. Moore, *J.C.S. Chem. Comm.*, 1974, 60.

mechanism. A subsequent demonstration that the reaction of Fe^{3+} with thiocyanate in methanol was more rapid than the analogous reaction in water could be explained by a bigger equilibrium constant for the pre-interchange association of the ions or by faster interchange arising from weaker iron to methanol bonding.[11] The methanol *vs.* water reactivity comparison did not establish the nature of the mechanism in either solvent. Now, following Parker's approach[12] to the connection between reactivities and solvent activity coefficients, particularly for substitution at cobalt(III) and platinum(II), Devia and Watts have analysed the kinetics of reaction of Fe^{3+} with thiocyanate in DMSO. As small anions tend to have much bigger chemical potentials in dipolar aprotic solvents, one would expect that a bimolecular, associative reaction with thiocyanate would go much faster in DMSO than in water. In fact this reaction is slower in DMSO than in water. This observation, along with the positive activation entropy of $+38$ cal deg^{-1} mol^{-1} and the dependence of rate constant on ionic strength found, indicate a dissociative-interchange mechanism here.[13] The activation parameters for this formation reaction differ more than would be expected from those for solvent exchange at Fe^{3+}, even allowing for their inclusion of the enthalpy and entropy of ion association and for the slightly different reactivity of an ion-pair from its parent ion {*cf.* methanol exchange at $[Co(MeOH)_5(OAc)]^+$ above[5]}.

Exchange Reactions.—Fluorine exchange, monitored by ^{18}F labelling, between alkali-metal fluorides and carbonyl fluoride is faster in acetonitrile, and much faster in diglyme, than in benzene or dimethyl ether. Although interpretation is complicated by the parallel homogeneous and heterogeneous exchange which is a consequence of the low solubilities of the alkali-metal fluorides, and by extensive ion aggregation, there is no doubt that the high dielectric constants and generally good solvating properties of acetonitrile and diglyme determined the observed higher reactivities in these media.[14]

Isomerization and Racemization.—The kinetics of isomerization of the trifluoroacetylacetone complex $[Cr(tfac)_3]$ in the gas phase are said to be rather similar to those in solution. The authors therefore suggest that the role of the solvent in determining isomerization rates for this type of complex is less significant than usually thought.[15] However, this point of view should be considered in conjunction with an earlier report that the activation energies for isomerization of $[Cr(tfac)_3]$ in the very similar solvents toluene and 1,2,4-trimethylbenzene differ by at least 3 kcal mol^{-1}.[16] The likely mechanism for this isomerization in the gas phase is a twisting process, in view of the high barrier to breaking chromium(III)–oxygen bonds. The modestly negative activation entropies, of -5.5 and -17.0 cal deg^{-1} mol^{-1} for *cis*→*trans* and *trans*→*cis*, respectively, are not inconsistent with an intramolecular twist mechanism.[15]

The two mechanisms usually considered for isomerization and racemization of tris-bidentate complexes of the type $[M(LL)_3]^{n+}$ are an intramolecular twist or a process in which one or more bidentate ligands become unidentate at some inter-

[11] J. Bjerrum and R. Poulson, *Nature*, 1952, **169**, 463.
[12] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.
[13] D. H. Devia and D. W. Watts, *Inorg. Chim. Acta*, 1973, **7**, 691.
[14] C. J. W. Fraser, D. W. A. Sharp, G. Webb, and J. M. Winfield, *J.C.S. Dalton*, 1974, 112.
[15] C. Kutal and R. E. Sievers, *Inorg. Chem.*, 1974, **13**, 897.
[16] R. Fontaine, C. Pommier, and G. Guiochon, *Bull. Soc. chim. France*, 1972, 1685.

mediate stage ('one-end-off' mechanism). A third possibility is that, in a strongly co-ordinating solvent, a molecule of the solvent may interact with the metal atom in the transition state or an intermediate. This possible, but as yet unobserved, mechanism has been christened the 'double-opposed-initiated-twist' and explored in a theoretical manner. It is a pathway which is distinguishable from the intramolecular twist or 'one-end-off' mechanisms for tris-complexes of asymmetric bidentate ligands.[17]

Two further reactions of this type in which the effects of solvent on reaction rates have been examined are the isomerization of $[Sn(acac)_2R_2]$ (R = Me or Ph)[18] and the racemization of the $[Si(acac)_3]^+$ cation.[19]

2 Mixed Solvents

Diagnosis of Mechanism.—*Competition.* In a solvent mixture which contains two (or more) 'good', *i.e.* potentially co-ordinating, solvents there will be competition for the transient intermediate in any reaction in which an intermediate of reduced co-ordination number is generated. Such an intermediate seems not to be involved in the normal uncatalysed aquation of cobalt(III) complexes of the amine-halide type, but may be generated in the relatively rapid catalysed solvolyses of halide complexes in the presence of mercury(II) and of azide complexes in the presence of nitrous acid. Results of competition experiments on nitrosation of the $[Co(NH_3)_5(N_3)]^{2+}$ and $[Co(NH_3)_5(O_2CNH_2)]^{2+}$ cations in aqueous acetonitrile or in aqueous DMSO suggest a common intermediate, presumed to be $[Co(NH_3)_5]^{3+}$. This study complements earlier competition studies in which anions rather than organic co-solvents were in competition with water for the proposed $[Co(NH_3)_5]^{3+}$ transient intermediate.[20] Competition studies, again involving anions competing with water, also indicate the intermediacy of $[Co(NH_3)_5]^{3+}$ in the NO^+-catalysed aquation of the newly characterized $[Co(NH_3)_5(NCO)]^{2+}$ cation.[21]

Dielectric Constant Correlations. There has been a resurgence of interest in the use of variations of rate constants with dielectric constants of aqueous solvent mixtures for the diagnosis of mechanisms of substitution. Most of the recently published papers have dealt with aquation of cobalt(III) bromide complexes, though two rhodium(III) chloride complexes have also been studied. The majority of investigations have involved plotting logarithms of rate constants against reciprocal dielectric constants and discussion of the slopes $[\partial \ln k/\partial(1/D)]$* of these plots. Values of $\partial \ln k/\partial(1/D)$, either taken directly from the literature or estimated graphically by the Reporter from the published kinetic results, are collected in Table 1.[22–28] The interpretation of

[17] D. L. Kepert, *Inorg. Chem.*, 1974, **13**, 2758.
[18] N. Serpone and R. Ishayek, *Inorg. Chem.*, 1974, **13**, 52.
[19] T. Inoue and K. Saito, *Bull. Chem. Soc. Japan*, 1973, **46**, 2417.
[20] D. A. Buckingham, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, 1974, **13**, 2165.
[21] D. A. Buckingham, D. J. Francis, and A. M. Sargeson, *Inorg. Chem.*, 1974, **13**, 2630.
[22] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Russ. J. Inorg. Chem.*, 1973, **18**, 838.
[23] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Russ. J. Inorg. Chem.*, 1973, **18**, 1296.
[24] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Russ. J. Inorg. Chem.*, 1973, **18**, 979.
[25] A. V. Ablov, A. A. Popova, and N. M. Samus', *Russ. J. Inorg. Chem.*, 1973, **18**, 1057.
[26] G. P. Syrtsova and T. S. Bolgar', *Russ. J. Inorg. Chem.*, 1973, **18**, 1438.
[27] G. P. Syrtsova and T. S. Bolgar', *Russ. J. Inorg. Chem.*, 1973, **18**, 1140.
[28] B. A. Bovykin, *Russ. J. Inorg. Chem.*, 1973, **18**, 1598.

* Occasionally $\partial \ln k/\partial[(D-1)/(2D+1)]$.

Table 1 *Slopes of* $\partial \ln k/\partial(1/D)$ *plots for substitution reactions of cobalt*(III) *and rhodium*(III) *halide complexes*

Complex	*Reaction*	$\partial \ln k/\partial(1/D)$	*Ref.*
cis-$[Co(en)_2(MeNH_2)Br]^{2+}$	aquation	−161	22
cis-$[Co(en)_2(Bu^nNH_2)Br]^{2+}$	aquation	−189	22
cis-$[Co(en)_2(PhNH_2)Br]^{2+}$	aquation	−32[a]	23
cis-$[Co(en)_2(py)Br]^{2+}$	aquation	−61[a]	23
cis-$[Co(en)_2(HOCH_2CH_2CH_2NH_2)Br]^{2+}$	aquation	−149	24
cis-$[Co(en)_2(HOCH_2CH_2NH_2)Br]^{2+}$	aquation/chelation	−77[a]	24
trans-$[Co(dmgH)_2(NCO)Br]^-$	aquation	−300	25
trans-$[Rh(dmgH)_2(SO_3)Cl]^{2-}$	aquation	−110	26
trans-$[Rh(dmgH)_2(NO_2)Cl]^-$	aquation	−160	27
trans-$[Rh(dmgH)_2(NO_2)(OH_2)]$	Cl^- substitution	~+100[a]	27
trans-$[Co(dmgH)_2(NO_2)(tu)]$	tu substitution	−85	28

[a] Poor correlation.

$\partial \ln k/\partial(1/D)$ plots and their slopes seems to be that a dissociative mechanism is characterized by a good linear correlation and a large negative slope, whereas an associative mechanism is characterized by a poorer correlation and a less negative or even positive slope. Authors generally, and wisely, try to provide some ancillary evidence, such as the value of the activation entropy or the dependence of rate constant on ionic strength or concentration of water present, to give some support to the mechanism diagnosis from the $\partial \ln k/\partial(1/D)$ plot slopes. In the case of the aquation of the complexes *cis*-$[Co(en)_2\{HO(CH_2)_nNH_2\}Br]^{2+}$, the difference in mechanism between the normal aquation of the complex with $n = 3$ and the intramolecular chelation reaction consequent on bromide loss for the complex with $n = 2$ is appropriately reflected in the respective $\partial \ln k/\partial(1/D)$ values.[24] The reaction which seems to fit least well into the pattern is that of *trans*-$[Co(dmgH)_2(NO_2)(tu)]$ with thiourea (tu), but here the leaving group (tu) is so different from the halide leaving groups in the other cases that direct comparisons of rate trends seem unwise.[28]

Other reactions for which the dependence of rate constants on dielectric constant for ranges of mixed aqueous solvents has been examined include the decomposition of the $[Cu(CN)_4]^{2-}$ anion,[29] the reaction of Ni^{2+} with the *NNN*-trimethylethylenediamine cation ($H_2NCH_2CH_2NMe_3^+$),[30] and the inner-sphere iron(II) reduction of the $[Co(NH_3)_5Br]^{2+}$ cation.[31] In the nickel(II) formation reaction, the primary interest was the role of the solvent dielectric properties in determining pre-interchange association constants. Plots of logarithms of rate constants for the iron(II) reduction against reciprocal dielectric constant, for a variety of aqueous alcohol solvent mixtures, are far from linear and indeed usually show extrema. These extrema are more marked at temperatures both higher (*e.g.* 36.8 °C, maxima) and lower (*e.g.* 11.9 °C, minima) than 25 °C. An isokinetic or compensation temperature in this region is apparently usual for systems in which solvent structural effects are important and in which solvating water molecules are released into bulk solvent.[32] The irregular behaviour observed in the present reaction does not seem unreasonable for a

[29] G. Nord and H. Matthes, *Acta Chem. Scand.*, 1974, **A28**, 13; O. Mønsted and J. Bjerrum, *ibid.*, 1967, **21**, 1116.
[30] Chin-Tung Lin and D. B. Rorabacher, *Inorg. Chem.*, 1973, **12**, 2402.
[31] R. Koren, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2341.
[32] R. Lumry and S. Rajender, *Biopolymers*, 1970, **9**, 1125.

process which in the present context can be considered as associative substitution at iron(II).

Grunwald–Winstein Analysis. Since Langford's estimation[33] of m values for the aquation of the *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(en)_2(NO_2)Br]^+$ cations from a Grunwald–Winstein analysis[34] of the variation of aquation rate constants in mixed aqueous solvents, there has been continuing interest in this method of diagnosing mechanisms of substitution at inorganic complexes.[35] Values of m of *ca.* 0.3 have normally been found for dissociative aquation of cobalt(III) ammine- or amine-halide complexes. Recently an m value of 0.32 has been obtained from kinetic measurements on the aquation of the *trans*-$[Co(en)_2Cl_2]^+$ cation in mixtures of water with methanol, ethanol, acetone, or dioxan containing up to 90% of the organic component.[36] This m value compares satisfactorily with those of 0.35 (ref. 37) and *ca.* 0.25 (ref. 33) reported earlier from studies in more restricted (water-rich) ranges of solvent composition. The m value for aquation of the *trans*-$[Co(en)_2(NO_2)Cl]^+$ cation is much smaller, at 0.09. This value may be compared with $m = 0.18$ for aquation of the *trans*-$[Co(en)_2(NO_2)Br]^+$ cation.[33] These low values, in other words low sensitivity of reaction rate to solvent composition variation, suggest less charge separation in the transition states. The authors[36] consider that the cobalt–chloride bond does not have to stretch so far in forming the transition state for aquation of the nitro-chloro-complex as does the cobalt–chloride bond in the case of aquation of the dichloro-complex. Incoming water is thought to assist to a greater extent in the aquation of the former complex. In other words, the electron-withdrawing nitro-group is encouraging water–cobalt interaction in the transition state, giving the process rather more associative character.

Close inspection of mY plots for aquation of metal ammine- or amine-halide complexes reveals that there is some pattern in the (relatively small) scatter of points about the best straight line. Usually rate constants for acetone–water mixtures lie on the opposite side of the line from those for alcohol–water mixtures; the rate constants for aquation in acetone–water mixtures vary slightly less with solvent Y values than expected. It is possible to accommodate this pattern by the use of a more sophisticated equation, such as that [equation (1)] established for organic reactions.[38]

$$\log k/k_0 = lN + mY \qquad (1)$$

Here the lN term permits allowance to be made for the nucleophilicity (N) of the solvent. The kinetics of aquation of the *trans*-$[Co(1,3\text{-diaminopropane})_2Cl_2]^+$ cation in mixtures of water with methanol, ethanol, or acetone can be analysed successfully according to equation (1): values of m are 0.36, 0.34, and 0.17, respectively.[39] It has also been found that earlier results[37,40] on similar complexes, *e.g.*

[33] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.
[34] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.
[35] See, for example, pp. 202—203 of Volume 1, pp. 150—151 of Volume 2, and pp. 322—323 of Volume 3.
[36] M. Pribanić, M. Biruš, D. Pavlović, and S. Ašperger, *J.C.S. Dalton*, 1973, 2518.
[37] J. Burgess and M. G. Price, *J.C.S. Dalton*, 1971, 3108.
[38] See, for example, A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1608; T. W. Bentley, F. L. Schadt, and P. von R. Schleyer, *ibid.*, 1972, **94**, 992.
[39] G. Thomas and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1974, 1688.
[40] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2703.

the *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ and $[Co(NH_3)_5Cl]^{2+}$ cations, can also be accommodated more successfully by equation (1) than by the simple Grunwald–Winstein expression, equation (2). The *trans*-[Co(1,3-diaminopropane)$_2$Cl$_2$]$^+$ cation was

$$\log k/k_0 = mY \qquad (2)$$

chosen for the recent work, in preference to the previously favoured *trans*-$[Co(en)_2Cl_2]^+$ cation, since the six-membered chelate rings in the former are likely to encourage dissociative activation in the rate-determining step.[39]

Whereas Grunwald–Winstein analysis of kinetic results for aquation of ammine or amine complexes of transition metals often seems to work satisfactorily when the leaving group is a halide ion, it seems to break down for other leaving groups. This has been found previously for thiocyanate leaving from chromium(III).[41] It has now been similarly found for the aquation of the $[Co(NH_3)_5(DMSO)]^{3+}$ cation,[42] where not only is the leaving group very different from chloride in its chemical composition but it is also uncharged.

The kinetic results discussed in an earlier section on the effect of dielectric constant on reactivity[22–28] can also be analysed by the Grunwald–Winstein method. In fact mY plots constructed from the reported rate constants are curved for the *cis*-$[Co(en)_2(amine)Br]^{2+}$ complexes listed in Table 1. Approximate m values, estimated from the results in water-rich mixtures, range from 0.2 to 0.45. They seem to cover a somewhat greater range than those for similar chlorocobalt(III) complexes, though they are distributed about a similar mean ($m \sim 0.3$ for Co^{III}—Cl aquation, see above). A more detailed analysis of the results using equation (1) might prove more fruitful. Better mY plots, both straighter and with less scatter, were obtained for the dimethylglyoximate complexes mentioned in Table 1; the respective m values are listed in Table 2. Values of Y for ethanol–water mixtures were interpolated (a weight composition to volume composition conversion is needed) from the Y value tabulation of a standard source.[34] For glycol–water mixtures Y values were estimated* from kinetic data on the solvolysis of t-butyl chloride in water[43] and in glycol–water mixtures.[44]

Table 2 *Grunwald–Winstein m values for reactions of cobalt*(III) *and rhodium*(III) *dimethylglyoximate complexes*

Complex	*Reaction*	*Co-solvents*	*m*	*Ref.*
trans-$[Co(dmgH)_2(NCO)Br]^-$	aquation	ethanol, glycol	*ca.* 0.3[a]	25
trans-$[Co(dmgH)_2(NO_2)(tu)]$	substitution of NO_2 by tu	ethanol, glycol	0.21	28
trans-$[Rh(dmgH)_2(NO_2)Cl]^-$	aquation	ethanol, glycol	0.32	27
trans-$[Rh(dmgH)_2(SO_3)Cl]^{2-}$	aquation	ethanol	0.22	26

[a] Curved plot; cited m value applies to water-rich mixtures.

[41] J. Burgess, *J.C.S. Dalton*, 1973, 825.
[42] W. L. Reynolds, M. Biruš, and S. Ašperger, *J.C.S. Chem. Comm.*, 1973, 822; *J.C.S. Dalton*, 1974, 716.
[43] E. A. Moelwyn-Hughes, R. E. Robertson, and S. Sugamori, *J. Chem. Soc.*, 1965, 1965.
[44] M. J. Blandamer and J. R. Membrey, unpublished observations.

* Values of Y of 3.28, 3.08, 2.90, 2.78, and *ca.* 2.6 for mixtures containing 10, 20, 30, 40, and 50% respectively by weight of glycol were estimated by interpolation from the kinetic data.

Other Methods. Rates of hydrolysis of pyro- and tripoly-phosphates are greater in aqueous dioxan, and smaller in aqueous formic or acetic acids, than in water. As water molecules are more easily available for incorporation into the transition state in aqueous dioxan than in water, but less available in the strongly intermolecularly hydrogen-bonded aqueous carboxylic acids, the observed rate trends are consistent with a bimolecular mechanism for hydrolysis of these phosphates.[45]

The comparison of rates of reaction of hydroxylamine-*O*-sulphonate with thiosulphate or thiourea in H_2O and in D_2O has already been mentioned.[1] The kinetics of the reactions of hydroxylamine-*O*-sulphonate and its parent acid with iodide and with triphenylphosphine have been examined in mixtures of water with methanol[46] or DMSO.[47] DMSO was chosen as co-solvent for the main study as its ability to solvate such species as sulphate differs greatly from that of water. The determined rate laws suggest that triphenylphosphine reacts only with the hydroxylamine-*O*-sulphonate anion, but that iodide reacts with the anion and with the free acid in parallel. The acid appears to exist in solution as $H_3\overset{+}{N}OSO_3^-$ rather than as H_2N-OSO_3H. The mechanism for these, as for related, reactions of the hydroxylamine-*O*-sulphonate anion is thought to be nucleophilic substitution at the nitrogen.[47] The variation of rate constant with solvent composition, in DMSO–water mixtures, for the reaction of the *S*-methyl-*S*-phenylsulphinium cation $Me(Ph)SNH_2^+$,[48] like that of the *SS*-dimethylsulphinium cation $Me_2SNH_2^+$,[49] with iodide [equation (3), R^1 = Me, R^2 = Me or Ph] or with thiourea parallels the variation of the pK of the *m*-nitroanilinium ion. This supports the importance of the pre-equilibrium of equation (4) before the rate-determining step [equation (5)].

$$R^1R^2SNH_2^+ + 3I^- + 2H^+ \longrightarrow R^1R^2S + NH_4^+ + I_3^- \quad (3)$$

$$R^1R^2SNH_2^+ + H^+ \rightleftharpoons R^1R^2SNH_3^{2+} \quad (4)$$

$$R^1R^2SNH_3^{2+} + I^- \longrightarrow R^1R^2SI^+ + NH_3 \quad (5)$$

Rate constants for bromide exchange with the *cis*-$[Ru(NH_3)_4Br_2]^+$ cation vary little with solvent composition in methanol–water mixtures. There is a shallow minimum at a mole fraction of *ca.* 0.08 water. It is claimed that at higher mole fractions of water the mechanism involves rate-determining S_N2 attack by water, but that at lower mole fractions of water the mechanism is dissociative.[50] This is not the only recent example of a suggestion of a change of mechanism in going from water-rich to water-poor solvent mixtures. Another such example is afforded by the aquation of the *cis*-$[Co(en)_2(py)Br]^{2+}$ cation (see above).[23]

Formation of ternary complexes from the $[Ni(phen)(OH_2)_4]^{2+}$ cation is unusually rapid when the incoming ligand can associate itself with the co-ordinated phen molecule and still retain a free nitrogen atom in a suitable place for bonding to the

[45] M. Watanabe, *Bull. Chem. Soc. Japan*, 1974, **47**, 2048.
[46] J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, 1973, **12**, 2714.
[47] B. A. Sudbury and J. H. Krueger, *Inorg. Chem.*, 1974, **13**, 1736.
[48] J. H. Krueger and R. J. Kikoyane, *Inorg. Chem.*, 1974, **13**, 2522.
[49] J. H. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 4974.
[50] A. Ohyoshi, T. Shinohara, Y. Hosoyamada, T. Yamada, and Y. Hiroshima, *Bull. Chem. Soc. Japan*, 1973, **46**, 2133.

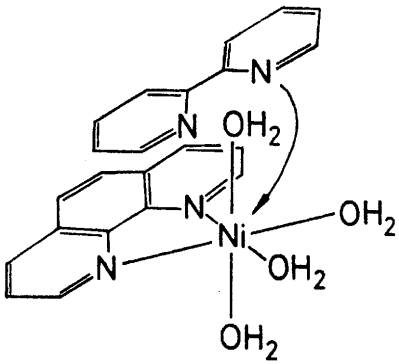


Figure *The association of the incoming ligand with the nickel(II) complex in the reaction of the* $[Ni(phen)(OH_2)_4]^{2+}$ *cation with 2,2′-bipyridyl*

nickel in an interchange step (Figure). Ligands such as bipy or terpy provide examples for such incoming ligands. The association or 'stacking' makes the value of the outer-sphere pre-interchange association constant for the Eigen–Wilkin mechanism very much larger than would normally be expected for a 2+ cation interacting with an uncharged incoming group. Thus the (second-order) formation rate constant is correspondingly larger than for the analogous reaction with, for instance, ammonia. This favourable interaction between the co-ordinated phen and the incoming ligand could arise from hydrophobic bonding or from polarization effects. The differences between the properties of water and of aqueous methanol have been used to distinguish between these two possibilities. The rate enhancements for ligands like bipy and terpy are very much less in 65% methanol than in water. This suggests that hydrophobic interactions are the dominant factor for these incoming groups. But the extra enhancement noted for methyl-substituted analogues, such as 4,4′-dimethyl-2,2′-bipyridyl, is less affected by the change in solvent. The electron-releasing methyl groups seem therefore to increase the polarization contribution to the 'stacking' phenomenon.[51]

Reactions of Known Mechanism.—There seem to have been singularly few studies of the kinetics of reactions of well established mechanism in which reactivity variations are correlated with, or explained by, established properties of solvent mixtures or their structural peculiarities. It was acknowledged that a consideration of solvent ordering beyond the primary co-ordination shell is necessary in rationalizing kinetic parameters, especially activation entropies, for trimethyl phosphate exchange at magnesium(II) in trimethyl phosphate–dichloromethane solvent mixtures, and in comparing these parameters with those for water, methanol, or ethanol exchange at this cation.[52] Similarly the composition of the secondary solvation shell seems to be important in determining reactivity in the I_d aquation of the $[Co(NH_3)_5(DMSO)]^{3+}$ cation in a variety of mixed aqueous solvents.[42] N.m.r. studies of suitable complexes in appropriate solvent mixtures often give valuable information about interactions

[51] G. R. Cayley and D. W. Margerum, *J.C.S. Chem. Comm.*, 1974, 1002.
[52] J. Crea, S. F. Lincoln, and R. J. West, *Austral. J. Chem.*, 1973, **26**, 1227.

between primary and secondary co-ordination spheres. Recently it has been shown that the complex [Co^{II}(pyrazolylborate)$_2$] is particularly suitable for this sort of investigation as not only are the ligands firmly bonded to the metal but also the magnetic anisotropy makes the dipolar shifts a sensitive probe of the secondary solvation shell.[53]

The bimolecular reaction of the $[Fe(terpy)_2]^{2+}$ cation with cyanide ion shows the expected increase in rate on going from water (k_2 = 0.019 l mol^{-1} s^{-1} at 35 °C) to 50% aqueous ethanol (k_2 = 0.068 l mol^{-1} s^{-1} at 35 °C). This increase can be ascribed to the decreased solvation, and thus increased chemical potential, of the cyanide ion in the aqueous ethanol.[54] It is interesting to contrast this situation with the dissociative-interchange reaction between iron(III) and thiocyanate mentioned above,[13] where the small decrease in rate in going from water to less-solvating DMSO was used as evidence against bimolecular attack by thiocyanate. The bimolecular substitution redox reaction of iron(II) with the $[Co(NH_3)_5Br]^{2+}$ cation shows a more complicated reactivity pattern in mixed aqueous solvents. The pattern is discussed in terms of the effects of the organic co-solvents on water structure and thence on reaction rates.[31]

3 Salt Effects

As in previous Volumes, we are concerned here primarily with specific effects of salts on rates of substitution reactions rather than on general salt effects of the Brønsted–Bjerrum type or on salt effects that can be assigned simply to the consequences of ion-pairing. However, it would be wrong to give the impression that such studies are no longer popular or useful. Plots of logarithms of rate constants against square roots of ionic strengths are still much used as an aid to the diagnosis of mechanism, as in several references cited above. Instances include aquation of the *trans*-$[Co(dmgH)_2(NCO)Br]^-$ anion,[25] the reaction of Fe^{3+} with thiocyanate in DMSO,[13] and the forward and backward reactions of (1)$\rightleftharpoons$(2) + Cl^-.[4] Markedly different rate constants for the aquation of the hexachloroiridate(III) anion in 3M-LiCl and in 3M-KCl were ascribed to ion-pairing differences,[55] though in such high concentrations of added salt one would imagine that the different hydration requirements of the Li^+ and K^+ cations would also be reflected in the solvation of the initial and transition states and thence in the observed rate constants. The effect of added barium chloride on the aquation rate of hexachloroiridate(III) has also been studied; equilibrium constants and the enthalpy and entropy of formation of the proposed ion-pair intermediate were estimated.[56] Effects of added sodium, lithium, or iron(II) perchlorate on the reaction of the $[Co(NH_3)_5Br]^{2+}$ cation with iron(II) cannot be accounted for by classical ionic strength considerations. They have been rationalized in terms of the specific effects of these various ions on the water structure.[31]

The addition of potassium, caesium, or tetra-alkylammonium (alkyl = methyl, ethyl, or n-butyl) salts has a marked effect on the rate of aquation of the tris-(5-nitro-1,10-phenanthroline)iron(II) cation. For a given concentration of added salt,

[53] D. R. Eaton and K. L. Chua, *Canad. J. Chem.*, 1973, **51**, 4137.
[54] J. Burgess and M. V. Twigg, *J.C.S. Dalton*, 1974, 2032.
[55] I. Lakatos-Varsanyi, A. N. Kochetkova, E. G. Tsventarnyi, and V. I. Kravtsov, *Russ. J. Inorg. Chem.*, 1973, **18**, 1603.
[56] V. I. Kravtsov, E. G. Tsventarnyi, and A. N. Kochetkova, *Russ. J. Inorg. Chem.*, 1973, **18**, 1060.

the effects of potassium and caesium bromides are very similar; Me_4NBr, Et_4NBr, and Bu^n_4NBr give increasingly enhanced rates in that order. The transition state for this dissociative reaction is thought to be more hydrophobic than the initial state, as more of the hydrophobic periphery of the ligand will be exposed to the solvent in the transition state. The observed kinetic pattern can be rationalized in terms of the hydrophilicity and hydrophobicity, K^+ and Cs^+ *vs.* R_4N^+, of the added cations and their differing effects on the initial state to transition state free-energy difference.[57]

Aquation of the oxalato-complexes $[Cr(ox)_3]^{3-}$ and $[Co(ox)_3]^{3-}$ is greatly accelerated, by up to 10^6 and up to 1500 times, respectively, in surfactant-solubilized water–benzene solutions. The surfactants used were octylammonium tetradecanoate and dodecylammonium propionate. The increased rates were ascribed to the enhanced activity of the water in the polar cavities of the surfactant aggregates. Rates are proportional to water concentration, which suggests an associative mechanism. The greater reluctance of cobalt(III) to undergo substitution by an associative process may explain the smaller rate enhancement for the $[Co(ox)_3]^{3-}$ than for the $[Cr(ox)_3]^{3-}$ anion. The nature of the ligands is of great importance, for in similar solvent media the rate enhancement for the aquation of the $[Co(en)_2(N_3)_2]^+$ cation is only up to 11-fold, while aquation of the $[Co(CN)_5(N_3)]^{3-}$ anion is actually slower in the surfactant–benzene–water mixtures than in pure water. The usefulness of this approach to the diagnosis of reaction mechanisms is discussed in this paper.[58]

[57] M. J. Blandamer, J. Burgess, and S. H. Morris, *J.C.S. Dalton*, 1974, 1717.
[58] C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J.C.S. Dalton*, 1974, 625.

Part III

REACTIONS OF BIOCHEMICAL INTEREST

By
D. N. HAGUE

1 General

Two monographs on the role of metals in biological systems have appeared during the review period.[1,2] A third is concerned with the biological and molecular properties of iron–sulphur proteins,[3] and Llinás has reviewed[4] the conformational state of iron proteins in general. Österberg has discussed[5] the origins of metal ions in biology and reviewed[6] models for copper–protein interaction based on solution and crystal-structure studies. In view of the increasing use of lanthanide binding as a model for calcium binding in protein studies, Silber's finding[7] that significant concentrations of inner-sphere lanthanide complexes exist in regions where the local dielectric constant is less than that of water (whereas Ca^{2+} will not form complexes under these conditions) is of interest. It seems, then, that lanthanide binding to a biochemical molecule at the calcium-binding site will not occur if the region surrounding this site has a dielectric constant lower than that of water and if the cation size is crucial. As in previous periods, there have been several kinetic studies on the interaction between metals and small biologically important molecules (such as amino-acids); these are generally discussed in Part II, Chapter 4.

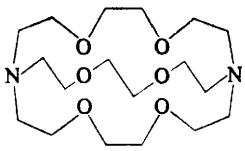
2 Metal Ion Transport

The mechanistic problems associated with the transport of cations (especially Na^+ and K^+) through membranes have continued to receive attention. The structures[8] of macrocyclic alkali-metal complexes and the thermodynamics of their formation[9] have been reviewed, as has the general question of the selectivity[10] of the carriers towards the metals. The role of hydration energy has been considered[11] and it has been suggested[12] that, at least in the case of the enniatin ionophores, sandwich

[1] 'Inorganic Biochemistry', ed. G. L. Eichhorn, Elsevier, New York, 1973.
[2] 'Metal Ions in Biological Systems', ed. H. Sigel, Dekker, New York, 1973.
[3] 'Iron–Sulphur Proteins', ed. W. Lovenberg, Academic Press, New York, 1973.
[4] M. Llinás, *Structure and Bonding*, 1973, **17**, 135.
[5] R. Österberg, *Nature*, 1974, **249**, 382.
[6] R. Österberg, *Coordination Chem. Rev.*, 1974, **12**, 309.
[7] H. B. Silber, *F.E.B.S. Letters*, 1974, **41**, 303.
[8] M. R. Truter, *Structure and Bonding*, 1973, **16**, 71.
[9] R. M. Izatt, D. J. Eatough, and J. J. Christensen, *Structure and Bonding*, 1973, **16**, 161.
[10] W. Simon, W. E. Morf, and P. C. Meier, *Structure and Bonding*, 1973, **16**, 113; B. C. Pressman, *Fed. Proc.*, 1973, **32**, 1698.
[11] B. H. Tredgold, *Biochim. Biophys. Acta*, 1973, **323**, 143.
[12] V. T. Ivanov, A. V. Evstratov, L. V. Sumskaya, E. I. Melnik, T. S. Chumburidze, S. L. Portnova, T. A. Balashova, and Yu. A. Ovchinnikov, *F.E.B.S. Letters*, 1973, **36**, 65.

complexes play an important part in the transport process. N.m.r. spectroscopy has been used[13] to detect the ionophore-mediated transport of praseodymium ions across phospholipid membranes, and Raman evidence has been produced[14] for a conformational difference between crystalline nonactin and uncomplexed nonactin in solution. (Differing effects on the frequency of the ester carbonyl stretch were also observed[14] as the nature of the cation was changed in the alkali-metal complexes of nonactin.) The far-i.r. spectra of alkali-metal complexes with valinomycin, beauvericin, and nonactin have been the subject of a preliminary note[15] and, from the ^{13}C n.m.r. and i.r. spectra of the highly stable K^+, Rb^+, and Cs^+ complexes of valinomycin in methanol, it has been concluded[16] that the ligand conformations in these complexes must be similar. In contrast, the weaker Na^+ complex of the antibiotic exhibits different spectral properties which bear a greater resemblance to those of the uncomplexed antibiotic in polar solvents, suggesting that the conformation of the ligand in the Na^+ complex is different from that in the other complexes. In particular, the structure of the Na^+ complex can be characterized by a reduced number of co-ordinated ester carbonyl groups and intramolecular hydrogen bonds between the amide groups as compared with the complexes with the larger cations. These findings are evidently of relevance in a discussion of the rate constants for the formation of these complexes (*cf.* below and Vol. 3, p. 332).

The kinetics have been reported for the formation of the Na^+ complexes of dibenzo-18-crown-6 (DBC) in DMF, methanol, and dimethoxyethane,[17] of dicyclohexyl-18-crown-6 (DCC)[17] and valinomycin[18] in methanol, and of (1)[19] in ethylenediamine. In all three studies, use was made of the difference between the nuclear



(1)

relaxation rates of ^{23}Na in the free and complexed forms of the metal; this is larger than that observed with the ^1H signal. With valinomycin the dissociation rate constant (25 °C) was in the range $1—3 \times 10^6\ s^{-1}$ and the activation energy 9.5 kcal mol^{-1}. Similar high activation energies were found for the dissociation of Na^+ from the other ligands (ranging from 8.3 kcal mol^{-1} for DCC in methanol to 12.6 kcal mol^{-1} for DBC in DMF) and are presumably the energies associated with the onfigurational changes occurring during decomplexation.

[13] M. S. Fernández, H. Célis, and M. Montal, *Biochim. Biophys. Acta*, 1973, **323**, 600.
[14] I. M. Asher, G. D. J. Phillies, and H. E. Stanley, *Biochem. Biophys. Res. Comm.*, 1974, **61**, 1356.
[15] V. T. Ivanov, G. A. Kogan, V. M. Tulchinsky, A. V. Miroshnikov, I. I. Mikhalyova, A. V. Evstratov, A. A. Zenkin, P. V. Kostetsky, Yu. A. Ovchinnikov, and B. V. Lokshin, *F.E.B.S. Letters*, 1973, **30**, 199.
[16] E. Grell, T. Funck, and H. Sauter, *European J. Biochem.*, 1973, **34**, 415.
[17] E. Shchori, J. Jagur-Grodzinski, and M. Shporer, *J. Amer. Chem. Soc.*, 1973, **95**, 3842.
[18] M. Shporer, H. Zemel, and Z. Luz, *F.E.B.S. Letters*, 1974, **40**, 357.
[19] J. M. Ceraso and J. L. Dye, *J. Amer. Chem. Soc.*, 1973, **95**, 4432.

3 Metal Complex Formation; Non-redox Systems

The question of the identity (and even the number) of binding groups in metal–ATP and related complexes continues to attract the attention of workers in the field. In a recent reinvestigation of the Mn^{2+}-induced broadening of the H-8 and H-2 n.m.r. signals of ATP, Wee *et al.* found[20] that this metal does not, contrary to previous reports, cause equal broadening of the H-8 signals of ATP and AMP. From the results of temperature-, pD-, and concentration-dependent studies, they concluded that both adenine H-8 protons in the 1 : 2 complex (Mn^{2+} : ATP) are approximately equidistant from the Mn^{2+} nucleus and couple with the metal magnetically. When the pD is lowered from 6.4 to 5.4 a drastic increase occurs in the Mn^{2+} broadening of both the H-8 and the H-2 signals (of 0.25 but not of 0.02 or 0.1M-ATP; $[Mn^{2+}] = 5 \times 10^{-5}$ mol l^{-1}). It is suggested[20] that the fundamental cause for the large pD effect is a transition in the triphosphate chelation, from $\alpha\beta\gamma$ to $\beta\gamma$, consequent upon phosphate protonation. The 1 : 2 structure proposed at pH 8 contains two water bridges connecting the metal with N-7 of the two adenine rings which are stacked, one on top of the other, in the outer sphere of the metal. As mentioned in Part II, Chapter 4, ^{31}P Fourier-transform n.m.r. spectroscopy has been used[21] to study the structure and dissociation kinetics of the Mn^{2+}–ATP complex. In this study, evidence was obtained for a principal structure at pH 8.5 in which the β and γ phosphorus atoms are closer to the metal than is the α phosphorus. As a result of an n.m.r. study using the ^{13}C resonance, on the other hand, Lam *et al.*[22] conclude that, at pD 7.0, the metal binding involves all three phosphate groups as well as the ring N-7 (bound directly to the metal). Clearly there is room for further discussion on this topic and it may well be that the full mapping procedure used recently by Williams and co-workers[23] on the conformations of AMP and cyclic 3′,5′-AMP in solution will help to clarify the situation. Certainly, the stabilizing influence of metal-bridged ternary complex formation with copper(II) and bipy against hydrolysis of ATP and ADP can be rationalized conveniently[24] in terms of the *lack* of an adenine–metal interaction (whereas such an interaction *is* possible in the binary complex, which is readily hydrolysed).

The interactions of ADP and the arginine enantiomers with arginine kinase have been investigated[25] by measuring the enhancement of the longitudinal water proton relaxation rate due to Mn^{2+} in the enzyme–substrate complexes. The geometry of the metal ion in the various enzyme–metal complexes (including the number of remaining water molecules in the inner co-ordination sphere as the various ligands are added) has been followed with the additional help of e.p.r. spectroscopy.

There have been several reports during the review period concerning the mode of action of carbonic anhydrase (CA). Lindskog and Coleman[26] have published a rebuttal of the proposition of Koenig and Brown[27] that mechanisms involving a zinc

[20] V. Wee, I. Feldman, P. Rose, and S. Gross, *J. Amer. Chem. Soc.*, 1974, **96**, 103.
[21] F. F. Brown, I. D. Campbell, R. Henson, C. W. J. Hirst, and R. E. Richards, *European J. Biochem.*, 1973, **38**, 54.
[22] Y. F. Lam, G. P. P. Kuntz, and G. Kotowycz, *J. Amer. Chem. Soc.*, 1974, **96**, 1834.
[23] C. D. Barry, J. A. Glasel, R. J. P. Williams, and A. V. Xavier, *J. Mol. Biol.*, 1974, **84**, 471.
[24] D. H. Buisson and H. Sigel, *Biochim. Biophys. Acta*, 1974, **343**, 45.
[25] D. H. Buttlaire and M. Cohn, *J. Biol. Chem.*, 1974, **249**, 5733, 5741.
[26] S. Lindskog and J. E. Coleman, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 2505.
[27] S. H. Koenig and R. D. Brown, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 2422.

hydroxide as the active group violate the principle of microscopic reversibility. (The latter authors had postulated[27] that H_2CO_3 must be the substrate with this enzyme.) This zinc-containing enzyme is one of the most widely investigated metallo-proteins (indeed, the crystal structure of the human C isoenzyme has been completed to a resolution of 2 Å), yet there is little direct evidence identifying the catalytic and substrate binding groups. It is known that an ionizing group on the enzyme with a pK_a near 7 is involved in catalysis and that the titration of this group results in changes in the environment of the metal ion, but its identity is as yet unknown. The two major contenders for the basic form of this group are a zinc-co-ordinated hydroxide ion and a basic amino-acid side-chain (*e.g.* imidazole) directly or indirectly linked to the metal ion. The proposal of Koenig and Brown[27] (which included the suggestion that the high-pH form of the enzyme contained an H_2O ligand on the metal rather than an OH^- ligand) was thus of considerable interest. In their paper disagreeing with this claim, Lindskog and Coleman[26] summarize the evidence in favour of the 'accepted' scheme and point out that the majority of it favours the assignment of the pK_a to the ionization of $ZnOH_2$, although the other assignment mentioned above cannot be ruled out.

In an attempt to decide between these two possibilities, Lanir *et al.*[28] have investigated the relaxation rates of the exchangeable water molecules in the inner co-ordination sphere of the metal in manganese-substituted bovine carbonic anhydrase B. Their conclusion is that one water molecule (and not a hydroxide ion) is directly bound to the metal at high pH values while below the pK_a there is no rapidly exchanging water bound to the metal ion (*cf.* the conclusions of Koenig and Brown based on the results of similar studies with the cobalt enzyme).

A ^{13}C study of the binding of CN^- to copper(II)–CA has indicated[29] that the anion is directly bound to the metal (through the carbon), as it appears to be[30] with the cobalt(II) enzyme. In the latter case, a certain flexibility of the ligands at the active site is indicated (either distorted trigonal bipyramidal or octahedral), as well as a difference in molecular conformation between the liquid and the frozen state. On the other hand, the e.s.r. spectra of various sulphonamide adducts of cobalt(II)–CA are consistent[31] with the kind of distorted tetrahedral metal ion co-ordination revealed by *X*-ray crystallography. It seems that benzocyclic and heterocyclic sulphonamides are held in the hydrophobic cleft at the active site in characteristic orientations which are independent of the nature of the side-chains. The effect on its pK_a of changing the environment of a metal-bound water molecule from hydrophilic to hydrophobic has been investigated by Coates *et al.*[32] In Table 1 are listed the differences in the thermodynamic parameters for water ionization in Me_6tren and tren complexes of Co^{2+}, Cu^{2+}, and Zn^{2+}, from which it is concluded that the suggestion is reasonable that the low pK_a values for the co-ordinated water molecules in carbonic anhydrase (and other metal-proteins) are, in part, a consequence of their hydrophobic environments. The pK_a of bovine carbonic anhydrase in which the zinc has been replaced by VO^{2+} is 7.1 and further evidence has been found[33] that the functional group is not a

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[29] P. H. Haffner and J. E. Coleman, *J. Biol. Chem.*, 1973, **248**, 6626.
[30] P. H. Haffner and J. E. Coleman, *J. Biol. Chem.*, 1973, **248**, 6630.
[31] S. A. Cockle, S. Lindskog, and E. Grell, *Biochem. J.*, 1974, **143**, 703.
[32] J. H. Coates, G. J. Gentle, and S. F. Lincoln, *Nature*, 1974, **249**, 773.
[33] J. J. Fitzgerald and N. D. Chasteen, *Biochemistry*, 1974, **13**, 4338.

Table 1 *Differences in apparent thermodynamic quantities between* Me_6tren *and* tren *complexes*[32]

Metal	$pK(Me_6tren) - pK(tren)$	$\Delta H°(Me_6tren) - \Delta H°(tren)$/ kJ mol^{-1}	$\Delta S°(Me_6tren) - \Delta S°(tren)$/ J K^{-1} mol^{-1}
Co	−1.42	33.0(±4.6)	138.2(±15.5)
Cu	−0.85	41.4(±3.8)	158.5(±12.8)
Zn	−1.26	37.3(±3.8)	149.3(±12.8)

metal-bound OH^- group. Rate constants have been reported for the binding of the vanadyl[33] and manganous[34] cations to bovine carbonic anhydrase B and for the interaction of the cyanate ion with the cobalt(II) enzyme.[35]

Carbonic anhydrase, carboxypeptidase A, thermolysin, and alkaline phosphatase in which Mn^{II} has been substituted for the native Zn^{II} all show[36] solid e.s.r. spectra typical of d^5 ions in environments with large rhombic distortions from spherical symmetry. It is suggested that such a spectrum can be used as a highly sensitive probe of conformation at the metal-binding site of a zinc metalloprotein since the binding of competitive inhibitors to the manganese causes significant changes in the transition probabilities and hyperfine structures of the spectra.

The evidence concerning the geometry of the metal co-ordination in Co^{II}-alkaline phosphatase has been discussed.[37] Of particular interest is the finding from magnetic circular dichroism that the favoured distorted tetrahedral geometry undergoes relatively little change as a function of pH or of arsenate or phosphate binding. It has been suggested[38] that the co-ordination geometry of the metal in alkaline phosphatase from *Bacillus subtilis* is approximately the same as in the *E. coli* enzyme. A preliminary report[39] has appeared on the use of ^{31}P n.m.r. for studying the binding of orthophosphate to the zinc, cobalt(II), and manganese(II) forms of *E. coli* phosphatase. Likewise, $^{35}Cl^-$ quadrupole relaxation has been used[40] to study the binding of zinc and phosphate to the same enzyme, and a proton relaxation rate study of the copper(II) enzyme indicates[41] that at least one water molecule or hydroxide ion has access to the inner co-ordination sphere of the metal and that phosphate does not displace it.

The use of the VO^{2+} ion as a probe of metal–protein interactions in carboxypeptidase A has been explored.[42]

4 Reactions involving Metals in Porphyrins and Related Ring Systems

Haemoglobin and Similar Molecules.—The reversible binding of molecular oxygen to the haem-proteins haemoglobin (Hb) and myoglobin (Mb) has long been a source of considerable interest but, although many of the general features are known, the

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[35] K. Gerber, F. T. T. Ng, R. Pizer, and R. G. Wilkins, *Biochemistry*, 1974, **13**, 2663.
[36] P. H. Haffner, F. Goodsaid-Zalduondo, and J. E. Coleman, *J. Biol. Chem.*, 1974, **249**, 6693.
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[41] R. S. Zukin and D. P. Hollis, *J. Biol. Chem.*, 1974, **249**, 656.
[42] R. J. de Koch, D. J. West, J. C. Cannon, and N. D. Chasteen, *Biochemistry*, 1974, **13**, 4347.

detailed step-by-step mechanism is not. The iron atoms in deoxyhaemoglobin are puckered out of the haem plane and are high-spin but they assume an in-plane, low-spin configuration on combination with oxygen, and the present hypothesis is that the iron geometrical positions and spin states are coupled to the interactions with the protein (leading to co-operativity of binding between the subunits). Certainly, recent evidence from resonance Raman spectroscopy supports[43] the assignment of a low-spin iron(III) configuration in oxyhaemoglobin. It has been suggested[44] that the single temperature-jump relaxation effect observed in methaemoglobin at pH 6 is associated with the change in spin state of the iron. Evidently quaternary structural effects perturb the spin dynamics since a longer relaxation time is observed in the case of the $\alpha\beta$ dimer than in the tetramer.

Several kinetic studies of the binding of O_2, CO, and other ligands to various forms of haemoglobin have been reported. The O_2–human Hb reaction is characterized[45] by two well-separated relaxation times which are both concentration-dependent. The detailed kinetic picture is rather complex, and it has not been possible to determine the rate constants for all the elementary steps. However, it has been possible to characterize three reactions kinetically: (i) a fast step at low oxygen saturation yielding an apparent k_{off} of *ca.* 1000 s^{-1} (20 °C) and k_{on} (per tetramer) of *ca.* 4×10^7 l mol^{-1} s^{-1}; (ii) a fast step at high oxygen saturation yielding an apparent k_{on} of *ca.* 4×10^7 l mol^{-1} s^{-1}; and (iii) a slow step which, at high oxygen concentration, yields an apparent rate constant of 5×10^6 l mol^{-1} s^{-1}. It therefore seems that the low oxygen affinity of deoxyHb arises mainly from the high dissociation rate constant (*i.e.* short lifetime) of Hb_4O_2. It is not possible to say whether the quoted rate constants apply equally to the α- and β-chains or if only one type of chain is involved in the fast phase of the relaxation spectrum. ^{13}C N.m.r. studies on the binding of CO to human haemoglobin do, however, allow us to distinguish between the two chains as far as the equilibrium binding parameters are concerned.[46] Previously published kinetic data are discussed[47] in terms of a new ligand-binding model which sees the initial stage as involving the β-chain alone (which, however, does not retain the oxygen for long). The kinetics have been reported for the binding of O_2,[48] CO,[48] and NO[49] to isolated Hb components from trout, of O_2 and CO to Hb Kansas,[50] of O_2, CO, and Bu^{n}NC to des-His(146β) human haemoglobin,[51] and of Bu^{n}NC to human Hb.[52] The binding of CO to simple haem proteins has been further studied[53] under photodissociating conditions, and it has been found[54] that the photolysis of CO and O_2 derivatives of Hb by a short laser pulse produces a

[43] T. Yamamoto, G. Palmer, D. Gill, I. T. Salmeen, and L. Rimai, *J. Biol. Chem.*, 1973, **248**, 5211.
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[45] G. Ilgenfritz and T. M. Schuster, *J. Biol. Chem.*, 1974, **249**, 2959.
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[50] Q. H. Gibson, A. Riggs, and T. Imamura, *J. Biol. Chem.*, 1973, **248**, 5976.
[51] K. Moffat, J. S. Olson, Q. H. Gibson, and J. V. Kilmartin, *J. Biol. Chem.*, 1973, **248**, 6387.
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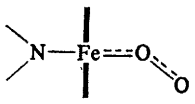
[53] C. Bonaventura, J. Bonaventura, E. Antonini, M. Brunori, and J. Wyman, *Biochemistry*, 1973, **12**, 3424.
[54] B. Alpert, R. Banerjee, and L. Lindqvist, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 558.

transient species which rapidly decays to normal deoxyHb. The effect has been interpreted as corresponding to structural changes in the haem pocket on ligand dissociation; it follows first-order kinetics with a rate constant of *ca.* 1×10^7 s^{-1}. It is found with single-chain proteins and non-co-operative aggregated forms as well as co-operative haemoglobins and, although the rate constant is pH-dependent in the latter case, it remains first or pseudo-first order at all wavelengths. This shows that the tertiary and quaternary structure changes are closely linked in normal haemoglobin.

The kinetics of the reaction of O_2 and CO with Hb and Mb have been studied[55] by the temperature-jump technique as a function of pressure. The volumes of activation $\Delta V^{\ddagger}$ for the binding of O_2 were both positive (Mb = 8 and Hb = 5 cm^3 mol^{-1}) and for CO were both negative (Mb = −9, Hb 'fast' and 'slow' reactions = −3 and −21 cm^3 mol^{-1}), suggesting that the interactions with the two ligands are different in the transition states. (The differing values of $\Delta V^{\ddagger}$ for the 'fast' and 'slow' reactions of Hb with CO indicate that different structural changes occur on binding.) It is, apparently, possible to rationalize the large negative volume of activation for the reaction of deoxyHb with CO since most of the processes which may appreciably affect $\Delta V^{\ddagger}$ (bond formation, solvation of hydrophobic residues, formation of solvent hydrogen bonds, and charge dispersal) would be expected to give negative contributions. The n.m.r. technique has been used[56] to study the binding of MeNC to the β-chains of Hb; values of 57 s^{-1} and 14 kcal mol^{-1}, respectively, have been quoted for k_{off} and its activation energy.

Until recently, there has been no direct evidence concerning the nature of the bonding between oxygen and the haem iron of Hb. The i.r. difference spectrum of packed human erythrocytes treated with $^{16}O_2$ *vs.* $^{18}O_2$ or with $^{16}O_2$ *vs.* CO has a unique band at 1107 cm^{-1} which has been assigned[57] to ^{16}O—^{16}O stretch for bound $^{16}O_2$. The frequency and intensity of the band indicate non-linear end-on binding of O_2 to Fe^{II} in oxyHb, and an O—O bond order of *ca.* 1.5 is suggested (2). The reduction in bond order on binding to the iron is analogous to those found when CO, NO,



(2)

and N_2 are similarly bound, and it therefore seems to be unnecessary to use a bond description for bound O_2 which is fundamentally different from those used for the other diatomics. The strong covalent bonding between Fe and O_2 resulting from π-donation from Fe^{II} to O_2 represents a sufficient reason for dioxygen to dissociate from oxyHb as O_2 rather than O_2^- and relegates the presence or absence of a non-polar or hydrophobic environment to a minor role. Similar i.r. results have been obtained[58] for the binding of O_2 to cobalt(II) and to iron(II) in reconstituted haemo-

[55] B. B. Hasinoff, *Biochemistry*, 1974, **13**, 3111.
[56] B. A. Manuck, J. G. Maloney, and B. D. Sykes, *J. Mol. Biol.*, 1973, **81**, 199.
[57] C. H. Barlow, J. C. Maxwell, W. J. Wallace, and W. S. Caughey, *Biochem. Biophys. Res. Comm.*, 1973, **55**, 91.
[58] J. C. Maxwell and W. S. Caughey, *Biochem. Biophys. Res. Comm.*, 1974, **60**, 1309.

globins, and *X*-ray studies indicate[59] that analogous 'end-on' binding with a bent Fe—O—O bond occurs in the O_2 complex of an iron(II) porphyrin.

Human oxyhaemoglobin (HbO_2) in the presence of excess nucleophile (*e.g.* N_3^-, SCN^-, F^-, Cl^-) has been shown[60] to form cleanly the oxidized methaemoglobin (metHb) with the nucleophile as the ligand. The rates, which are sensitive to pH and the nucleophilicity of the anionic nucleophile (N^-), obey the law Rate $= k[HbO_2][N^-][H^+]$. This autoxidation process therefore appears to involve the nucleophilic displacement of superoxide from a protonated intermediate and can reasonably account for normal metHb formation in the erythrocyte where Cl^- can serve as the nucleophile. [MetHb formation by electron-transfer agents such as NO_2^-, which are not normally present, can follow a different course, *e.g.* direct electron transfer to bound O_2 to form iron(III) peroxide.]

Baldwin and Huff[61] have invoked mechanistic ideas in designing an iron(II) complex which should share with haemoglobin the ability to bind oxygen reversibly in solution rather than suffer the irreversible autoxidation to iron(III) species experienced by all other known complexes of Fe^{II}. Studies on the autoxidation mechanism for iron(II) salts have suggested that an initial 1 : 1 binding of dioxygen by the metal [step *a*, equation (1)] is followed by a rapid bimolecular redox process

$$Fe^{II} + O_2 \overset{a}{\rightleftharpoons} Fe^{II}O_2 + Fe^{II} \xrightarrow{b} Fe^{II}O{-}OFe^{II} \longrightarrow Fe^{III} \qquad (1)$$

(step *b*), which eventually leads irreversibly to iron(III) species. It is argued that if the second process (step *b*) were impeded by the molecular geometry of the iron(II) ligand it should be possible to obtain reversible behaviour (step *a*). This might be possible by constructing a molecular cavity containing a suspended iron(II) atom, which would thereby approximate to each of the four porphyrin-containing clefts of haemoglobin. Indeed, compound (3) (in which models indicate that the benzo substituents provide an open-sided cavity of depth 5 Å) was found to bind oxygen reversibly (with a 1 : 1 mole ratio) in THF–dimethoxyethane containing pyridine at −78 °C. Chang and Traylor[62] have synthesized a simple haem-imidazole compound (4), having the same geometry as the haem-imidazole complex in myoglobin, which reversibly binds oxygen in the solid state or when dissolved in a polystyrene film. These authors concluded that the principal factors governing reversible oxygen binding are the electronic nature of the base (imidazole), neighbouring-group effects of the basic group, and immobilization of the haem group; they have discussed their proposition further in subsequent notes.[63]

The kinetics of the rebinding of CO to myoglobin and to cytochrome P450 after removal by a light flash have been reported.[64] Above 240 K the reaction is second order while between 240 and 200 K the rebinding becomes exponential and independent of the CO concentration; below 150 K the reaction follows a power law

[59] J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1326.
[60] W. J. Wallace, J. C. Maxwell, and W. S. Caughey, *Biochem. Biophys. Res. Comm.*, 1974, **57**, 1104.
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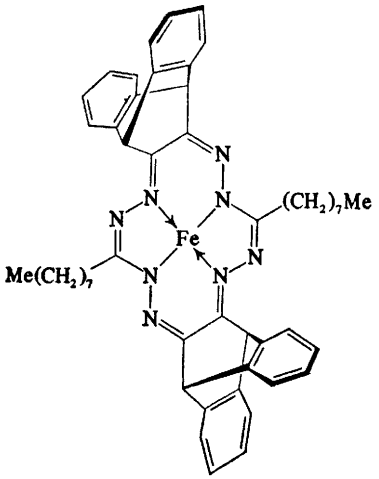
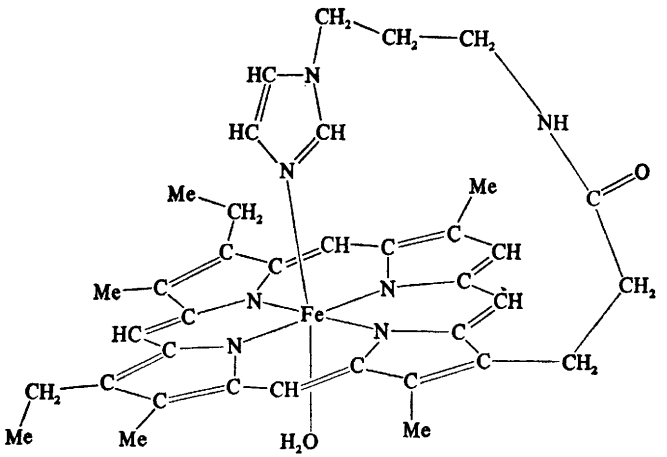
[62] C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 2647.
[63] C. K. Chang and T. G. Traylor, *J. Amer. Chem. Soc.*, 1973, **95**, 8475, 8477.
[64] R. H. Austin, K. Beeson, L. Eisenstein, H. Frauenfelder, I. C. Gunsalus, and V. P. Marshall, *Science*, 1973, **181**, 541.



(3)



(4)

and is *ca.* 10^3 times faster for cytochrome P450 than for Mb. The mechanism of the anation of ferric myoglobin [equation (2), where L = CN^-, N_3^-, OCN^-, SCN^-,

$$Mb{-}OH_2 + L \rightleftharpoons Mb{-}L + H_2O \qquad (2)$$

NO_2^-, *etc.*) is thought to be dissociative in character, as with most octahedral metal complexes. If the normal I_d mechanism is operating, it is to be expected that ligand substitution [equation (3)] would involve aquation followed by anation. This

$$Mb{-}L + Y \rightleftharpoons Mb{-}Y + L \qquad (3)$$

prediction has recently been confirmed[65] where the (L,Y) combinations are (SCN^-, N_3^-), (OCN^-, N_3^-), (SCN^-, CN^-), and (NO_2^-, SCN^-).

[65] D. A. Sweigart and C. Bern, *Inorg. Chem.*, 1974, **13**, 3033.

The interconversion of the high-spin and low-spin states of iron(III) myoglobin hydroxide has been shown[66] to have a lifetime of less than 5 μs, indicating that such spin-state changes can be sufficiently rapid to participate in coupled electron transport.

The reversible oxygenation of a series of cobalt myoglobins, haemoglobins, and other porphyrin ring compounds has been studied[67] by the temperature-jump technique. Values of k_{on} in the range $3—7 \times 10^7$ l mol^{-1} s^{-1} and k_{off} in the range $1—3 \times 10^3$ s^{-1} were obtained. (The former are comparable to those obtained with the corresponding iron ring compounds, while the latter are about a hundred times larger). The authors are unable to comment on the likely molecular mechanisms of these reactions but note that the oxygenation rate constants are in a range similar to typical enzyme–substrate association–dissociation reactions. Artificial myoglobins and haemoglobins containing cobalt(II) and their interactions with oxygen have been studied[68] by e.p.r. spectroscopy. The signals for deoxy-CoMb and -CoHb are consistent with a five-co-ordinate, square-pyramidal configuration of the low-spin cobaltous ion while the signals of the oxygenated compounds are of a 'free radical' type with axial symmetry, indicating a substantial transfer of the unpaired spin density from the cobaltous ion to the bound oxygen. The resonance Raman spectra of oxy- and deoxy-CoHb suggest[69] that the displacement of the cobalt atom on oxygenation is no greater than the out-of-plane distance in five-co-ordinate Co^{II} porphyrins (*ca.* 0.15 Å). However, contraction of the cobalt–histidine distance on oxygenation is likely to be substantial; crystal structures of cobalt porphyrin derivatives suggest a value of 0.22 Å. Thus the displacement of the proximal histidine with respect to the haem plane may amount to 0.37 Å, about one-third of the corresponding displacement estimated for iron haemoglobin. The estimated free energy of co-operativity for CoHb is also one-third that for FeHb so that, on the basis of the distributed energy model (which predicts proportionality of these quantities), displacement of the proximal histidine on oxygenation could serve, as Perutz has suggested,[70] to trigger the quaternary structure change associated with co-operativity in both iron and cobalt haemoglobin.

Preliminary evidence has been obtained[71] to suggest that the binding of NO to manganese haemoglobin is allosteric. The catalytic effect of copper on the autoxidation of haemoglobin has been studied in detail.[72]

Coenzyme B_{12} and Similar Molecules.—5′-Deoxyadenosylcobalamin and methylcobalamin function as coenzymes in enzymatic reactions involving the transfer of, respectively, hydrogen or a methyl group. The most striking feature of these corrinoid coenzymes is the carbon–cobalt bond which is alternately cleaved and re-formed during the catalytic process. The chemical and physical properties of the organometallic bond are markedly influenced by the axial ligand *trans* to it and, in order to obtain some quantitative measure of the electronic rearrangements in the Co—C

[66] J. K. Beattie and R. J. West, *J. Amer. Chem. Soc.*, 1974, **96**, 1933.
[67] H. Yamamoto, F. J. Kayne, and T. Yonetani, *J. Biol. Chem.*, 1974, **249**, 691.
[68] T. Yonetani, H. Yamamoto, and T. Iizuka, *J. Biol. Chem.*, 1974, **249**, 2168.
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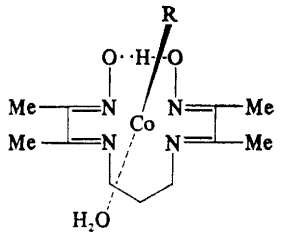
[70] M. F. Perutz, *Nature*, 1970, **228**, 726; 1972, **237**, 495.
[71] Q. H. Gibson, B. M. Hoffman, R. H. Crepeau, S. J. Edelstein, and C. Bull, *Biochem. Biophys. Res. Comm.*, 1974, **59**, 146.
[72] J. M. Rifkind, *Biochemistry*, 1974, **13**, 2475.

bond accompanying co-ordination in the *trans* position, Needham *et al.*[73] have determined the ^{13}C n.m.r. spectra of methylcobalamins, methylcobinamides, and cyanocobinamides. The nature of the cobalt centre in methylcobaloxime (one of the series of B_{12} model compounds) has been given detailed consideration,[74] and it has been found[75] that the character of allylcobaloximes is dependent on the nature of the other axial ligand.

The pressure dependence of the rate constants for the formation and dissociation of the iodide complex of cobalamin has been determined;[76] the activation volumes for the two processes are, respectively, $+5.5$ and $+11.5$ cm^3 mol^{-1}. The positive value for the formation reaction, after appropriate correction for the volume change associated with formation of the outer-sphere complex, is consistent with a dissociative mechanism in which the metal–water bond is stretched in the activated complex. An analogous mechanism has been proposed[77] for formation of the 1 : 1 adducts between ethylaquobis(dimethylglyoximato)cobalt and $[M(CN)_6]^{n-}$ (M = Fe^{II}, Co^{III}, Fe^{III}, or Cr^{III}). The product in each case, $[EtCo(dmgH)_2NCM(CN)_5]^{n-}$, corresponded simply to displacement of the water molecule in the cobaloxime (except that a slower secondary process was noted in the case of Cr^{III}) and the data were found to be inconsistent with a limiting S_N1 mechanism. Preliminary kinetic studies on the replacement of H_2O in (5; R = alkyl) provide evidence[78] for an outer-sphere intermediate when the incoming ligand contains an aromatic group; when it does not, a limiting S_N1 mechanism applies.



(5)

The rapidity of substitution reactions at a metal surrounded by a porphyrin or corrin group seems to be connected with π-delocalization and a strong in-plane ligand field which is not present in 'normal' complexes. The substitution reactions (4) of five-co-ordinate neutral dithiolen complexes (where M is iron or cobalt and L and

$$[M(S_2C_2Ph_2)_2X] + L \longrightarrow [M(S_2C_2Ph_2)_2L] + X \quad (4)$$

X are unidentate phosphines or phosphites) are likewise several orders of magnitude faster than normal. The kinetics of a series of reactions of the type shown in equation (4) have been reported[79] and the results are shown in Table 2. The mechanism followed by reaction (4) is probably mainly associative, although the existence of non-zero

[73] T. E. Needham, N. A. Matwiyoff, T. E. Walker, and H. P. C. Hogenkamp, *J. Amer. Chem. Soc.*, 1973, **95**, 5019.
[74] R. L. Courtright, R. S. Drago, J. A. Nusz, and M. S. Nozari, *Inorg. Chem.*, 1973, **12**, 2809.
[75] D. Dodd and M. D. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 2279.
[76] B. B. Hasinoff, *Canad. J. Chem.*, 1974, **52**, 910.
[77] J. H. Espenson and R. Russell, *Inorg. Chem.*, 1974, **13**, 7.
[78] G. Tauzher, R. Dreos, G. Costa, and M. Green, *J.C.S. Chem. Comm.*, 1973, 413.
[79] D. A. Sweigart, D. E. Cooper, and J. M. Millican, *Inorg. Chem.*, 1974, **13**, 1272.

Table 2 *Rate data for five-co-ordinate* $[M(S_2C_2Ph_2)_2PR_3]$ *substrates* (M = Fe *or* Co)[a]

Substrate	*Nucleophile*[b]	$10^3 \times$ *range of* [nucl][c]/mol l^{-1}	k_{obs}/s^{-1}
$[Fe(S_2C_2Ph_2)_2PPh_3]$	$P(p\text{-tol})_3$	1.5—18	116[nucl]
$[Fe(S_2C_2Ph_2)_2PPh_3]$	$P(OBu)_3$	1.0—13	445[nucl]
$[Fe(S_2C_2Ph_2)_2PPh_3]$	$P(OEt)_3$	1.0—13	472[nucl]
$[Fe(S_2C_2Ph_2)_2PPh_3]$	PBu_3	0.2—2.6	5.16×10^4[nucl]
$[Fe(S_2C_2Ph_2)_2P(OBu)_3]$	PBu_3	0.2—2.6	2.30×10^5[nucl]
$[Co(S_2C_2Ph_2)_2PPh_3]$	$P(p\text{-tol})_3$	5.0—30	0.07+11.8[nucl]
$[Co(S_2C_2Ph_2)_2PPh_3]$	$P(OEt)_3$	2.0—12	0.05+42.5[nucl]
$[Co(S_2C_2Ph_2)_2PPh_3]$	$P(OBu)_3$	2.0—13	0.03+44.0[nucl]
$[Co(S_2C_2Ph_2)_2PPh_3]$	PPh_2OMe	2.0—16	678[nucl]
$[Co(S_2C_2Ph_2)_2PPh_3]$	PBu_3	0.5—5.0	1.01×10^4[nucl]
$[Co(S_2C_2Ph_2)_2P(OBu)_3]$	PBu_3	0.5—3.0	8.27×10^4[nucl]

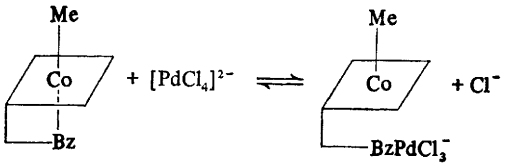
[a] Data, from ref. 79, refer to 25 °C and benzene solvent. [b] All butyl groups are Bu^n; tol = tolyl. [c] [nucl] is concentration of nucleophile.

intercepts in the plots of k_{obs} *vs.* concentration of nucleophile for the cobalt series suggests that a dissociative pathway does contribute a small amount. (The fact that excess leaving group affects some of the cobalt reactions but not others also suggests that a dissociative pathway exists; a purely associative mechanism predicts that excess leaving group will have no effect.) It appears that steric effects are important in determining the relative rates of nucleophilic substitution in these compounds.

Pulse radiolysis has been used[80] to study the reaction of hydrated electrons with various cobalamins (vitamins B_{12}, B_{12a}, and B_{12r}). The rate constant for B_{12} (cyanocobalamin), 3.8×10^{10} l mol^{-1} s^{-1}, is similar to those found with several other Co^{III} complexes and is close to the diffusion-controlled value. The efficiency of reaction with the cobalt atom appears to be only about two-thirds (the product being vitamin B_{12r}) and it therefore appears that the molecule possesses one or more additional electron sinks. Since ribose and phosphate are both unreactive towards hydrated electrons it seems most likely that these sinks are provided by the amide groups. When the lower axial co-ordination position in a vitamin B_{12} derivative is occupied by a strong ligand (*e.g.* the benzimidazole nucleotide in 'base on' cobalamins), the cobalt(II)–cobalt(I) interconversion is irreversible[81] because of the slow reduction of the Co^{II}; when it is free of a strong ligand (*e.g.* in most cobinamides or in 'base off' cobalamins) the interconversion is effectively reversible. The mechanism of the oxygenation of cobalt(II) complexes, including those of biochemical interest, has been reviewed.[82]

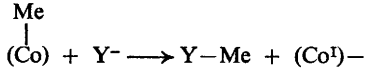
Further studies have been reported on the transfer of the methyl group from methylcobalamin and models. There are two kinetically distinct steps[83] in the methyl-transfer process from MeB_{12} to tetrachloropalladate(II): the initially established equilibrium process involves a relatively rapid complexation between $[PdCl_4]^{2-}$ and

[80] R. Blackburn, A. Y. Erkol, G. O. Phillips, and A. J. Swallow, *J.C.S. Faraday I*, 1974, **70**, 1693.
[81] P. G. Swetik and D. G. Brown, *Biochim. Biophys. Acta*, 1974, **343**, 641.
[82] E. I. Ochiai, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3375.
[83] W. M. Scovell, *J. Amer. Chem. Soc.*, 1974, **96**, 3451.



(5)

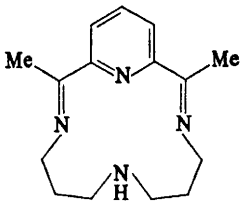
the methylcobalamin at the 5,6-dimethylbenzimidazole nitrogen [equation (5)], while the subsequent slower step involves the methyl transfer itself. The chloride ion dependence of the overall rate process is consistent with the predominant route of methyl transfer being the reaction of $[PdCl_4]^{2-}$ with uncomplexed MeB_{12}. The initial complexation reaction, therefore, converts much of the reactive MeB_{12} into the much less reactive complex. There appear to be similarities between this reaction and the methyl-transfer reactions involving Hg^{II}. The cobalt-bound methyl group in methylcobalamin and in most Me—Co derivatives of common B_{12} models is susceptible[84] to attack by a variety of medium-to-strong nucleophiles [equation (6) with



(6)

Y = RS^-, Cl^-, Br^-, I^-, CN^-, PBu^n_3, PPh_3, Se^{2-}, *etc.*). Higher alkyl-cobalt derivatives also react with strong nucleophiles, but here olefin elimination occurs rather than nucleophilic displacement. The reaction of *N*-alkylcobalamins and *N*-alkyl cobalt derivatives of five different B_{12} models with mercaptide ions produces thioethers, and it has been found[85] that the relative rates of S-alkylation follow a pattern which is typical of S_N2 displacement rather than a free-radical reaction.

The use of the cobalt complex of (6) (a B_{12} model) to mediate the hydrolysis of DDT has been reported,[86] and it has been shown[87] that the product of the reaction



(6)

between pyridinatocobaloxime(I) and DDT contains a chlorovinyl group σ-bonded to the metal. It is more reasonable[88] to regard the reaction of Cr^{2+} with alkylcobaloximes as a homolytic substitution at carbon than as a chromium–cobalt electron transfer. An e.p.r. spectrum has been obtained[89] in a reaction mixture

[84] E. A. Stadlbauer, R. J. Holland, F. P. Lamm, and G. N. Schrauzer, *Bioinorg. Chem.*, 1974, **4**, 67.
[85] G. N. Schrauzer and E. A. Stadlbauer, *Bioinorg. Chem.*, 1974, **3**, 353.
[86] R. H. Prince and D. A. Stotter, *Nature*, 1974, **249**, 286.
[87] R. H. Prince, G. M. Sheldrick, D. A. Stotter, and R. Taylor, *J.C.S. Chem. Comm.*, 1974, 854.
[88] R. H. Prince and M. G. Segal, *Nature*, 1974, **249**, 246.
[89] W. H. Orme-Johnson, H. Beinert, and R. L. Blakley, *J. Biol. Chem.*, 1974, **249**, 2338.

containing coenzyme B_{12}, an equivalent concentration of ribonucleotide reductase, dGTP, and dihydrolipoate which, it is suggested, is a cobamide intermediate in the ribonucleotide reduction (possibly a B_{12r}-deoxyadenosyl radical–enzyme complex).

Cytochrome *c* and other Porphyrin-containing Systems.—Reviews have appeared concerning the oxidation states and reversible redox reactions of metalloporphyrins,[90] the biochemical significance of porphyrin π-cation radicals,[91] and the interaction of histidine and other imidazole derivatives with metal ions in chemical and biological systems[92] (including those containing porphyrin rings). The resonance Raman technique has been used to determine[93] the oxidation and spin states of the haem iron in cytochrome *c*, microperoxidase, and horseradish peroxidase (HRP) and to provide evidence[94] for an anomalous haem structure in the latter case. It seems that the doming of the porphyrin ring, which is characteristic of high-spin haem, is less pronounced in native HRP than in aquomethaemoglobin. Perhaps this is related to the mechanism of the peroxidase reaction, which appears to involve oxidation of the haem iron to Fe^{IV}; in a less domed high-spin haem, one electron would be in a relatively high-energy orbital and might therefore be susceptible to easy removal.

The decay of oxyferroperoxidase to ferriperoxidase has been studied[95] by rapidly mixing solutions of ferroperoxidase with various amounts of oxygen and following the time-course of appearance of oxyferroperoxidase and its subsequent decay to ferriperoxidase by reaction with ferroperoxidase. The scheme proposed is

$$Fe^{II} + O_2 \longrightarrow Fe^{II},O_2$$

$$Fe^{II},O_2 + 3Fe^{II} \longrightarrow 4Fe^{III} + [O_2^{4-}]$$

for which no intermediates were detected in the millisecond time range.

Cytochrome *c*, a haem protein of molecular weight *ca.* 12 000, functions as an electron transport unit in the mitochondria of all aerobic organisms and yeasts, as well as in the chloroplasts of yeasts. Amino-acid sequences and *X*-ray crystallographic studies of cytochromes from different sources have indicated that in all cases the fifth and sixth co-ordination positions of the iron are occupied by histidine-imidazole and methionine-sulphur, the first four co-ordination sites being provided by protoporphyrin IX. Furthermore, the haem unit is attached covalently to the protein which sheaths it almost entirely, with only the porphyrin edge being exposed to solution. Previous studies with comparatively simple oxidizing and reducing agents have indicated that ligand binding and electron transfer can occur with a form of horse heart cytochrome *c* which contains a haem-crevice, although other electron-transfer reactions may involve attack at the exposed porphyrin edge. Creutz and Sutin[96] have recently compared the kinetics of ligand-binding and oxidation–reduction reactions of cytochromes *c* from horse heart and *Candida krusei* (a yeast), and have found that common mechanisms (and similar rates) apply for a given reaction in the two cases.

[90] J. H. Fuhrhop, *Structure and Bonding*, 1974, **18**, 1.
[91] D. Dolphin and R. H. Felton, *Accounts Chem. Res.*, 1974, **7**, 26.
[92] R. J. Sundberg and R. B. Martin, *Chem. Rev.*, 1974, **74**, 471.
[93] T. M. Loehr and J. S. Loehr, *Biochem. Biophys. Res. Comm.*, 1973, **55**, 218.
[94] G. Rakshit and T. G. Spiro, *Biochemistry*, 1974, **13**, 5317.
[95] C. F. Phelps, E. Antonini, G. Giacometti, and M. Brunori, *Biochem. J.*, 1974, **141**, 265.
[96] C. Creutz and N. Sutin, *J. Biol. Chem.*, 1974, **249**, 6788.

The kinetics of electron transfer between cytochrome *c* and iron hexacyanides and their derivatives have been measured.[97,98] In the oxidation of the reduced cytochrome by $[Fe(CN)_5X]^{n-}$ (X = PPh_3, SCN^-, CN^-, NH_3, or N_3^-), the reaction was found[98] to be first order in each reactant and the rate constant decreased with the reduction potential (3.0×10^7, 1.0×10^7, 8.0×10^6, 2.5×10^6, and 9.0×10^5 l mol^{-1} s^{-1}, respectively). The oxidation rate decreased markedly as the ionic strength increased and also decreased somewhat in 10% propan-1-ol. The entropy of activation (*ca.* -20 cal K^{-1} mol^{-1}) was almost independent of the nature of the oxidizing agent but the energy of activation was found to decrease with increasing rate constant from a value of 3.5 kcal mol^{-1} for $[Fe(CN)_5N_3]^{3-}$ to *ca.* 1 kcal mol^{-1}. The abnormally low value of E_a was explained in terms of two possible mechanisms, one in which the rapid binding of the oxidizing agent to the cytochrome *c* is followed by slow electron transfer, and the other in which the cytochrome *c* exists in a labile equilibrium with another more easily oxidized conformation. The kinetic parameters for the oxidation of ferrocytochrome *c* by tris-(1,10-phenanthroline)cobalt(III) are markedly different[99] although the rate law is the same. The rate constant is considerably lower (1.5×10^3 l mol^{-1} s^{-1} for the horse heart protein) whereas $\Delta H^{\ddagger}$ (11.3 kcal mol^{-1}) and $\Delta S^{\ddagger}$ (-6.2 cal K^{-1} mol^{-1}) are more 'normal'. Good agreement is found between these results and those predicted by the Marcus theory, suggesting that electron transfer from the reduced cytochrome *c* occurs by the same mechanism as employed in the protein self-exchange reaction. The exposed haem edge is proposed as the likely site of electron transfer from the metalloprotein.

The reduction of ferricytochrome *c* by hydrated electrons[100] and by several free radicals[101] has been studied by pulse radiolysis. The reduction of oxidized cytochrome *c* by $[Fe(edta)]^{2-}$ follows first-order kinetics for both protein and reductant,[102] with a rate constant of 2.57×10^4 l mol^{-1} s^{-1} at pH 7 and activation enthalpy and entropy of 6.0 kcal mol^{-1} and -18 cal K^{-1} mol^{-1}, respectively. These values are comparable to those for outer-sphere cytochrome *c* reductions and redox reactions involving simple iron complexes, and are compatible with outer-sphere attack of $[Fe(edta)]^{2-}$ at the exposed haem edge, although the possibility of adjacent attack through the haem pocket is not ruled out. The rate data at pH 9 are consistent with $[Fe(edta)]^{2-}$ reduction of two slowly interconverting forms of the protein, native ($k_f = 2.05\times10^4$ l mol^{-1} s^{-1}) and high-pH ($k_f = 2.67\times10^1$ l mol^{-1} s^{-1}) isomers. A possible route for the transfer of the electron from Cr^{2+} to ferricytochrome *c* has been suggested[103] as a result of the chemical analysis of the chromium(III) product. The reduction by Cr^{2+} of the native protein and of ferricytochrome *c* carboxymethylated at the haem-linked methionine (residue 80) has been studied kinetically.[104] At pH 6.5 the former process is simple and corresponds to a second-order rate constant of 1.21×10^3 l mol^{-1} s^{-1}. The latter, however, is complex – two chromium-

[97] E. Stellwagen and R. G. Shulman, *J. Mol. Biol.*, 1973, **80**, 559; R. M. Zabinski, K. Tatti, and G. H. Czerlinski, *J. Biol. Chem.*, 1974, **249**, 6125.
[98] J. C. Cassatt and C. P. Marini, *Biochemistry*, 1974, **13**, 5323.
[99] J. V. McArdle, H. B. Gray, C. Creutz, and N. Sutin, *J. Amer. Chem. Soc.*, 1974, **96**, 5737.
[100] E. J. Land and A. J. Swallow, *Biochim. Biophys. Acta*, 1974, **368**, 86.
[101] A. Shafferman and G. Stein, *Science*, 1974, **183**, 428.
[102] H. L. Hodges, R. A. Holwerda, and H. B. Gray, *J. Amer. Chem. Soc.*, 1974, **96**, 3132.
[103] C. J. Grimes, D. Piskiewicz, and E. B. Fleischer, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1408.
[104] T. Brittain, M. T. Wilson, and C. Greenwood, *Biochem. J.*, 1974, **141**, 455.

dependent steps (1.5×10^4 and 1.3×10^3 l mol^{-1} s^{-1}) leading to formation of an intermediate which decays by a first-order process (0.15 s^{-1}) to form the normal fully reduced material. A model is proposed in which reduction of low-spin ferric carboxymethyl-cytochrome *c* to high-spin ferrous carboxymethyl-cytochrome *c* involves a low-spin ferrous intermediate. The unimolecular step involving the decay of this low-spin Fe^{II} intermediate (associated with an activation energy of *ca.* 126 kJ mol^{-1}) is thought to involve a change both of spin state and of protein conformation. The kinetics of isomerization of horse heart ferricytochrome *c* at alkaline pH have been determined,[105] and it has been suggested[106] that, for native cytochrome *c*, polymerization has an effect on the lability of the haem crevice, rendering the iron available for ligand binding.

Cytochrome *c* peroxidase is an enzyme which catalyses the oxidation of ferrocytochrome *c* by hydrogen peroxide. At low concentrations of ferrocytochrome *c* the catalysis follows the classical peroxidase mechanism developed for horseradish peroxidase (HRP) by Chance and George. Two oxidized cytochrome *c* peroxidase intermediates have been identified in the oxidation of ferrocytochrome *c* and ferrocyanide, and (at low substrate concentrations) the reaction scheme is as shown in equation (7) (where CcP represents the native enzyme, CcP-I represents compound I

$$\begin{aligned} \text{CcP} + \text{H}_2\text{O}_2 &\longrightarrow \text{CcP-I} \\ \text{CcP-I} + \text{Fe}^{\text{II}} &\longrightarrow \text{CcP-II} + \text{Fe}^{\text{III}} \\ \text{CcP-II} + \text{Fe}^{\text{II}} &\longrightarrow \text{CcP} + \text{Fe}^{\text{III}} \end{aligned} \qquad (7)$$

of cytochrome *c* peroxidase which is oxidized two equivalents higher than the native enzyme, CcP-II represents compound II of the enzyme, oxidized one equivalent above the native enzyme, and Fe^{II}, Fe^{III} represent ferrous and ferric iron in either cytochrome *c* or the hexacyanide complex). Jordi and Erman[107] have determined the apparent bimolecular rate constants for the oxidation of ferrocyanide by CcP-I and CcP-II over the pH range 4.0—9.5 and at different ionic strengths in the range 0.005—0.1 mol l^{-1}. Under all conditions, compound I oxidizes ferrocyanide about three times more rapidly than does compound II and the effects of pH and ionic strength on the rate constants could be explained by the contribution of electrostatic interactions to a single intrinsic rate constant and to variation of the activity coefficients of the reactants with charge and ionic strength. The intrinsic rate constants for CcP-I and CcP-II oxidation of ferrocyanide are, respectively, 3.8×10^5 and 1.4×10^5 l mol^{-1} s^{-1}.

The binding of several small molecules to cytochrome *c* peroxidase has been studied kinetically. In the case of fluoride,[108] the data are consistent with the interaction of F^- with the protonated form of the enzyme (pK_a 5.5) or with the interaction of HF with the ionized form of the protein. The latter is the preferred interpretation, giving a pH-independent rate constant for binding of 5.1×10^7 l mol^{-1} s^{-1}. With cyanide[109] the situation is rather more complex; the maximum value of the association rate constant, which occurs between pH 6 and 8, is 1.1×10^5 l mol^{-1} s^{-1}.

[105] L. A. Davis, A. Schejter, and G. P. Hess, *J. Biol. Chem.*, 1974, **249**, 2624.
[106] S. Dupré, M. Brunori, M. T. Wilson, and C. Greenwood, *Biochem. J.*, 1974, **141**, 299.
[107] H. C. Jordi and J. E. Erman, *Biochemistry*, 1974, **13**, 3734.
[108] J. E. Erman, *Biochemistry*, 1974, **13**, 34.
[109] J. E. Erman, *Biochemistry*, 1974, **13**, 39.

The kinetics of the binding of azide (at low concentrations) to oxidized cytochrome *c* oxidase are biphasic:[110] a fast bimolecular step, strongly pH-dependent, is followed by a slow first-order reaction which is essentially pH-independent. The authors suggested that the active form of the ligand is HN_3 and determined a value of 2.5×10^6 l mol^{-1} s^{-1} for the rate constant of binding. The unimolecular process yields a rate constant of 0.03 s^{-1} and is interpreted in terms of an azide-induced conformational change in the protein. Low-temperature e.p.r. spectra show[111] that the binding of CO to reduced cytochrome a_3 (one of the two types of cytochrome contained in cytochrome *c* oxidase) changes the oxidized cytochrome *a* (the other type) from high-spin to low-spin. The haem–haem interaction demonstrated in this reaction is very fast since, even at 5 K, the measured change in oxidized cytochrome is complete within 5 ms. Cytochrome *c* oxidase also contains two atoms of copper, and the involvement of one of these (the so-called 'invisible' copper) in the binding of CO has recently been indicated.[112] Additional evidence for haem–haem interaction in this enzyme has been obtained[113] from kinetic studies on the binding of CO and O_2; it seems that the ligand-binding behaviour of cytochrome a_3 depends on the redox state of its partners.

The reduction of cytochrome *c* oxidase by hydrated electrons has been studied[114] in the absence and in the presence of cytochrome *c*. In the former case the haem group of the enzyme is not readily reduced, confirming a previous suggestion that haem *a* is not directly exposed to the solvent. In the presence of cytochrome *c* the latter is first reduced by e_{aq}^- ($k = 4 \times 10^{10}$ l mol^{-1} s^{-1} at 22 °C and pH 7.2) and then transfers electrons to the cytochrome *c* oxidase ($k = 6 \times 10^7$ l mol^{-1} s^{-1}). It was found that two equivalents of cytochrome *c* are oxidized initially per equivalent of haem *a* reduced, showing that one electron is accepted by a second group, probably one of the copper atoms in the enzyme.

Further kinetic studies have been reported on the incorporation of metal ions into porphyrin molecules. In most cases the results can be explained[115] in terms of a dissociative-interchange mechanism by taking into account porphyrin deformation. Evidence has been given[116] for the non-existence of 'sitting atop' complexes in aqueous solutions of metal porphyrins, while their involvement has been invoked[117] in the replacement of zinc by copper(II) in the tetrasulphonated tetraphenylporphyrin complex (for which the rate constant at 30 °C is 4.76×10^{-1} l mol^{-1} s^{-1}). The displacement of oxygen from [Fe(TPP)(base)(O_2)] (TPP = tetraphenylporphyrin) in CH_2Cl_2 is a dissociative process[118] in which the axial base exerts a *trans* effect with the lability of the co-ordinated oxygen decreasing in the order pyridine > piperidine ≫ 1-methylimidazole. In water, cobalt(II) tetrasulphophthalocyanine forms an adduct

[110] R. A. Wever, A. O. Muijsers, and B. F. van Gelder, *Biochim. Biophys. Acta*, 1973, **325**, 8.
[111] J. S. Leigh, D. F. Wilson, and C. S. Owen, *Arch. Biochem. Biophys.*, 1974, **160**, 476.
[112] J. G. Lindsay and D. F. Wilson, *F.E.B.S. Letters*, 1974, **48**, 45.
[113] C. Greenwood, M. T. Wilson, and M. Brunori, *Biochem. J.*, 1974, **137**, 205.
[114] K. J. H. van Buuren, B. F. van Gelder, J. Wilting, and R. Braams, *Biochim. Biophys. Acta*, 1974, **333**, 421.
[115] H. Baker, P. Hambright, L. Wagner, and L. Ross, *Inorg. Chem.*, 1973, **12**, 2200; P. Hambright and P. B. Chock, *J. Amer. Chem. Soc.*, 1974, **96**, 3123.
[116] H. Baker, P. Hambright, and L. Wagner, *J. Amer. Chem. Soc.*, 1973, **95**, 5942.
[117] S. K. Cheung, F. L. Dixon, E. B. Fleischer, D. Y. Jeter, and M. Krishnamurthy, *Bioinorg. Chem.*, 1973, **2**, 281.
[118] C. J. Weschler, D. L. Anderson, and F. Basolo, *J.C.S. Chem. Comm.*, 1974, 757.

with O_2 in which the stoicheiometry (Co : O_2) is 2 : 1. It has been shown[119] that the rate-determining step in this process is formation of the 1 : 1 adduct. The kinetics of binding of thiocyanate to a water-soluble cobalt(III) porphyrin[120] and of formation of the peroxidatic intermediate from deuterioferrihaem and hydrogen peroxide[121] have also been reported.

Six-co-ordinate low-spin iron(II) phthalocyanine complexes of the type L_2FePc (L = imidazole, pyridine, piperidine, or 2-methylimidazole) reversibly bind carbon monoxide in toluene solution. The reaction has a dissociative mechanism and it is found[122] that the limiting first-order rate constants for the dissociation of L parallel the equilibrium constants for reaction (8), *viz.* 2-MeIm > pip > py ≫ Im. A substantial

$$L_2FePc + CO \rightleftharpoons LFePc(CO) + L \qquad (8)$$

trans effect is observed for imidazole in the dissociation of CO from LFePc(CO).

The mechanisms of reduction of haematoporphyrin and its zinc complex have been investigated by pulse radiolysis.[123]

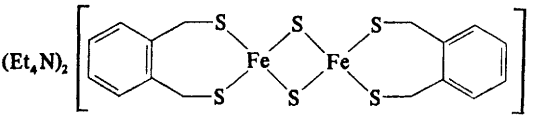
5 Redox Reactions involving Metals in other Biological and Model Systems

In addition to the monograph on the iron–sulphur proteins,[3] there have been two reviews[124,125] on this important class of macromolecule, and the IUPAC–IUB commission on biochemical nomenclature has published[126] recommendations on their nomenclature. A method has been described[127] for the interpretation of e.p.r. spectra of reduced dinuclear iron–sulphur proteins which will allow both the symmetry and the extent of covalency at the paramagnetic site to be parameterized. The parameters can then be related to the chemical composition of the paramagnetic centre, the protein-dependent charge delocalization of the unpaired electron, and the geometrical arrangement at the reduced iron atom – an analysis which, it is hoped, will ultimately be useful in rationalizing the redox behaviour of these important metalloproteins.

Clostridial ferredoxin, which is characterized by two clusters containing four sulphur-linked iron atoms each, has been studied[128] by Mössbauer and e.s.r. spectroscopy. The iron of oxidized ferredoxin is high-spin Fe^{III} and reduction leads to an uptake of one electron per cluster. The two Fe^{III} centres in oxidized spinach ferredoxin are not equivalent[129] and it seems that the metal co-ordination geometry at the non-reducible site is basically tetrahedral. The first well-defined synthetic analogue of the active sites of two-iron ferredoxins has been prepared and charac-

[119] D. M. Wagnerová, E. Schwertnerová, and J. Vepřek-Šiška, *Coll. Czech. Chem. Comm.*, 1974, **39**, 1980.
[120] R. F. Pasternack and M. A. Cobb, *J. Inorg. Nuclear Chem.*, 1973, **35**, 4327.
[121] P. Jones, K. Prudhoe, T. Robson, and H. C. Kelly, *Biochemistry*, 1974, **13**, 4279.
[122] D. V. Stynes and B. R. James, *J. Amer. Chem. Soc.*, 1974, **96**, 2733.
[123] Y. Harel and D. Meyerstein, *J. Amer. Chem. Soc.*, 1974, **96**, 2720.
[124] S. J. Lippard, *Accounts Chem. Res.*, 1973, **6**, 282.
[125] R. Mason and J. A. Zubieta, *Angew. Chem. Internat. Edn.*, 1973, **12**, 390.
[126] *J. Biol. Chem.*, 1973, **248**, 5907.
[127] W. E. Blumberg and J. Peisach, *Arch. Biochem. Biophys.*, 1974, **162**, 502.
[128] K. Gersonde, H. E. Schlaak, M. Breitenbach, F. Parak, H. Eicher, W. Zgorzalla, M. G. Kalvius, and A. Mayer, *European J. Biochem.*, 1974, **43**, 307.
[129] J. Rawlings, O. Siiman, and H. B. Gray, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 125.

terized.[130] Compound (7) contains two tetrahedrally co-ordinated ferric ions bridged by two sulphide ions and separated by 2.70 Å. Comparison of electronic, Mössbauer, and ^1H n.m.r. spectra and magnetic susceptibility of the anion with the corresponding properties of the oxidized forms of the proteins shows significant similarity. The



(7)

anion also exhibits the essential redox capacity of the proteins and the conclusion is that it possesses the same total oxidation level and electronic configuration as the active site of the oxidized proteins, and that its structure provides a feasible representation of the minimal structure of the active site.

Although we are beginning to build up a structural and electronic picture of the active site of the iron–sulphur proteins, very little is known about their kinetic properties. The rate parameters have recently been reported[131] for the second-order reduction of oxidized clostridial rubredoxin by $[Ru(NH_3)_6]^{2+}$, V_{aq}^{2+}, and Cr_{aq}^{2+} (Table 3). Rubredoxin is the least complex of the Fe–S proteins (mol. wt. *ca.* 6000;

Table 3 *Kinetic data for the reduction of clostridial rubredoxin*[131]

Reductant	k (25 °C)/ l mol^{-1} s^{-1}	*Ionic strength*/ mol l^{-1}	pH	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
$[Ru(NH_3)_6]^{2+}$	9.5×10^4	0.10	6.3—7.0	(1.4)	(−31)
$[V(H_2O)_6]^{2+}$	1.1×10^4	0.50	3.5—4.5	0.1	−40
	1.6×10^4	0.10	4.0		
	4.0×10^4	0.010	4.0		
$[Cr(H_2O)_6]^{2+}$	1.2×10^3	0.10	3.5—4.0	≃(0)	≃(−44)

1 Fe per molecule), and it is known that the Fe is co-ordinated close to the surface of the crystalline protein by four cysteine sulphurs at the apices of a distorted tetrahedron; moreover, there is evidence that the immediate environment of the metal is little different in solution and in the crystal. The ionic-strength dependence of the V^{2+} rate constant suggests that there is a direct interaction between the reductants and the $[Fe(SR)_4]^-$ site and it is proposed that an outer-sphere mechanism operates in all three cases. Evidence is presented in support of an absolute entropy decrease of *ca.* 7.5 cal K^{-1} mol^{-1} on going from oxidized to reduced rubredoxin, which is presumably attributable to the charge increase from −1 to −2 at the redox site. In a preliminary note it is reported[132] that both e_{aq}^- and CO_2^- reduce the redox centre of spinach ferredoxin directly and without any detectable intermediates, in contrast to their behaviour with various oxidases.

Ferritin, the iron-storage protein, has a unique structure consisting of a microcrystalline sphere, *ca.* 70 Å in diameter, of hydroxy-iron(III) phosphate surrounded

[130] J. J. Mayerle, R. B. Frankel, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 2429.
[131] C. A. Jacks, L. E. Bennett, W. N. Raymond, and W. Lovenberg, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1118.
[132] I. Pecht, *F.E.B.S. Letters*, 1973, **33**, 259.

by a protein shell. (A review has recently appeared[133] on the subject.) The kinetics of liberation of iron from ferritin as Fe^{II} have been reported,[134] and structure–function relationships have been given[135] for ferritin iron uptake and release. A model has been made[136] which, it is hoped, will help in the elucidation of the mechanism of iron(III) transport through the ferritin protein shell.

The two components of the Fe–Mo protein nitrogenase, which is responsible for the fixation of nitrogen by microbes, have been purified and characterized from several sources.[137] It seems that the enzyme acts through an elaborate mechanism which involves electron transport from one protein to the other promoted by reaction with Mg-ATP. Further results with a nitrogenase model have been reported.[138]

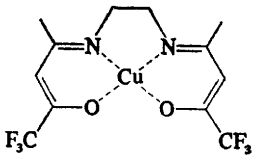
Haemerythrins and haemocyanins are large non-haem respiratory proteins (the former containing iron, the latter copper) about which relatively little is known. The binding of oxygen to each of them has recently been studied by resonance Raman spectroscopy. With haemerythrin, resonances assigned to bound O_2^{2-} and Fe—O were observed,[139] and with haemocyanin[140] resonances assigned to bound O_2^{2-} and a vibration involving magnetically coupled Cu^{II}–Cu^{II} centres. The kinetics of the binding of oxygen to haemocyanin from *Helix pomatia* have been reported[141] under conditions where ligand binding is co-operative and under conditions where it is non-co-operative. In the first case, the initial rate constant for oxygen combination to the fully deoxygenated state is $2—3 \times 10^5$ l mol^{-1} s^{-1} but as the reaction progresses this increases to a value higher than 10^6 l mol^{-1} s^{-1}. At fractional saturations between 0.7 and 0.97 only a single relaxation process is observed, suggesting that no structural transition is occurring under these conditions (the $R \rightleftharpoons T$ transition being relatively slow). The binding of CO to three haemocyanins has also been studied kinetically, and large differences have been observed[142] compared with the binding of O_2.

The kinetics of formation of the intermediate complex between catalase and H_2O_2 have been re-examined,[143] and reports of pulse radiolysis experiments with superoxide dismutase[144] and its manganese-containing form[145] have appeared. Bovine superoxide dismutase is known to contain two Cu^{II} and two Zn^{II} atoms per molecule and it has been shown that the copper site, which is directly involved in the catalytic activity, comprises three nitrogens and a water molecule bound to the metal in a field with less than axial symmetry. Less is known of the zinc site but it has recently been shown,[146] by e.p.r. spectroscopy with the cobalt–copper form of the enzyme, that the

[133] R. R. Crichton, *Structure and Bonding*, 1973, **17**, 67.
[134] S. Sirivech, E. Frieden, and S. Osaki, *Biochem. J.*, 1974, **143**, 311.
[135] P. M. Harrison, T. G. Hoy, I. G. Macara, and R. J. Hoare, *Biochem. J.*, 1974, **143**, 445.
[136] B. A. Sommer, D. W. Margerum, J. Renner, P. Saltman, and T. G. Spiro, *Bioinorg. Chem.*, 1973, **2**, 295.
[137] R. R. Eady and J. R. Postgate, *Nature*, 1974, **249**, 805.
[138] G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. A. Doemeny, *J. Amer. Chem. Soc.*, 1974, **96**, 641.
[139] J. B. R. Dunn, D. F. Shriver, and I. M. Klotz, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 2582.
[140] J. S. Loehr, T. B. Freedman, and T. M. Loehr, *Biochem. Biophys. Res. Comm.*, 1974, **56**, 510.
[141] R. van Driel, M. Brunori, and E. Antonini, *J. Mol. Biol.*, 1974, **89**, 103.
[142] C. Bonaventura, B. Sullivan, J. Bonaventura, and S. Bourne, *Biochemistry*, 1974, **13**, 4784.
[143] E. Zidoni and M. L. Kremer, *Arch. Biochem. Biophys.*, 1974, **161**, 658.
[144] E. M. Fielden, P. B. Roberts, R. C. Bray, D. J. Lowe, G. N. Mautner, G. Rotilio, and L. Calabrese, *Biochem. J.*, 1974, **139**, 49.
[145] M. Pick, J. Rabani, F. Yost, and I. Fridovich, *J. Amer. Chem. Soc.*, 1974, **96**, 7329.
[146] G. Rotilio, L. Calabrese, B. Mondoví, and W. E. Blumberg, *J. Biol. Chem.*, 1974, **249**, 3157.

two metal centres are magnetically coupled [but the two cobalt (zinc) sites are non-interacting]. The e.p.r. spectrum of the Co^{II} can only be seen after reduction of the Cu^{II}, and it is typical of tetrahedral co-ordination which is distorted in a particular way. Anions such as CN^- and N_3^- do not affect the e.p.r. spectrum of the Co^{II} significantly, but they do modify the spectrum of the Cu^{II}. Interestingly, the e.p.r. spectrum of the cobalt enzyme is similar to that of the 1 : 1 CN^- complex of human carbonic anhydrase B.

The copper(II) in superoxide dismutase is of the so-called Type 2 in that it exhibits properties similar to those of small Cu^{II} complexes. It has recently been suggested[147] that a distinguishing feature of Types 1 and 2 copper(II) is that the latter is accessible to exchangeable water molecules whereas the former is not. The copper(II) of stellacyanin is of Type 1 (or 'blue') and it has been shown[148] that addition of the metal to the apoprotein occurs in two steps. The first stage is rapid and involves binding of copper to the protein in a non-native, though specific way. All the spectroscopic properties of native stellacyanin are recovered in a slower unimolecular process ($k = 7.5 \times 10^{-3}\ s^{-1}$ at 25 °C) characterized by a high activation energy (22 kcal mol^{-1}) and low activation entropy (3 cal $K^{-1}\ mol^{-1}$). The second step parallels a conformational change of the copper-bound protein, and ammonia or univalent anions (N_3^-, SCN^-, Cl^-) have a catalytic effect on it which approximately parallels their first binding constant to Cu_{aq}^{2+}. It is suggested that they may compete for a non-native bond of the copper to the protein, thereby facilitating the conformational change. From the spectrum of the cobalt(II) form of the protein, it is suggested[149] that one of the metal-binding groups is a cysteine sulphur atom. A similar suggestion has been made[150] for the other Type 1 copper(II) proteins plastocyanin and azurin. Galactose oxidase is one of the simplest Type 2 Cu^{II} proteins known inasmuch as it only contains one Cu^{2+} per molecule. In an attempt to understand the nature of the metal binding in this enzyme it has been proposed,[151] largely on the basis of e.p.r. results, that (8) represents a good model for the equatorial co-ordination in the



(8)

enzyme. The authors conclude that the differences between the optical properties of Type 1 and Type 2 copper(II) cannot be equated merely to differences in the degree of distortion of the copper ligand field, suggesting that some contribution related to the chemical identity of the ligand must also be taken into account.

[147] N. Boden, M. C. Holmes, and P. F. Knowles, *Biochem. Biophys. Res. Comm.*, 1974, **57**, 845.
[148] L. Morpurgo, G. Rotilio, A. Finazzi-Agró, and B. Mondovì, *Arch. Biochem. Biophys.*, 1974, **161**, 291.
[149] D. R. McMillin, R. A. Holwerda, and H. B. Gray, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 1339.
[150] D. R. McMillin, R. C. Rosenberg, and H. B. Gray, *Proc. Nat. Acad. Sci. U.S.A.*, 1974, **71**, 4760.
[151] R. S. Giordano and R. D. Bereman, *J. Amer. Chem. Soc.*, 1974, **96**, 1019; R. S. Giordano, R. D. Bereman, D. J. Kosman, and M. J. Ettinger, *ibid.*, p. 1023.

Part IV

ORGANOMETALLIC COMPOUNDS

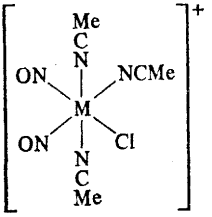
By
R. D. W. KEMMITT
M. A. R. SMITH

1
Substitution

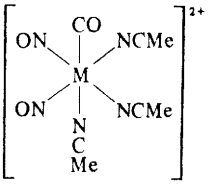
BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Exchange Reactions

Initial substitution of MeCN by [$^2H_3$]MeCN in *cis*-[$M(NO)_2(MeCN)_4$]$^{2+}$ (M = Mo or W) takes place specifically in the equatorial positions, although under forcing conditions complete substitution is possible. This is considered to arise as a result of the *trans*-labilizing influence of the nitrosyl ligands, a conclusion supported by the failure of *trans*-[$Cr(NO)_2(MeCN)_4$]$^{2+}$ to undergo exchange and by exchange of only one or two MeCN ligands respectively in (1) and (2). The mechanism itself is dis-



(1)



(2)

sociative, whereas metal–nitrosyl complexes are commonly observed to react *via* associative pathways. That the present reaction should not be considered surprising follows from the authors' observation that, in those reactions which do follow an associative course, loss of NO itself is observed.[1] This is illustrated in the case of ^{15}NO exchange with [$Fe(NO)_2IL$] (L = $AsPh_3$ or PPh_3), which follows second-order kinetics, although in the analogous cobalt complexes rate laws indicating first- and second-order processes were derived. The results may be accounted for in terms of the increased σ-donor ability of PPh_3 compared with $AsPh_3$ and the effect of this on the π-component of the M—NO bond.[2]

Infrared analysis indicates that the photolytically assisted mono- or di-substitution of ^{13}CO in [$M(CO)_4$(nbd)] (M = Cr, Mo, or W; nbd = norbornadiene) occurs stereospecifically in the axial position(s). On standing in the dark conversion into the equatorially substituted complexes takes place. The proposed mechanism initially involves dissociative exchange with labelled carbonyl, and subsequently axial–equatorial equilibration of carbonyls *via* opening of the norbornadiene chelate ring, rather than by carbonyl scrambling.[3] A brief report of intermolecular redistribution

[1] B. F. G. Johnson, A. Khair, C. G. Savory, and R. H. Walter, *J.C.S. Chem. Comm.*, 1974, 744.
[2] G. Innorta, S. Torroni, and A. Foffani, *J. Organometallic Chem.*, 1974, **66**, 459.
[3] D. J. Darensbourg and H. H. Nelson, *J. Amer. Chem. Soc.*, 1974, **96**, 6511.

of carbonyl, halide, and phosphine in complexes of the type $[M(CO)X(PR_3)_2]$ (M = Rh or Ir; X = Cl or Br) proposes that carbonyl and halogen exchange occurs *via* dihalogeno- and dicarbonyl-bridged dimers in which each metal atom is five-co-ordinate.[4]

Lineshape analysis of variable-temperature n.m.r. spectra of the benzyl methylene protons indicate that exchange of 3,5-lutidine between $[M(CH_2Ph)_4]$ (M = Hf or Zr) and $[(3,5\text{-lutidine})M(CH_2Ph)_4]$ occurs *via* rate-determining dissociation of the base. This is supported by the values obtained for $\Delta S^{\ddagger}$, 13.0 ± 1.5 cal K^{-1} mol^{-1} (M = Hf) and 23.7 ± 3.0 cal K^{-1} mol^{-1} (M = Zr). In the presence of excess base, however, rapid bimolecular exchange of free and complexed base occurs and this could not be arrested even at 238 K.[5]

2 Substitution in Carbonyls: Carbon Monoxide Replacement

Simple Carbonyls.—The co-ordinatively unsaturated species $[Cr(CO)_5]$ can be generated by flash or conventional photolysis of $[Cr(CO)_6]$ (see Volumes 2 and 3 of these Reports). In the current period the reaction of this species with several common solvents L, to afford $[Cr(CO)_5L]$, has been described. The systems studied and the rate constants found for the formation process (1) are summarized in Table 1. In the

$$[Cr(CO)_5] + L \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Cr(CO)_5L] \qquad (1)$$

Table 1 *Rate constants and stability constants for reaction of* $Cr(CO)_5$ *with* L (*from ref.* 6)

L	k_1/l mol^{-1} s^{-1}	k_2/s^{-1}	K/l mol^{-1}
Benzene	7.0×10^6	2.1×10^5	3.4×10^1
Diethyl ether	1.1×10^7	1.4×10^2	7.6×10^4
Methanol	3.1×10^7		
Ethyl acetate	9.2×10^7	8.1×10^1	1.1×10^6
Acetone	1.3×10^8	1.4×10^1	9.3×10^6
Acetonitrile	1.6×10^8	$< 1 \times 10^{-2}$	$> 1 \times 10^{10}$

case of L = MeOH, unlike the other 'ligands', k_2 was found to depend on MeOH; more precisely, plots of k_2 against 1/[MeOH] are linear. The authors suggest that this could arise by reaction of $[Cr(CO)_5(MeOH)]$ with a further molecule of methanol. The exact nature of the resultant species {$[Cr(CO)_4(MeOH)_2]$ and $[Cr(CO)_5(\bar{O}Me\cdots\overset{+}{M}eOH_2)]$ are suggested} must, however, await further investigation.[6] Reaction of $[M(CO)_6]$ with Bu_4NX (X = Cl, Br, or I) in chlorobenzene to give $[Bu_4N][M(CO)_5X]$ proceeds according to second-order rate laws for M = Mo or W. In the case of M = Cr an additional first-order pathway corresponding to rate-determining dissociation of CO is found in the rate law. Comparison of the relative rates of the second-order paths with earlier results leads to the conclusion that, prior to fast rearrangement to the products, rate-determining attack of X^- takes place at the metal for M = Mo or W but on a carbonyl carbon in the chromium complex.[7]

[4] P. E. Garrou and G. E. Hartwell, *J.C.S. Chem. Comm.*, 1974, 381.
[5] J. J. Felten and W. P. Anderson, *Inorg. Chem.*, 1973, **12**, 2334.
[6] J. M. Kelly, D. V. Bent, H. Hermann, D. Schulte-Frohlinde, and E. Koerner von Gustorf, *J. Organometallic Chem.*, 1974, **69**, 259.
[7] J. E. Pardue, M. N. Memering, and G. R. Dobson, *J. Organometallic Chem.*, 1974, **71**, 407.

A rather recent concept, at least in the field of inorganic and organometallic kinetics, is activation volume. This can be defined as the product of the cross-sectional area of the molecule in question and the increase in bond length in going to the transition state. Instead of studying the effect of varying the temperature at constant pressure on reaction rates the alternative situation, the effect of varying the pressure at constant temperature, is examined. From this can be derived values of $\Delta V^{\ddagger}$ as the slope of plots of p *versus* ln $(k_p/k_{1\ \mathrm{atm}})$ in agreement with equation (2).

$$RT\left(\frac{\partial \ln k}{\partial p}\right)_T = -\Delta V^{\ddagger} \qquad (2)$$

It has been suggested that, in the absence of serious electrostrictive effects, this parameter can indicate with less ambiguity than $\Delta S^{\ddagger}$ (its 'equivalent' at constant pressure) whether a reaction is associative or dissociative, a value of *ca.* -10 ml mol^{-1} indicating the former and *ca.* $+10$ ml mol^{-1} the latter.[8] This supposition has been tested for several already well characterized substitution reactions that should not be subject to any severe electrostriction with, as shown by the data in Table 2,

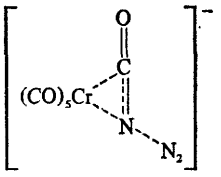
Table 2 *Volumes of activation for several known substitution reactions (from ref.* 9)

Substrate	*Ligand*	*Kinetic order*	*Solvent*	$\Delta V^{\ddagger}$/ml mol^{-1}
$[Ni(CO)_4]$	$(EtO)_3P$	first	heptane	8 ± 1
$[Mo(CO)_6]$	Ph_3P	first	'iso-octane'	10 ± 1
$[Cr(CO)_6]$	Ph_3P	first	cyclohexane	15 ± 1
$[W(CO)_6]$	Bu_3P	second	cyclohexane	-10 ± 1

considerable success. In the case of the reaction

$$[Cr(CO)_6] + N_3^- \longrightarrow [Cr(CO)_5(NCO)]^- + N_2$$

a value of $\Delta V^{\ddagger}$ close to 0 was found. This was interpreted in terms of a possible transition state structure (3) to which bond-making and -breaking contribute about equally.[9]



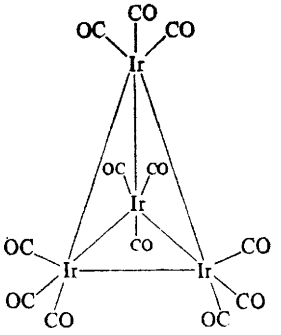
(3)

Polynuclear Carbonyls.—It has been shown that substitution reactions of $[Ru_3(CO)_{12}]$ with Group Vb donors follow the rate law $k_{obs} = k_1 + k_2[L]$, where L = PPh_3, $AsPh_3$, $P(OPh)_3$, $P[(OCH_2)_3CEt]$, $P(OEt)_3$, or PBu^n_3, and that contrary to earlier reports the k_2 term contributes significantly to the overall rate. A recent, more detailed analysis has now appeared. The nature of the reaction products varies considerably but the kinetic equation above is quite clear. The first-order path corresponds

[8] See, *e.g.*, D. R. Stranks, 15th International Conference on Coordination Chemistry, *Pure Appl. Chem.*, 1974, **38**, 303.

[9] K. R. Brower and T.-s. Chen, *Inorg. Chem.*, 1973, **12**, 2198.

to a simple dissociative mechanism and this is amply confirmed by rate inhibition by added CO. The importance of bond making in these (and a varied set of other) reactions was probed by a linear free-energy relationship which involved plotting log k_2 against Δ(hnp) (the relative half neutralization potentials when titrating the nucleophile L against perchloric acid in nitromethane), the latter providing a measure of the basicity of the nucleophile. A considerable degree of bond-making was thereby indicated, most probably in the form of straightforward nucleophilic attack at ruthenium. Deviation from the relationship in the case of PPh_3 and $P(C_6H_{11})_3$ can be ascribed to the steric effects arising from their large cone angles.[10] Reaction of $[Ir_4(CO)_{12}]$ (4) with PPh_3 gives $[Ir_4(CO)_9(PPh_3)_3]$ (7) with no evidence for intermediate substitution products. However, by effectively commencing the substitution



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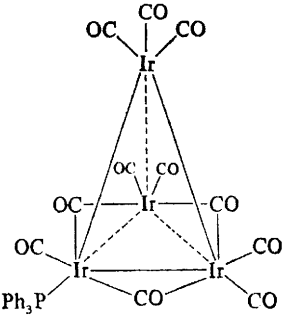

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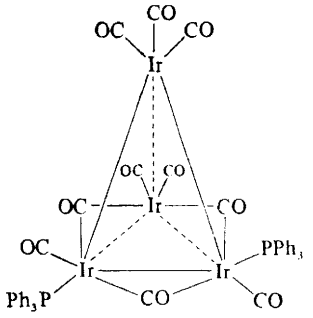

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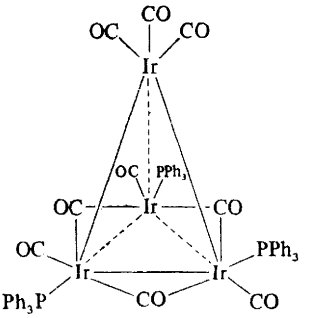


(7)

at each stage, *i.e.* with (5) and (6) [which all lead to (7)], information about the relative rates of individual stages can be derived. Data are summarized in Table 3. The relative magnitudes of the specific rates of the reactions (4)→(5) and (5)→(6), together with the change of mechanism, are consistent with the change from a non-bridged to a bridged structure, promotion of dissociative lability by such being already well known. However, since this acceleration is passed on to the reaction

[10] A. Poë and M. V. Twigg, *J.C.S. Dalton*, 1974, 1860.

Table 3 *Progressive substitution of* $[Ir_4(CO)_{12}]$ *by* PPh_3 (*from ref.* 11)

Reaction	*Rate law*	*Rate constant*	*Specific rate* $\times 10^6$/s^{-1} (348 K)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
(4)→(5)	k_1 [(4)][PPh_3]	5.6×10^{-3} l mol^{-1} s^{-1} (379 K)	1.5[b]	20.6	−22
(5)→(6)	k_2 [(5)]	8.8×10^{-5} s^{-1} (348 K)	44	31.8	+14
(6)→(7)	k_3 [(6)]	1.4×10^{-3} s^{-1} (348 K)	1380	31.0	+17

[a] Corrected for the number of available symmetry-related carbonyl sites, *i.e.* 12 for (4), 2 for (5), and 1 for (6). [b] Extrapolated from higher temperatures at $[PPh_3] = 3.82\times10^{-2}$ mol l^{-1}.

(6)→(7), enhanced lability promoted by substitution must be occurring. This contrasts with the classical example of dissociative substitution of $[Ni(CO)_4]$ by PPh_3, where progressive substitution slows down the rate of each successive reaction. A possible explanation here could be in terms of increasing ease of formation of semi-bridging carbonyl groups in the transition state (see ref. 30 of Chapter 7).[11] The complex reaction whereby $[Co_2(CO)_8]$ is converted into $[Co_4(CO)_{12}]$ in heptane proceeds according to the rate equation

$$d[Co_4(CO)_{12}]/dt = k_{obs}[Co_2(CO)_8]^2[CO]^{-2}$$

The only real possibility to emerge from the data is the intermediacy, as in other reactions of $[Co_2(CO)_8]$, of $[Co_2(CO)_7]$ in the mechanism.[12]

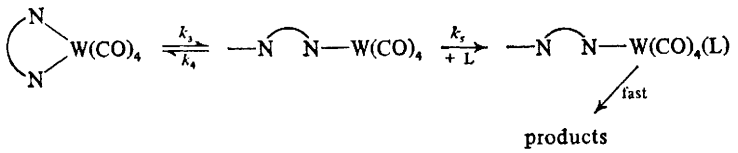
Mixed-ligand Carbonyls.—*Groups VI and VII.* Continuing kinetic studies of the chelation reaction

$$[(PP)M(CO)_5] \longrightarrow [(PP)M(CO)_4] + CO$$

[M = Cr or Mo; PP = $Ph_2PC_2H_4PPh_2$ (dpe) or $Me_2PC_2H_4PMe_2$ (dmpe)] confirm previous observations that chelation is more rapid in the molybdenum complexes and also reveal that this is doubly so in the case of dmpe compared with the phenyl analogue. For a given metal, however, dpe chelates faster than dmpe. Enthalpy considerations suggest that a dissociative pathway may be more important in the chromium complexes although a concerted mechanism in both cases seems likely.[13] Previous examination of the reaction of Lewis bases L with $[(bipy)M(CO)_4]$ (M = Mo or W) resulted in the proposed rate law $k_{obs} = k_1 + k_2[L]$, where the respective k_1 and k_2 terms were attributed to the normal dissociative and associative mechanisms. Two obvious inconsistencies were apparent, however. Firstly k_1 varies with the nature of L and secondly values of $\Delta S^{\ddagger}$ were rather negative for a reaction involving a large degree of bond-breaking in the transition state. A re-examination [M = W; L = $P(O_3C_6H_9)$ or $P(OEt)_3$] now proposes an additional mechanism (Scheme 1) involving dechelation of bipyridyl, which on steady-state treatment of $[(N\frown N)W(CO)_4]$ yields the combined rate law

$$k_{obs} = \frac{k_1k_4 + (k_2k_4 + k_1k_5 + k_3k_5)[L] + k_2k_5[L]^2}{k_4 + k_5[L]}$$

[11] K. J. Karel and J. R. Norton, *J. Amer. Chem. Soc.*, 1974, **96**, 6812.
[12] F. Ungvary and L. Marko, *J. Organometallic Chem.*, 1974, **71**, 283.
[13] J. A. Connor and G. A. Hudson, *J. Organometallic Chem.*, 1974, **73**, 351.



Scheme 1

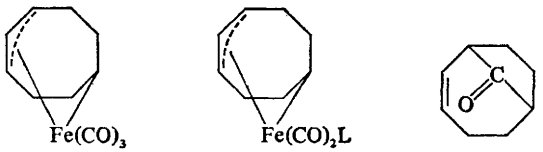
Accordingly, for high concentrations (> 0.2 mol l^{-1}) of the stronger base $P(O_3C_6H_9)$, $k_5[L]$ becomes significant, and plots of k_{obs} *versus* [L] diverge from linearity, an observation which cannot be accounted for by the previous rate law. Linear plots for L = $P(OEt)_3$ are consistent with a lower value of $k_5[L]$, thereby reducing the contribution of Scheme 1 to the overall ligand-dependent term. In addition, unlike the previous study but in agreement with the k_1 pathway, identical intercepts for $P(O_3C_6H_9)$ and $P(OEt)_3$ were found. Finally, the observation of *trans*-$[L_2W(CO)_4]$ in the products also testifies to the operation of the dechelation mechanism.[14]

Substitution of one carbonyl ligand in $[MnRe(CO)_{10}]$ by PPh_3 predominantly leads to *ax*-$[(CO)_5MnRe(CO)_4(PPh_3)]$. However, evidence was obtained from spectroscopic and kinetic measurements for the existence in solution of *ax*-$[(PPh_3)(CO)_4MnRe(CO)_5]$. Consistent with a lower degree of kinetic stability in the Mn–PPh_3 isomer, reaction with PPh_3 to give $[MnRe(CO)_8(PPh_3)_2]$ is considerably faster than in the case of the Re–PPh_3 isomer.[15]

Group VIII. Iron. Products of the reaction of tricarbonyl-(1,2,3,6-h^4-cyclo-octadiene)-iron (8) with phosphines depend on the nucleophilicity of the base. In the case of PPh_3 and $P(OPh)_3$, (9) is formed by carbonyl dissociation followed by addition of the base. This leads to the familiar rate law

$$k_{obs} = \frac{k_1k_2[L]}{k_{-1}[CO] + k_2[L]}$$

which is further evidenced by the approach to a limiting rate as [L] is increased and by values of $\Delta S^{\ddagger} = 15.2 \pm 0.5$ cal K^{-1} mol^{-1} and $\Delta H = 29.21 \pm 0.16$ kcal mol^{-1}. Reaction with stronger nucleophiles (alkylphosphines and alkyl phosphites) leads to the rate law $k_{obs} = k_1 + k_2'[L]$, in which k_1 is shown to correspond to the dissociative pathway above. The bimolecular process characterized by k_2' is associated with formation of $[FeL_3(CO)_2]$ and the transannular ketone (10). Activation para-



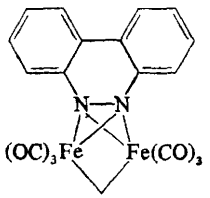
(8) (9) (10)

meters $\Delta S = -27.0 \pm 1.6$ cal K^{-1} mol^{-1} and $\Delta H = 13.7 \pm 0.5$ kcal mol^{-1} [L = $P(OEt)_3$] again typify the proposed mechanism. Examination of product and rate-

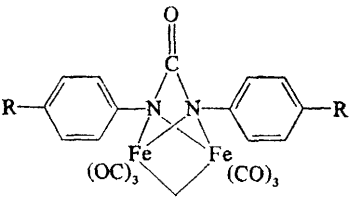
[14] M. N. Memering and G. R. Dobson, *Inorg. Chem.*, 1973, **12**, 2490.
[15] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **61**, 315.

constant ratios obtained by monitoring the reactant [L = $P(OEt)_3$] or the two metal carbonyl products confirms that formation of (9) and [$FeL_3(CO)_2$] [L = $P(OEt)_3$] takes place exclusively by the k_1 and k_2' paths. The ruthenium analogue of (8) reacts with a range of phosphines [PPh_3, $P(OPh)_3$, $P(OEt)_3$, PBu^n_3] only by the CO-dissociative mechanism but at a rate *ca.* 40 times that of the corresponding reaction in the iron system. As in the case of the iron complex this is confirmed by values of $\Delta S^* = 13.8$ cal K^{-1} mol^{-1} and $\Delta H^* = 26.5$ kcal mol^{-1}. The greater reactivity of the ruthenium complex can be reconciled with the more favourable enthalpy of activation.[16] Substitution reactions of [(η-C_3H_4X)$Fe(CO)_2(NO)$] with phosphorus bases L are found to depend on the nature and position of X and on L. When X = 1-Me, 1-Ph, or 2-Me and L = PPh_3 or $P(OEt)_3$, [(η-C_3H_4X)Fe(CO)-(NO)L] is formed according to an associative mechanism, with the exception that for X = 2-Me, L = PPh_3 a parallel dissociative route operates. On the other hand, for X = 1-Cl, 1-CN, 2-Cl, or 2-Br and L = PPh_3, PBu^n_3, PPh_2Et, $P(OEt)_3$, or $P(OCH_2)_3CEt$, first of all [(σ-C_3H_4X)$Fe(CO)_2(NO)$L] is formed by a second-order associative mechanism, and this species subsequently rearranges *via* a first-order associative intramolecular chelation process to give [(1-σ-2,3-η-C_3H_4X)Fe(CO)-(NO)L]. Examination of the relative rates of all these processes indicates that the most important factors in determining the reaction course are the basicity and electronic properties of L. Parallel to the rearrangement described above, [(σ-C_3H_4X)$Fe(CO)_2(NO)$L] [X = 1-Cl, 2-Cl, or 2-Br; L = $P(OEt)_3$ or $P(OMe)_3$] also undergo disubstitution, giving the but-3-enoyl complexes [(σ-XC_3H_4CO)Fe(CO)-(NO)L_2]. The fact that disubstitution only occurs with the strongest nucleophiles and best π-acceptors indicates the dominance of these factors in determining the reaction course.[17] Carbonyl substitution reactions of [$Fe_2(CO)_6(S_2C_6H_3Me)$] and [$Fe_2(CO)_6$-($S_2C_2H_4$)] by Group Vb bases proceed according to second-order kinetics. Whether mono- or di-substitution occurs, substitution of the first carbonyl is rate determining. The picture is complicated somewhat in the case of substitution of [$Fe_2(CO)_6(SR)_2$] (R = Me, Et, CH_2Ph, Ph, or p-C_6H_4Me) by PPh_3 since the bridging organothio-groups are not rigid, unlike those above, and can exist in *syn* and *anti* configurations. Although *syn–anti* equilibration did interfere somewhat (with the equilibrium probably favouring the *anti*-isomer), it was still possible to show that the same second-order rate law applied to substitution in each isomer. Substitution in the *anti*-form was found to be considerably slower than in the *syn*. Thus the original site of nucleophilic attack is possibly indicated as that afforded shelter in the *anti*-isomer. This in turn leads to a speculative indication that the structure of the activated complex in the transition state is an octahedral wedge in which the entering and leaving groups occupy an edge parallel to that defined by the sulphur atoms.[18] This hypothesis is supported, however, by a study of carbonyl substitution in isostructural nitrogen-bridged complexes (11), (12; R = H or OMe), and (13) by Group Vb nucleophiles. In the case of (11) and (12) similar results and conclusions apply, *i.e.* second-order kinetics, an S_N2 or I_a mechanism, and an analogous octahedral wedge in the transition state. In (13) formation of such a structure is blocked by the conformation

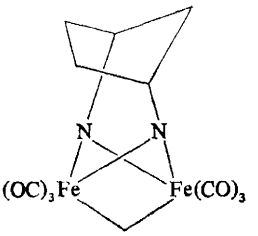
[16] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1974, 241.
[17] G. Cardaci, *J.C.S. Dalton*, 1974, 2452.
[18] P. C. Ellgen and J. N. Gerlach, *Inorg. Chem.*, 1973, **12**, 2526.



(11)



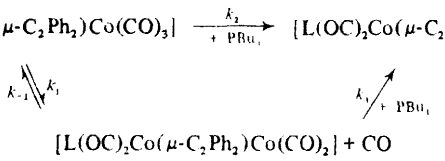
(12)



(13)

adopted by the nitrogen ligand, and, consistent with its formation in the reactions above, this complex is substitution inert.[19]

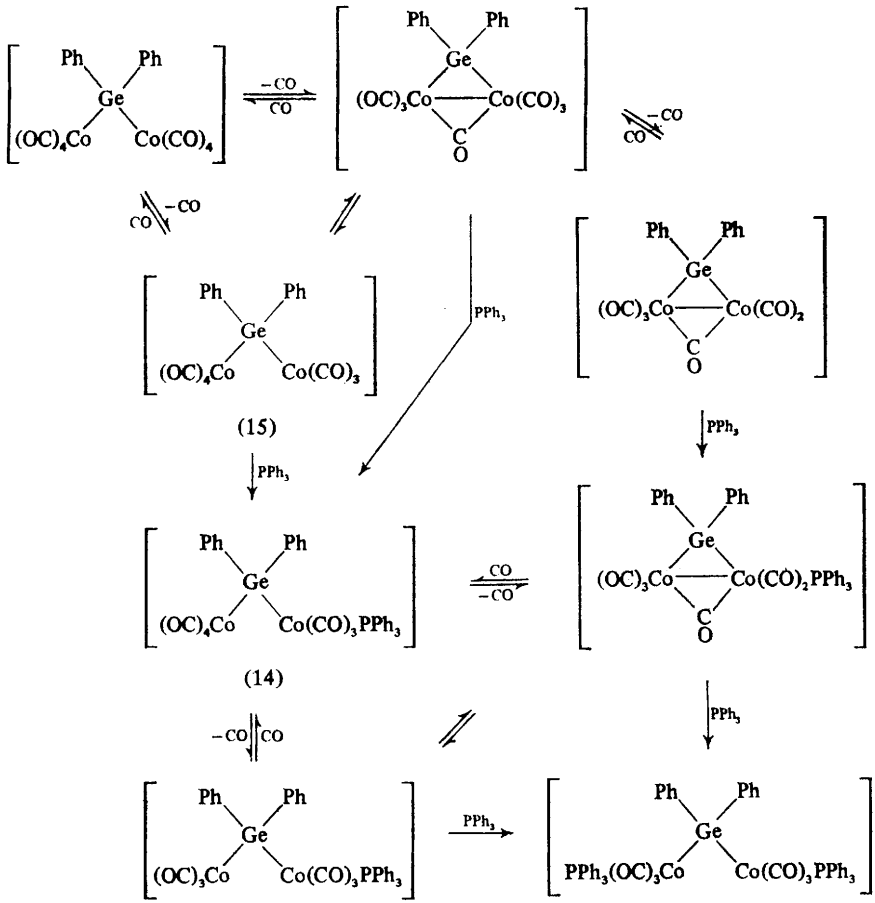
Cobalt. The reaction between $[(CO)_3Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ and tri-n-butylphosphine proceeds in two separately identifiable stages. The kinetics of both stages are consistent with concurrent dissociative and associative pathways (Scheme 2;



Scheme 2

L = CO for the first stage and PBu^n_3 for the second). Activation parameters for the two stages for the first-order path are very similar [$\Delta H_1^{\ddagger} = 136.3 \pm 4.2$ kJ mol^{-1}, $\Delta S_1^{\ddagger} = 100 \pm 13$ J K^{-1} mol^{-1} (first stage) and $\Delta H_1^{\ddagger} = 130.0 \pm 1.7$ kJ mol^{-1}, $\Delta S_1^{\ddagger} = 75 \pm 4$ J K^{-1} mol^{-1} (second stage)]. However, those for the associative path ($\Delta H_2^{\ddagger} = 52 \pm 0.6$ kJ mol^{-1}, $\Delta S_2^{\ddagger} = -122 \pm 2$ J K^{-1} mol^{-1} (first stage), and $\Delta H_2^{\ddagger} = 107.4 \pm 4.2$ kJ mol^{-1}, $\Delta S_2^{\ddagger} = 6 \pm 13$ J K^{-1} mol^{-1} (second stage)] reveal either that bond-making in the second stage is much less pronounced than in the first or that some disorder must become apparent in the molecule before the second carbonyl is replaced.[20] A rather more complicated situation exists in the reactions of $[(CO)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_3]$ with PPh_3 to give $[(PPh_3)(CO)_3Co(\mu\text{-}GePh_2)\text{-}Co(CO)_3(PPh_3)]$ and with CO to give $[(CO)_4Co(\mu\text{-}GePh_2)Co(CO)_4]$. The kinetics of the reaction with CO are first order in [CO] and [complex] whilst those for the reaction with PPh_3 indicate a carbonyl-dissociation pathway before attack by a second molecule of PPh_3 in a fast ring-opening reaction. Both reactions are summarized in the proposed mechanism shown in Scheme 3. Several additional reactions and intermediate experiments endorse this Scheme. For instance a bimolecular pathway was also observed in the case of attack by PPh_3, leading directly to (14), which then reacts further with PPh_3 but in a manner zero order with respect to $[PPh_3]$ to give $[(PPh_3)\text{-}(CO)_3Co(\mu\text{-}GePh_2)Co(CO)_3(PPh_3)]$. In addition reaction of $[(CO)_4Co(\mu\text{-}GePh_2)\text{-}Co(CO)_4]$ with PPh_3 involves rate-determining formation of $[(CO)_3Co(\mu\text{-}GePh_2)\text{-}$

[19] P. C. Ellgen and J. N. Gerlach, *Inorg. Chem.*, 1974, **13**, 1944.
[20] M. Basato and A. Poë, *J.C.S. Dalton*, 1974, 456.



Scheme 3

(μ-CO)Co(CO)$_3$] before substitution by PPh_3 occurs by the paths shown in the Scheme. The reaction with PBu^n_3, as might be expected on account of its greater nucleophilicity, showed a greater tendency to second-order kinetics than the corresponding reactions with PPh_3, for instance attack on [(CO)$_4$Co(μ-$GePh_2$)-Co(CO)$_4$] or (14), were independent of [PPh_3].[21] In contrast to the reactions of [(CO)$_3$Co(μ-Ph_2C_2)Co(CO)$_3$] and [(CO)$_3$Co(μ-$GePh_2$)(μ-CO)Co(CO)$_3$] described above, where the Ph_2C_2 and $GePh_2$ ligands retain their bridging roles, $GePh_2$ as well as the bridging carbonyl are displaced from [(CO)$_3$Co(μ-$GePh_2$)(μ-CO)Co(CO)$_3$] by the alkynes C_2Ph_2, MeC_2H, PhC_2H, and $C_2(CO_2Et)_2$ to give [(CO)$_3$Co(μ-alkyne)-Co(CO)$_3$]. However, retardation of the reaction rate (alkyne = C_2Ph_2) by CO indicates the intermediate (15), previously postulated in the case of reaction with PPh_3, PBu^n_3, or CO.[22]

[21] M. Basato, J. P. Fawcett, and A. Poë, *J.C.S. Dalton*, 1974, 1350.
[22] M. Basato, J. P. Fawcett, S. A. Fieldhouse, and A. J. Poë, *J.C.S. Dalton*, 1974, 1856.

Nickel. The reaction of $[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2]$ with diphenylacetylene,

$$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2] + Ph_2C_2 \longrightarrow [Ni_2(Ph_2C_2)(h^5\text{-}C_5H_5)_2] + 2CO \quad (3)$$

has been the subject of some controversy. Early work (see Volume 3) proposed a two-stage mechanism involving an active intermediate:

$$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ni_2(CO)_2(h^5\text{-}C_5H_5)_2]^*$$

$$[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2]^* + Ph_2C_2 \xrightarrow{k_2} [Ni_2(Ph_2C_2)(h^5\text{-}C_5H_5)_2] + 2CO$$

which leads to the rate law

$$k_{obs} = \frac{k_1k_2[Ph_2C_2]}{k_{-1} + k_2[Ph_2C_2]} \quad (4)$$

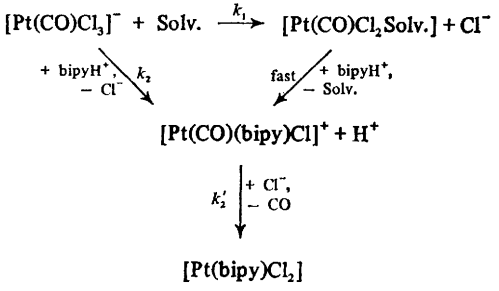
and which of course predicts, as was found, a limiting value of k_{obs} (equal to k_1) at high values of $k_2[Ph_2C_2]$. Criticism of these proposals was based on (*a*) failure to observe a limiting rate at $[Ph_2C_2] = 0.50$ mol l^{-1} and (*b*) that decomposition of $[Ni_2(CO)_2(h^5\text{-}C_5H_5)_2]$ or its reaction with the free CO generated would contribute significantly to the kinetics. This last led to the proposal that $k_{obs} = k_d + k_r[Ph_2C_2]$, where k_d is the rate constant for substrate decomposition in the absence of acetylene and k_r is twice the rate constant for bimolecular attack of the acetylene on nickel.[23] In the current period the picture has cleared somewhat. Values of k_{obs} from reactions analogous to (3) with Et_2C_2, MeC_2Ph, HC_2Ph, and HC_2CO_2Me did not reach limiting values at high [alkyne]. Analysis of the curves obtained revealed in addition to equation (4) the simultaneous operation of a bimolecular rate law. In fact for $MeO_2CC_2CO_2Me$ only this second-order law was found.[24] In the light of these results a re-examination of the reaction with Ph_2C_2, under the same conditions of temperature, verified that a limiting rate is not found at high $[Ph_2C_2]$ (up to 0.5 mol l^{-1}). However, by virtue of the same kinetic analysis used for the acetylenes above this can be accounted for by the additional second-order mechanism. The same work also failed to detect any spurious kinetic effects from the previously postulated side products.[25] Additionally, the current data reveal that the most likely rate-determining step in the first-order path is homolytic Ni—Ni cleavage and that in acetylene co-ordination the π-acceptor ability is more important than the capacity of the acetylene as a σ-donor.[24]

Platinum. Replacement of the carbonyl ligand in the reaction between $AsPh_4[Pt(CO)Cl_3]$ and bipyridyl in acidic 95% aqueous methanol occurs in two stages. The product from the first stage $[Pt(CO)(bipy)Cl][Pt(CO)Cl_3]$ can in fact be isolated and is formed according to the rate law $k_{obs} = k_1 + k_2[bipyH^+]$. Kinetics for the second stage,

$$[Pt(CO)(bipy)Cl]^+ + Cl^- \longrightarrow [PtCl_2(bipy)] + CO$$

are given by $k'_{obs} = k'_2[Cl^-]$. These data are consistent with the mechanism shown in Scheme 4.[26]

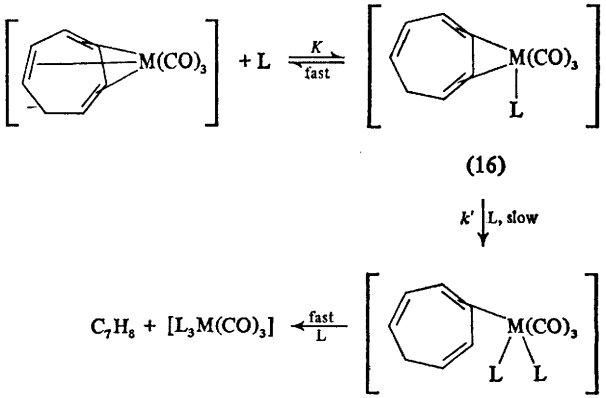
[23] P. C. Ellgen, *Inorg. Chem.*, 1972, **11**, 2279 (see also Volume 3, p. 360).
[24] P. L. Stanghellini, R. Rossetti, O. Gambino, and G. Cetini, *Inorg. Chim. Acta*, 1973, **7**, 445.
[25] P. L. Stanghellini, R. Rossetti, O. Gambino, and G. Cetini, *Inorg. Chim. Acta*, 1974, **10**, 5.
[26] R. Pietropaolo, F. Faraone, D. Pietropaolo, and P. Piraino, *J. Inorg. Nuclear Chem.*, 1974, **36**, 369.



Scheme 4

3 Substitution in Carbonyls: Replacement of other Ligands

Group VI.—Acetonitrile displaces the organic ligands from $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, or W; C_7H_7 = tropylium cation)[27] and $[RM(CO)_3]$ [R = mesitylene ($C_6H_3Me_3$) or cycloheptatriene (C_7H_8); M = Cr, Mo, or W][28] to give, under oxygen-free conditions $[M(CO)_3(MeCN)_3]$. In the first two complexes second-order kinetics were observed, whereas cycloheptatriene is displaced according to the third-order rate law $k_{obs} = k[MeCN]^2$. The mechanism proposed is substantially similar in all cases, *i.e.* progressive reduction of the number of bonding pairs and finally elimination of the organic ligand by MeCN. In the case of the second-order rate laws, the rate-determining step is probably attack by the first MeCN ligand. The third-order law is accommodated by the mechanism shown in Scheme 5. Pre-equilibrium



Scheme 5

addition of the first MeCN molecule before slow addition of the second leads to the rate law

$$\text{Rate} = k'K[\text{complex}][\text{MeCN}]^2$$

[27] K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1973, 1683.
[28] K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1974, 428.

It should be noted that this is a true pre-equilibrium since third-order kinetics are maintained even at high [MeCN]. Steady-state treatment of [(16)] leads to

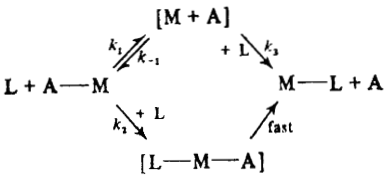
$$\text{Rate} = \frac{k'K[\text{complex}][\text{MeCN}]^2}{1 + K[\text{MeCN}]}$$

which reduces to a second-order law at high [MeCN]. The change in mechanism can be rationalized in terms of steric favourability of formation of a seven-co-ordinate intermediate from $[(C_7H_8)M(CO)_3]$.

Substitution of the amine ligand in [(amine)$M(CO)_5$] (A–M) by L [M = Mo, amine = piperidine, L = $P(OMe)_3$, PPh_3, or $AsPh_3$;[29] M = W, amine = aniline, L = PPh_3 [30]] are consistent with the rate law

$$-\text{d[A–M]}/dt = k_1[\text{A–M}] + k_2[\text{A–M}][\text{L}]$$

the second-order term arising probably from an I_d process.[29] This is consistent with the mechanism shown in Scheme 6. Thus the first-order term arises under conditions



Scheme 6

of large excess of L, *i.e.* when $k_3[\text{L}] \gg k_{-1}[\text{A}]$ in the equation derived by steady-state treatment of [M]:

$$\frac{-\text{d[A–M]}}{dt} = \frac{k_1k_3[\text{A–M}][\text{L}]}{k_{-1}[\text{A}] + k_3[\text{L}]}$$

The competition ratio for M, k_{-1}/k_3, was found to vary over a very narrow range close to unity, thereby revealing a lack of discrimination for M by L and A.[29] Further evidence that $k_{-1} \approx k_3$ is shown by inhibition of the rate under conditions of large excess of A ([A]/[L] up to 184), *i.e.* when $k_{-1}[\text{A}]$ becomes progressively greater than $k_3[\text{L}]$.[30] Variations in ΔS^* for the second-order process for the displacement of a series of amines by PPh_3 [−38.0 cal K^{-1} mol^{-1} (quinuclidine), −20.1 cal K^{-1} mol^{-1} (piperidine), and −18.1 cal K^{-1} mol^{-1} (aniline) (M = W)] reflect the importance in this process of the steric requirements of the leaving group.

Iron.—Exchange of the phosphorus bases L [L = PBu^n_3, $P(OPh)_3$, or $P(C_6H_{11})_3$] with the triphenylphosphine ligand in the carbene complexes *trans*-[$(PPh_3)Fe(CO)_3$-{C(OEt)R}] (R = Ph or Me) proceeds *via* a dissociative course. This is clearly shown by values of ΔS^* (*ca.* +10 cal K^{-1} mol^{-1}) and by the insensitivity of the rate to the nature or concentration of L. Reactions were normally conducted in heptane. The use of THF reveals a greater degree of disorder and a lower degree of stabilization by THF in the transition state ($\Delta S^*_{\text{THF}} = 15.3 \pm 2.4$ cal K^{-1} mol^{-1}, $\Delta H^*_{\text{THF}} = 29.6 \pm 0.8$ kcal mol^{-1}, $\Delta S^*_{\text{heptane}} = 10.5 \pm 1.4$ cal K^{-1} mol^{-1}, $\Delta H^*_{\text{heptane}} = 27.6 \pm 0.4$ kcal mol^{-1}, R = Ph). The more electron-withdrawing carbene C(OEt)Ph is

[29] W. D. Covey and T. L. Brown, *Inorg. Chem.*, 1973, **12**, 2820.
[30] G. R. Dobson, *Inorg. Chem.*, 1974, **13**, 1790.

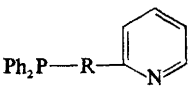
found to labilize the PPh_3 ligand to a greater extent than C(OEt)Me.[31] Identical kinetic behaviour was found in the analogous reaction with iron carbonyl acylates,

$$L + \textit{trans}\text{-}[(PPh_3)Fe(CO)_3\{C(O)Ph^-Li^+\}] \longrightarrow \textit{trans}\text{-}[LFe(CO)_3\{C(O)Ph^-Li^+\}] + PPh_3$$
$$L = P(OPh)_3 \text{ or } PBu^n_3$$

although the rates were lower. Thus the dissociative mechanism described for the carbene complexes seems likely here also. Over longer periods the acyl moiety is itself displaced to give $[L_2Fe(CO)_3]$ but with indeterminate kinetics. The rate of acyl displacement, however, is found to depend on the nature of L in the parent compound $[LFe(CO)_3\{C(O)Ph^-Li^+\}]$ in the order $L = PBu^n_3 > PPh_3 > P(OPh)_3$. The paper also describes reactions of the co-ordinated acylate ligand.[32] Thermolysis of $[(\sigma\text{-allyl})(CO)(\eta\text{-}C_5H_5)(PPh_3)Fe]$ to give $[(\eta\text{-allyl})(CO)(\eta\text{-}C_5H_5)Fe]$ and PPh_3 occurs cleanly above 313 K and follows solvent-independent first-order kinetics. Small positive values of $\Delta S^{\ddagger}$ (3.9 cal K^{-1} mol^{-1} in cyclohexane, 2.3 cal K^{-1} mol^{-1} in THF) are postulated to indicate an associative mechanism, although no detailed description of this interesting reaction is available at present.[33]

4 Formation of Carbonyls

Reaction with carbon monoxide causes dechelation of the N-donor end of the phosphorus–nitrogen bidentate ligands (P–N) in $[M(CO)_4(P\text{–}N)]$ (M = Cr, Mo, or W; P–N = $Ph_2PCH_2CH_2NMe_2$, $Ph_2PCH_2CH_2NEt_2$, $Ph_2PCH_2CH_2NH_2$, or $Ph_2PCH_2CH_2CH_2NMe_2$)[34] and in $[Mo(CO)_4(P\text{–}N)]$ [P–N = (17; R = NH, CH_2, CH_2CH_2, or

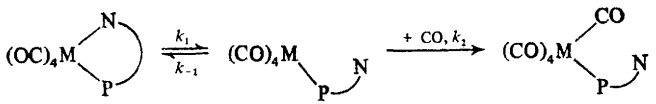


(17)

$CH_2CH_2CH_2$)][35] to afford $[M(CO)_5(P\text{–}N)]$. The observed kinetics are second order, first order both in complex and in carbon monoxide. This is considered, however, to be the limiting form ($k_{-1} \gg k_2[CO]$) of the familiar rate law,

$$k_{obs} = \frac{k_1 k_2[CO]}{k_{-1} + k_2[CO]}$$

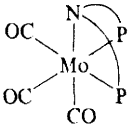
derived by steady-state treatment of the intermediate in Scheme 7. If the reaction is conducted in the presence of acid, the rate becomes greater and independent of [CO].



Scheme 7

[31] D. J. Darensbourg and H. L. Conder, *Inorg. Chem.*, 1974, **13**, 374.
[32] H. L. Conder and M. Y. Darensbourg, *Inorg. Chem.*, 1974, **13**, 506.
[33] K. R. Aris, J. M. Brown, and K. A. Taylor, *J.C.S. Dalton*, 1974, 2222.
[34] W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, 1974, **13**, 627.
[35] W. J. Knebel and R. J. Angelici, *Inorg. Chem.*, 1974, **13**, 632.

In this case the product is the amine-protonated complex $[M(CO)_5(P\text{–}\overset{+}{N}H)]$ in which the k_{-1} path is effectively blocked, with the result that k_{obs} becomes equal to k_1. Since k_{obs} in the absence of acid is equal to $k_1k_2[CO]/k_{-1}$, the value of k_1 obtained in acid solution enables calculation of the competition ratio k_{-1}/k_2. This shows that there is a considerable preference for ring closure in the intermediate over reaction with CO. It is generally found that the rate of N-donor dissociation increases with increasing size of the chelate ring and with the bulkiness of the substituents on nitrogen. Since k_{-1}/k_2 ratios are quite similar in the first set of complexes studied,[34] N-donor dissociation appears to control the overall rate of chelate ring-opening. In the pyridyl phosphine complexes, however, the ratio is 0.75 (five-membered ring), 210 (six-membered), and 71 (seven-membered). The value for the six-membered ring is particularly surprising in that it seems to indicate a large k_{-1} value, whereas k_1 values found in the presence of acid indicated that the five-membered rings were the most stable. The terdentate P–N–P-containing complex *fac*-$[Mo(CO)_3\{Ph_2P(CH_2)_2NEt(CH_2)_2PPh_2\}]$ (18) reacts with CO to give (19). The kinetics suggest a mechanism



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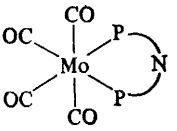


(19)

analogous to the $[M(CO)_4(P\text{–}N)]$ complexes above.[35] I.r. and ^{13}C n.m.r. analysis of the product of this reaction and also of that of $[Mo(CO)_4\{Ph_2P(CH_2)_2NMe_2\}]$ with ^{13}CO show that the incoming carbonyl ligand locates always stereospecifically *cis* to the phosphorus atom(s) in the position vacated by nitrogen. The intermediate in Scheme 7, therefore, has either square-pyramidal geometry resulting directly from nitrogen dissociation or, if it has trigonal-bipyramidal geometry, attack by CO is limited to a position *cis* to the phosphorus atom(s).[36]

A brief study of the equilibrium

$$[V(h^5\text{-}C_5H_5)I] + CO \rightleftharpoons [V(h^5\text{-}C_5H_5)I(CO)]$$

reports that $\Delta H^\circ = -13.1 \pm 1.0$ kcal mol^{-1} and $\Delta S^\circ = -34.6 \pm 3.4$ cal K^{-1} mol^{-1}.[37]

5 Cyclopentadienyls

The exchange reaction between nickelocene and deuterium-labelled lithium cyclopentadienide,

$$[Li(^2H_5\text{-}Cp)] + [NiCp_2] \longrightarrow [NiCp(^2H_5\text{-}Cp)] + [LiCp$$

proceeds in THF according to a two-term rate law. Both terms are first order in $[NiCp_2]$ but differ according to first- or second-order dependence on [LiCp]. Each term is considered to represent an associative pathway, more explicitly to involve respectively rate-determining association of $NiCp_2$ and LiCp or a dimer $(LiCp)_2$. If the

[36] W. J. Knebel, R. J. Angelici, O. A. Gansow, and D. J. Darensbourg, *J. Organometallic Chem.*, 1974, **66**, C11.

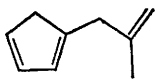
[37] F. Calderazzo, G. Fachinetti, and C. Floriani, *J. Amer. Chem. Soc.*, 1974, **96**, 3695.

exchange is conducted using LiCp,tmeda the rate law reduces to the term first order in each reactant. The rate is *ca.* 40 times greater than that found with LiCp, but a comparison of activation parameters indicates that the mechanism is probably similar to that involving the LiCp monomer. Presumably use of the adduct precludes formation of the dimeric lithium cyclopentadienide. Similarly, exchange between $[MnCp_2]$ and $[Ni(^2H_5\text{-}Cp)_2]$ in benzene follows second-order kinetics but at a rate ten times lower than in the LiCp–$NiCp_2$ system above. Attempts at a direct comparison by conducting the reaction in THF were prevented by what appeared to be formation of an exchange-inert $[MnCp_2]$–THF solvate.[38]

In Volume 3 of these Reports we examined a report on the reaction

$$[(h^3\text{-}C_3H_5)M(h^5\text{-}C_5H_5)] + 4L \longrightarrow ML_4 + C_8H_{10}$$
$$M = Ni \text{ or } Pd;\ L = P(OEt)_3 \text{ or } P(OPh)_3$$

The kinetics showed first- or second-order dependence on [L] depending on whether M is Pd or Ni, respectively. These results were interpreted in terms of two limiting forms of a rate law derived by steady-state treatment of an intermediate $[(C_3H_5)M(C_5H_5)(L)]$. The kinetic data, however, gave no information about the nature of this intermediate. N.m.r. results in the current period [L = $P(OEt)_3$, $P(OMe)_3$, or $P(OPh)_3$; M = Pd] show that it comes about by π–σ rearrangement of the allylic rather than cyclopentadienyl ligand. Addition of the second L ligand does, however, promote formation of a cyclopentadienide structure before final elimination of both organic ligands. N.m.r. results below 223 K indicate that the initial organic product is the 5-substituted allyl cyclopentadiene. Under normal conditions, however, the 4-substituted isomer (20) is obtained.[39]

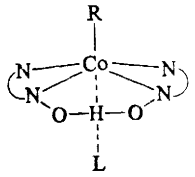


(20)

6 Phosphite Complexes

The rate of dissociation of $P(OMe)_3$ from the dimethylglyoximato-cobalt(III) complexes $[RCo(dmg)_2P(OMe)_3]$ is found to depend on the nature of R such that $CH_2SiMe_3 > Me > CH_2F > CHF_2 > CH_2Cl > CF_3 \sim CHCl_2 > CH_2Br > CHBr_2$. The relative rates, which span a range from 1.8 s^{-1} ($CHBr_2$) to 380 s^{-1} (CH_2SiMe_3) follow the known order of the axial ligand's *trans* effect. As predicted by consideration of inductive effects, electron-withdrawing halogenoalkyl ligands reduce the rate (compared with Me) whereas the electron-releasing group CH_2SiMe_3 increases it. Within the range of halogenoalkyl groups, however, the results do not follow the normal order of inductive effects and cannot be accounted for on such simple grounds. Neither can steric effects be invoked: rather a larger group is found to inhibit phosphite dissociation. The problem was eventually rationalized in terms of steric repulsion between the non-bonding halogen orbitals and the non-bonding d_{xz} and d_{yz} electrons on cobalt. This interaction would, of course, be more pronounced for Br than for Cl. Since the proposed structure of the transition state (21) would place

[38] M. E. Switzer and M. F. Rettig, *Inorg. Chem.*, 1974, **13**, 1975.
[39] G. Parker and H. Werner, *Helv. Chim. Acta*, 1973, **56**, 2819.



(21)

increased electron charge density on the alkyl side of the metal, the interaction above argues that the tolerable limit for a stable transition state would be reached sooner for, say, Br than for Cl, thereby slowing the reaction in the case of the bromoalkyls.[40] The equilibrium constant for the reaction

$$[NiL_3] + \text{olefin} \overset{K}{\rightleftharpoons} [NiL_2(\text{olefin})] + L \quad [L = P(O\text{-}o\text{-tolyl})_3]$$

has been evaluated for 38 different olefins. The variation in K extends from 10^{-4} to 4×10^8. Of primary importance in determining the stability of the olefin complexes is metal-*d*–olefin-π^* back donation and resonance interaction of the substituents on the double bond. Those substituents better able to donate electrons to the double bond by resonance interaction destabilize the olefin complex. Since the values of ΔS obtained are close to zero the values of K directly reflect changes in ΔH and thus the strength of the metal–olefin bond.[41] The actual mechanism of the reaction was examined in the case of olefin = C_2F_4. Second order kinetics were taken to indicate an associative pathway.[42]

7 Olefin Complexes

Substitution of the olefin ligand in $[Fe(CO)_4(CH_2{=}CHPh)]$ by $AsPh_3$, $SbPh_3$, or pyridine in toluene solution follows the same mechanistic course noted previously for substitution by CO (see Volume 3). The intermediate $[Fe(CO)_4]$ is generated by a dissociative pathway and subsequently combines with the ligand, L. In the case of substitution by the strong nucleophile PPh_3, however, the situation is complicated somewhat. The products in this case are $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$. No effect on the ratio of these products is observed on varying the concentration of PPh_3, the olefin, or temperature. These results and the usual mass-effect tests for a dissociative mechanism are deemed indicative of two possible reaction paths. In both $[Fe(CO)_4(PPh_3)]$ is produced by a mechanism identical with that described above for the weaker nucleophiles. $[Fe(CO)_3(PPh_3)_2]$, however, can arise by reaction of $[Fe(CO)_4]$ with PPh_3, either after an isomerization of the expected T_d structure to a C_{2v} form of different reactivity or after further dissociation to $[Fe(CO)_3]$.[43] In an additional paper, which describes the effects of differing solvents on the reaction, only the latter mechanism is considered.[44] In the preceding section the replacement of one L in $[NiL_3]$ by olefins was described. In the presence of large excesses of certain

[40] R. J. Guschl, R. S. Stewart, and T. L. Brown, *Inorg. Chem.*, 1974, **13**, 417.
[41] C. A. Tolman, *J. Amer. Chem. Soc.*, 1974, **96**, 2780.
[42] C. A. Tolman and W. C. Seidel, *J. Amer. Chem. Soc.*, 1974, **96**, 2774.
[43] G. Cardaci, *Inorg. Chem.*, 1974, **13**, 368.
[44] G. Cardaci, *J. Organometallic Chem.*, 1974, **76**, 385.

olefins [NiL_2(olefin)$_2$] can be formed. Except in the case of some chelating olefins, and possibly *trans*-hex-2-ene, the equilibrium constants for co-ordination of the second olefin bond are smaller than for the first.[41]

8 Amine Complexes

This section deals with papers involving formation as well as substitution of amine groups in complexes not including carbonyl ligands.

Substitution.—The reaction

$$[(cod)RhCl(amine)] + bipy \longrightarrow [(cod)Rh(bipy)]^+ Cl^- + amine$$

proceeds according to the two-term rate law: $k_{obs} = k_s + k_y[bipy]$. Furthermore, plots of log k_s or log k_y against the basicity (pK_a) of the amine are linear, and large negative values of $\Delta S^{\ddagger}$ are apparent for both paths. Mechanistically k_s is said to characterize displacement of amine by the solvent and k_y direct attack by bipyridyl on the substrate. However, the authors prefer not to indicate the dominance of bond-making or bond-breaking in the former process.[45] This dilemma seems to be further compounded as a result of the behaviour of the analogous reaction in which piperidine is displaced from [(cod)RhCl(pip)] by a series of uni- and bi-dentate amines. The rate law is the same and the k_y pathway clearly associative in nature. The best that can be said of the solvent-assisted route, however, is that bond-making and bond-breaking cannot, in this instance, be considered as independent steps.[46]

Formation.—Amongst substitution reactions of platinum(II) complexes the reaction of *trans*-[$Pt(PEt_3)_2$(R)Cl] (R = *o*-tolyl) with pyridine in methanol solution is anomalous. In dealing with this reaction in Volume 3 we reported on the nature of the anomaly and its explanation in terms of the mechanism

$$trans\text{-}[Pt(PEt_3)_2(R)Cl] + MeOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Pt(PEt_3)_2(R)(MeOH)]^+ Cl^-$$

$$trans\text{-}[Pt(PEt_3)_2(R)(MeOH)]^+ + py \underset{k_4}{\overset{k_3}{\rightleftharpoons}} trans\text{-}[Pt(PEt_3)_2(R)(py)]^+ + MeOH$$

which at constant [py] and [Cl^-] leads to the rate law

$$k_{obs} = \frac{k_1[py] + (k_4k_2/k_3[Cl^-])}{(k_2/k_3[Cl^-]) + [py]}$$

Under conditions where $(k_2/k_3[Cl^-]) \gg [py]$, k_{obs} reduces to $k_{obs} = k' + k''[py]$, the latter expression having the same form as the rate law normally found for substitution at platinum(II) but with a very different meaning in this case. In the current period the reaction has been examined for a series of substituted pyridines, and shows the same kinetics. The competition ratio for the solvated intermediate, k_3/k_2 is found to be relatively unaffected for 3-, 4-, and 5-substituted pyridines but is considerably lower in the case of pyridines having substituents in the *ortho* position. This is quite clearly a steric effect rather than a consequence of any differences in nucleophilicity.[47] A more detailed examination of the k_3 path (R = Ph, *o*-tolyl, or mesityl) shows, in addition, a rate-retarding effect which derives from the presence of *ortho* substituents on the *trans* ligand R. Retardation by *ortho* substituents either on

[45] W. Robb and C. G. Nicholson, *Inorg. Chim. Acta*, 1973, **7**, 645.
[46] C. G. Nicholson and W. Robb, *Inorg. Chim. Acta*, 1974, **8**, 41.
[47] V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 927.

the pyridine or on R is accompanied by an increase in $\Delta H^{\ddagger}$ which is almost always compensated for by an increase in $\Delta S^{\ddagger}$. This so-called 'compensation effect' is generally held to be common for reactions dominated by solvation changes.[48] The reaction of DL-α-alanine (alaH) with Zeise's salt,

$$[Pt(C_2H_4)Cl_3]^- + alaH \longrightarrow \textit{N-trans}\text{-}[Pt(ala)C_2H_4)Cl] + 2Cl^-$$

proceeds in two stages, involving prior co-ordination of the nitrogen group to platinum before ring closure at the carboxylate end. The aquo-species $[Pt(C_2H_4)(H_2O)Cl_2]$ also participates in the first stage.[49]

[48] R. Romeo, M. L. Tobe, and M. Trozzi, *Inorg. Chim. Acta*, 1974, **11**, 231.
[49] G. Carturan, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1974, **13**, 542.

2

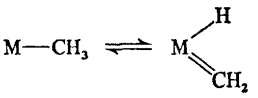
Metal-Alkyl, -Aryl, and -Allyl Bond Formation and Cleavage

BY R. D. W. KEMMITT AND M. A. R. SMITH

1 General

As in previous volumes, the formation and cleavage of transition-metal–carbon bonds are discussed in this chapter. Metal–carbon bond formation *via* oxidative addition of alkyl halides to low-valent metal complexes is discussed in Chapter 6.

Reversible elimination of hydrogen from a carbon which is in a β-position relative to the transition metal has become a widely established mechanism for the cleavage of metal–carbon bonds. Until recently, however, it had been assumed that α-hydrogen elimination (Scheme 1) was not a likely process. This situation has now



Scheme 1

changed and several examples of α-hydrogen elimination from W—CH_3, Co—CH_3, Rh—CH_3, and Ta—CH_2CMe_3 bonds are known.[1-4]

Formation and cleavage reactions of transition-metal–carbon σ-bonds have been reviewed.[5-7] It is apparent that the cleavage of such bonds by halogens can proceed by inversion, retention, or epimerization of the configuration at carbon, the stereochemical course being dependent on structure and reaction conditions. It is therefore not possible to relate configurations of organometallic complexes to products formed in such reactions.

2 Group IV

Titanium.—Cleavage of the titanium–carbon bond in $TiCl_3CH_3$ in the presence of $AlEt_3$ in toluene solution shows a first-order dependence on the concentration of [$TiCl_3Me$], the pseudo-first-order rate constants being roughly proportional to the

[1] N. J. Cooper and M. L. H. Green, *J.C.S. Chem. Comm.*, 1974, 761.
[2] L. S. Pu and A. Yamamoto, *J.C.S. Chem. Comm.*, 1974, 9.
[3] R. R. Schrock, *J. Amer. Chem. Soc.*, 1974, **96**, 6796.
[4] A. Sanders, L. Cohen, W. P. Giering, D. Kennedy, and C. V. Maggatti, *J. Amer. Chem. Soc.*, 1973, **95**, 5430.
[5] P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, **7**, 209.
[6] M. C. Baird, *J. Organometallic Chem.*, 1974, **64**, 289.
[7] P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271.

concentration of organoaluminium compound. The rate constant also increases in the order $AlEt_2(OEt) < AlPr^n_3 < AlEt_3$, *i.e.* activation of the Ti—CH_3 bond increases with the Lewis acidity of the aluminium alkyl.[8]

3 Group VI

Chromium.—Further details have appeared on the reactions of organic radicals R· with $[Cr(H_2O)_6]^{2+}$ (see Vol. 3, p. 373). Formation of $[CrR(H_2O)_5]^{2+}$ follows pseudo-first-order kinetics. No dependence of the rate constant on H_3O^+ concentration is observed. Hydrolysis of the chromium–carbon bonds follows a rate law which is first order in the chromium–carbon compound and independent of the $[Cr(H_2O)_6]^{2+}$ concentration, consistent with a heterolytic mechanism:[9]

$$[CrR(H_2O)_5]^{2+} + H_2O \longrightarrow [Cr(OH)(H_2O)_5]^{2+} + RH$$
$$[CrR(H_2O)_5]^{2+} + H_3O^+ \longrightarrow [Cr(H_2O)_6]^{3+} + RH$$

Excess iodoform reacts with chromium(II) to form $[Cr(CHI_2)(H_2O)_5]^{2+}$. However, with excess chromium(II), $[Cr(CH_2I)(H_2O)_5]^{2+}$ is identified as a major product. The reaction of $[Cr(CHI_2)(H_2O)_5]^{2+}$ with $[Cr(H_2O)_6]^{2+}$ proceeds quantitatively according to the equation

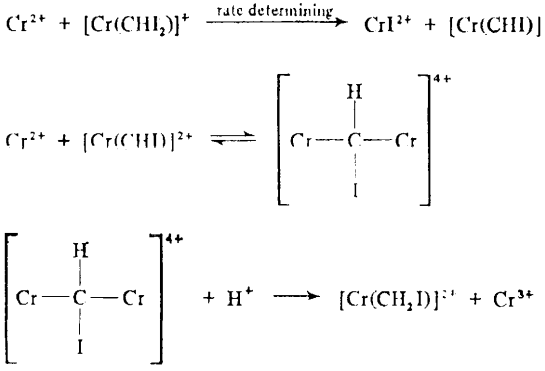
$$2[Cr(H_2O)_6]^{2+} + [Cr(CHI_2)(H_2O)_5]^{2+} + H^+ \longrightarrow [CrI(H_2O)_5]^{2+} + [Cr(H_2O)_6]^{3+} + [Cr(CH_2I)(H_2O)_5]^{2+}$$

The disappearance of Cr^{2+} is independent of H^+ and follows the rate law

$$-d[Cr^{2+}]/dt = k_1[Cr(CHI_2)^{2+}][Cr^{2+}]$$

The calculated value of k at 25 °C is 11.2 $mol^{-1}\ s^{-1}$. The activation parameters are $\Delta H^{\ddagger} = 6.5 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -32 \pm 1$ cal $deg^{-1}\ mol^{-1}$. The rate-determining step of the reaction involves abstraction of an iodine atom by Cr^{2+} *via* a bridged transition state $[Cr—C(HI)—Cr]^{4+}$.

Experiments with isotopically labelled Cr^{2+} reveal that the label appears in all the chromium-containing products and a carbon-bridged intermediate would explain this observation.[10] The overall mechanism is shown in Scheme 2. The breakdown of



Scheme 2

[8] T. Yamamoto and A. Yamamoto, *J. Organometallic Chem.*, 1973, **57**, 127.
[9] H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434.
[10] R. S. Nohr and L. O. Spreer, *J. Amer. Chem. Soc.*, 1974, **96**, 2618.

the intermediate $[CrC(HI)Cr]^{4+}$ involves a homolytic chromium–carbon bond cleavage.

The bromination of some alkylchromium complexes takes place according to the following reaction:

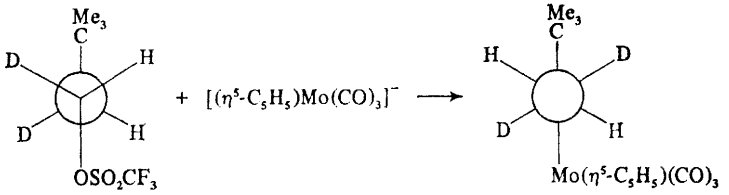
$$[CrR(H_2O)_5]^{2+} + Br_2 + H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + RBr + Br^-$$

Kinetic measurements on these reactions in perchloric acid solutions are consistent with the rate law

$$-d[CrR^{2+}]/dt = k[CrR^{2+}][Br_2]$$

For $[CrCH_2Cl]^{2+}$ the activation parameters are $\Delta H^{\ddagger} = 33.1 \pm 1.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -134 \pm 6$ J mol^{-1} K^{-1}. For $[CrC_2H_5]^{2+}$ $\Delta H^{\ddagger} = 44.8 \pm 3.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 15 \pm 11$ J mol^{-1} K^{-1}.[10] The absence of the kinetically stable $[CrBr(H_2O)_6]^{2+}$ in the products suggests that an S_Ei mechanism and other mechanisms involving a closed four-centre transition state are not involved in the cleavage reaction. The results are consistent with an S_E2 mechanism, as is the observation that the presence of methyl groups on the α-carbon atom increases the rate of cleavage. It is suggested that the reaction may proceed with inversion of configuration at carbon.[11]

Molybdenum.—The reaction of *threo*-3,3-dimethyl[1,2-$^2H_2$]butyl triflate with $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (Scheme 3) proceeds with inversion of configuration at



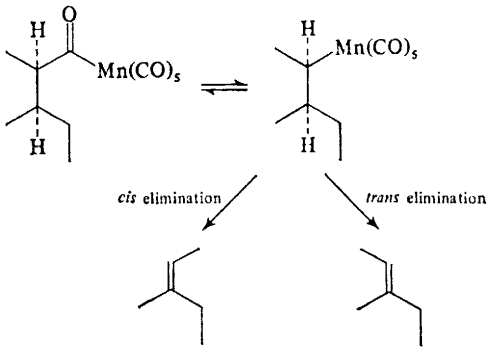
Scheme 3

carbon.[12] However, it should be noted that the stereochemical outcome of this type of experiment with organometallic systems can be sensitive to the structure of the organic groups involved.

4 Group VII

Manganese.—Elimination of transition-metal hydride from metal alkyls and addition of metal hydrides to alkenes are usually considered to be *cis*-processes. Since acylmanganese compounds undergo stereospecific reversible decarbonylation, thermal decomposition of (*erythro*-2,3-dimethylpentanoyl)(pentacarbonyl)manganese(I) should allow the determination of the stereochemistry of elimination of $[MnH(CO)_5]$ (Scheme 4). However, both the *erythro* and a mixture of the *erythro* and *threo* acyl complexes decompose thermally to give the same mixture of *cis*- and *trans*-3-methylpent-2-ene and 3-methylpent-1-ene under conditions which do not isomerize these alkenes. It is suggested that the mechanism involves interconversion of

[11] J. H. Espenson and D. A. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 1008.
[12] P. L. Bock and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 2826.

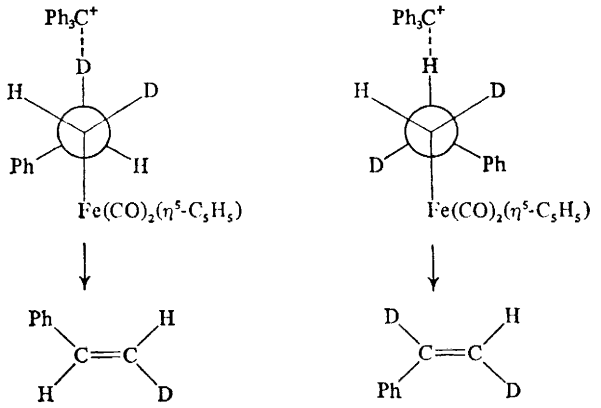


Scheme 4

[Mn(alkyl)(CO)$_4$] and [MnH(alkene)(CO)$_4$] species at a greater rate than loss of alkene from the complex.[13]

5 Group VIII

Iron.—Formation of iron–carbon σ-bonds in [(η^5-C_5H_5)Fe(CO)$_2${(*erythro* or *threo*)-CHDCHDCMe$_3$}] by the reaction of the *p*-bromobenzene-sulphonate esters of *threo*- and *erythro*-3,3-dimethyl[1,2-$^2H_2$]butan-1-ol with [(η^5-C_5H_5)Fe(CO)$_2$]-Li, -Na, or -MgBr proceeds with inversion of configuration at carbon, consistent with an S_N2 mechanism. Further, it is apparent from this series of experiments that, in contrast to reactions with [SnMe$_3$]$^-$, the stereochemistry of formation of the iron–carbon bond is independent of the nature of the counter-cation.[14] The cleavage of the iron–carbon bond of [(η^5-C_5H_5)Fe(CO)$_2$(CHDCHDCMe$_3$)] with bromine or iodine proceeds with inversion of configuration and the stereochemistry of the reaction is not significantly solvent dependent.[14] However, the stereochemical course of these



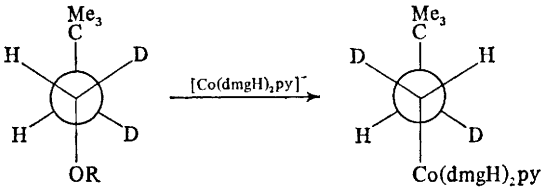
Scheme 5

[13] C. P. Casey, C. R. Cyr, and J. A. Grant, *Inorg. Chem.*, 1974, **13**, 910.
[14] P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 2814.

cleavage reactions can be dependent upon structure. Thus halogenation of [(η^5-C_5H_5)Fe(CO)$_2$(*threo*-CHDCHDPh)] proceeds with retention of configuration.[15] The larger Bu^t group may inhibit direct attack at iron. Cleavage of both the Ph and Bu^t derivatives with mercury(II) chloride proceeds with retention of configuration.[12,15]

Reaction of *threo*-[Fe(CHDCHDPh)(CO)$_2$(η^5-C_5H_5)] with $Ph_3C^+BF_4^-$ results in β-hydride abstraction to give deuteriated styrene complexes, [Fe(CO)$_2$(alkene)(η^5-C_5H_5)]$^+$[BF_4]$^-$ and triphenylmethane. Liberation of the alkenes from their iron complexes by addition of triphenylphosphine followed by n.m.r. analysis showed that hydride abstraction occurs *via* a predominantly *trans* elimination process from the less stable *gauche*-isomers (Scheme 5).[15]

Cobalt.—Formation of the cobaloximes (1) *via* the reactions in Scheme 6 proceeds

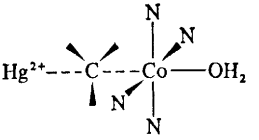


threo (1) *erythro*

R = *p*-$SO_2C_6H_4Br$ or H

Scheme 6

with inversion of configuration at carbon, in agreement with the earlier assignment that these reactions proceed *via* an S_N2 inversion mechanism.[12,16] Cleavage of the cobalt–carbon bond in (1) with mercury(II) ($k = 1.9 \times 10^{-3}$ s^{-1} at 25 °C) also proceeds with inversion of configuration at carbon, establishing an S_E2 inversion process for this reaction. An 'open' transition state such as (2) is proposed for this



(2)

reaction.[16] Metal–alkyl cleavage reactions with mercury(II) usually proceed with retention of configuration. However, the sterically hindered macrocyclic ligand of the cobaloxime may prevent close approach of the mercury(II) to the carbon atom, thus inhibiting an S_E2 'cyclic' mechanism. Cleavage of *trans*-4-t-butylcyclohexylcobaloxime with mercury(II) chloride also proceeds with inversion of configuration.[17]

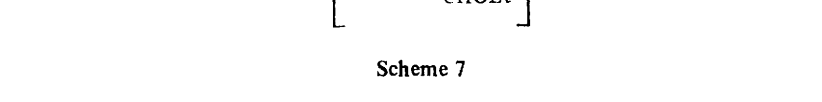
Secondary alkyl cobaloximes do not undergo electrophilic cleavage with mercury-

[15] D. Slack and M. C. Baird, *J.C.S. Chem. Comm.*, 1974, 701.
[16] H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *J. Amer. Chem. Soc.*, 1974, **96**, 2378.
[17] M. Tada and H. Ogawa, *Tetrahedron Letters*, 1973, 2639.

(II), in contrast to the ready homolysis by photolytic processes.[16] Kinetic studies on the dealkylation of the alkylcobalt complexes $[Co(BDMBg)R]^+$ with mercury(II) are also consistent with an S_E2 mechanism. The rates of reaction decrease in the order $R = Me \gg Et > Ph > Bu^n \simeq Pr^n$. The ligand $BDMBg^-$ is formed by the condensation of two moles of butane-2,3-dionemonoxime with one mole of propane-1,3-diamine or ethane-1,2-diamine.[18]

The reaction of methylcobalamin with mercury(II) is extremely rapid and has been studied by stopped flow kinetics.[19] However, methyl transfer from methylcobalamin to tetrachloropalladate(II) is slower.[20] In both methyl transfer reactions there are two kinetically distinct steps. The initial step involves a rapid association of the metal species with methylcobalamin, resulting in a 'base-on', 'base-off' pre-equilibrium, the electrophilic metal system competing with the cobalt(III) for the lone pair of electrons on the benzimidazole nitrogen. There follows a slower demethylation step in which the electrophilic metal species attacks the Co—C bond in the uncomplexed methylcobalamin. The more rapid transfer with mercury(II) is a consequence of the greater electrophilicity of mercury(II) than palladium(II), and the mercury(II) produces slightly more of the 'base-off' species.[20]

The reaction of cobaloximes and cobalamines with vinyl ethers in the presence of alcohols to give acetals *via* intermediate cobalt(III)–alkene complexes (Scheme 7),



Scheme 7

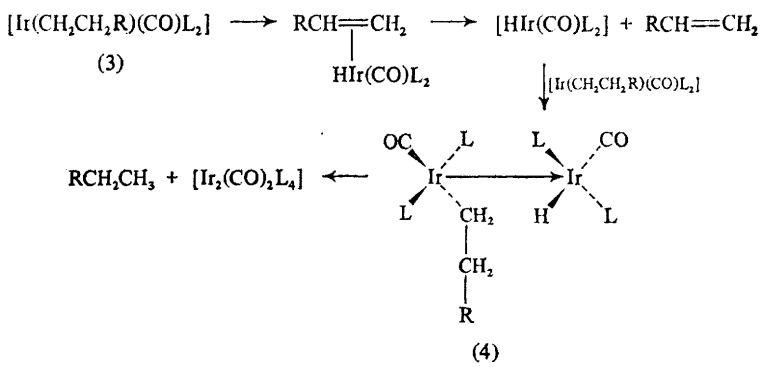
reported in Volume 3, has been questioned.[21] However, further studies reveal that the reactions shown in Scheme 7 are correct.[22]

An MO treatment suggests that the mechanism of reductive cleavage of organic halides by $[Co(CN)_5]^{3-}$ proceeds *via* electron migration from the highest occupied lone-pair halogen orbital to the singly occupied d_{z^2} cobalt orbital, and from the highest occupied $d_{xz}(d_{yz})$ cobalt orbital to the lowest occupied antibonding $p\sigma^*$ orbital of the R—X bond.[23]

Iridium.—The thermal decomposition of the octyl iridium complex (3) gives predominantly octene. Octane, however, is also produced in substantial amounts which are dependent on the concentration of triphenylphosphine (L). It is proposed that octane is lost from the bimolecular intermediate (4) (Scheme 8).[24]

Nickel.—Cleavage of the nickel–carbon bond in $[NiR_2(bipy)]$ (R = Me or Et) by aluminium alkyls is first order in nickel complex, the first-order rate constants being

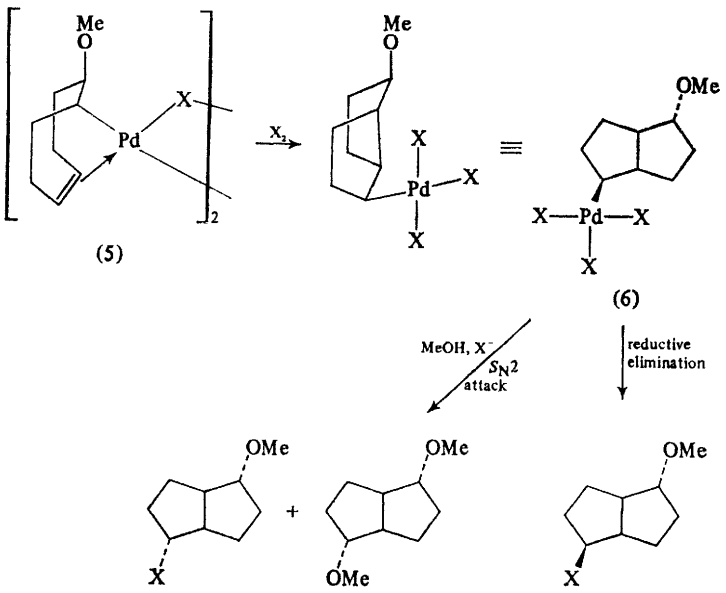
[18] V. E. Magnuson and J. H. Weber, *J. Organometallic Chem.*, 1974, **74**, 135.
[19] R. E. DeSimone, M. W. Penley, L. Charconneau, S. G. Smith, J. M. Wood, H. A. O. Hill, J. M. Pratt, S. Ridsdale, and R. J. P. Williams, *Biochim. Biophys. Acta*, 1973, **304**, 851.
[20] W. M. Scovell, *J. Amer. Chem. Soc.*, 1974, **96**, 3451.
[21] W. J. Michaely and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1973, **95**, 5771.
[22] R. B. Silverman and D. Dolphin, *J. Amer. Chem. Soc.*, 1974, **96**, 7094.
[23] K. Ohkubo, H. Kanaeda, and K. Tsuchihashi, *Bull. Chem. Soc. Japan*, 1973, **46**, 3095.
[24] J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, 1974, **96**, 2276.



Scheme 8

proportional to $[AlR_3]$ at high concentrations. Activation of the Ni—C bond increases with increase of Lewis acidity of the aluminium alkyl in the order $AlEt_2(OEt) < AlEt_3 < AlCl_3$. A mechanism involving co-ordination of the aluminium alkyl to $[NiR_2(bipy)_2]$ followed by Ni—R bond cleavage is proposed. Co-ordination of a Lewis acid is considered to lower the energy of the nickel *d*-orbitals, thus facilitating electron promotion from the Ni—C bonding orbital.[8] Electronegative olefins also cause cleavage of the Ni—C bonds probably *via* a similar mechanism.

Palladium.—Halogenation of the enyl complexes (5) proceeds with retention of configuration at the C—Pd bond (Scheme 9).[25] Reductive elimination from the



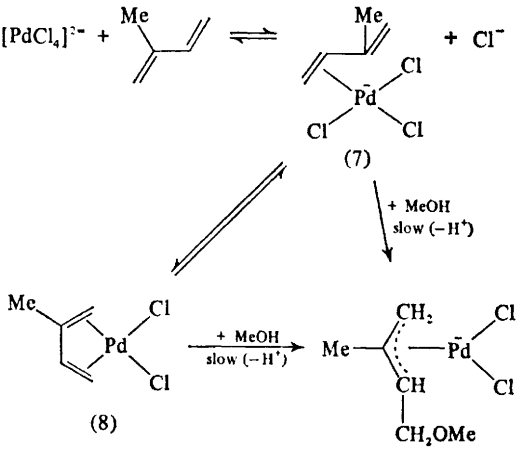
Scheme 9

[25] P. K. Wong and J. K. Stille, *J. Organometallic Chem.*, 1974, **70**, 121.

intermediate (6) also proceeds with retention of configuration. Inversion of configuration in the presence of added halide in methanol may result *via* S_N2 attack at carbon.

Studies on the cleavage of palladium–carbon bonds by $LiAlH_4$ provide further evidence that hydride cleavage proceeds with a high degree of stereospecificity.[26]

Pseudo-first-order conditions are observed in the reaction of isoprene with $[PdCl_4]^{2-}$ in methanol in the presence of lithium chloride.[27] A possible mechanism



Scheme 10

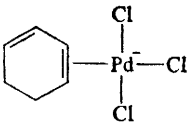
consistent with the rate law is shown in Scheme 10. The kinetic law observed is

$$k_{obs} = \left(\frac{k_1}{[Cl^-]^2} + \frac{k_2}{[Cl^-]}\right)[\text{isoprene}]$$

However, the analogous reaction between $[PdCl_4]^{2-}$ and cyclohexa-1,3-diene follows the rate law

$$k_{obs} = k[\text{cyclohexa-1,3-diene}]/[Cl^-]$$

The absence of the term $1/[Cl^-]^2$ in this rate equation suggests that the only reaction intermediate present in this example is (9).[28] However, isoprene can exist in both



(9)

[26] B. Akermark, J. E. Bäckvall, K. Siirala-Hansen, K. Sjöberg, and K. Zetterberg, *Tetrahedron Letters*, 1974, 1363.

[27] R. Pietropaolo, F. Faraone, D. Pietropaolo, and P. Piraino, *J. Organometallic Chem.*, 1974, **64**, 403.

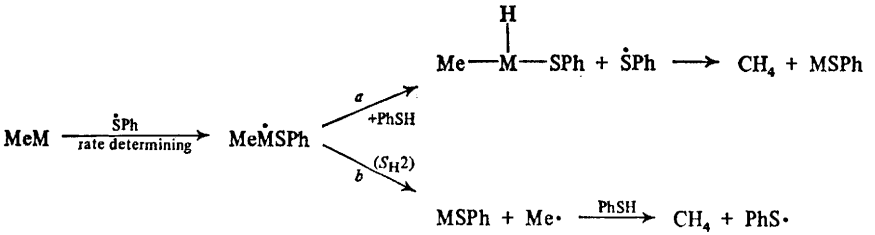
[28] R. Pietropaolo, E. Rotondo, F. Faraone, and D. Pietropaolo, *J. Organometallic Chem.*, 1973, **60**, 197.

cisoid and transoid forms and the intermediates (7) and (8) can be involved in the reaction.

Platinum.—Benzenethiol reacts with methylplatinum(II) compounds according to the equations (L = PMe_2Ph)

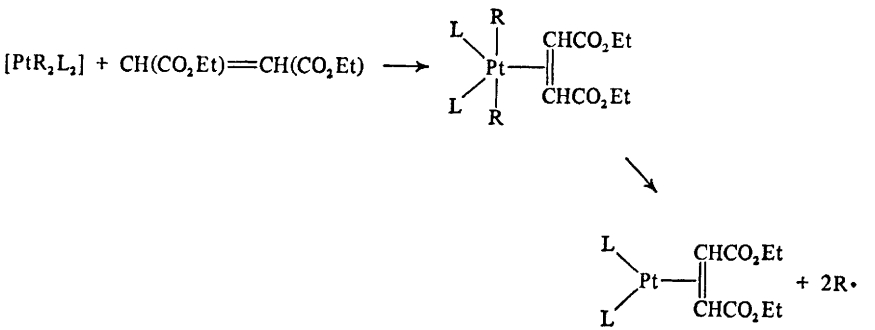
$$cis\text{-}[PtMe_2L_2] + PhSH \longrightarrow trans\text{-}[PtMe(SPh)L_2] + CH_4$$
$$trans\text{-}[PtMe(SPh)L_2] + PhSH \longrightarrow trans\text{-}[Pt(SPh)_2L_2] + CH_4$$

These reactions are totally inhibited on addition of the radical scavenger galvinoxyl, and are enhanced by the initiator azobis(isobutyronitrile).[29] The metal–carbon bond is therefore considered to be cleaved by a free-radical chain mechanism (Scheme 11).



Scheme 11

The radical trap Bu^tNO has little effect on overall reaction rates and mechanism (*a*) therefore predominates. However, the radical $Bu^t(Me)NO$ can be detected so mechanism (*b*) must be operative to some extent. Attack of PhS· at the metal centre is considered to be the rate-determining step. Homolytic cleavage of platinum(II)–alkyl bonds also results when the complexes $[PtR_2L_2]$ (R = CH_3, CD_3, or C_2H_5; L = 2,2′-bipy; R = Me, L_2 = 1,10-phen or cyclo-octa-1,5-diene) are treated with diethyl fumarate, free alkyl radicals being detected by the radical trap $Bu^tN{=}O$.[30] The reactions proceed according to the equations in Scheme 12.



Scheme 12

[29] N. G. Hargreaves, A. Johnson, R. J. Puddephatt, and L. H. Sutcliffe, *J. Organometallic Chem.*, 1974, **69**, C21.

[30] N. G. Hargreaves, R. J. Puddephatt, L. H. Sutcliffe, and P. J. Thompson, *J.C.S. Chem. Comm.*, 1973, 861.

Formation of the complex (+)-*trans*-$[PtCl(SiR_3)(PMe_2Ph)_2]$ occurs with a high degree of retention of configuration at silicon from (+)-R_3Si^*H [R_3Si^* = Me(1-$C_{10}H_7$)PhSi] and *cis*-$[PtCl_2(PMe_2Ph)_2]$ in the presence of triethylamine.[31] The Pt—Si bond is cleaved by lithium aluminium hydride with 93% overall retention of configuration at silicon. Smaller degrees of retention are observed when the Pt—Si bond is cleaved with benzenethiol or triethylsilane. Similar results are found with Pt—Ge-bonded compounds.[31]

6 Group I

Copper and Silver.—Copper(II) complexes are rapidly reduced by $PbEt_4$ even at low temperatures in protic as well as aprotic media:

$$PbEt_4 + CuX_2 \longrightarrow Et_3PbX + CuX + Et\cdot$$

$$Et\cdot + CuX_2 \xrightarrow[\text{fast}]{} CuX + \text{oxidation products of Et}\cdot$$

The reduction of copper(II) can occur either *via* an outer-sphere electron-transfer mechanism (Scheme 13) or *via* an inner-sphere process (Scheme 14). Mass spectral

$$Et_4Pb + Cu^{II}X_2 \longrightarrow Et_4Pb^+ + Cu^IX_2^-$$

$$Et_4Pb^+ \longrightarrow Et_3Pb^+ + Et\cdot \quad etc.$$

Scheme 13

$$Et_4Pb + Cu^{II}X_2 \longrightarrow Et_3PbX + EtCu^{II}X$$

$$EtCu^{II}X \longrightarrow Cu^IX + Et\cdot \quad etc.$$

Scheme 14

studies reveal that fragmentation of alkyl-lead compounds from PbR_4^+ follows the order Et > Me. However, the rate of cleavage of alkyl–lead bonds by copper(II) follows the order Me > Et, and these different reactivity patterns reveal that the reaction occurs *via* Scheme 14 in which the transalkylation process is rate-determining.[32]

Organocopper(I) intermediates are involved in the copper(I)-catalysed decomposition of $PbEt_4$ in acetic acid, the following mechanism operating:

$$PbEt_4 + CuOAc \longrightarrow Pb(OAc)Et_3 + CuEt$$

$$CuEt + AcOH \longrightarrow EtH + CuOAc$$

Ethane is also formed in the alkylation of $AgOSO_2CF_3$ by $PbEt_4$ in acetic acid, but the reaction is not truly catalytic since the ethylsilver intermediate is thermally unstable.[33,34]

Studies on the thermal decomposition of $[Ag(Bu^n)(PBu^n_3)]$ indicate that octane is formed *via* a concerted process involving carbon–carbon bond formation and carbon–silver bond breaking. n-Butyl free radicals and silver(I) hydride intermediates are not

[31] C. Eaborn, D. J. June, and D. R. M. Walton, *J.C.S. Dalton*, 1973, 2255.
[32] N. A. Clinton and J. K. Kochi, *J. Organometallic Chem.*, 1973, **56**, 243.
[33] N. A. Clinton and J. K. Kochi, *J. Organometallic Chem.*, 1972, **42**, 229.
[34] N. A. Clinton and J. K. Kochi, *J. Organometallic Chem.*, 1973, **61**, 433.

involved to any significant extent in the decomposition. However, in the presence of light or, more interestingly, the nitrosyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl, radicals *are* involved. The thermal decomposition of $[Ag(Bu^s)(PBu^n_3)]$ occurs *via* a different pathway which may involve silver(I) hydride elimination.[35]

Gold.—Cleavage of the gold(I)–carbon bond in the complexes $[AuMe(PR_3)]$ by benzenethiol occurs *via* the free-radical chain mechanism discussed above for the reactions of benzenethiol with platinum(II)–carbon bonded complexes (Scheme 11).[29] However, no radicals could be detected in the following reaction with gold(III) complexes:

$$[AuMe_3(PR_3)] + PhSH \longrightarrow cis\text{-}[AuMe_2(SPh)(PR_3)] + CH_4$$

The reactivity series found for these reactions, $[AuMe(PMe_3)] > cis\text{-}[PtMe_2(PMe_2Ph)_2] > [AuMe(PMePh_2)]$, $[AuMePPh_3] > trans\text{-}[PtMe(SPh)(PMe_2Ph)_2] \gg [AuMe_3(PMe_3)] > [AuMe_3(PMePh_2)]$, appears to be determined largely by steric effects of the phosphines. The series is similar to those found for the reactivity of transition-metal–alkyl complexes towards oxidative addition and reactions with alkenes also known to occur *via* free-radical chain processes.[29]

Thermolysis of $[AuMe(PPh_3)]$ in decalin follows first-order kinetics and is retarded by added triphenylphosphine. The following mechanism is suggested:

$$AuMeL \overset{k_1}{\rightleftharpoons} AuMe + L$$

$$AuMe + AuMeL \longrightarrow MeMe + 2Au + L$$

However, it is not yet clear whether this mechanism can be applied to other gold(I)–alkyl derivatives.[36]

Thermolysis of gold(III) complexes $AuR_3(PPh_3)$ proceeds *via* a dissociative process involving a three-co-ordinate gold(III) intermediate:

$$[AuR_3(PPh_3)] \rightleftharpoons AuR_3 + PPh_3$$

$$AuR_3 \longrightarrow \text{products}$$

Addition of triphenylphosphine retards the decomposition. Analysis of the products reveals that the three-co-ordinate intermediate maintains sufficient stereochemical integrity to allow *cis* elimination of alkyl groups.[37]

Table *Rate constants and free energies of activation for the thermolysis of* $[UR(\eta\text{-}C_5H_5)_3]$ *compounds in toluene solution*[38]

R	$k \times 10^4/h^{-1}$	$\Delta G^{\ddagger}$/kcal mol^{-1}
Bu^t	51 000 ± 5100	24.8
C_6F_5	1890 ± 50	27.0
Allyl	167 ± 3	28.7
Pr^i	34 ± 1	29.8
neo-C_5H_{11}	25.7 ± 0.2	32.2
Bu^n	6.10 ± 0.3	33.3
Me	1.10 ± 0.1	34.5
trans-But-2-enyl	1.03 ± 0.1	34.6

[35] G. M. Whitesides, D. E. Bergbreiter, and P. E. Kendall, *J. Amer. Chem. Soc.*, 1974, **96**, 2806.
[36] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1973, **61**, 441.
[37] A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 6487.

7 Actinides

Uranium.—The thermolysis reactions of the alkyl complexes $[UR(\eta\text{-}C_5H_5)_3]$ are first order in uranium complex.[38] Rate constants and free energies of activation are given in the Table. The order of stability of the alkyl compounds is primary > secondary > tertiary. In the thermolysis reaction intramolecular abstraction of hydrogen from a cyclopentadienyl occurs, giving RH with retention of configuration at carbon.[38]

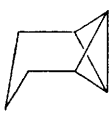
[38] T. J. Marks, A. M. Seyam, and J. R. Kolb, *J. Amer. Chem. Soc.*, 1973, **95**, 5529.

3
Homogeneous Catalysis

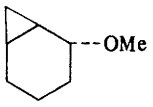
BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Isomerization

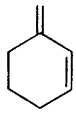
Strained Carbocyclic Systems.—Addition of $[Rh(CO)_2Cl]_2$ to methanol solutions of tricyclo[4,1,0,0]heptane (1) (and similar compounds substituted at the bicyclobutane fragment) caused first a rapid fall then a slower rise in pH. The proportion of the products (2) and (3) was found to depend on the rate of addition of solutions of the hydrocarbon to $[Rh(CO)_2Cl]_2$ or on the presence of $NaHCO_3$, slower addition or $NaHCO_3$ favouring (3). These and i.r. results suggest the intermediate (4), from



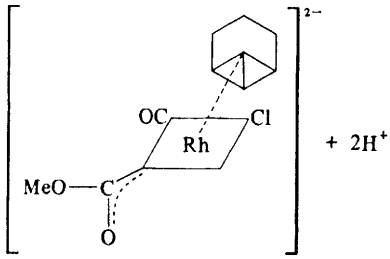
(1)



(2)



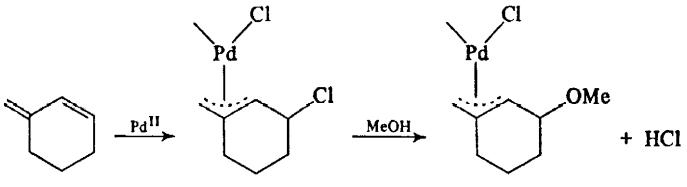
(3)



(4)

which two routes are possible. Disproportionation to $[Rh(CO)_2Cl]_2$ and methanol would be accompanied by formation of the diene (3) and would account for the rise and fall in acidity. Alternatively, acid-catalysed ring-opening of the bicyclobutane system would give (2). A fairly similar situation probably applies to catalysis by $[PdCl_2(PhCN)_2]$, except that the diene (3) forms first and co-ordinates to palladium as an h^3-allyl complex (5). Since this can generate HCl in the presence of methanol (Scheme 1), ring-opening of the bicyclobutane can then occur.[1] The Ag^+-catalysed conversion of benzene solutions of *endo*-2-methoxytricyclo[4,1,0,0]heptane (6) into (7) or of the norcanyl ether (8) to give predominantly (9) takes place *via* ionization of the methoxy-group; a typical configuration of the intermediate carbonium ion being

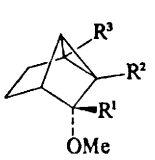
[1] W. G. Dauben, A. J. Kielbania, jun., and K. N. Raymond, *J. Amer. Chem. Soc.*, 1973, **95**, 7166



(5)

Scheme 1

(10). In similar reactions with (11) or (12), however, 'demethanolization' takes place to give (13) or cycloheptatriene, respectively. Whereas differences in structure might have been expected to promote a radical difference in the reaction course of (6)



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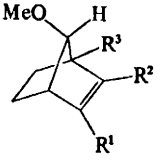

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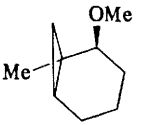

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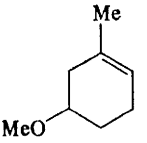

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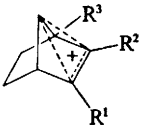

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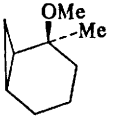

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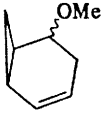
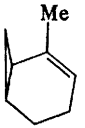


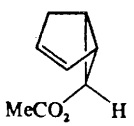
(12)



(13)

compared with, for instance, (12), a difference produced merely by the position of the substituents in (8) compared with (11) or (12) was considered surprising. During the reaction of (8) autocatalytic production of acid was observed. Mainly on account of its uniqueness the authors ascribe the difference in reactions to this although the detailed mechanism remains as yet unexplored.[2]

The passage of oxygen through solutions of (14) and $[(PPh_3)_3RhCl]$ or $[(PPh_3)_2Rh(CO)Cl]$ has been found to accelerate considerably the catalysed ring-opening reaction which affords (15) and (16). At present the active catalyst has not been completely identified. However, in solutions from which oxygen has been rigorously excluded, $[(PPh_3)_2Rh(O_2)Cl]_2$ catalyses the ring-opening at a rate comparable to that



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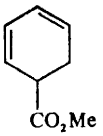
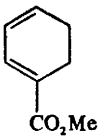


(15)



(16)

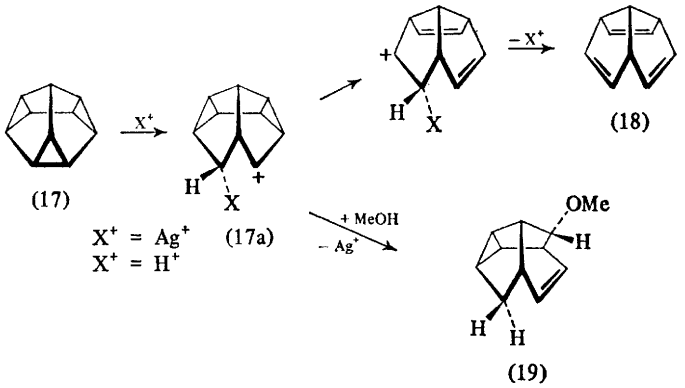
[2] G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, 1974, **96**, 5478.

found when oxygen is passed through solutions of (14) and $[(PPh_3)_3RhCl]$. In addition, $[(PPh_3)_2RhCl]_2$, which can be produced in the reaction

$$2[(PPh_3)_3RhCl] + O_2 \longrightarrow [(PPh_3)_2RhCl]_2 + 2Ph_3PO$$

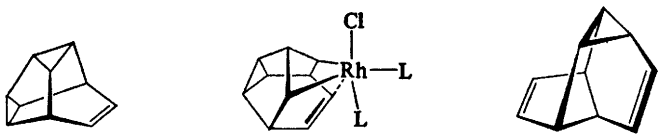
does not catalyse the reaction at all in the absence of oxygen and only ineffectively in its presence. Thus, it can at least be said that the catalyst precursor is an oxygen-containing complex.[3]

Silver ion catalyses the rearrangement of 'diademane' (17) to triquinacene (18). The reaction is also catalysed by protons and apparently proceeds according to Scheme 2 (X = Ag^+ or H^+). In the presence of a nucleophile such as methanol the



Scheme 2

initial intermediate carbenium ion (17a) is trapped before it can rearrange, thereby giving (19). In contrast to the silver-catalysed pathway, rhodium catalysts $[Rh(nor)Cl]_2$ or $[Rh(CO)_2Cl]_2$ lead to formation of 'snoutene' (20). It is proposed that initial oxidative addition occurs from the side of one of the five-membered rings to give (21).[4] Snoutene then rearranges further to give up to 55% of (22). The mechanism is

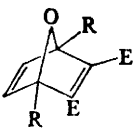


(20) (21) (22)

substantially the same as that observed for diademane and conforms to the general hypothesis that the bicyclopropyl unit linked by ring bridges will rearrange to a cyclohexene unit in the presence of transition-metal ions able to undergo oxidative addition. It was further shown that the size of the bridge can determine the predominant direction in which the rearrangement will proceed.[5]

[3] K. W. Barnett, D. L. Beach, D. L. Garin, and L. A. Kaempfe, *J. Amer. Chem. Soc.*, 1974, **96**, 7127.
[4] A. de Meijere, *Tetrahedron Letters*, 1974, 1845.
[5] A. de Meijere and L.-U. Meyer, *Tetrahedron Letters*, 1974, 1849.

In the presence of $[Rh(CO)_2Cl]_2$, 3-oxaquadricyclanes or 7-norbornadienes rearrange to 6-hydroxyfulvenes (see Vol. 3). For instance (23; R = Me, E = CO_2Me in all following examples) rearranges to (24).[6] It has been reported that, depending on the amount or nature of the catalyst {$[Rh(CO)_2Cl]_2$ or $[PtCl_2(PhCN)_2]$}, on the solvent, or on temperature, (23) rearranges not only to (24) but also to various amounts of (25) and (26). It is postulated that the mechanism involves formal migration of the ethereal oxygen. This can occur *via* (27) which is part of an acid-catalysed path (provided by traces of protic solvent) and leads exclusively to (24), or *via* a symmetry-forbidden route involving (28) which owes its viability to metal



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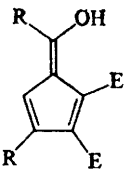

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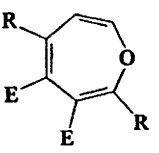

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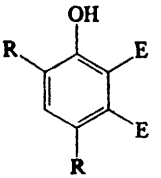

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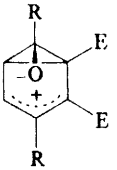

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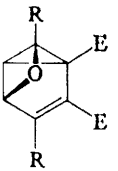
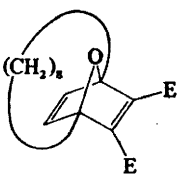


(28)

catalysis and which leads predominantly to (25) but with the alternative of an acid-catalysed route to (26).[7] The rearrangement of (29) to (30) in the presence of $[Rh(CO)_2Cl]_2$ proceeds at the same rate as (23) to (24). Complexation of the ethereal oxygen by rhodium as part of the mechanism therefore seems unlikely, since it is



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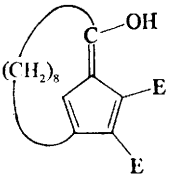


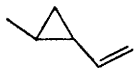
(30)

very effectively shielded by the octane bridge in (29).[6] Although not strictly applicable to catalysis, of related interest to these systems is the silver(I)-promoted production of intermediate bridgehead radicals during the course of substitution of the 1-chloroformyl group in (31).[8]

[6] H. Hogeveen and T. B. Middlekoop, *Tetrahedron Letters*, 1973, 4325.
[7] R. Roulet, J. Wenger, M. Hardy, and P. Vogel, *Tetrahedron Letters*, 1974, 1479.
[8] P. Beak and B. R. Harris, *J. Amer. Chem. Soc.*, 1974, **96**, 6363.

The *trans*- (32) and *cis*-2-methylcyclopropanes (33) are isomerized by *trans*-$[NiCl_2(PBu^n_3)_2]$–Bu^i_2AlCl and $[Ni(C_2H_4)\{P(o\text{-tolyl})_3\}_2]$–HCl catalysts to yield mixtures of *trans*-2-methylpenta-1,3-diene and *trans,trans*- and *trans,cis*-hexa-2,4-dienes. It was found also that reaction rates and product distribution were markedly

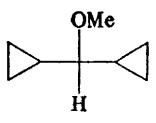
(31)



(32)

(33)

affected by the introduction of free ethylene in the former system. The authors' aim was to establish a model to demonstrate the role of cyclopropylcarbinylnickel intermediates in the catalysed isomerization of *cis*-hexa-1,4-dienes. Such intermediates can be readily inferred from the necessary presence of the co-catalyst, since a metal–hydride precursor is needed to generate the metal carbinyl. The results are discussed successfully in terms of the proposed model, particularly with reference to the stereochemistry of the intermediates.[9] Addition of $[Rh(CO)_2Cl]_2$ to a large variety of phenyl and vinyl cyclopropanes causes rearrangement mainly to *trans*-penta-1,3-diene derivatives. Once again the intermediacy of a metal cyclopropylcarbinyl species is proposed.[10] The interest in these species has in fact been extended to a direct study. Paquette *et al.* have noted the partial rearrangement of dicyclopropylcarbinyl methyl ether (34) to (35) (86%) and its *syn*-isomer (10%) catalysed by $AgClO_4$. Kinetic data indicate that the reaction is autocatalytic, but since reproducibility of data caused problems detailed mechanistic conclusions were not forthcoming.[8]



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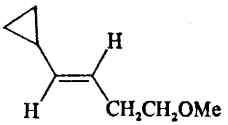


(35)

Transition-metal catalysis of rearrangement of internal epoxides to give ketones is rare. Particularly, rhodium catalysts normally act as Lewis acids and catalyse conversion into aldehydes; *cis*- and *trans*-stilbene oxide, for example, give diphenylacetaldehyde or its decarbonylation product diphenylmethane. It is interesting, therefore, that a large range of ruthenium, rhodium, iridium, palladium, and platinum catalysts have been found to catalyse the rearrangement of the *trans*-isomer to the ketone desoxybenzoin, $PhCOCH_2Ph$, (although in some cases a significant contribution from the acid-catalysed path was noted). Mechanistic details are promised at a later date.[11]

Alkenes.—The isomerization of pent-1-ene to pent-2-ene has received considerable attention during the period under review. Catalysis by (i) $[IrH(CO)(PPh_3)_3]$–O_2, (ii)

[9] P. A. Pinke, R. D. Stauffer, and R. G. Miller, *J. Amer. Chem. Soc.*, 1974, **96**, 4229.
[10] H. W. Voigt and J. A. Roth, *J. Catalysis*, 1974, **33**, 91.
[11] D. Milstein, O. Buchman, and J. Blum, *Tetrahedron Letters*, 1974, 2257.

$[IrHCl_2(PEt_2Ph)_3]$–O_2, (iii) $[IrCl(CO)(PPh_3)_2]$–O_2, (iv) $[IrCl(CO)(O_2)(PPh_3)_2]$–O_2, (v) $[PtH(SnCl_3)(PPh_3)_2]$,[12] (vi) $[RuHCl(CO)(PPh_3)_3]$, and (vii) $[RuHCl(PPh_3)_3]$[13] has been examined with particular emphasis on the catalyst-dependent preferential formation of the *cis*- or *trans*-2-ene. Systems (i), (ii), and (v) favour the *cis* olefin, whereas the *trans* is preferred in (iii) and (iv). The ruthenium catalysts both lead to the *cis* product at high catalyst concentrations but a change to preference for the *trans* is observed as the catalyst concentration is reduced. As in the case of nickel catalysis of this system (see Vol. 3) the isomerization is deemed to proceed *via* pentyl complex intermediates. Variation in *cis* : *trans* ratios are ascribed to the varying interactions of the bulky phosphine with the pentyl group. This may arise *via* the intervention of oxygen in such interactions, or *via* dissociation of the phosphine in the case of the ruthenium catalysts. $[Fe_3(CO)_{12}]$ and $[PdCl_2(PhCN)_2]$ also catalyse the isomerization, both leading preferentially to *trans*-pent-2-ene. Deuterium redistribution studies with [1,2-$^2H_2$]pent-1-ene indicate that in these examples the reaction proceeds *via* the well-known h^3-allyl–metal hydride mechanism.[14]

Previous studies of alkene isomerization have been noted in many cases for the requirement of acid co-catalysts. It is interesting, therefore, that isomerization of pent-1-ene by $[PdCl_2(\text{pent-1-ene})]_2$ requires a basic co-catalyst. This may be the free olefin itself or an added reagent such as ethanol.[15] A well-described system requiring an acid co-catalyst is $[NiL_4]$–H^+. This has now been supplemented by $[Ni\{P(OEt)_2Ph\}_4]$–H^+ which catalyses the conversion of 3-methylpent-1-ene into the *cis*- and *trans*-2-ene. Addition of the optically active phosphine (−)-*R*-P(Me)(Pr^n)(Ph) caused a retardation in the rate, a fact which is consistent with the previous postulate[16] that these complexes generate the active catalyst by dissociation. However, if the reaction is stopped by oxygen poisoning of the catalyst, it is found that the remaining starting olefin was enriched as the (+)-*S*-isomer, the optical yield of which is independent of the extent of conversion, but dependent on the amount of added phosphine. Furthermore, at high phosphine : nickel ratios the optical yield approaches a limiting value. This might indicate a limit in the extent of dissociation of the phosphite in the catalytic mechanism since this would be related to exchange with phosphine.[17] Finally, a word of caution about the extensive practice of performing catalytic studies under nitrogen when an inert atmosphere is necessary. Molecular nitrogen both inhibits and promotes the isomerization of pent-1-ene in the respective cases of catalysis by $[RuH_2(N_2)(PPh_3)_3]$[18] and $[CoH(N_2)(PPh_3)_3]$,Et_2O.[19] Other recent studies of the homogeneous catalysis of alkenes are summarized in Table 1.

2 Disproportionation

Activation of WCl_6 in benzene solution with alkylating reagents gives alkene disproportionation catalysts whose reactivities decrease in the order (WCl_6–EtOH–$4EtAlCl_2$) > (WCl_6–$2EtAlCl_2$) > (WCl_6–$2Bu^nLi$) > (WCl_6–R_2Zn). Solids are present

[12] D. Bingham, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1974, 1514.
[13] D. Bingham, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1974, 1519.
[14] D. Bingham, B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1974, 1521.
[15] F. Conti, L. Raimondi, and G. F. Pregaglia, *J. Organometallic Chem.*, 1974, **70**, 107.
[16] C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94**, 2994.
[17] G. Strukul, M. Bonivento, R. Ros, and M. Graziani, *Tetrahedron Letters*, 1974, 1791.
[18] F. Pennella and R. L. Banks, *J. Catalysis*, 1974, **35**, 73.
[19] F. Pennella, *J. Organometallic Chem.*, 1974, **78**, C10.

Table 1 *Homogeneous catalysis of the isomerization of alkenes*

Catalyst	*Substrate*	*Ref.*
$[NiCl_2(Bu^n{}_3P)_2]$–$Bu^i{}_2AlCl$	2- or 3-methyl or 2,3-dimethylpenta-1,4-diene, 3- or 4-methylhexa-1,4-diene	20
$PdCl_2$–$MeCO_2H$	allylbenzene	21
$[PdX_2(RCN)_2]$	hex-1-ene, pent-1-ene, but-1-ene	22
$[PtH(ClO_4)(PPh_3)_2]$	allyl ethers	23
$[PtH(SnCl_3)(PPh_3)_2]$		
$[PtH(NO_3)(PPh_2Me)_2]$		
$[PtH(PPh_3)_2(acetone)]^+BF_4^-$		
Ag^+	maleylacetones	24

in all these systems and it is possible that they should all be considered as heterogeneous systems. These catalysts are essentially inactive for the disproportionation of terminal alkenes, and reactions of internal alkenes are inhibited by the presence of terminal alkenes. The wide variation found for the reactivity of the above systems suggests that the other metal present is involved in the disproportionation reaction.[25] The low activity of heterogeneous disproportionation catalysts derived from $[W(CO)_6]$ is probably associated with poor ability of the hexacarbonyl to form tungsten. Thus treatment of silica or γ-alumina with the more reactive WMe_6 gives catalyst systems of comparable reactivity to $[Mo(CO)_6]$.[26]

3 Oligomerization

Oligomerization, co-oligomerization, and cyclo-oligomerization reactions catalysed by transition-metal complexes have been reviewed.[27–30]

Copper(I) triflate, $CuSO_3F$, is an efficient catalyst for the photodimerization of norbornene. The proposed mechanism of this reaction (Scheme 3), which is supported by quantum-yield studies, involves photoexcitation of a 2 : 1 alkene–$CuSO_3F$ complex followed by unimolecular collapse to products. An alternative mechanism involving photoexcitation of a 1 : 1 copper(I)–alkene complex and a subsequent termolecular interaction with two ground-state alkenes to give the dimer, a mechanism proposed for the photodimerization of norbornene-catalysed by copper(I) halides, is not consistent with the present studies.[31] Photodimerizations catalysed by CuCl have only been observed with strained cycloalkenes. However, $CuSO_3F$ is an efficient catalyst for the photodimerization of simple alkenes *e.g.* cyclopentene,

[20] H. J. Golden, D. J. Baker, and R. G. Miller, *J. Amer. Chem. Soc.*, 1974, **96**, 4235.
[21] B. I. Cruikshank and N. R. Davies, *Austral. J. Chem.*, 1973, **26**, 2635.
[22] S. Sakaki, H. Kanai, and K. Tarama, *Canad. J. Chem.*, 1974, **52**, 2857.
[23] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1973, **12**, 1566.
[24] R. A. Johnson and S. Seltzer, *J. Amer. Chem. Soc.*, 1973, **95**, 5700.
[25] E. L. Muetterties and M. A. Busch, *J.C.S. Chem. Comm.*, 1974, 754.
[26] W. Mowat, J. Smith, and D. A. Whan, *J.C.S. Chem. Comm.*, 1974, 34.
[27] P. Heimbach, *Angew. Chem. Internat. Edn*, 1973, **12**, 975.
[28] K. Fischer, K. Jonas, P. Misbach, R. Stabba, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1973, **12**, 943.
[29] H. Bonnemann, C. Grard, W. Kopp, W. Pump, K. Tanaka, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1973, **12**, 964.
[30] R. Baker, *Chem. Rev.*, 1973, **73**, 487.
[31] R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 1137.

$$Cu{-}A + A \overset{K}{\rightleftharpoons} Cu{-}A_2$$

$$Cu{-}A + h\nu \xrightarrow{\Phi_1} Cu{-}A^*$$

$$Cu{-}A_2 + h\nu \xrightarrow{\Phi_2} Cu{-}A_2$$

$$Cu{-}A^* + A \xrightarrow{k_1} \text{dimer}$$

$$Cu{-}A_2 \longrightarrow \text{dimer}$$

$$Cu{-}A^* \xrightarrow{k_2} Cu{-}A$$

(A = alkene)

Scheme 3

cyclohexene, and cycloheptene. The major products from cyclohexene and cycloheptene are the thermodynamically less stable *trans*-fused [2 + 2] cyclodimers.[32]

A brief kinetic study on the cyclo-oligomerization of allene with nickel(0) complexes has been reported.[33] The rate of reaction increases in the order Ni^0–$P(OPh)_3$ < Ni^0–PPh_3 < Ni^0. Initial rates for pentamerization and tetramerization are first-order in allene concentration but the trimerization reaction is nearly zero order. The mechanisms illustrated in Scheme 4 are proposed. The complex $[Ni(cod)_2]$ produces complexes of allene trimer and tetramer below −30 °C but at higher temperatures the nickel(0) complexes catalyse the pentamerization reaction. In the presence of 1 to 2 mol of a phosphorus ligand only the trimer complex is formed.[34]

Trimerization

$$Ni{-}P(OAr)_3 + 3C_3H_4 \longrightarrow [Ni(C_9H_{12})\{P(OAr)_3\}]$$

$$[Ni(C_9H_{12})\{P(OAr)_3\}] \longrightarrow Ni{-}P(OAr)_3 + C_9H_{12}$$

Tetramerization

$$Ni{-}PR_3 + 3C_3H_4 \xrightarrow{\text{fast}} [Ni(C_9H_{12})PR_3]$$

$$[Ni(C_9H_{12})PR_3] + C_3H_4 \xrightarrow{\text{slow}} [Ni(C_{12}H_{16})PR_3]$$

$$[Ni(C_{12}H_{16})PR_3] \xrightarrow{\text{fast}} Ni{-}PR_3 + C_{12}H_{16}$$

Pentamerization (labile ligands not shown)

$$Ni + 4C_3H_4 \xrightarrow{\text{fast}} [Ni(C_{12}H_{16})]$$

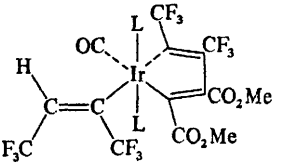
$$[Ni(C_{12}H_{16})] + C_3H_4 \xrightarrow{\text{slow}} [Ni(C_{15}H_{20})]$$

$$[Ni(C_{15}H_{20})] \xrightarrow{\text{fast}} Ni + C_{15}H_{20}$$

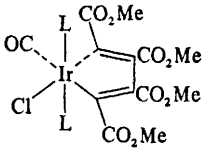
Scheme 4

[32] R. G. Salomon, K. Folting, W. E. Streib, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 1145
[33] S. Otsuka, K. Tani, and T. Yamagata, *J.C.S. Dalton*, 1973, 2491.
[34] W. H. Baddley and G. B. Tupper, *J. Organometallic Chem.*, 1974, **67**, C16.

Metallocyclopentadiene complexes are often involved in cyclotrimerization reactions of alkynes. Studies on the complex (36) reveal that these alkenyl-metallocyclopentadiene complexes are more efficient catalysts for cyclotrimerization reaction than (37).[35] The significant enhancement of catalysis by the alkenyl ligand may be a



(36)



(37)

consequence of the higher *trans* influence of alkenyl as compared to chloride. Weakening of the *trans*-metal–carbon bond of the metallocyclopentadiene might thus enhance further insertion of an alkyne to produce the benzene derivative.

Studies on the reactions of various alkenes with iron complexes of the type $[Fe(alkyl)_2(dipy)_2]$ have shown that electronegative alkenes undergo polymerization. Less electronegative alkenes do not react. A similar but less marked trend is observed in reactions with $[CoH(N_2)(PPh_3)_3]$ except that less electronegative alkenes *e.g.* styrene or isobutyl vinyl ether give alkene cobalt complexes. The carbonyl complex $[CoH(CO)(PPh_3)_3]$ is, in general, less reactive than the dinitrogen complex. However, styrene and isobutyl vinyl ether are polymerized with this carbonyl complex. The reactions are first order with respect to the complexes, and the pseudo-first-order rate constants are given by the equations

$$\frac{1}{k(N_2)} = \frac{1}{k_1} + A\{B + C[N_2]\}\frac{[PPh_3]}{[alkene]}$$

$$\frac{1}{k(CO)} = \frac{1}{k} + D\frac{[PPh_3]}{[alkene]}$$

The reactions are inhibited by added triphenylphosphine and a mechanism involving dissociation of a phosphine ligand followed by alkene co-ordination is proposed.[36,37]

It is well known that systems containing organometallic compounds and organic halides are sources of free radicals which initiate free-radical polymerizations. The overall reaction involves ligand exchange followed by one or more redox processes in which free radicals are produced (Scheme 5). Absolute rate constants for these redox processes have now been determined. Activation entropies of the redox reactions of $[Mo(CH_2{=}CHCO_2Me)(CO)_5]$ with CCl_4, CCl_3CO_2Et, and CBr_4 are more positive than expected for a bimolecular process involving a polar transition state in a polar solvent. Weakening of a Mo—CO band in the transition state may be responsible for this effect.[38] The system *trans*-$[RhCl(CO)(PPh_3)_2]$ and an organic halide can also initiate free-radical polymerization of methyl methacrylate.[39]

[35] Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1973, **60**, 165.
[36] Y. Kubo, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Japan*, 1974, **47**, 393.
[37] C. H. Bamford and I. Sakamoto, *J.C.S. Faraday I*, 1974, **70**, 330.
[38] C. H. Bamford and I. Sakamoto, *J.C.S. Faraday I*, 1974, **70**, 344.
[39] N. Kameda and N. Itagaki, *Bull. Chem. Soc. Japan*, 1973, **46**, 2597.

$$NiL_4 \underset{\text{dissociation}}{\overset{S_N1}{\rightleftharpoons}} NiL_3 + L \qquad [L = P(OPh)_3]$$

$$NiL_3 + CH_2{=}CHCO_2Me \overset{K}{\rightleftharpoons} [Ni(CH_2{=}CHCO_2Me)L_3]$$

(A)

$$(A) + CCl_4 \longrightarrow CCl_3\cdot + (A)^+$$

$$[Mo(CO)_6] + CH_2{=}CHCO_2Me \rightleftharpoons [Mo(CH_2{=}CHCO_2Me)(CO)_5] + CO$$

(B)

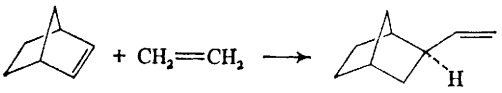
$$(B) \longrightarrow \text{inactive products}$$

$$(B) + CCl_4 \longrightarrow (B)^+ + CCl_3\cdot + CO$$

Scheme 5

4 Co-addition and Co-oligomerization

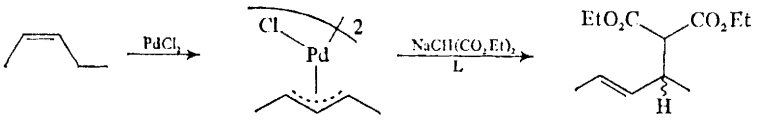
η^3-Allylnickel halide–Lewis acid–chiral phosphine catalyst systems have been developed which can induce the asymmetric formation of 3-vinylcyclo-oct-1-ene and 3-methylpent-1-ene. Catalytic codimerizations of norbornene, norbornadiene, and (±)-2-bornene with ethylene are also possible (*e.g.* Scheme 6) and these types of



(+)-(1*S*, 2*S*, 4*R*)

Scheme 6

reactions have been reviewed.[40] Alkylation of an η^3-allylpalladium complex has also been shown to lead to high optical yields of the C—C bonded product (38) (Scheme 7) when the ligand L is (+)-2,2-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenyl-



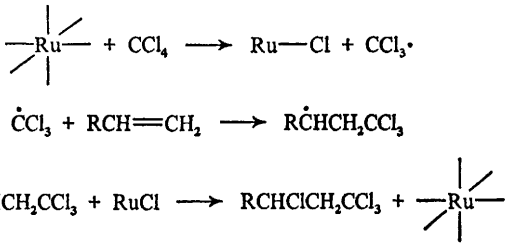
(38)

Scheme 7

phosphino)butane, (+)-*o*-anisylcyclohexylmethylphosphine, (−)-dimethylisopropylphosphine or (−)-sparteine. In these reactions the proximity of the asymmetry to the complexing atom in the ligand rather than steric effects appears to dominate the asymmetric synthesis.[41]

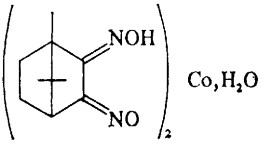
[40] B. Bogdanovic, B. Henc, A. Losler, B. Meister, H. Pauling, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1973, **12**, 954.
[41] B. M. Trost and T. J. Dietsche, *J. Amer. Chem. Soc.*, 1973, **95**, 8200.

The ruthenium(II) complexes $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PPh_3)_4]$ catalyse the addition of carbon tetrachloride or chloroform to terminal alkenes. Support for a homolytic mechanism (Scheme 8) is provided by the observation that reaction is completely inhibited by a small amount of galvinoxyl.[42]



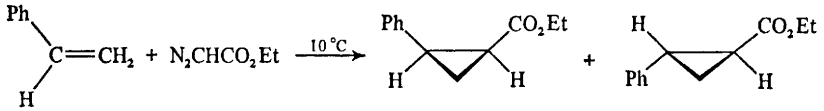
Scheme 8

Treatment of cobalt(II) chloride in alkaline aqueous methanol with (+)-camphorquinone-α-dioxime under nitrogen gives the air-sensitive complex (39) which is an



(39)

effective catalyst for the cyclopropanation of alkenes (Scheme 9). The *cis*- and *trans*-esters are formed in a nearly 1 : 1 mole ratio. Hydrolysis gives at least 68% of the *cis*

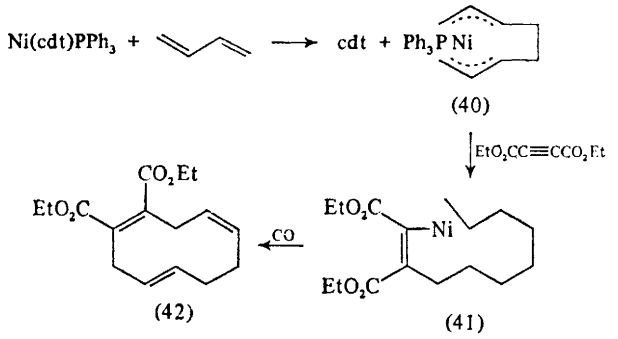


Scheme 9

acid with the (1*S*,2*R*) configuration. Similarly the *trans*-acid can be obtained in excess of 78% in the 1*S*,2*S* configuration. Cobalt catalysts containing achiral dioxime ligands and a chiral axial base give essentially optically inactive products.[43]

The reaction of butadiene with alkynes to give cyclodecatrienes is catalysed by zerovalent nickel complexes. Evidence that these reactions proceed in a stepwise manner and involve an αω-bisallyl-C_8 nickel complex has now been obtained. Thus addition of $EtO_2CC{\equiv}CCO_2Et$ to the αω-octadienediylnickel complex (40) at −30 °C gives a yellow complex (41) which on treatment with carbon monoxide gives the cyclodecatriene derivative (42) (Scheme 10).[44]

[42] H. Matsumoto, T. Nakano, and Y. Nagai, *Tetrahedron Letters*, 1973, 5147.
[43] Y. Tatsuno, A. Konishi, A. Nakamura, and S. Otsuka, *J.C.S. Chem. Comm.*, 1974, 588.
[44] B. Büssemeier, P. W. Jolly, and G. Wilke, *J. Amer. Chem. Soc.*, 1974, **96**, 4726.

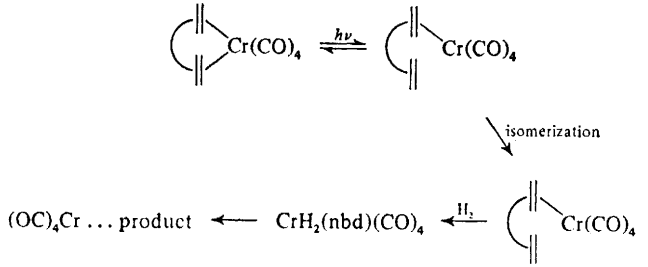


Scheme 10

5 Homogeneous Hydrogenation

The homogeneous hydrogenation and asymmetric hydrogenation of organic compounds catalysed by transition-metal complexes and salts have been reviewed.[40,45]

Chromium.—The photoinduced hydrogenation of norbornadiene is catalysed by $[Cr(CO)_4(nbd)]$. Kinetic studies on this system are consistent with the mechanism illustrated in Scheme 11. The first-order kinetics found at low norbornadiene concentrations are consistent with competitive pathways involving the substrate on one

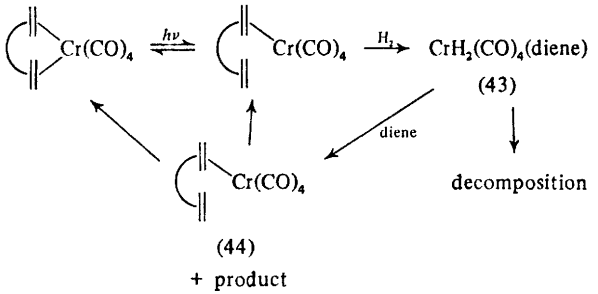


Scheme 11

side in a rate-determining step. However, the mechanism must also involve thermal catalytic cycles, *e.g.* reaction of free norbornadiene with (43) to generate (44) (Scheme 12), since the first-order behaviour coincides with a quantum yield higher than 0.1.[46] Similar hydrogenation reactions with hexa-2,4-diene are slower and the absence of first-order kinetics has been interpreted in terms of a mechanism not involving free $[Cr(CO)_4]$ (Scheme 12).[47]

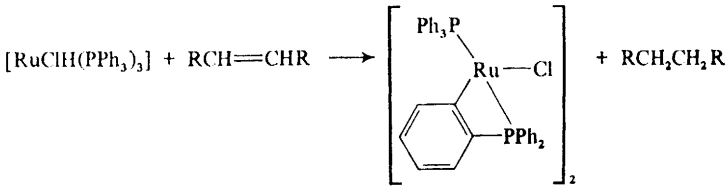
Ruthenium.—Use of the phenyl hydrogen of triphenylphosphine metal complexes has been suggested for alkene hydrogenation on the basis of results of exchange studies

[45] G. Dolcetti and N. W. Hoffman, *Inorg. Chim. Acta*, 1974, **9**, 269.
[46] G. Platbrood and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1974, **70**, 393.
[47] G. Platbrood and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1974, **70**, 407.



Scheme 12

for some homogeneous catalytic systems.[48] It has now been found that [RuClH-$(PPh_3)_3$] stoicheiometrically hydrogenates alkenes with the formation of the *ortho*-metallated complex (45). However, this stoicheiometric reaction is unimportant in hydrogenations with hydrogen gas catalysed by [RuClH$(PPh_3)_3$] which occur much more rapidly.[49]



(45)

Hydrated 'ruthenium trichloride' which is a mixture of ruthenium(III) and ruthenium(IV) reacts with hydrogen in *NN*-dimethylacetamide solution under mild conditions in stepwise stoicheiometric processes to give ruthenium(I) species.

$$Ru^{IV} \xrightarrow{1} Ru^{III} \xrightarrow{2} Ru^{II} \xrightarrow{3} Ru^{I}$$

Reactions 1 and 2 involve heterolytic activation of hydrogen by a catalyst of ruthenium(III) and probably involve a ruthenium(III) hydride intermediate. The ruthenium(III) catalyst also catalyses reduction of oxygen to water. However, a heterolytic splitting *via* a ruthenium(V) dihydride intermediate cannot be ruled out. Activation parameters for these reactions are given in Table 2. The kinetics of the H_2

Table 2 *Rates and activation parameters for ruthenium*(III) *catalysed hydrogen reductions*[50]

Substrate	k_1 (55 °C)/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
Ru^{IV}	1.64	19.9	+3.3
O_2	2.29	19.3	+2.3
Ru^{III}	0.04	15.5	−16.4

[48] R. A. Schunn, *Inorg. Chem.*, 1970, **9**, 2567.
[49] B. R. James, L. D. Markham, and D. K. W. Wang, *J.C.S. Chem. Comm.*, 1974, 439.
[50] B. C. Hui and B. R. James, *Canad. J. Chem.*, 1974, **52**, 348.

reduction of Ru^{II} to Ru^{I} are similar to those observed for the Ru^{III}–H_2 activations, except that a ruthenium(II) hydride intermediate is involved.[50]

The ruthenium(II) complex $[RuCl_2(PPh_3)_3]$ can catalyse transformation of a saturated ketone into an equilibrium mixture of the carbonyl compound and corresponding carbinol:

$$PhCH_2COCH_2Ph + PhCH(OH)Me \rightleftharpoons PhCOMe + PhCH_2CH(OH)CH_2Ph$$

Kinetic studies in the presence of the catalyst at 180 °C show that at constant concentration of the carbinol, the rate of equilibration changes from first-order (at 0.1 mol l^{-1} ketone) to a maximum and constant value above 0.3 mol l^{-1} dibenzylketone. If the ketone concentration is constant, the rate reaches its highest (constant) value only when the carbinol concentration exceeds 7 mol l^{-1}.

Studies with other systems show that the rate is virtually independent of the nature of the ketone but depends upon the steric and electronic nature of the carbinol. The steps in Scheme 13 are considered to be important in the reaction mechanism.[51]

$$R^1_2CO + Ru \rightleftharpoons Ru(R^1_2CO)$$

$$Ru(R^1_2CO) + R^2R^3CHOH \rightleftharpoons Ru(OCHR^2R^3)(R^1_2CO) + H^+$$

$$Ru(OCHR^2R^3)(R^1_2CO) \rightleftharpoons RuH(R^2R^3CO)(R^1_2CO)$$

$$RuH(R^2R^3CO)(R^1_2CO) \rightleftharpoons Ru(OCHR^1_2)(R^2R^3CO)$$

$$Ru(OCHR^1_2)(R^2R^3CO) + H^+ \rightleftharpoons Ru + R^1_2CHOH + R^2R^3CO$$

Scheme 13

Cobalt.—Aromatic hydrocarbon hydrogenations with a discrete metal complex have now been achieved for the first time. Thus hydrogenation of benzene to cyclohexane proceeds slowly at 25 °C and < 760 mmHg pressure in the presence of $[Co(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}_3]$. Alkylbenzenes are converted into alkylcyclohexanes, anisole into methoxycyclohexane, and ethylbenzoate into ethyl cyclohexenylcarboxylate. The suggested mechanism of reaction is summarized in Scheme 14.[52]

$$[Co(\eta^3\text{-}C_3H_5)L_3] \rightleftharpoons [Co(\eta^1\text{-}C_3H_5)L_3]$$

$$[Co(\eta^1\text{-}C_3H_5)L_3] + H_2 \rightleftharpoons [CoH_2(\eta^1\text{-}C_3H_5)L_3]$$

$$[CoH_2(\eta^1\text{-}C_3H_5)L_3] + C_6H_6 \rightleftharpoons [Co(\eta^1\text{-}C_3H_5)L_3] + C_6H_8$$

$$[CoH_2(\eta^1\text{-}C_3H_5)L_3] + C_6H_8 \rightleftharpoons [Co(\eta^1\text{-}C_3H_5)L_3] + C_6H_{10}$$

$$[CoH_2(\eta^1\text{-}C_3H_5)L_3] + C_6H_{10} \rightleftharpoons [Co(\eta^1\text{-}C_3H_5)L_3] + C_6H_{12}$$

$$L = P(OMe)_3$$

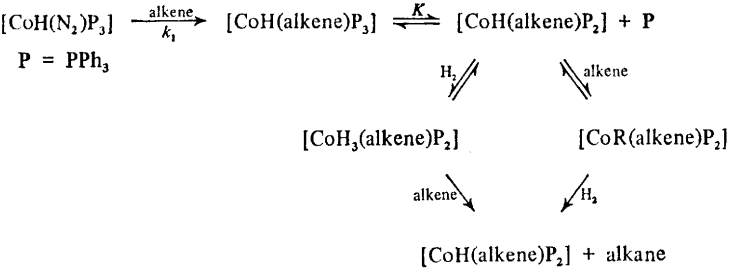
Scheme 14

[51] Y. Sasson, P. Albin, and J. Blum, *Tetrahedron Letters*, 1974, 833.
[52] E. L. Muetterties and F. J. Hirsekorn, *J. Amer. Chem. Soc.*, 1974, **96**, 4063.

A study of the kinetics of homogeneous hydrogenation of cyclohexene catalysed by cobalt hydride complexes formed *in situ* from $[CoH(N_2)(PPh_3)_3]$ and hydrogen at room temperature and atmospheric pressure has revealed the following rate equation

$$\text{Rate} = \frac{k_{obs}[H_2][\text{alkene}][\text{catalyst}]}{[PPh_3]}$$

The kinetic data are interpreted in terms of Scheme 15.[53]



Scheme 15

Two types of mechanism have been suggested for the hydrogenation of conjugated alkenes catalysed by $[Co(CN)_5]^{3-}$. In Scheme 16 organocobalt intermediates

$$2Co + H_2 \rightleftharpoons 2CoH$$

$$CoH + A \rightleftharpoons CoAH$$

$$CoAH + CoH \longrightarrow 2Co + AH_2$$

Scheme 16

are involved, while in Scheme 17 free-radical intermediates have been proposed. The hydrogenation of butadiene and isoprene follows Scheme 16. However, Scheme 17

$$2Co + H_2 \rightleftharpoons 2CoH$$

$$CoH + A \rightleftharpoons Co + AH\cdot$$

$$CoH + AH\cdot \longrightarrow Co + AH_2$$

$$Co + AH\cdot \rightleftharpoons CoAH$$

$$Co = [Co(CN)_5]^{3-};\ CoH = [CoH(CN)_5]^{3-};\ A = \text{alkene}$$

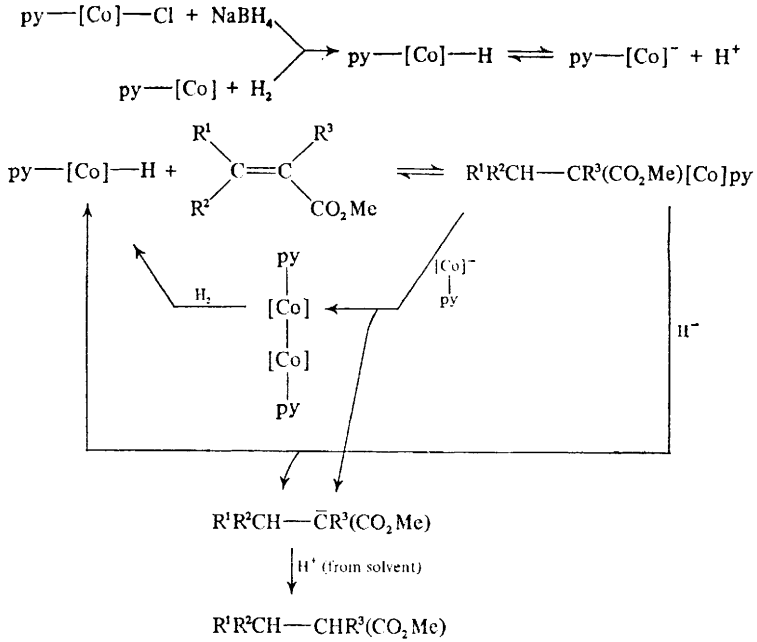
Scheme 17

has been suggested for the hydrogenation of activated alkenes such as styrene and cinnamate. Support for the radical mechanism has been obtained from kinetic studies, radical trapping experiments, and the non-stereoselectivity of hydrogen addition.

[53] E. Balogh-Hergovich, G. Speier, and L. Marko, *J. Organometallic Chem.*, 1974, **66**, 303.

Kinetic evidence has now shown that the hydrogenation of *trans*-1-phenylbuta-1,3-diene in water follows Scheme 16. In glycerol–methanol and ethylene glycol–water mixtures the products are still mainly formed *via* Scheme 16. However, products may also probably be formed *via* radical intermediates in these solvents. The solvents can affect the rate and equilibrium constants in each reaction.[54]

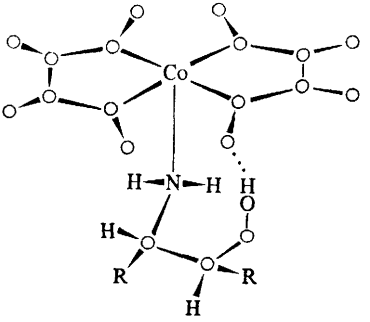
The complexes (pyridinato)cobaloxime(II), chloro(pyridinato)cobaloxime(III), and vitamin B_{12} catalyse the hydrogenation of $\alpha\beta$-unsaturated esters by hydrogen or sodium borohydride. The hydrogenation is not stereospecific and the proposed mechanism is outlined in Scheme 18.[55]



Scheme 18

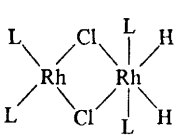
Complexes of bis(dimethylglyoximato)cobalt(II) and optically active amines, [Co(dmgH)$_2$(amine)], can catalyse the asymmetric hydrogenation of alkenes, α-diketones, and α-ketocarboxylic esters. It has been suggested that the Co(dmgH)$_2$ plane is twisted by hydrogen bonding between an oxygen of a dmgH ligand and the hydroxy-group of the amine (46). The direction of this twist will be determined by the configuration of the amine, and the resulting asymmetry about the cobalt could then be transferred to the hydrogenated products during the catalytic reaction. However, the crystal structure of β-cyanoethyl[D-(−)-*erythro*-1,2-diphenyl-2-hydroxyethylaminebis(dimethylglyoximato)]cobalt is different from the assumed structure in (46) and the mechanism of asymmetric induction is not clear.[56]

[54] T. Funabiki, M. Mohri, and K. Tarama, *J.C.S. Dalton*, 1973, 1813.
[55] M. N. Ricroch and A. Gaudemer, *J. Organometallic Chem.*, 1974, **67**, 119.
[56] Y. Ohashi, Y. Sasada, Y. Tashiro, Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Japan*, 1973, **46**, 2589.

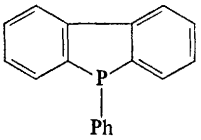


(46)

Rhodium.—In addition to the studies[57] on the alkene hydrogenation catalyst $[RhCl(PPh_3)_3]$ (see Vol. 3), some other very detailed studies on this system have appeared.[58] It is now apparent that the complexes $[RhClL_3]$ [L = PPh_3 or P(*p*-tolyl)$_3$] do not dissociate to a spectroscopically detectable extent. However, despite its low concentration a species of composition $[RhClL_2]$ must be postulated, as previously reported,[57] in order to explain the kinetics of H_2 reactions with solutions of $[RhClL_3]$. The complexes $[RhClL_3]$, however, are in equilibrium with the dimers, $[RhClL_2]_2$. The dimer reacts with H_2 to form (47) and is also readily cleaved with ethylene or L, but not cyclohexene, to form $[RhCl(C_2H_4)L_2]$ or $[RhClL_3]$.[58]



(47)



(48)

The complex, [RhH(dbp)$_4$] (dbp = 5-phenyl-5*H*-dibenzophosphole) (48) is a very effective and selective catalyst for the homogeneous hydrogenation of terminal alkenes at 20 °C and less than 1 atm of hydrogen pressure. In its activity and selectivity the complex resembles $[RuClH(PPh_3)_3]$ but has the advantage of being more stable in the solid state. The kinetic studies of hydrogenation of hex-1-ene are consistent with the mechanism in Scheme 19.[59]

$$[RhH(dbp)_4] \longrightarrow [RhH(dbp)_3] + dbp$$

$$[RhH(dbp)_3] \overset{K}{\rightleftharpoons} [RhH(dbp)_2] + dbp$$

$$[RhH(dbp)_2] + alkene \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} [Rh(alkyl)(dbp)_2]$$

$$[Rh(alkyl)(dbp)_2] \xrightarrow{k_2} [RhH(dbp)_2] + alkane$$

Scheme 19

[57] J. Halpern and C. S. Wong, *J.C.S. Chem. Comm.*, 1973, 629.
[58] C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 2762.
[59] D. E. Budd, D. G. Holah, A. N. Hughes, and B. C. Hui, *Canad. J. Chem.*, 1974, **52**, 775.

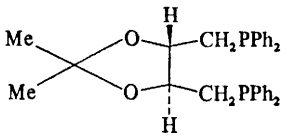
The activity of the hydrogenation catalyst $[RhH(CO)(PPh_3)_3]$ decreases with time. However, under weak u.v. irradiation the catalyst can be reactivated.[60]

The asymmetric reduction of α-keto-esters has been achieved *via* catalytic hydrosilylation followed by hydrolysis (Scheme 20). The rhodium catalysts used in these

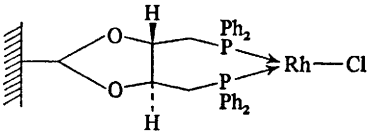
$$R^1COCO_2R^2 + R^3R^4S_1H_2 \xrightarrow{[Rh]^*} R^1\overset{*}{C}HCO_2R^2 \xrightarrow{MeOH-H^+} R^1\overset{*}{C}HCO_2R^2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad OSiHR^3R^4 \qquad\qquad OH$$

Scheme 20

reactions are prepared by addition of either (+)-benzylmethylphenylphosphine or (+)-2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop) (49) to $[RhCl(1,5\text{-cod})]_2$.[61] Similarly the asymmetric hydrogenation of ketones to carbinols can be achieved *via* catalytic hydrosilylation.[62] Although the insoluble chiral polymer-supported rhodium complex (50) is just as efficient as the soluble rhodium catalyst for hydrosilylation the insoluble system (suspended in benzene) catalyses asymmetric hydrogenation of α-ethylstyrene and methyl atropate with a much lower efficiency than in solution.[62]



(49)



(50)

Iridium.—Buta-1,3-diene is catalytically hydrogenated to a mixture of butenes and butane by $[IrH(CO)(PPh_3)_3]$ and $[IrH_3(CO)(PPh_3)_2]$ at 50 °C in DMF. The rates observed can be predicted from the empirical rate equation

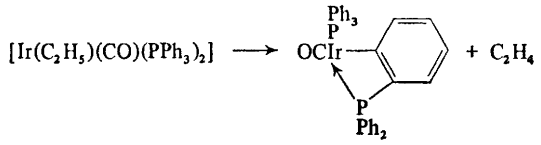
$$\frac{-d[C_4H_6]}{dt} = \frac{\{1.86\times10^{-3} + 0.681[PPh_3]\}[Ir][C_4H_6]}{\{1 + 4.2\times10^{4}[PPh_3]\}}$$

where Ir = $[IrH(CO)(PPh_3)_3]$ + $[IrH_3(CO)(PPh_3)_2]$.

Butadiene reacts with $[IrH_3(CO)(PPh_3)]$ to form $[Ir(\eta^3\text{-}C_4H_7)(CO)(PPh_3)_2]$ and its much slower formation from $[IrH(CO)(PPh_3)_3]$ has been established. Although the rate of formation of the allyl is inhibited by triphenylphosphine its equilibrium is not greatly reduced. The allyl reacts rapidly with hydrogen to form butene and $[IrH_3(CO)(PPh_3)_2]$. The reaction is dramatically inhibited by triphenylphosphine. The hydrogenation of ethylene occurs by a very similar mechanism. Decomposition of $[IrEt(CO)(PPh_3)_2]$ to an *ortho*-metallated product (51) could be the rate-determining step.[63]

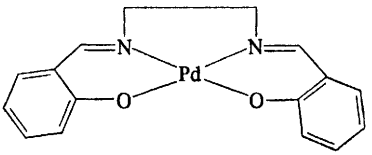
Under weak u.v. irradiation the activity of the hydrogenation catalyst *trans*-$[IrCl(CO)(PPh_3)_2]$ can be increased considerably.[64]

[60] W. Strohmeier and G. Csontos, *J. Organometallic Chem.*, 1974, **67**, C27.
[61] I. Ojima, T. Kogure, and Y. Nagai, *Tetrahedron Letters*, 1974, 1889.
[62] W. Dumont, J. C. Poulin, T.-P. Dand, and H. B. Kagan, *J. Amer. Chem. Soc.*, 1973, **95**, 8295.
[63] M. G. Burnett, R. J. Morrison, and C. J. Strugnell, *J.C.S. Dalton*, 1974, 1663.
[64] W. Strohmeier and G. Csontos, *J. Organometallic Chem.*, 1974, **72**, 277



(51)

Palladium.—A variety of micro-organisms activate molecular hydrogen. The palladium(II) complex (52) has been shown to behave in several respects as a hydro-



(52)

genase and it can therefore be considered as a suitable model system. The hydrogenation of hex-1-ene catalysed by (52) in DMF solution proceeds by the mechanism illustrated in Scheme 21.

$$[Pd] + H_2 \overset{K_1}{\rightleftharpoons} H{-}[Pd]{-}H$$

$$H{-}[Pd]{-}H + \text{alkene} \overset{K_2}{\rightleftharpoons} \text{alkyl}{-}[Pd]{-}H \xrightarrow{k} [Pd] + \text{alkane}$$

Scheme 21

The rate law following from Scheme 21

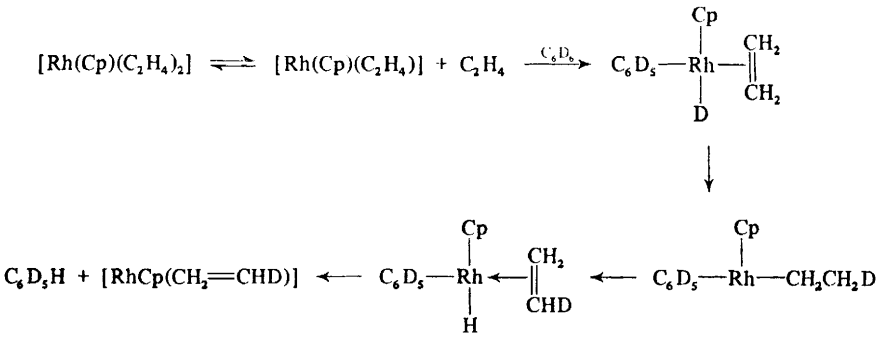
$$\text{Rate} = \frac{kK_1K_2[H_2][\text{alkene}][Pd]}{1 + K_1[H_2] + K_1K_2[H_2][\text{alkene}]}$$

is in excellent agreement with the kinetic measurements.[65]

6 Hydrogen Exchange

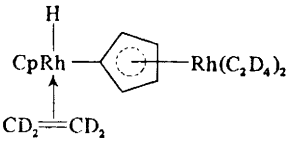
A novel isotopic hydrogen exchange reaction occurs when [$^2H_6$]benzene and [Rh(η^5-C_5H_5)(C_2H_4)$_2$] are heated together at 130 °C. Under these conditions deuterium is introduced into both the cyclopentadienyl and ethylene protons. The rhodium complex can be recovered and mass spectroscopy shows no non-deuteriated complex to be present. The other major exchange species is C_6D_5H. Free ethylene inhibits the exchange reaction and the initial step in the reaction is probably dissociation. The proposed overall mechanism is outlined in Scheme 22. Oxidative addition of a C—H bond of a cyclopentadienyl ligand to give the intermediate (53) can be envisaged as a key step in the exchange reaction of the η^5-C_5H_5 ligand. The alkene complexes [Rh(acac)(C_2H_4)$_2$], [Rh(η^5-C_5Me_5)(C_2H_4)$_2$], and [Rh(η^5-C_5H_5)(CH_2=CHCN)$_2$] also undergo the exchange reaction. The methyl protons of [Rh(η^5-C_5Me_5)(C_2H_4)$_2$] do not

[65] G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1974, **13**, 549.



Cp = η^5-C_5H_5

Scheme 22



(53)

undergo the exchange reaction but the complex is as reactive as [Rh(η^5-C_5H_5)-(C_2H_4)$_2$]. Much less exchange is observed with [Rh(acac)(C_2H_4)$_2$], [Rh(η^5-C_5H_4CN)-(C_2H_4)$_2$], and [Rh(η^5-C_5H_5)(1,5-cod)]. The reactivity of other arenes decreases in the order $C_6D_6 \geq C_5D_5N > C_5D_5NO_2 \geq C_6D_5CD_3$, pyridine exchanging mainly with co-ordinated ethylene.[66]

The kinetics of D_2–C_2H_5OH exchange catalysed by [RhCl(PPh_3)$_3$] have been studied in benzene–ethanol solution. The rate of exchange is low, the rate-limiting step being transfer of deuterium from [$RhClD_2(PPh_3)_3$] to the solvent. The activation energy for the overall process is 35 kJ mol^{-1}.[67] The reaction in chloroform–ethanol solution is complicated by a side-reaction of the solvent to yield HCl, C_2H_5Cl, CH_2Cl_2, [$RhHCl_2(PPh_3)_2$], Ph_3PO, and other phosphorus(v) species. The D_2 exchange reaction is very solvent dependent and between 6 and 96% of ethanol in chloroform, the rate of exchange decreases by a factor of *ca.* 30. The rate of but-1-ene hydrogenation decreases by only a factor of 3.4. However, the relative magnitudes of the rates of these reactions may not be significant since the concentration of but-1-ene is low. The activation energy for exchange is 101 ± 9 kJ mol^{-1} at 58 mol % ethanol and 86 ± 8 kJ mol^{-1} at 6 mol % ethanol and hence solvent-catalyst bonding interactions are probably not important. The exchange rate with [$RhBr(PPh_3)_3$] is roughly twice that for [RhCl(PPh_3)$_3$].[68]

Hydrogen–deuterium exchange of alkanes catalysed by platinum(II) in AcOD and D_2O is thought to involve hydrido(alkyl)platinum intermediates which in hydrogenation reactions may revert to the parent alkene. However, attempts to function-

[66] L. P. Seiwell, *J. Amer. Chem. Soc.*, 1974, **96**, 7134.
[67] G. Strathdee and R. Given, *Canad. J. Chem.*, 1974, **52**, 2216.
[68] G. Strathdee and R. Given, *Canad. J. Chem.*, 1974, **52**, 2226.

alize the alkane in these systems have not been successful. Thus n-decane gives no decyl acetate, norbornane gives no norbornyl acetate, and protoadamantane did not rearrange to adamantane. However, with dibenzyl some *trans*-stilbene is formed.[69]

Benzene and substituted benzenes react with $[PtCl_6]^{2-}$ in aqueous acetic acid to give chlorinated aromatic compounds, diphenyls, and $[PtCl_4]^{2-}$.[70] In deuteriated solvent extensive hydrogen–deuterium exchange takes place, the active catalyst being $[PtCl_4]^{2-}$.

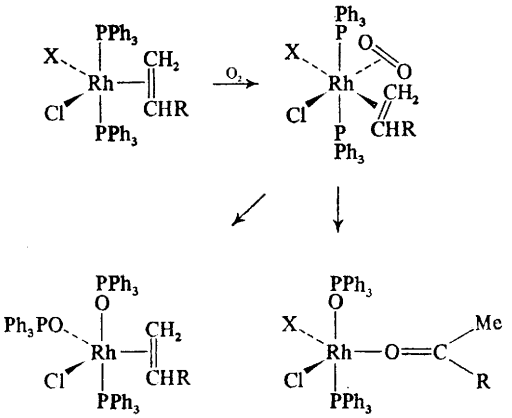
7 Homogeneous Oxidation

The kinetics of the aqueous oxidation of alkenes by palladium(II) chloride have been studied by a number of workers. It has been proposed that the overall rate of reactions obeys the equation[71]

$$\frac{-\mathrm{d[alkene]}}{\mathrm{d}t} = \frac{k_1[PdCl_4]^{2-}\,[\mathrm{alkene}]}{[Cl^-]^2\,[H_3O^+]} + \frac{k_{11}[PdCl_4]^{2-}\,[\mathrm{alkene}]}{[Cl^-]^3\,[H_3O^+]}$$

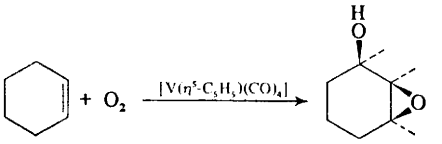
However, doubt has been raised[72] as to the existence of the second term on the grounds that no systematic growth of the first-order rate constant is observed on increasing the concentration of palladium(II) up to 0.2 mol l^{-1}. However, these experiments have been criticized and it is suggested that the discrepancies may be ascribed to the increasing part played by diffusion factors with increasing rate of chemical reaction in the transition region.[71]

Hex-1-ene, hept-1-ene, and oct-1-ene can be oxidized to the corresponding methyl ketones with oxygen at ambient temperature and pressure in the presence of the complexes $[RhH(CO)PPh_3)_3]$ and $[RhCl(PPh_3)_3]$. Radical-chain processes have not been detected and the reactions appear to involve co-oxygenation of co-ordinated phosphine and alkene at the metal centre (Scheme 23).[73] Higher yields of ketone are obtained with $[RhCl(PPh_3)_3]$. The complex, $[V(\eta^5\text{-}C_5H_5)(CO)_4]$, is an efficient catalyst



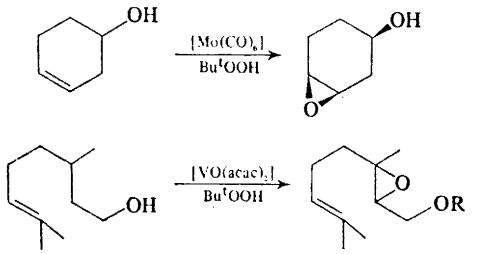
Scheme 23

[69] G. W. Littlecott and F. J. McQuillin, *Tetrahedron Letters*, 1973, 5013.
[70] J. L. Garnett and J. C. West, *Austral. J. Chem.*, 1974, **27**, 129.
[71] I. I. Moiseev, O. G. Levanda, and M. N. Vargaftik, *J. Amer. Chem. Soc.*, 1974, **96**, 1003.
[72] P. M. Henry, *J. Amer. Chem. Soc.*, 1972, **94**, 4437.
[73] C. W. Dudley, G. Read, and P. J. C. Walker, *J.C.S. Dalton*, 1974, 1926.



(54)

for the stereoselective oxidation of cyclohexene to *cis*-1,2-epoxycyclohexane-3-ol (54) in good yield in contrast to $[VO(acac)_2]$ or vanadium naphthenate.[74] However, highly stereo- and regio-selective epoxidations of alkenic alcohols by t-butyl hydroperoxide can be achieved in the presence of $[VO(acac)_2]$ or $[Mo(CO)_6]$ (Scheme 24).[75]



Scheme 24

The cobalt dithiolene complex, $[Co(mnt)_2]_2^{2-}$, (mnt = maleonitriledithiolate) is an efficient catalyst for the reaction

$$2PhCH_2SH + O_2 \longrightarrow PhCH_2SSCH_2Ph + H_2O_2$$

in acetonitrile, acid-buffered with excess of $PhMe_2N$–$PhMe_2NH^+ClO_4^-$. The initial rate of autoxidation is given by the equation in Scheme 25. The function of the

$$\frac{-d(pO_2)}{dt} = \frac{Co[X]_T[PhCH_2SH]_T pO_2}{C_1 + C_2 pO_2 + C_3[PhCH_2SH]_T + C_4[PhCH_2SH]_T pO_2}$$

$$RSH + B \overset{K_1}{\rightleftharpoons} RSHB$$

$$X^{2-} + RSHB \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X{-}SR^{3-} + BH^+$$

$$BH^+ + O_2 + X{-}SR^{3-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} BH{-}O_2{-}SR^{2-}$$

$$BH_2{-}O_2{-}X{-}SR^{2-} \xrightarrow{k_4} B + HO_2\cdot + X^{2-} + RS\cdot$$

$$HO_2\cdot + RSH \xrightarrow{fast} H_2O_2 + RS\cdot$$

$$RS\cdot + RS\cdot \xrightarrow{fast} RS{-}SR$$

$$B = NMe_2Ph,\ RSH = PhCH_2SH,\ X^{2-} = [Co(mnt)_2]_2^{2-}$$

Scheme 25

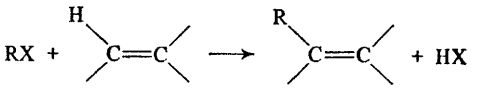
[74] J. E. Lyons, *Tetrahedron Letters*, 1974, 2737.
[75] K. B. Sharpless and R. C. Michaelson, *J. Amer. Chem. Soc.*, 1973, **95**, 6136.

cobalt dithiolene catalyst is to activate both reductant and oxidant by co-ordination so that electron shift can occur in the direction:[76]

$$RS^- \longrightarrow [Co(mnt)_2]_2^{2-} \longrightarrow O_2 \longrightarrow H\overset{+}{N}Me_2Ph$$

8 Exchange Reactions

The exchange reactions of aryl or alkenyl bromides or iodides with alkenes (Scheme 26) is catalysed by a palladium acetate–triphenylphosphine catalyst in the presence



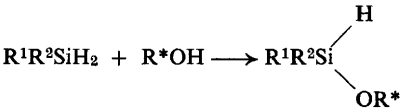
Scheme 26

of a tertiary amine. The reaction has a high degree of stereospecificity with *cis*- and *trans*-1-phenylprop-1-ene in contrast to the reactions catalysed with palladium metal.[77]

The asymmetric cross-coupling reaction

$$R^1R^2CHMgX + R^3X \rightarrow R^1R^2R^3CH + MgX_2$$

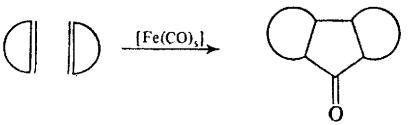
can be catalysed using the nickel catalyst $[NiCl_2\{(-)\text{-diop}\}]$, where diop is the phosphine (49).[78] Similarly the asymmetric synthesis of alkoxysilanes



is catalysed by a rhodium(I) complex of (49).[79]

9 Carbonylation and Hydroformylation

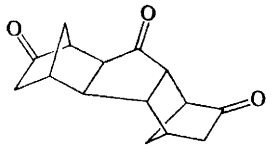
Pentacarbonyliron reacts with alkenes, particularly strained alkenes, to produce carbonyl-inserted dimers (Scheme 27).[80,81] When 2-(*RS*)-norbornen-5-one is treated



Scheme 27

with $[Fe(CO)_5]$ the only adduct which is formed is the isomer (55). It is therefore apparent that the (*R*)-enantiomer of norbornen-5-one-2 combines only with another

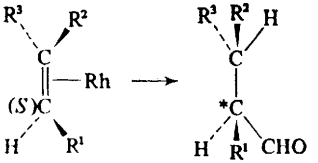
[76] I. G. Dance, R. C. Conrad, and J. E. Cline, *J.C.S. Chem. Comm.*, 1974, 13.
[77] H. A. Dieck and R. F. Heck, *J. Amer. Chem. Soc.*, 1974, **96**, 1133.
[78] Y. Kiso, K. Tamao, N. Miyake, K. Yamamoto, and M. Kumada, *Tetrahedron Letters*, 1974, 3.
[79] R. J. P. Corriu and J. J. E. Moreau, *Tetrahedron Letters*, 1973, 4469.
[80] J. Mantzaris and E. Weissberger, *J. Amer. Chem. Soc.*, 1974, **96**, 1880.
[81] J. Grandjean, P. Laszlo, and A. Stockis, *J. Amer. Chem. Soc.*, 1974, **96**, 1622.



(55)

(*R*)-enantiomer and similarly the (*S*)-enantiomer only recognizes another (*S*)-enantiomer.[81] In other studies it is also found that the cyclopentanones formed have the *exo-trans-exo* stereochemistry.[80] The intermediate or transition state for the reaction is considered to have a trigonal-bipyramidal geometry with two alkenes as equatorial ligands, the inserted carbonyl resulting from an axial position.[80,81] The observation that the adducts have the *exo-trans-exo* stereochemistry is consistent with the generalization that norbornyl systems are subject to exo-attack by reagents unless bulky substituents are present at the bridge system. However, the observation that the thermal coupling of 7,7-dimethoxybenzonorbornadiene with $[Fe(CO)_5]$ in di-n-butyl ether gives the *exo-trans-endo*-product suggests that methoxy-complexation and endo-complexation is induced by presence of the methoxy-groups, as has been observed in some chromium compounds.[82,83]

The hydroformylation of (*E*)-3-methylpent-2-ene and (*Z*)-3-methylpent-2-ene in the presence of $[RhH(CO)PPh_3)_3]$ reveal that there is a *cis* addition of hydrogen and formyl group in the reaction. Deuterioformylation also establishes that the stereospecificity of the reaction is very high.[84] Asymmetric hydroformylation of aliphatic alkenes can also be achieved using a catalyst system prepared from $[RhH(CO)(PPh_3)_3]$ and (−)-diop (49). In the case of prochiral alkene formylation the predominating enantiomer of the aldehyde is always formed by addition of CO and H to the same prochiral side of the alkene (Scheme 28).[85]



Scheme 28

The results of carbonylation of *cis*- and *trans*-but-2-ene in methanol in the presence of palladium(II)–copper(II) Wacker type catalyst show that in the initial stages of reaction, stereospecific *trans*-methoxypalladation is observed giving exclusively the *threo*- and *erythro*-methoxyesters, respectively.[86]

[82] A. Speert, J. Gelan, M. Anteunis, A. P. Marchand, and P. Laszlo, *Tetrahedron Letters*, 1973, 2271.
[83] D. Wege and S. P. Wilkinson, *J.C.S. Chem. Comm.*, 1972, 1335.
[84] A. Stefani, G. Consiglio, C. Botteghi, and P. Pino, *J. Amer. Chem. Soc.*, 1973, **95**, 6504.
[85] G. Consiglio, C. Botteghi, C. Salomon, and P. Pino, *Angew. Chem. Internat. Edn.*, 1973, **12**, 669.
[86] I. H. Elson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 5062.

10 Decarbonylation

In the decarbonylation of *para*-substituted benzoyl chlorides and phenylacetyl chlorides intermediate acyl complexes, $[RhCl_2(COR)(PPh_3)_2]$, can be isolated. The kinetics of the rearrangement of these acyl complexes to alkyl complexes and alkyl complexes to *trans*-$[RhCl(CO)(PPh_3)_2]$ have been measured and the results are summarized in Table 3. The entropies of activation for these reactions are small, as

Table 3 *Rates at* 25 °C *and activation parameters for the rearrangement of* $[RhCl_2(COR)(PPh_3)_2]$ *to* $[RhCl_2(R)(CO)(PPh_3)_2]$ (k_1) *and* $[RhCl_2(R)(CO)PPh_3)_2]$ *to* RCl *and* trans-$[RhCl(CO)(PPh_3)_2]$ (k_2)[87]

R	$k_1 \times 10^4$/ $mol^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal $K^{-1}\,mol^{-1}$	$k_2 \times 10^4$/ $mol^{-1}\,s^{-1}$	$\Delta H^{\ddagger}_2$/ kcal mol^{-1}	$\Delta S^{\ddagger}_2$/cal $K^{-1}\,mol^{-1}$
p-ClC_6H_4	5.27	22.8	2.1	0.59	25.9	9.0
p-$ClC_6H_4CH_2$	0.50	21.3	−6.8	9.59	20.5	−3.6

expected for intramolecular rearrangements, and linear free energy relationships for each of the steps reveal that the amount of charge developed in these rearrangements is very small and is in the range observed for free-radical reactions. The results obtained in this kinetic study show that the acyl–alkyl rearrangement for a benzyl group is reversible. The loss of RCl from phenyl and benzyl complexes is enhanced by electron-withdrawing substituents in the phenyl ring.[87]

The stoicheiometric decarbonylation of (*S*)-(−)-α-trifluoromethylphenylacetyl chloride with $[RhCl(PPh_3)_3]$ affords a 71% yield of the racemic α-trifluoromethylbenzyl chloride. Racemization probably takes place in the rearrangement of the intermediate acyl complex, $[RhCl_2\{COCH(CF_3)(Ph)\}(PPh_3)_2]$, to the alkyl complex $[RhCl_2\{CH(CF_3)(Ph)\}(CO)(PPh_3)_2]$.[88] However, the decarbonylation of *erythro*- and *threo*-2,3-diphenylbutanoyl chloride with $[RhCl(PPh_3)_3]$ gives exclusively *trans*- and *cis*-methylstilbene, respectively, results which can be explained either by an acyl–alkyl rearrangement with retention and a *cis*-β-hydride elimination or a concerted *cis*-elimination. Decarbonylation of these acyl chlorides generated alkenes since the intermediate rhodium alkyl complex can eliminate a β-hydrogen to generate a rhodium(III) hydride intermediate and the alkene. Studies with a series of acyl chlorides reveal that the tendency toward β-hydrogen elimination follows the order secondary hydrogen abstraction is preferred over primary and tertiary over secondary or primary, *i.e.* Saytzeff elimination is preferred.[89]

11 Hydrosilylation

Asymmetric hydrosilylation of acetophenone, methylbenzyl ketone, and isobutyrophenone can be achieved using soluble chiral rhodium(I)–diop complexes (49) and polymer-supported catalyst. The optical yield is dependent on the silane used, dihydrosilanes giving higher yields than monohydrosilanes.[62] Similar results are obtained with α-keto-esters.[61]

[87] J. K. Stille and M. T. Regan, *J. Amer. Chem. Soc.*, 1974, **96**, 1508.
[88] J. K. Stille and R. W. Fries, *J. Amer. Chem. Soc.*, 1974, **96**, 1514.
[89] J. K. Stille, F. Huang, and M. T. Regan, *J. Amer. Chem. Soc.*, 1974, **96**, 1518.

The rate of addition of triethylsilane to hex-1-ene catalysed by the complexes $[RhClL_3]$ increases in the order $L = PCy_3 \ll PMe_2Ph < PCy_2Ph \approx PPh_3 < PCyPh_2 \approx PEt_2Ph$. However, discussion of the mechanism of these reactions must await further data.[90]

The additions of monohydrosilanes to terminal alkynes catalysed by chloroplatinic acid involves stereoselective (100%) *cis*-addition. However, in the presence of $[RhCl(PPh_3)_3]$ as catalyst stereoselective *trans*-addition is observed, results which resemble peroxide-catalysed reaction of trichlorosilanes with alkynes. The rhodium-catalysed reactions may involve radical species.[91]

[90] R. N. Haszeldine, R. V. Parish, and R. J. Taylor, *J.C.S. Dalton*, 1974, 2311.
[91] I. Ojima, M. Kumagai, and Y. Nagai, *J. Organometallic Chem.*, 1974, **66**, C14.

4
Insertion Reactions

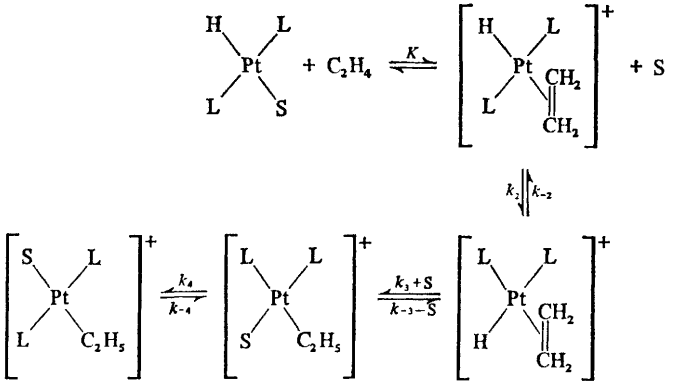
BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Alkenes and Alkynes

The reversible insertion of ethylene into the platinum–hydrogen bond of *trans*-$[PtH(acetone)(PEt_3)_2]^+$ to give *trans*-$[Pt(C_2H_5)(acetone)(PEt_3)_2]^+$ follows the rate law

$$\frac{-d[Pt\text{–}H]}{dt} = \frac{k'[C_2H_4][Pt\text{–}H]}{1 + K[C_2H_4]}$$

The suggested mechanism is depicted in Scheme 1. However, the kinetic data observed taken alone do not distinguish between insertion from a rearranged four-coordinate intermediate (Scheme 1) and an associative mechanism involving a five-coordinate intermediate of the type $[PtH(ethylene)(PEt_3)_2(Z)]$, where Z is a coordinated solvent molecule, alkene, or counterion, a mechanism which may become competitive for poor leaving groups *trans* to hydride ligand.[1]



Scheme 1

If the mechanism in Scheme 1 operates, reaction of C_2D_4 with $[PtH(C_2H_4)L_2]^+$ might be expected to lead to a PtC_2H_5 complex whereas an associative mechanism might be expected to yield a mixture containing PtC_2D_4H and PtC_2H_5 complexes. Experiments of this type, however, are inconclusive since a PtC_2D_4H complex is the initial major product, indicating that alkene exchange is faster than insertion. An

[1] H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, 1974, **13**, 2213; H. C. Clark, J. Halpern, A. Mantovani, and T. A. Weil, *Inorg. Chem.*, 1974, **13**, 1541.

important feature of the associative mechanism is that ligands which stabilize five-co-ordinate platinum(II) should also promote insertion. Such a ligand is $[SnCl_3]^-$ and the kinetics of the reaction

$$\textit{trans}\text{-}[PtHCl(PEt_3)_2] + C_2H_4 \rightleftharpoons \textit{trans}\text{-}[PtEtCl(PEt_3)_2]$$

catalysed by $SnCl_2$ have been studied in methanol solution.[1] The data are consistent with the mechanism

$$[PtHClL_2] + SnCl_2 \rightleftharpoons [PtH(SnCl_3)L_2]$$

$$SnCl_2 + Cl \rightleftharpoons [SnCl_3]^-$$

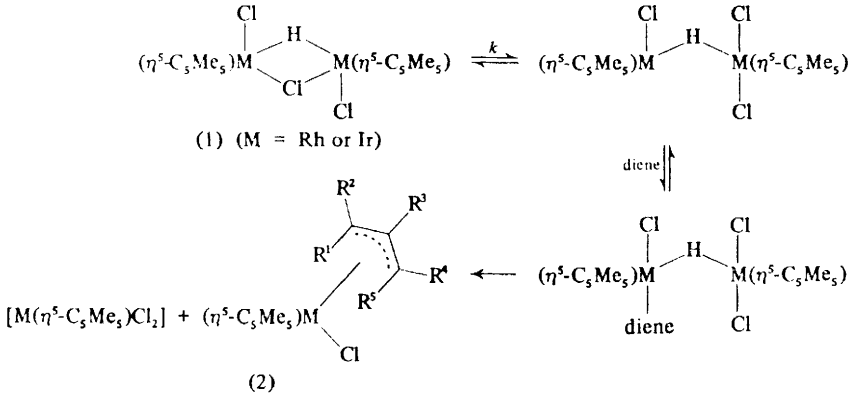
$$[PtH(SnCl_3)L_2] + [SnCl_3]^- \rightleftharpoons [PtH(SnCl_3)_2L_2]^-$$

$$[PtH(SnCl_3)L_2] + C_2H_4 \xrightarrow{\text{rate determining}} [Pt(C_2H_5)(SnCl_3)L_2]$$

$$[Pt(C_2H_5)(SnCl_3)L_2] \rightleftharpoons [Pt(C_2H_5)ClL_2] + SnCl_2$$

Since excess Cl^- does not inhibit $SnCl_2$ catalysis of this reaction the catalytic role of $SnCl_2$ is not that of promoting chloride displacement to form $[PtH(C_2H_4)(PEt_3)_2]^+$. However, these results still do not differentiate between mechanisms involving either $[PtH(C_2H_4)L_2]^+$ or $[PtH(C_2H_4)L_2Z]$.[1]

Kinetic studies on the reactions of the bridged hydride complexes (1) with 1,3-dienes to give the η-allylic complexes (2) are consistent with a mechanism involving rate-determining chloride-bridge cleavage (Scheme 2).[2] Activation parameters for the

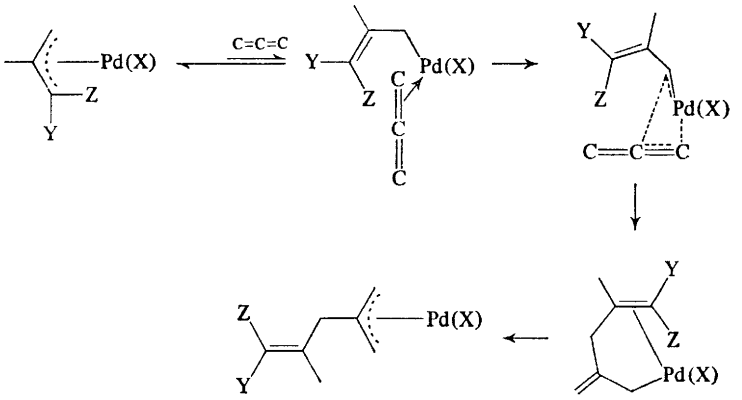


Scheme 2

reactions of (2) with cyclo-octa-1,5-diene, which are first order in (2) and zero order in diene, are $\Delta H^{\ddagger} = 93.3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -18.4$ J K^{-1} mol^{-1} (M = Rh) and $\Delta H^{\ddagger} = 89.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = -15.5$ J K^{-1} mol^{-1} (M = Ir), the small negative values of $\Delta S^{\ddagger}$ being consistent with the bridge-opened intermediate.[2] In order for the allylic complexes (2) to eliminate HCl readily to form a diene complex the stereochemistry of the allyl must be such that it can readily form a *cisoid* diene. It is also apparent that 1,3-dienes must react in the *s-transoid* form with (1) *via* 1,2-addition. In analogous reactions with $[NiHL_4]^+$ such dienes react in the *cisoid* form.

[2] H.-B. Lee and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1974, 601.

Studies on the insertion of 1,2-dienes into allyl–palladium bonds are consistent with the mechanism depicted in Scheme 3. The rate-determining step is considered to



Scheme 3

be migration of the σ-allylic group to the central carbon atom of the co-ordinated allylic grouping.[3]

Carbon monoxide insertion into allyl–palladium bonds is known to be second order in carbon monoxide concentration, a second molecule of carbon monoxide presumably being required to fill the vacant co-ordination site resulting from migration of the allyl group. However, since the insertions of 1,2-dienes exhibit a first-order dependence on the concentration of 1,2-diene this system must be able to maintain a four-co-ordinate palladium complex during the rate-determining step.[3] The rate of formation of the insertion product decreases in the order 2-chloroallyl > allyl > 2-methylallyl > 2-t-butylallyl; 1,3-dimethylallene > 1,1-dimethylallene > methylallene > allene ≫ tetramethylallene ≈ 1,3-di-t-butylallene; X = hfac > acac ≈ Cl. Co-ordination of the allene to the palladium occurs *via* the least substituted olefinic function. There may be a small degree of polarization of the palladium–allene bond in the transition state for σ-allyl migration.[3]

Co-ordination of monoalkenes to complexes of the type [Pd(hfac)(allyl)] occurs rapidly and reversibly in solution at room temperature. However, the introduction of strain into the alkene promotes a ready insertion of the alkene into allyl–palladium and –platinum bonds.[4] Initial rapid and reversible formation of [Pd(hfac)(σ-allyl)(η-olefin)] is involved in the reaction, the rate-determining step again involving migration of a σ-allylic group from palladium to the co-ordinated alkene *via* a concerted *cis-exo* addition of Pd—C across the double bond.

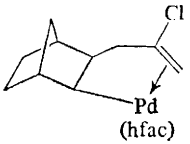
The reaction of norbornene with [Pd(hfac)(η-CH_2CClCH_2)] to give (3) follows the second-order rate law

$$-\text{d[complex]}/\text{d}t = k\text{[complex][norbornene]}$$

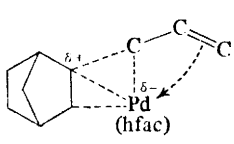
being the same in $CDCl_3$ and C_6D_6. Since the reaction is first order in alkene and

[3] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1973, **60**, 409.
[4] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1973, **60**, 387.

independent of solvent it is suggested that co-ordination of the alkene function of the σ-allyl group to the palladium and migration of the σ-allyl group occur in a concerted process. The effect of remote electronegative substituents on the alkene, which inhibit the migration process, can be rationalized in terms of polarization of the Pd–alkene bond in the transition state (4).[4] Second-order rate constants have also been



(3)



(4)

obtained for the insertion of norbornadiene into the allyl complexes [Pd(allyl)-{$CF_3COCHCS$(2-thienyl)}] and [Pd(allyl){$CF_3COCHCO$(2-thienyl)}],[5] and a similar mechanism may operate.

Further studies have appeared on the reaction of dimethyl acetylenedicarboxylate with *trans*-[PtClMe(PMe_2Ph)$_2$] in chloroform solution reported in Volume 3. The reaction has now been shown to lead to the β-chlorovinyl compound *trans*-[PtCl{$C(CO_2Me)$=$CCl(CO_2Me)$}(PMe_2Ph)$_2$] rather than *trans*-[PtCl{$C(CO_2Me)$=$CMe(CO_2Me)$}(PMe_2Ph)$_2$].[6] The radical aspects of this unusual reaction can be attributed to radically induced formation of HCl, probably formed from the chloroform solvent. The suggested mechanism is shown in Scheme 4.

$$[PtCl(Me)L_2(dma)] + HCl \longrightarrow CH_4 + [PtCl_2L_2(dma)]$$

$$\downarrow$$

$$trans\text{-}[PtCl\{C(CO_2Me)=CCl(CO_2Me)\}L_2] \longleftarrow [PtClL_2(dma)]^+ Cl^-$$

L = PMe_2Ph dma = $MeO_2CC{\equiv}CCO_2Me$

Scheme 4

The insertion of dimethyl acetylenedicarboxylate into the iron–carbon bond of the *erythro*- and *threo*-isomers of [Fe(CHDCHDCMe$_3$)(η^5-C_5H_5)(CO)$_2$] occurs with 80% retention of configuration at carbon.[7]

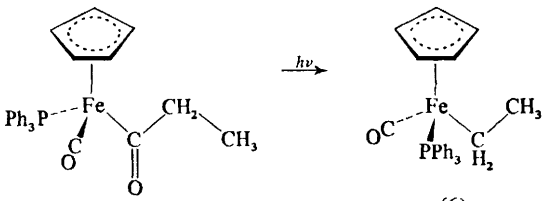
2 Carbon Monoxide

Treatment of *erythro*-[Fe(CHDCHDCMe$_3$)(CO)$_2$(η^5-C_5H_5)] with Bu^tNC leads to the carbonyl-insertion product with retention of stereochemistry. Reactions of the iron complex with the oxidizing agents bromine, ceric ammonium nitrate, and oxygen, all in methanol, and chlorine in chloroform also give derivatives of 4,4-dimethyl-[2,3-$^2H_2$]pentanoic acid with >90% retention of configuration at carbon. The

[5] J. A. Sadownick and S. J. Lippard, *Inorg. Chem.*, 1973, **12**, 2659.
[6] T. G. Appleton, M. H. Chisholm, H. C. Clark, and K. Yasufuku, *J. Amer. Chem. Soc.*, 1974, **96**, 6600.
[7] P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 2814.

mechanism of these oxidatively induced carbonyl-insertion reactions is not known but electron transfer is probably an important step.[7] With the possibility of one exception[8] all carbonylations and decarbonylations of known stereochemical outcome proceed with retention of configuration at carbon. It is therefore possible that carbonylation and decarbonylation reactions may provide processes of dependable stereochemical course.[7]

The photochemical decarbonylation of each pair of enantiomers of [Fe($COCH_2$-CHMePh)(η^5-C_5H_5)(CO)(PPh_3)] gives the alkyl complexes with a high degree of stereospecificity at iron but it has not been possible to establish the configurations of the reactants and products.[9] However, studies on the photochemical decarbonylation of (5) to (6) reveal that the high degree of stereoselectivity in this process results in



(5) (6)

largely an inversion of configuration at iron (in a topological sense, $R \rightarrow S$). This result does not necessarily imply that there is a Walden inversion taking place since ethyl migration to the site vacated by the leaving terminal carbonyl group is consistent with this result.[10]

The reaction of [PtI(Me)(CO)(PPh_3)] with a number of tertiary-arsine and -stibine ligands has now been studied.[11] The proposed mechanism of reaction proceeds as follows:

$$[PtI(Me)(CO)(PPh_3)] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [PtI(COMe)(PPh_3)]$$

$$[PtI(COMe)(PPh_3)] + L \xrightarrow{k_3} [PtI(COMe)(PPh_3)L]$$

The rate-determining step involves neither the incoming ligand nor solvent and is considered to involve formation of a three-co-ordinate intermediate. The rate equation is

$$k_{obs} = \frac{k_1 k_3[L]}{(k_2 + k_3[L])}$$

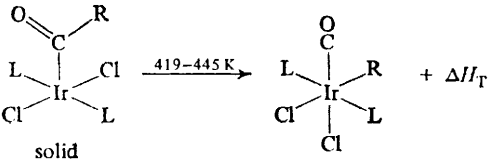
and activation parameters for the k_1 step (L = $AsPh_3$) are $\Delta H^{\ddagger} = 18.3 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.3 \pm 1.1$ cal K^{-1} mol^{-1}. The rate of attack of L on the intermediate increases in the order $AsPh_3 < AsMe(o\text{-}MeC_6H_4)_2 < SbPh_3 < As(p\text{-}MeC_6H_4)_3$.[11]

[8] F. Calderazzo and K. Noack, *Coordination Chem. Rev.*, 1966, **1**, 118.
[9] P. Reich-Rohrwig and A. Wojcicki, *Inorg. Chem.*, 1974, **13**, 2457.
[10] A. Davison and N. Martinez, *J. Organometallic Chem.*, 1974, **74**, C17.
[11] C. J. Wilson, M. Green, and R. J. Mawby, *J.C.S. Dalton*, 1974, 1293.

In contrast to the above process rates of carbonyl insertion with complexes of the types $[MnR(CO)_5]$, $[FeR(\eta^5\text{-}C_5H_5)(CO)_2]$, and $[MoR(\eta^5\text{-}C_5H_5)(CO)_3]$ are solvent-dependent and it has been suggested that the co-ordinating power of the solvent is important in promoting these reactions. However, studies on the rates of reaction of the complexes $[FeR(\eta^5\text{-}C_5H_5)(CO)_2]$ (R = cyclohexyl or cyclohexylmethyl) with triphenylphosphine in a variety of solvents show no correlation with solvent donicity. Further, although dissolution of the complexes in DMSO leads to a solvent-co-ordinated acyl, $[Fe(COR)(\eta^5\text{-}C_5H_5)(CO)(DMSO)]$, there is no specific rate acceleration in DMSO as solvent. It is therefore suggested that the first intermediate in these reactions is the co-ordinatively unsaturated species $[Fe(COR)(\eta^5\text{-}C_5H_5)(CO)]$. This intermediate can then react readily with phosphine or be trapped by a solvent of high co-ordinating ability.[12]

The rate of thermal decarbonylation of the molybdenum acetyls $[Mo(COMe)(\eta^5\text{-}C_5H_5)(CO)_2L]$ decreases in the order of the ligands L = $P(cyclohexyl)_3 > PPh_2Pr^i > PPh_3 > P(p\text{-}MeC_6H_4)_3 > PPh_2Me > PBu^i_3 > PPhMe_2 \gg PBu^n_3$. There is a good correlation between the observed decarbonylation rate and the steric bulk of the ligand as measured by its cone angle. Activation parameters for the decarbonylation reactions are $\Delta H^{\ddagger} = 29.3 \pm 1.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = 4.2 \pm 3.0$ cal K^{-1} mol^{-1} for L = PPh_3 and $\Delta H^{\ddagger} = 30.3 \pm 1.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = 7.4 \pm 3.0$ cal K^{-1} mol^{-1} for L = PBu^n_3. The activation enthalpies are consistent with values obtained for dissociative reactions of a variety of similar metal carbonyl compounds and suggest that the rate-determining step is loss of a terminal carbonyl ligand. The absence of solvent polarity effects and the observed steric effects are also consistent with this mechanism.[13]

Migration of *para*-substituted benzyl and trifluoromethyl groups in the complexes (7) occurs[14] in the solid state and the enthalpy change is opposite in sign to that found



solid (7) solid

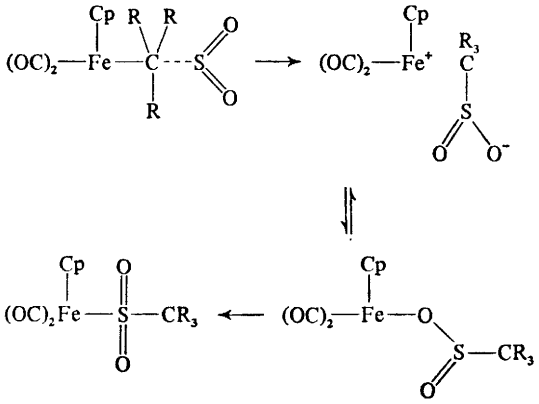
for the decarbonylation of $[PtCl(COC_6H_4X)(PPh_3)_2]$[15] and there is an inverse correlation between the migration rate and the enthalpy change.

3 Sulphur Dioxide

Cleavage of the iron–carbon bond in reactions of sulphur dioxide with complexes of the type $[FeR(\eta^5\text{-}C_5H_5)(CO)_2]$ is an electrophilic process which proceeds with a large and negative entropy of activation and with inversion of configuration at the α-carbon. The inversion of stereochemistry observed on insertion of sulphur dioxide

[12] K. Nicholas, S. Raghu, and M. Rosenblum, *J. Organometallic Chem.*, 1974, **78**, 133.
[13] K. W. Barnett and T. G. Pollmann, *J. Organometallic Chem.*, 1974, **69**, 413.
[14] D. M. Blake, J. de Faller, Y. L. Chung, and A. Winkelman, *J. Amer. Chem. Soc.*, 1974, **96**, 5568.
[15] S. J. Ashcroft, G. Beech, and A. Maddock, *J.C.S. Dalton*, 1974, 462.

into the iron–carbon bond of $[Fe(CHDCHDCMe_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ is consistent with direct electrophilic backside attack on the iron–carbon bond. A mechanism consistent with the available data is depicted in Scheme 5.[7,16]



Scheme 5

Studies with the complex $[Fe(CH_2CHMePh)(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ show that the insertion reaction occurs with high stereospecificity at iron. Hence each step in Scheme 5 must also be highly stereospecific.[9] The high configurational stability of the proposed contact ion pair, $Fe^+ O_2SR^-$, is surprising, especially as the iron is only bound to three ligands. However, the low dielectric constant of the solvent medium may restrict mobility of the ion O_2SR^- which might therefore stabilize the cation.[11] Studies with the related complex $[Fe\{CH_2C(O)OC_{10}H_{19}\}(\eta^5\text{-}C_5H_5)(CO)(PPh_3)]$ [$C_{10}H_{19}O$ = (−)-mentholate] suggest that sulphur dioxide insertion occurs with retention at iron.[17]

Studies on the cleavage of iron–carbon σ-bonds by sulphur dioxide have usually been carried out in neat sulphur dioxide. In chloroform solution the reaction of $[Fe(CHMe_2)(\eta^5\text{-}C_5H_5)(CO)_2]$ with SO_2 is first order in the iron-alkyl and SO_2, with $\Delta H^{\ddagger} = 8.7 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -45 \pm 2$ cal K^{-1} mol^{-1}.[18] The second-order rate constants decrease with the alkyl group in the order $CHMe_2 > CH_2CMe_3 \gtrsim CH_2SiMe_3 > Me \gg CH_2Ph$, CMe_3. The rate of reaction is some 7—8 times larger in chloroform or propan-2-ol than in benzene and a polar nature for the transition state is further indicated by an enhancement of the rate in propan-2-ol upon addition of $LiClO_4$. The above data are consistent with an associative mechanism which involves a polar, constrained transition state. However, a striking difference is observed between the insertion reaction of $[Fe(CH_2CMe_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ in organic solvents and in liquid SO_2. In neat SO_2 at −10 °C this complex is 700—1800 times less reactive than its methyl analogue. However, in chloroform solution at 26 °C it is 30 times as reactive. Usually reactions involving backside attack at the α-carbon atom of R proceed some 2000—3 000 000 times faster for R = Me than for

[16] S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, 1973, **95**, 6962.
[17] T. C. Flood and D. L. Miles, *J. Amer. Chem. Soc.*, 1973, **95**, 6460.
[18] S. E. Jacobson and A. Wojcicki, *Inorg. Chim. Acta*, 1974, **10**, 229.

R = CH_2CMe_3. Reactions involving frontside attack usually have comparable rates for neopentyl and methyl complexes. Insertion reactions with dilute solutions of sulphur dioxide may therefore well proceed *via* a different mechanism to those occurring in liquid sulphur dioxide. It is suggested that under these conditions reaction occurs *via* a bimolecular electrophilic process of S_E2 retention or S_Ei inversion (Scheme 6) rather than S_E2 inversion proposed for insertion in liquid sulphur dioxide.[18]

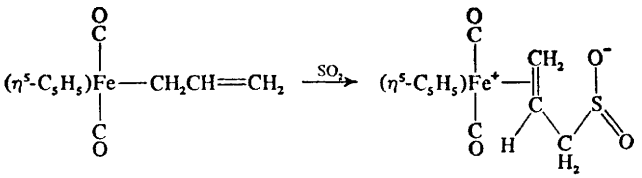
S_E2 S_Ei

Scheme 6

Although reactions of sulphur dioxide with $[Fe(CHDCHDCMe_3)(\eta^5\text{-}C_5H_5)(CO)_2]$ proceed with inversion in organic solvents[7] the concentrations of sulphur dioxide are apparently higher than those used in the kinetic studies described above where a different mechanism may operate. Similarly the report that $[Fe(Me)(\eta^5\text{-}1\text{-}Me\text{-}3\text{-}Ph\text{-}C_5H_3)(CO)(PPh_3)]$ inserts sulphur dioxide with high stereospecificity at iron (probably retention) both in liquid sulphur dioxide and in methylene chloride solution does not resolve this problem.[19]

A comparative study of the cleavage of the metal–carbon bond in a variety of complexes in liquid sulphur dioxide reveals that the pseudo-first-order rate constants decrease in the order $[FeMe(\eta^5\text{-}C_5H_5)(CO)_2] > [ReMe(CO)_5] > [RuMe(\eta^5\text{-}C_5H_5)(CO)_2] \approx [MnMe(CO)_5] \gtrsim [MoMe(\eta^5\text{-}C_5H_5)(CO)_3] \gg [WMe(\eta^5\text{-}C_5H_5)(CO)_3]$; $[Cr(CH_2Ph)(\eta^5\text{-}C_5H_5)(NO)_2] \gg [Mo(CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_3] \gtrsim [Fe(CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_2] \gtrsim [Mn(CH_2Ph)(CO)_5] > [Ru(CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_2] \gg [W(CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_3]$; $[FeEt(\eta^5\text{-}C_5H_5)(CO)_2] > [MoEt(\eta^5\text{-}C_5H_5)(CO)_3] \gg [WEt(\eta^5\text{-}C_5H_5)(CO)_3]$; and $[CrPh(\eta^5\text{-}C_5H_5)(NO)_2] \gg [FePh(\eta^5\text{-}C_5H_5)(CO)_2]$. In general cleavage of the methyl complexes occurs more rapidly than that of the analogous benzyl complexes.[20]

Reactions of sulphur dioxide with $[Fe(\eta^1\text{-allyl})(\eta^5\text{-}C_5H_5)(CO)_2]$ are known to afford S-bonded sulphinate complexes. It is generally accepted that these reactions proceed *via* dipolar metal–alkene intermediates, and low-temperature n.m.r. studies have now provided evidence for this reaction intermediate (8).[21] The rates of re-



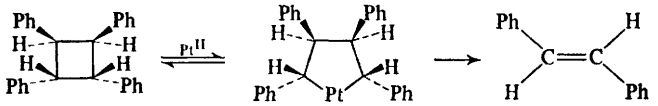
(8)

[19] T. G. Attig and A. Wojcicki, *J. Amer. Chem. Soc.*, 1974, **96**, 262.
[20] S. E. Jacobson and A. Wojcicki, *J. Organometallic Chem.*, 1974, **72**, 113.
[21] L. S. Chen, S. R. Su, and A. Wojcicki, *J. Amer. Chem. Soc.*, 1974, **96**, 5655.

arrangement of intermediates of type (8) to *S*-sulphinate products increase on increasing the number of alkyl groups in the alkene fragment, which is consistent with metal–alkene bonding being destabilized by such alkyl substitution.[21]

4 Metals

Tetraphenylcyclobutane has been shown to undergo reaction in the presence of platinum(II) to give *trans*-stilbene. Insertion of platinum(II) into a C—C bond is thought to be an important step in this reaction (Scheme 7).[22]



Scheme 7

[22] I. J. Harvie and F. J. McQuillin, *J.C.S. Chem. Comm.*, 1974, 806.

5
Reactions of Co-ordinated Ligands

BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Carbonyls and Nitrosyls

Carbonyls.—Studies on the reactions of strong nucleophiles such as alkoxides, azides, Grignard reagents, and organolithium reagents with metal carbonyls have led to the suggestion that nucleophilic attack occurs at a carbonyl carbon atom. Carbonyl stretching force constants may be used as a guide to predict relative reactivities of the carbonyl ligand, high CO stretching force constants correlating with a more positive carbon and low CO stretching force constants correlating with the addition of electrophiles to oxygen. Studies on the reaction of benzylmagnesium chloride with the compounds $[ML(CO)_5]$ (M = Cr, Mo, or W, L = phosphine, phosphite, or CO) are in agreement with the force constant–reactivity proposal, nucleophilic addition occurring at the *cis*-carbonyl ligand except where L is the bulky ligand tri-*o*-tolylphosphine. However, relative rate constants for the additions are dependent on the steric requirements of the phosphorus substituent. Similarly, for a given L rates decrease in the order $W \gtrsim Mo > Cr$, again consistent with steric requirements. In the series $[FeL(CO)_4]$ addition occurs at the *trans*-carbonyl ligand and the rates correlate with electronic factors and not with steric requirements. It is therefore suggested that addition occurs at an axial rather than an equatorial site although rapid intramolecular exchange can occur in these systems.[1] Activation parameters for the reactions

$$[ML(CO)_x] + PhCH_2MgCl \xrightarrow{THF} LM(CO)_{x-1}C(O^-)(CH_2Ph)\,\overset{+}{M}gCl$$

$x = 5$, M = Cr, Mo, or W
$x = 4$, M = Fe

are given in Table 1.

The reactions of methyl-lithium with the hexacarbonyls $[M(CO)_6]$ (M = Cr, Mo, or W) and the derivatives $[ML(CO)_5]$ have been studied using stopped-flow techniques. The reactions obey the rate law

$$-d[\text{substrate}]/dt = k[\text{substrate}][MeLi]^{1/4}$$

which is consistent with the mechanism

$$(MeLi)_4 \rightleftharpoons 4MeLi$$

$$MeLi + [(OC)_5M(CO)] \xrightarrow{k_\alpha} Li[M\{C(O)Me\}(CO)_5]$$

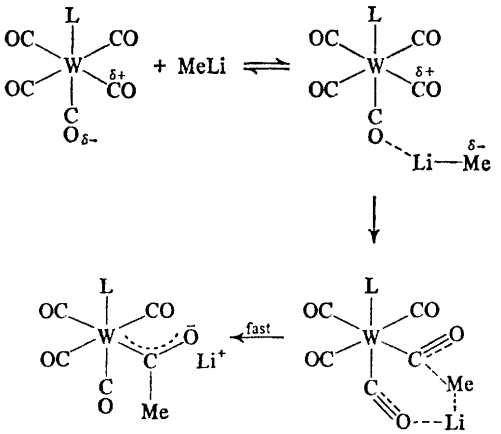
[1] M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, and C. Hasday, *J. Amer. Chem. Soc.*, 1973, **59**, 5919.

Table 1 *Rate constants and activation parameters for the reactions of* $PhCH_2MgCl$ *with metal carbonyls in THF solution (from ref. 1)*

Carbonyl	$k_2 \times 10^3$ l mol^{-1} s^{-1} *at* 25 °C[a]	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
$[Fe(CO)_4(PBu^n_3)]$	0.212	9.4±0.9	−44±3.2
$[Fe(CO)_4(PPh_3)]$	1.84	8.3±0.6	−43±2.1
$[Fe(CO)_4\{P(OPh)_3\}]$	15.30	8.4±0.8	−38.5±2.7
$[W(CO)_6]$	108	7.4±0.8	−38.1±2.8
$[W(CO)_5(PPh_3)]$	4.96	6.17±1.11	−47.9±4.0

[a] $k_2 = k_{obs}[PhCH_2MgCl]^{-1}$.

Reactions with the substituted derivatives $[WL(CO)_5]$ give the products *cis*-$Li[W\{C(O)Me\}L(CO)_5]$, and in the series L = PBu^n_3, PPh_3, or P(cyclohexyl)$_3$ only minor differences in rate are observed, in contrast to the studies with $PhCH_2MgCl$. A mechanism which accounts for the observed lack of steric and electronic effects upon reactivity (Scheme 1) involves interaction of the LiMe with the oxygen of a

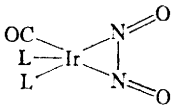


Scheme 1

carbonyl *trans* to L (an oxygen which would be expected to bear the greater negative charge) followed by rate-determining attack of the methyl at a radial carbonyl carbon.[2] This mechanism is considered to be an intermediate case between two *limiting mechanisms* of interaction of carbonyls with strong nucleophiles. In the limit of high electron density (low carbonyl stretching frequencies) at the carbonyl ligands only M—CO···LiMe interaction should occur, *e.g.* the formation[3] of such adducts as $[Mo(o\text{-phen})(PPh_3)_2(CO,AlR_3)_2]$. However, for substrates having high carbonyl stretching frequencies (low electron density at the carbonyl ligand) direct attack of nucleophile at carbon can occur, *e.g.* the studies with $[FeL(CO)_4]$ and $PhCH_2MgCl$.[1]

[2] G. R. Dobson and J. R. Paxson, *J. Amer. Chem. Soc.*, 1973, **95**, 5925.
[3] D. F. Shriver and A. Alich, *Inorg. Chem.*, 1972, **11**, 2984.

Nitrosyls.—Treatment of the nitrosyl complex $[Ir(NO)_2(PPh_3)_2]^+[PF_6]^-$ with carbon monoxide results in the formation of CO_2 and N_2O and $[Ir(CO)_3(PPh_3)_2]^+[PF_6]^-$. The initial step in this reaction is believed to involve the coupling of two NO ligands to generate the intermediate (1).[4,5] The overall sequence shown in Scheme 2 is proposed.



(1)

$$[M(NO)_2L_2]^+ + CO \rightleftharpoons [M(N_2O_2)L_2(CO)]^+$$

$$[M(N_2O_2)L_2(CO)]^+ + CO \rightleftharpoons [ML_2(CO)_2]^+ + N_2O_2$$

$$[M(N_2O_2)L_2(CO)]^+ + 2CO \rightleftharpoons [ML_2(CO)_2]^+ + N_2O + CO_2$$

$$N_2O_2 \rightleftharpoons 2NO$$

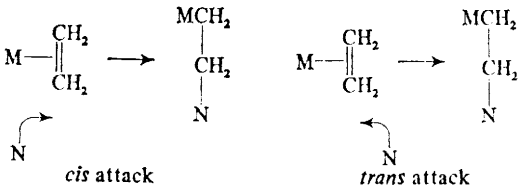
$$[ML_2(CO)_2]^+ + CO \rightleftharpoons [ML_2(CO)_3]^+$$

M = Rh or Ir

Scheme 2

2 Alkenes and Alkynes

Linear Alkenes and Alkynes.—Nucleophilic addition to co-ordinated alkenes can either occur on the same side as the metal (*cis* attack) or on the side remote from the metal (*trans* attack) (Scheme 3). A study on the oxidative hydrolysis of alkenes in the



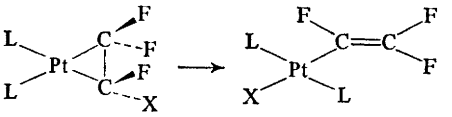
Scheme 3

presence of $[Pd(dien)(H_2O)]^{2+}$ and $[Pd(en)(H_2O)_2]^{2+}$ suggests that where possible nucleophilic attack by hydroxide on the alkene involves prior co-ordination of the hydroxide to the palladium. The observation that alkene oxidation occurs more rapidly in the presence of $[Pd(en)(H_2O)_2]^{2+}$ than with $[Pd(dien)(H_2O)]^{2+}$ can be rationalized in terms of the formation of an intermediate $[Pd(en)(alkene)(H_2O)]^{2+}$,

[4] B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 3325.
[5] S. Bhaduri, B. F. G. Johnson, C. J. Savory, J. A. Segal, and R. H. Walter, *J.C.S. Chem. Comm.*, 1974, 809.

which can transfer hydroxide *via cis* attack. With the dien complex [Pd(dien)-(alkene)]$^{2+}$ there is no vacant co-ordination site and only *trans* addition (the higher-energy pathway) can take place.[6] Studies on the palladium-promoted amination of but-2-enes show that the reaction proceeds *trans*.[7]

Activation parameters have been measured for the rearrangement of the fluoroalkene complexes (2) to the alkenyl complexes (3). The results (Table 2) indicate that



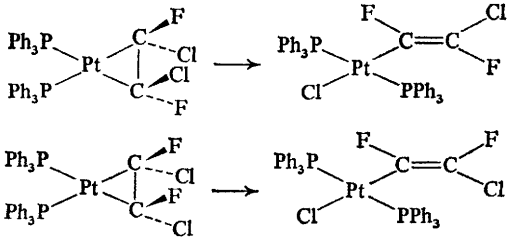
(2) (3)

L = PPh_3, X = Cl or Br
L = $PMePh_2$, X = Cl or Br

Table 2 *Activation parameters for rearrangement of* [$\overline{PtCF_2CFX(L_2)}$] *in ethanol (from ref. 8)*

Complex	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
[$\overline{PtCF_2CFCl(PPh_3)_2}$]	29.3±1.3	−9±5
[$\overline{PtCF_2CFCl(PMePh_2)_2}$]	24.9±0.6	+2±3
[$\overline{PtCF_2CFBr(PMePh_2)_2}$]	24.6±0.8	+2±3

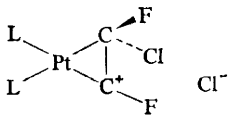
both the nature of the migrating halide and the relative σ-donor and π-acceptor properties of the phosphine ligand affect the reactivity of the complexes.[8] A major factor in determining relative reaction rates is the value of the activation enthalpy. A comparison of these data with analogous data found for the complexes [Pt(C_2Cl_4)-(PPh_3)$_2$] ($\Delta H^{\ddagger}$ = 21.4±1 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −9±4 cal K^{-1} mol^{-1}) and [Pt-(C_2Cl_3H)(PPh_3)$_2$] ($\Delta H^{\ddagger}$ = 17.6±1 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −10±4 cal K^{-1} mol^{-1}) shows that the fluoroalkene complexes are less reactive, a consequence of higher activation enthalpies and a more positive activation entropy.[9] A high degree of



Scheme 4

[6] C. Burgess, F. R. Hartley, and G. W. Searle, *J. Organometallic Chem.*, 1974, **76**, 247.
[7] B. Åkermark, J. E. Bäckvall, K. Siirala-Hansén, K. Sjöberg, and K. Zetterberg, *Tetrahedron Letters*, 1974, 1363.
[8] M. Green and G. J. Parker, *J.C.S. Dalton*, 1973, 2099.
[9] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **15**, 217; *ibid.*, 1969, **18**, 199.

retention of stereochemistry about the carbon–carbon bond of the fluoroalkene is observed during the rearrangement both in n-butanol and in the presence and absence of lithium acetate (Scheme 4).[8] Although the activation parameters and solvent dependency of these rearrangements are consistent with an S_N1 dissociative process the retention of stereochemistry about the carbon–carbon bond is not consistent with the formation of a carbonium ion species (4) in which the positive carbon becomes either sp^3- or *sp*-hybridized. It is suggested that a tight ion-pair is formed such that the stereochemistry at carbon is retained.[8]



(4)

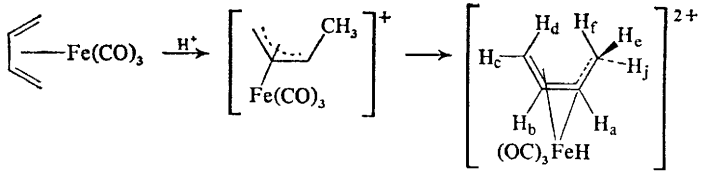
The reactions of $[Pd(CF_3C{\equiv}CCF_3)(Ph_2PCH_2CH_2PPh_2)]$ with CF_3CO_2H, CF_2HCO_2H, and CCl_3CO_2H in chloroform solution follow second-order kinetics, the activation parameters for the reaction with trifluoroacetic acid being $\Delta H^{\ddagger} = 11.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -35$ cal mol^{-1} K^{-1}. There is a qualitative correlation between acid strength and rate, and a possible sequence for the reaction is

$$[Pd(C_4F_6)(diphos)]^+ + H^+ \xrightarrow{\text{rate determining}} [Pd(C_4F_6)(diphos)(H)]^+$$

$$[Pd(C_4F_6)(diphos)(H)]^+ \xrightarrow[\text{halogenoacetate}]{\text{fast}} [Pd(OCOCX_3)(CF_3C{=}CHCF_3)(diphos)]$$

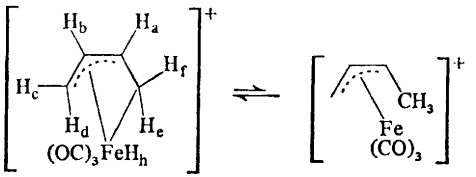
However, it is not known at which point in the alkyne complex proton attack occurs.[10] The kinetic pattern for analogous reactions of the complex $[Pd(CF_3C{\equiv}CCF_3)(PPh_3)_2]$ is more complicated and this is probably a consequence of reversible loss of triphenylphosphine.

Treatment of [Fe(butadiene)$(CO)_3$] with fluorosulphonic acid in liquid SO_2 has been reported to result in the formation of a diprotonated species (5).[11] This diprotonated species, however, can be reformulated as a σ–π species (6). The proton scrambling of H_f, H_e, and H_h can then occur *via* an equilibrium involving (6) and a small concentration of (7).[12]



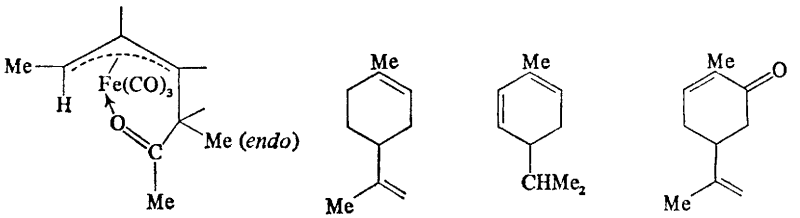
(5)

[10] J. Burgess, R. D. W. Kemmitt, and G. W. Littlecott, *J. Organometallic Chem.*, 1973, **56**, 405.
[11] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.
[12] M. Brookhart and D. L. Harris, *Inorg. Chem.*, 1974, **13**, 1540.



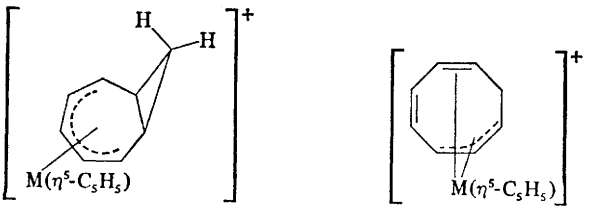
(6) (7)

An *X*-ray structure determination of a cationic intermediate (8) isolated during the acylation of [Fe(CO)$_3$(*trans,trans*-hexa-2,4-diene)] establishes that Friedel–Crafts acylation involves stereospecific *endo* attack.[13] The stereochemistry of reaction parallels protonation of tricarbonyl(diene)iron, cyclopentadienyl(cyclohexa-1,3-diene)rhodium complexes, and (η^5-cyclopentadienyl)rhodium complexes of limonene (9), α-phellandrene (10), and carvone (11).[14]



(8) (9) (10) (11)

Cyclic Alkenes.—The cyclo-octatetraene complexes [M(η^5-C_5H_5)(η-C_8H_8)] (M = Co or Rh) form unstable solutions in concentrated sulphuric acid. However, in trifluoroacetic acid the stable cationic species [M(η^5-C_5H_5)(C_8H_9)]$^+$ are produced. When M = Co, two isomeric forms (12) and (13) are formed upon initial protonation but over a period of two days irreversible isomerization of (12) to (13) occurs. Kinetics of the isomerization of (12) to (13) for M = Rh are first order in (12). The activation parameters found for this process are $\Delta H^{\ddagger} = 28 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 12 \pm 3$ cal K^{-1} mol^{-1}.[15]

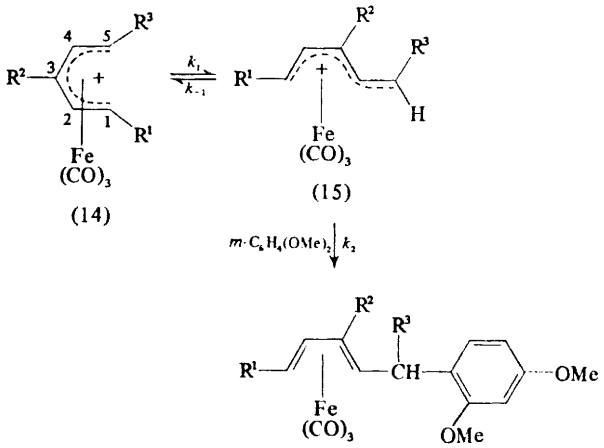


(12) (13)

[13] E. O. Greaves, G. R. Knox, P. L. Pauson, S. Toma, G. A. Sim, and D. I. Woodhouse, *J.C.S. Chem. Comm.*, 1974, 257.
[14] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1974, 1054.
[15] J. Evans, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1974, 2375.

The absence of a kinetic isotope effect is consistent with the C—H bond formed during protonation being retained during isomerization. The high value of ΔS^{+} suggests that in the rate-determining step a transition state more disordered than (12) is produced. These reactions probably proceed *via endo* attack. At low temperatures a hydride intermediate, $[IrH(\eta^5\text{-}C_5H_5)(C_8H_8)]$, may be detected when M = Ir. This proton may then be directly transferred to the ligand on elevation of temperature. Alternatively, a second proton may attack the cyclo-octatetraene with loss of the proton from the iridium. However, studies on [Fe(butadiene)$(CO)_3$] suggest that diprotonation may not occur.[12]

In Volume 3 it was reported that the cyclohexadienyl cation $[Fe(\eta^5\text{-}C_6H_7)(CO)_3]^+$ behaves as an electrophile towards activated aromatic systems. The reactions of open-chain pentadienyltricarbonyliron cations (14) with 1,3-dimethoxybenzene have now been shown to be considerably faster than those of their cyclic analogues and to show different kinetic characteristics. Rates for the reactions occurring in Scheme 5 are given in Table 3. Only the compounds (14a), (14b), and (14c) obey second-order



(14) (15)

Scheme 5

Table 3 *Rates of reaction of substituted* [Fe(pentadienyl)$(CO)_3$][BF_4] *with* 1,3-*dimethoxybenzene* (*DMB*) *in nitromethane at* 25 °C (*from ref.* 16)

	Compound (14)	k_2/l mol^{-1} s^{-1}	k_{obs}/s^{-1} (0.1M-DMB)	k_{obs}/s^{-1} (0.5M-DMB)
(14a)	cyclohexadienyl[a]	1.5×10^{-6}	—	—
(14b)	1,3,5-trimethyl	3.3×10^{-5}	—	—
(14c)	1,5-dimethyl	1.0×10^{-3}	—	—
(14d)	5-methyl	—	4.0×10^{-4}	1.3×10^{-3}
(14e)	1-phenyl-5-methyl	—	5.1×10^{-4}	1.4×10^{-3}
(14f)	1-phenyl-2,5-dimethyl	—	5.6×10^{-4}	1.4×10^{-3}

[a] At 20.8 °C.[17]

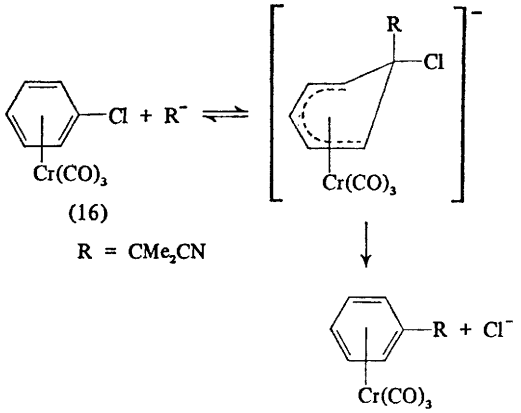
[16] T. G. Bonner, K. A. Holder, and P. Powell, *J. Organometallic Chem.*, 1974, **77**, C37.
[17] L. A. P. Kane-Maguire, personal communication quoted in ref. 16.

kinetics. The compounds (14d), (14e), and (14f) follow a different rate law,

$$\text{Rate} = \frac{k_1 k_2[\text{cation}][\text{ArH}]}{k_{-1} + k_2[\text{ArH}]}$$

In these reactions a reactive intermediate is presumably formed which is considered to be the *trans*-pentadienyltricarbonyliron cation (15). The enhanced reactivity of these systems compared with those with cyclic ligands may be ascribed to the ability of the open-chain ligands to form the *trans*-cations.[16]

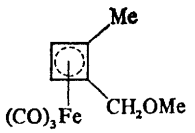
Co-ordination of the $Cr(CO)_3$ unit to halogenobenzenes enhances nucleophilic attack by carbanions at the co-ordinated benzene ring. A plausible mechanism for this process might be attack of the carbanion to form an η^5-cyclohexadienyl cation (Scheme 6). Preliminary studies, however, indicate that nucleophilic attack can



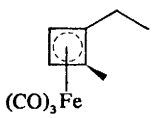
Scheme 6

occur at each of the ring carbons in (16) with the exception of the *para*-position.[18] Addition of protons to the reaction mixture can also lead to dihydrobenzene derivatives.

Alkenes and alkynes undergo cycloaddition reactions with cyclobutadiene produced *via* decomposition of [$Fe(CO)_3$(cyclobutadiene)]. Further studies on the oxidative decomposition of the optically active complexes (17) and (18) in the presence of dienophiles show that racemic adducts are formed. It would therefore appear that during the addition of the dienophile the iron is not sufficiently close to the cyclobutadiene to maintain the original chiral surroundings of the complex.[19,20]



(17)

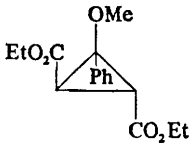


(18)

[18] M. F. Semmelhack and H. T. Hall, *J. Amer. Chem. Soc.*, 1974, **96**, 7092.
[19] R. H. Grubbs and R. A. Grey, *J. Amer. Chem. Soc.*, 1973, **95**, 5765.
[20] E. K. G. Schmidt, *Angew. Chem. Internat. Edn.*, 1973, **12**, 777.

3 Other Ligands

Treatment of the carbene complex [Cr{C(OMe)Ph}$(CO)_5$] with certain alkenes yields cyclopropanes by transfer of the carbene entity. The reaction of diethyl fumarate with (−)-(*R*)-methylphenylpropylphosphine(phenylmethoxycarbene)tetracarbonylchromium produces the optically active cyclopropane (19), the formation of which demonstrates that no free carbene is involved in the mechanism for the reaction.[21]



(19)

[21] M. D. Cooke and E. O. Fischer, *J. Organometallic Chem.*, 1973, **56**, 279.

6
Oxidative Addition and Reductive Elimination

BY R. D. W. KEMMITT AND M. A. R. SMITH

1 Group VI

Molybdenum.—The reaction of GeI_4 with $[Mo(CO)_4(o\text{-phen})]$ follows the rate law

$$-d[Mo(CO)_4(o\text{-phen})]/dt = k_2[Mo(CO)_4(o\text{-phen})][GeI_4]$$

Adduct formation is considered to be the rate-determining step, the overall mechanism being[1]

$$[Mo(CO)_4(o\text{-phen})] + GeI_4 \xrightarrow{k_2} [(o\text{-phen})(CO)_4Mo,GeI_4] \xrightarrow{\text{fast}} [MoI(GeI_3)(CO)_3(o\text{-phen})] + CO$$

Tungsten.—The reactions of $[W(CO)_4(bipy)]$ with $PhSnCl_3$, Bu^nSnCl_3, and Ph_2SnCl_2 can be encompassed in the rate law

$$-d[W(CO)_4(bipy)]/dt = k_1[W(CO_4)(bipy)] + k_3[W(CO)_4(bipy)][R_nSnCl_{4-n}]^2$$

The first-order term, observed only at elevated temperatures and only for Ph_2SnCl_2, can be ascribed to rate-determining loss of carbon monoxide followed by attack of Ph_2SnCl_2 at the five-co-ordinate activated complex. Activation parameters for this process in chlorobenzene are $\Delta H_1^{\ddagger} = 30.7 \pm 2.6$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = 5.3 \pm 7.2$ cal K^{-1} mol^{-1}, the positive entropy of activation providing support for the mechanism. The third-order term observed for all three oxidizing agents is consistent with the overall mechanism proposed for analogous reactions with $HgCl_2$. The mechanism is presumed to involve successive formation of 1 : 1 and 1 : 2 adducts (Scheme 1).[1] The activation parameters for this process using Ph_2SnCl_2 in chlorobenzene are $\Delta H_3^{\ddagger} = 11.3 \pm 0.2$ kcal mol^{-1} and $\Delta S_3^{\ddagger} = -37.6 \pm 0.5$ cal K^{-1} mol^{-1}. The rates of reaction are in the order $Ph_2SnCl_2 < Bu^nSnCl_3 < PhSnCl_3 < SnCl_4$.[1]

$$[W(CO)_4(bipy)] + Sn{-}X \rightleftharpoons [W(CO)_4(bipy),SnX]$$

$$[W(CO)_4(bipy),SnX] + Sn{-}X \rightleftharpoons [W(CO)_4(bipy),2SnX] \xrightarrow{\text{fast}} Sn{-}X + CO + [W(X)(Sn)(CO)_3(bipy)]$$

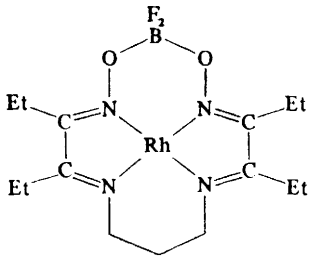
$$Sn{-}X = R_nSnCl_{4-n}$$

Scheme 1

[1] M. N. Memering, A. M. Araghi, and G. R. Dobson, *J. Coordination Chem.*, 1973, **2**, 271.

2 Group VIII

Rhodium.—The macrocyclic rhodium(I) complex (1) appears to be the most reactive neutral d^8 complex toward oxidative addition yet reported.[2] The very air-sensitive

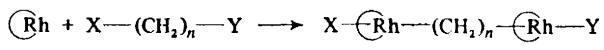


(1)

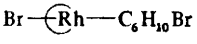
green complex (1) reacts smoothly with alkyl halides and sulphonates to give *trans*-rhodium(III) complexes, the reactions following the rate law

$$-\mathrm{d[Rh^I]/d}t = k_2[\mathrm{Rh^I}][\mathrm{RX}]$$

Evidence for an ionic intermediate is obtained by conducting the reaction of (1) with n-butyl bromide in the presence of LiCl, which yields only the *trans*-chloro-alkyl complex. The bromo-alkyl complex does not exchange with LiCl under the same conditions. Previous attempts to obtain evidence for ionic intermediates in oxidative additions with Vaska's complex have not been successful. The order of reactivity of (1) with alkyl halides, Me > Et > secondary > cyclohexyl, implies nucleophilic (S_N2), two-electron attack of carbon by rhodium. The order I > OTs ~ Br > Cl is consistent with either a one- or a two-electron mechanism. However, 1-bromoadamantane fails to react over a four day period and the overall results are consistent with an S_N2 mechanism.[2] Reactions with α,ω-dichloro-alkyls give the bis-rhodium complex (2) (X = Y = Br; n = 2, 3, 4, or 6). Second-order rate constants are also found for these reactions, and the second oxidative addition is even more rapid than the first. Even ICH_2CH_2Cl affords (2; X = I, Y = Cl, n = 2) as the major product. This second oxidative addition is also probably a two-electron reaction and the observation that 1,4-dibromocyclohexane gives only a mono-rhodium complex (3) suggests a cyclic intermediate in this neighbouring-group effect.[2]



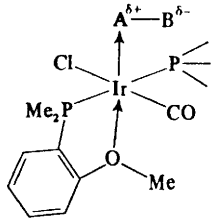
(2)



(3)

Iridium.—The tendency for iridium(I) complexes of the type *trans*-$[IrCl(CO)L_2]$ to undergo oxidative addition can be enhanced by decreasing the bulk of the ligand L and increasing the donor power of L. It has now been shown that when the ligand L is *o*-methoxyphenyl(dimethyl)phosphine the tendency for oxidative addition is enhanced over that found for *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ since there is a possibility

[2] J. P. Collman and M. R. MacLaury, *J. Amer. Chem. Soc.*, 1974, **96**, 3019.



(4)

for the ether oxygen to donate electron density to the iridium in the complex (4), so lowering the activation energy required for oxidative addition.[3] The addition of methyl iodide to the complexes *trans*-[IrCl(CO)L_2] [L = PMe_2Ph, PMe_2(*o*-$MeOC_6H_4$), or PMe_2(*p*-$MeOC_6H_4$)] follows the rate law

$$-d[IrCl(CO)L_2]/dt = k_1[IrCl(CO)L_2] + k_2[IrCl(CO)L_2][MeI]$$

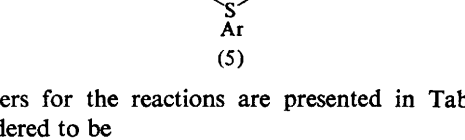
The contribution of the k_1 path to the overall reaction is less than 3% and may represent reaction of the iridium complex with traces of oxygen. The reactions rates are not changed significantly by addition of the efficient radical scavenger *p*-t-butylcatechol. Activation parameters are given in Table 1. The considerably lower

Table 1 *Second-order constants and activation parameters for the oxidative addition of* MeI *to* trans-[IrCl(CO)$(PPh_3)_2$] *in toluene at* 25.3 °C (*from ref.* 3)

L	$k_2 \times 10^2$/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
PMe_2Ph	4.7±0.15	46.4±0.8	−114±3
PMe_2(*o*-$MeOC_6H_4$)	530±25	27.6±0.8	−133±3
PMe_2(*p*-$MeOC_6H_4$)	6.75±0.2	38.1±7.5	−133±25

value of $\Delta H^{\ddagger}$ for the PMe_2(*o*-$MeOC_6H_4$) complex is considered to be a consequence of the interaction of methoxy oxygen with iridium.

The reactions of the disulphides *p*-$YC_6H_4SSC_6H_3$-2,4-$(NO_2)_2$ (Y = Br, F, H, Me, or MeO) with *trans*-[IrCl(CO)$(PPh_3)_2$] follow simple second-order kinetics. The reactions lead to the bridged complex (5), triphenylphosphine being liberated.



(5)

Activation parameters for the reactions are presented in Table 2. The overall mechanism is considered to be

$$trans\text{-}[IrCl(CO)(PPh_3)_2] + Ar^1SSAr^2 \xrightarrow[k_2]{\text{slow}} [IrCl(SAr^1)(SAr^2)(CO)(PPh_3)_2]$$

$$[IrCl(SAr^1)(SAr^2)(CO)(PPh_3)_2] \xrightarrow{\text{fast}} [IrCl(SAr^1)(SAr^2)(CO)(PPh_3)] + PPh_3$$

$$2[IrCl(SAr^1)(SAr^2)(CO)(PPh_3)] \xrightarrow{\text{fast}} [IrCl(SAr^1)(SAr^2)(CO)(PPh_3)]_2$$

[3] E. M. Miller and B. L. Shaw, *J.C.S. Dalton*, 1974, 480.

Table 2 *Activation parameters for the reactions of the disulphides* p-$YC_6H_4SSC_6H_3$-2,4-$(NO_2)_2$ *with* trans-$[IrCl(CO)(PPh_3)_2]$ *in toluene (from ref.* 4)

Y	$\Delta H^{\ddagger}$ (± 1 kcal mol^{-1})	$\Delta S^{\ddagger}$ (± 3 cal K^{-1} mol^{-1})
Br	17.0	−20.6
F	17.7	−18.2
H	17.8	−19.0
Me	18.0	−18.0
MeO	17.3	−19.2

The values of $\Delta H^{\ddagger}$ suggest that dissociation of the S—S bond is not a distinguishable step during the reaction. The rate-determining step is considered to be nucleophilic attack by iridium at the sulphur bonded to the 2,4-dinitrophenyl group since reaction rates are insensitive to the group Y. Addition of triphenylphosphine to the reaction increases the rate of reaction but the exact nature of the product formed from this reaction is not known. However, any mechanism involving triphenylphosphine in a dissociative step can be discounted. It is also now considered that in reactions of thiols ArSH with *trans*-$[IrCl(CO)(PPh_3)_2]$ the step leading to the activated complex involves attack of iridium(I) at the hydrogen bonded to sulphur.[4]

The oxidative addition of methyl fluorosulphonate to *trans*-$[IrX(CO)(PPh_3)_2]$ (X = Cl or Br) follows the rate law

$$-d[IrX(CO)(PPh_3)_2]/dt = k_2[IrX(CO)(PPh_3)_2][MeOSO_2F]$$

Activation parameters for the reaction when X = Cl are $\Delta H^{\ddagger} = 17.0 \pm 0.45$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11 \pm 2$ cal K^{-1} mol^{-1}. The reactivity sequence is Cl > Br, although the difference is rather small. The reaction presumably involves nucleophilic attack at carbon by iridium(I) but in view of the relative leaving-group properties of SO_3F^- and I^- it is surprising that the activation enthalpy for the addition of methyl fluorosulphonate is appreciably larger than that found for the addition of methyl iodide.[5] The marked difference between the activation parameters for reaction of *trans*-$[IrCl(CO)(PPh_3)_2]$ with oxygen or hydrogen on the one hand, transition state (6), and with methyl iodide, transition state (7), on the other, suggests that activation parameters may be diagnostic of mechanisms. However, a plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ for various oxidative addition reactions to *trans*-$[IrCl(CO)(PPh_3)_2]$ shows that it is not possible to draw this conclusion.[5]

(6)

Ir---Me---I

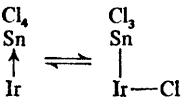
(7)

The reaction of optically active $MeCHBrCO_2Et$ with *trans*-$[IrCl(CO)(PMePh_2)_2]$ has been reported to proceed with substantial retention of stereochemistry.[6] However, further studies show that racemization occurs and that this reaction

[4] C. T. Lam and C. V. Senoff, *Canad. J. Chem.*, 1973, **51**, 3790.
[5] J. Burgess, M. J. Hacker, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1974, **72**, 121.
[6] R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5519.

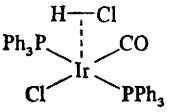
proceeds *via* a free-radical pathway[7] as reported for analogous oxidative additions in Volume 3 of this Report.

A number of oxidative-addition reactions of mercury(II) and tin(IV) halides proceed *via* the formation of metal donor–metal acceptor complexes. Evidence has now been presented which suggests that the adducts $[(Ph_3P)_2(CO)ClIr]\rightarrow SnCl_4$ and $[(Ph_3P)_2(CO)ClIr]\rightarrow SnCl_3Me$ undergo an intramolecular oxidation–reduction isomerization (Scheme 2).[8] The addition of hydrogen chloride to solid *trans*-$[IrCl(CO)(PPh_3)_2]$ is



Scheme 2

considered probably to proceed *via* a five-co-ordinate transition state (8).[9] The relative rates of the addition of oxygen to the complexes *trans*-$[IrX(CO)(PRPh_2)_2]$ (X = F, Cl, Br, or I; R = Ph, Me, or Et) follow the order R = Ph < Et < Me and X = F < Cl < Br < I.[10]



(8)

Palladium.—The reaction of $[Pd(PPh_3)_4]$ with α-phenylethyl bromide in the presence of carbon monoxide gives the acyl complex $[PdBr(COCHMePh)(PPh_3)_2]$ with greater than 90% inversion of configuration at carbon. This result is consistent with a mechanism involving oxidative addition to palladium with inversion of configuration followed by insertion of carbon monoxide with retention of configuration.[11] However, it is possible that this reaction could involve direct nucleophilic attack by a palladium carbonyl species at the benzylic carbon and that in the absence of carbon monoxide addition of benzyl halides to $[Pd(PPh_3)_4]$ may occur *via* a radical pathway. However, the oxidative addition of PhCHDCl to $[Pd(PPh_3)]_4$ has now been shown to proceed with inversion of configuration, and a radical pathway can be dismissed.[12] It is particularly noteworthy that the addition of the spin trap Bu^tNO to $[PdCl(CH_2Ph)(PPh_3)_2]$ produces the radical $Bu^t(PhCH_2)NO$. Thus the observation that the formation of $Bu^t(PhCH_2)NO$ can be detected in the reaction of benzyl chloride with $[Pd(PPh_3)_4]$ provides no evidence for a radical mechanism in this particular oxidative addition reaction.[12] It is also noteworthy that no inhibition by scavengers is observed in the reactions of $[Pd(PEt_3)_3]$ with MeX (X = Br or I), PhX (X = CN,

[7] J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 7908.
[8] C. B. Dammann, J. L. Hughey, D. C. Jicha, T. J. Meyer, P. E. Rakita, and T. R. Weaver, *Inorg. Chem.*, 1973, **12**, 2206.
[9] M. C. Ball and J. M. Pope, *J.C.S. Dalton*, 1973, 1802.
[10] C. A. McAuliffe and R. Pollock, *J. Organometallic Chem.*, 1974, **77**, 265.
[11] K. S. Y. Lau, R. W. Fries, and J. K. Stille, *J. Amer. Chem. Soc.*, 1974, **96**, 4983.
[12] P. K. Wong, K. S. Y. Lau, and J. K. Stille, *J. Amer. Chem. Soc.*, 1974, **96**, 5956.

Cl, Br, or I), $PhCH_2X$ (X = Cl or Br), $BrCH_2CH_2CO_2Et$, $CH_2{=}CHX$ (X = Cl or Br), *cis*- and *trans*-PhCH=CHBr, $CH_2{=}CHCH_2X$ (X = Cl or Br), or $CH_2{=}CHCH_2CH_2Br$. However, inhibition is observed for $Me(CH_2)_nX$ (X = Br or I, n = 1—5), Me_2CHCH_2Br, Me_3CCH_2Br, $Ph(CH_2)_nBr$ (n = 2 or 3), cyclo-$C_6H_{11}Br$, cyclo-C_5H_9Br, cyclo-C_4H_7Br, cyclo-C_3H_5Br, $MeCHBrCH_2Me$, $MeCHXCO_2Et$ (X = Cl or Br), and $CH_2{=}CH(CH_2)_4Br$.[13]

Platinum.—Evidence that the oxidative addition of MeI, CD_3I, EtI, or $PhCH_2Br$ to $[Pt(PPh_3)_3]$ involves free radicals has been obtained by using Bu^tNO as a spin trap.[14] A non-chain mechanism is proposed for these reactions with the formation of $[Pt^IX(PPh_3)_2]\cdot$ as rate limiting (Scheme 3). This scheme, however, is at variance with

$$[Pt(PPh_3)_3] \rightleftharpoons [Pt(PPh_3)_2] + PPh_3$$

$$[Pt(PPh_3)_2] + RX \overset{\text{slow}}{\rightleftharpoons} [PtX(PPh_3)_2]\cdot + R\cdot$$

$$[PtX(PPh_3)_2]\cdot + R\cdot \xrightarrow{\text{fast}} \textit{trans}\text{-}[PtX(R)(PPh_3)_2]$$

Scheme 3

other studies on the reaction of EtI with $[Pt(PPh_3)_3]$, which reveal that this reaction is inhibited by radical scavengers, suggesting a predominantly chain mechanism.[13] Indeed the major (but not only) pathway for the addition of alkyl halides to the complex $[Pt(PEt_3)_3]$ appears to involve a radical chain pathway.[7,13] Such addition reactions are often quite complex. Thus 1-bromobutane reacts with $[Pt(PEt_3)_3]$ to produce *trans*-$[PtBr(R)(PEt_3)_2]$, *trans*-$[PtBr(H)(PEt_3)_2]$, and *trans*-$[PtBr_2(PEt_3)_2]$ in the relative amounts 95 : 4 : 1 in addition to small quantities of butane and but-1-ene. Further reaction increases the quantity of the dibromide at the expense of the alkyl complex. Eventually the reaction products consist of alkene, alkane, and *trans*-$[PtBr_2(PEt_3)_2]$. Reactions with secondary alkyl bromides occur more slowly. In general the reactions of $[Pt(PEt_3)_3]$ follow the same patterns as those found for $[Pd(PEt_3)_3]$ described above.[13] Kinetic studies on the reaction of methyl iodide with $[Pt(PPh_3)_{3 \text{ or } 4}]$ are consistent with a nucleophilic-type mechanism[15] and these reactions show no inhibition with galvinoxyl.[7] However, methyl radicals have been detected in this reaction by use of the spin trap Bu^tNO and further experiments on these systems are clearly required.[14] *X*-Ray crystallographic studies confirm that there is retention of configuration upon oxidative addition of *trans*-*β*-bromostyrene to $[Pt(PPh_3)_3]$.[16] The reaction is not inhibited by galvinoxyl[13,16] and a free-radical intermediate may not be involved. However, it should be noted that alkenyl free radicals do not isomerize immediately.[16]

The oxidative-elimination reaction of (+)-R_3Si^*H [R_3Si^* = $Me(1\text{-}C_{10}H_7)PhSi$] with $[Pt(C_2H_4)(PPh_3)_2]$ to give *cis*-$[PtH(^*SiR_3)(PPh_3)_2]$ occurs with little loss of optical activity and probably proceeds with retention of configuration at silicon.

[13] A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1974, **96**, 7145.
[14] M. F. Lappert and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 948.
[15] R. G. Pearson and J. Rajaram, *Inorg. Chem.*, 1974, **13**, 246.
[16] J. Rajaram, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 2103.

Similarly the oxidative-addition–reductive-elimination sequences of reactions occurring in the formation of *trans*-[PtCl(*SiR$_3$)(PMe$_2$Ph)$_2$] from R$_3$Si*H and *cis*-[PtCl$_2$(PMe$_2$Ph)] in the presence of triethylamine occur with retention of configuration at silicon.[17]

Activation energies of 8.6 and 8.5 kcal mol^{-1} have been determined for the second-order oxidative-addition reactions of methyl iodide and acetyl chloride to *cis*-[PtMe$_2$(*p*-CNC$_6$H$_4$Me)$_2$] in chloroform solution. These low activation energies show that the platinum is very electron rich and a polar transition state is suggested for this reaction. In benzene solution there is no sign of reaction even after several hours.[18]

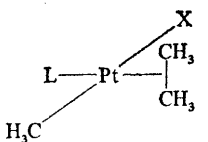
The oxidative-addition reactions of bromine to the complexes *trans*-[PtCl$_2$(PR$_3$)L] (R = Et, L = py, 3,5-Me$_2$-py, 4-Bu^t-py, or PEt$_3$; R = Bu^n, L = py) do not involve simple *trans* addition of bromine. ^{31}P N.m.r. spectra show that halogen exchange occurs to give complexes *trans*-[PtBr$_x$Cl$_{4-x}$(PEt$_3$)L] (x = 0—4).[19]

Although there has been considerable interest in oxidative-addition reactions there is less information available on the reverse reaction, reductive elimination. Kinetic studies of the decomposition of *fac*-[PtXMe$_3$L$_2$] (X = Cl or Br, L = PMe$_2$Ph; X = I, L = PMe$_3$, PMe$_2$Ph, or PMePh$_2$) are consistent with a mechanism involving dissociation of a phosphine ligand followed by elimination of ethane from the five-co-ordinate intermediate. Activation parameters are given in Table 3. Methyl

Table 3 *Activation parameters for the loss of ethane from the complexes* fac-[PtXMe$_3$L$_2$] *in* 1,4-*dioxan at* 353 K (*from ref.* 20)

X	L	$E^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
Cl	PMe$_2$Ph	116±5	15±10	108
Br	PMe$_2$Ph	125±5	46±5	106
I	PMe$_2$Ph	132±5	68±5	105
I	PMe$_2$Ph	150±5	185±15	82
I	½diphos	69±5	−125±5	109

groups are eliminated more readily from the platinum(II) complexes than CD$_3$ groups, the average secondary kinetic isotope effect k_H/k_D being 1.07. These results suggest considerable weakening of the Pt—C bonds in the transition state which may resemble an ethane complex of platinum(II) (9).[2] The different activation parameters found for the diphos complex suggest that ethane elimination occurs without cleavage of a Pt—P bond.[2]



(9)

[17] C. Eaborn, D. J. Tune, and D. R. M. Walton, *J.C.S. Dalton*, 1973, 2255.
[18] T. G. Appleton, H. C. Clark, and L. E. Manzer, *J. Organometallic Chem.*, 1974, **65**, 275.
[19] B. T. Heaton and K. J. Timmins, *J.C.S. Chem. Comm.*, 1973, 931.
[20] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1974, 2457.

3 Other Elements

Gold.—The mechanism described above for the loss of ethane from the complexes *fac*-$[PtXMe_3L_2]$ is analogous to that found for the reductive elimination of ethane from the gold(III) complexes $[AuMe_3L]$,[21] and it is evident that dissociation of a phosphine ligand lowers the activation energy for reductive elimination. Methyl iodide oxidatively adds to $[AuMe(PMe_3)]$ five times faster than to $[AuMe(PPh_3)]$. The resulting triphenylphosphine adduct then takes part in a series of reactions (Scheme 4).[22] However, $[AuMe_3(PMe_3)]$ is more stable to reductive elimination than

$$[AuMeL] + MeI \longrightarrow [AuIMe_2L]$$

$$[AuIMe_2L] + [AuMeL] \longrightarrow [AuMe_3L] + [AuIL]$$

$$[AuMe_3L] \longrightarrow [AuMeL] + CH_3{-}CH_3$$

$$L = PPh_3$$

Scheme 4

the triphenylphosphine analogue and therefore is able to take part in a slow reaction with $[AuI(PMe_3)]$ and MeI to give $[AuIMe_2(PMe_3)]$.[22]

[21] A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 6487.
[22] A. Tamaki and J. K. Kochi, *J. Organometallic Chem.*, 1974, **64**, 411.

7

Isomerization: Intramolecular Processes

BY R. D. W. KEMMITT AND M. A. R. SMITH

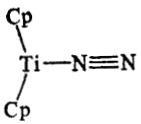
The efforts over recent years of several groups appear to have come to fruition during the current period. We refer in particular to the immense efforts by Cotton and co-workers to elucidate the exchange mechanisms of $[(h^5\text{-}C_5H_5)ML_2]_2$ species. This problem has now received a satisfactory answer in terms of a generally applicable and already well tested scheme. Trigonal-bipyramidal five-co-ordinate complexes have previously resisted investigation by virtue of their very low activation barriers. This property is not shown by a large series of Co, Rh, Ir, Ni, Pd, and Pt tertiary phosphite complexes and this has permitted the first extensive study of such systems. An interesting development in this area has been the successful use of olefin rotation coupled to the accepted Berry rearrangement to raise activation barriers in $[Fe(CO)_4(olefin)]$ and similar complexes. This promises well for future work in the field.

Rather less success has attended continuing efforts to label the mechanism of *cis–trans* isomerization in $[MCl_2(PR_3)_2]$ and related complexes. The best that can be said in view of current data is that a unique mechanism seems unlikely.

Finally we should add that, as in previous years, we have remained flexible in choosing subject headings. Apart from main headings by group, these reflect the trends in the period under review rather than conforming to a predetermined pattern.

1 Groups IV and V

At 211 K the ^{15}N n.m.r. spectrum of the ^{15}N-enriched titanocene dinitrogen adduct of stoicheiometry $[N_2Ti(Me_5C_5)_2]$ consists of two doublets and a sharp singlet. The results indicate that below 228 K the complex exists as an equilibrium of two forms (1) and (2), (1) giving rise to the two doublets and having $^1J(^{15}N\text{–}^{15}N) = 7 \pm 2$ Hz.



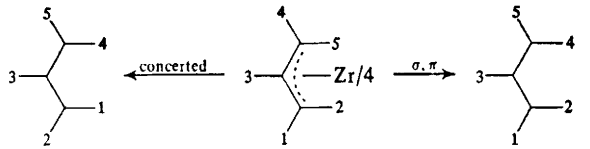
(1)

(2)

The variable-temperature behaviour of the ^1H and ^{13}C n.m.r. spectra supports this interpretation and also serves to dismiss the presence below 228 K of alternative disproportion products.[1] Eight-co-ordination can engender three structural forms (D_{2d}, D_{4d}, and C_{2v}), interconversion between which is readily feasible. Attempts to

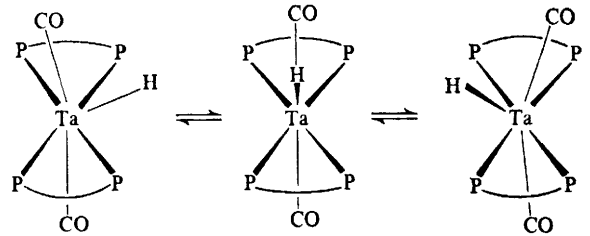
[1] J. E. Bercaw, E. Rosenberg, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1974, **96**, 612.

use as stereochemical labels the alkyl groups in eight-co-ordinate dithiocarbamate complexes $[M(S_2CNR_2)_4]$ (R = Et or Pr; M = Ti, Zr, or Nb^{IV}) and similar unsymmetrically N-substituted complexes were thwarted by the persistence of apparently non-rigid forms to the lowest temperatures attained. Although the alkyl groups may have initially appealed both as labels and chemically in terms of inducement of high solubility, the author concludes that their remoteness from sites of substantial stereochemical change negates these advantages. This supposition seems adequately supported by the close similarity between the ^1H n.m.r. of a mixture $[Zr(S_2CNEt_2)_x(S_2CNPr_2)_{4-x}]$ (x = 1, 2, or 3) and the combined spectra of the pure diethyl and dipropyl complexes.[2] Previous studies of the exchange of *syn* and *anti* protons in h^3-allyl complexes have chiefly favoured three interchange mechanisms. Before the appropriate site interchanging rotation, the first (referred to as the σ–π mechanism) involves the intermediacy of a *monohapto*-allyl moiety whilst the second and third involve respectively 1,2- and 1,3-*dihapto*-allyl complexes. The last, 'concerted' mechanism is distinguishable from the other two in that both pairs of terminal protons must exchange simultaneously. In comparison, in the σ–π mechanism interchange occurs at one terminus at a time (Scheme 1). This distinction has



Scheme 1

been employed by Whitesides *et al.*[3] in elucidating the interchange mechanism in the case of $[Zr(h^3\text{-allyl})_4]$. It is comprehensively rationalized that the mechanisms above will involve differing effects on certain nuclear transitions. Based on those considerations the generation of theoretical variable-temperature ^1H n.m.r. spectra of the 2-proton favours the σ–π mechanism. The second non-concerted mechanism mentioned above could not be finally dismissed, however.[3] ^{31}P and ^1H n.m.r. spectra of $[TaH(CO)_2(Me_2PC_2H_4PMe_2)_2]$ in the low-temperature limit are consistent with the solid-state structure derived by *X*-ray analysis, *i.e.* a distorted octahedron capped by the hydride ligand (3). Warming results in the onset of a 'mutual' exchange process (Scheme 2) having $\Delta G^{\ddagger}_{300} = 12.8$ kcal mol^{-1}. The inclusion of a low concentration



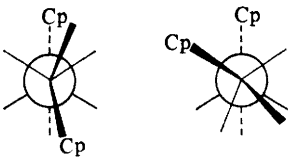
Scheme 2

[2] E. L. Muetterties, *Inorg. Chem.*, 1973, **12**, 1963.
[3] J. K. Krieger, J. M. Deutch, and G. M. Whitesides, *Inorg. Chem.*, 1973, **12**, 1535.

of the isomer (4) is vital to the fitting of the asymmetric n.m.r. patterns observed for the hydride ligand to those calculated when the system is in the intermediate exchange limit. The detailed mechanism of exchange probably involves dechelation of the phosphine ligand.[4]

2 Group VI

Group Trends.—We deal in this section with papers in which the effect of all three metals on a single non-rigid structure is detailed. The most obvious correlation, however, is the general lack of effect. The species $[M(h^5\text{-}C_5H_5)(CO)_3]_2$ (M = Cr,[5] Mo,[6,*] or W[7]) exist in solution in solvent-dependent rotational equilibria involving *anti-* (5) and *gauche-* (6) isomers. Variable-temperature ^1H n.m.r. and crystallographic investigations of these compounds reveal the trends Cr ≫ Mo > W for the



(5) (6)

metal–metal distances and Cr < Mo ≤ W for the free energies of activation of the rotational interconversion. Data are summarized in Table 1. Relative intramolecular

Table 1 gauche–anti *Rotational activation parameters* (298 K) *and* M—M *distances for the complexes* $[(h^5\text{-}C_5H_5)M(CO)_3]_2$ (*from ref.* 7)

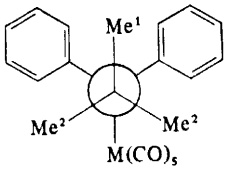
M	d(M—M)/Å	log A	E_a/ kcal mol^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
Cr	3.281	14.2	13.7	12.1	13.1	+4.5
Mo	3.235	13.0	15.3	15.0	14.7	−1.0
W	3.222	12.1	15.2	16.2	14.7	−5.2

contacts in the series might have been expected to predict the inverse order of the rotational barriers. However, the observed order can be rationalized on the basis of the weakness of the Cr—Cr bond at its equilibrium length,[5] the barrier to rotation then being comparatively lower by virtue of easier stretching. The expected increased freedom in the transition state induced by easier stretching is reflected in the value of $\Delta S^{\ddagger}$. At 144 K the t-butyl group in the complexes $[(Bu^tPh_2P)M(CO)_5]$ (M = Cr, Mo, or W) is undergoing sufficiently slow rotation about the P—C bond that line-shape analysis of the ^1H n.m.r. spectrum reveals the composite presence of two

[4] P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1025.
[5] R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1974, **96**, 749.
[6] R. D. Adams and F. A. Cotton, *Inorg. Chim. Acta*, 1973, **7**, 153.
[7] R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1086.

* In dealing with this reference in Volume 3 of this series the formula $[Mo(h^5\text{-}C_5H_5)(CO)_3]_2$ was omitted after (6) on p. 462.

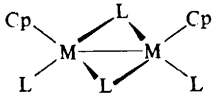
doublets, one (3H,Me^1) having ^3J(PCCH) = 10.0 Hz and the other (6H,Me^2) having ^3J(PCCH) = 17.5 Hz [see (7)]. Activation parameters were obtained after



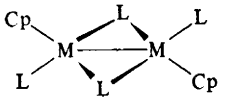
(7)

inducement of significant rotation by warming and show substantial insensitivity to the metal–carbonyl moiety [$\Delta G^{\ddagger}_{159}$ = 8.4 ± 0.2 kcal mol^{-1} (M = Cr), $\Delta G^{\ddagger}_{163}$ = 8.3 ± 0.2 kcal mol^{-1} (M = Mo), and $\Delta G^{\ddagger}_{159}$ = 8.3 ± 0.2 kcal mol^{-1} (M = W)]. The apparently similar steric effect on rotation of the t-butyl group can be reconciled, however, with equally similar intramolecular distances previously noted for these complexes in the solid state.[8] The exchange process responsible for coalescence of the ^{1}H n.m.r. spectra of the chelate in [(CO)$_4$MSePr^{i}C$_2$H$_4$SePr^i] (M = Cr or Mo) in the high-temperature limit is also insensitive to the remainder of the molecule [*e.g.* $\Delta G^{\ddagger}_{300}$ = 59.1 kJ mol^{-1} (M = Cr) and $\Delta G^{\ddagger}_{295}$ = 58.4 kJ mol^{-1} (M = Mo)]. In this example conformational interchange is favoured over lone-pair inversion about selenium, the former process being more likely to be unaffected by the metal. In the complex having M = W the spectrum remains unperturbed by increased temperature. This result was interpreted as arising from a system based on considerable involvement of the selenium lone pair in the co-ordinate bond and two resulting enantiomeric conformations between which exchange would remain slow on the n.m.r. time-scale.[9] Preferred conformations of the six-membered chelate ring in [(CO)$_4$MAsMe$_2$CH$_2$(CHR)CH$_2$AsMe$_2$] (M = Cr, Mo, or W) depend on the nature of R. When R = H fast exchange takes place between symmetric chairs whereas the introduction of a bulky group (R = Bu^t) 'locks' the ring in the chair conformation with R equatorial. The n.m.r. studies were conducted at *ca.* 295 K. Although low-temperature effects were noted, no detailed results are forthcoming.[10]

Chromium.—The intramolecular rearrangement processes inherent in such systems as [(h^5-C$_5$H$_5$)ML$_2$]$_2$ are now well documented. They are known to involve equilibration of *cis* (8) and *trans* (9) bridged forms by virtue of non-bridged intermediates (10) and (11), the latter being the immediate progenitors of a bridge–terminal interchange

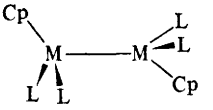


(8)



(9)

[8] C. H. Bushweller and M. Z. Lourandos, *Inorg. Chem.*, 1974, **13**, 2514.
[9] R. Donaldson, G. Hunter, and R. C. Massey, *J.C.S. Dalton*, 1974, 288.
[10] W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, *J. Amer. Chem. Soc.*, 1974, **96**, 410.



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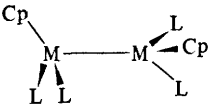


(11)

or scrambling process. In the later section on iron we review a recent paper by Cotton (ref. 23) in which is expounded a general rationale for these systems. Here we include comments on an investigation of the isoelectronic series $[(h^5\text{-}C_5H_5)Cr(NO)_2]_2$, $[(h^5\text{-}C_5H_5)Mn(NO)(CO)]_2$, and $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$.[11] The natures of the manganese[12] and iron[13] systems are well known and were dealt with in Volume 3. The inclusion of this paper in this section is therefore based on the new solution data presented for the chromium compound. As is often found in these systems, *cis–trans* interconversion in $[(h^5\text{-}C_5H_5)Cr(NO)_2]_2$ is solvent-dependent (Table 2). There is no

Table 2 *Solvent dependence of the* cis–trans *equilibrium in* $[(C_5H_5)Cr(NO)_2]_2$; $T = 308$ K, $K = [trans]/[cis]$ (from ref. 11)

Solvent	K^a
Cyclohexane	21.8
Carbon disulphide	19.2
[$^2H_8$]Toluene	15.4
Nitrobenzene	5.0
[$^2H_6$]Acetone	3.2
Acetonitrile	3.0
[$^2H_6$]Dimethyl sulphoxide	2.1

[a] ±5%.

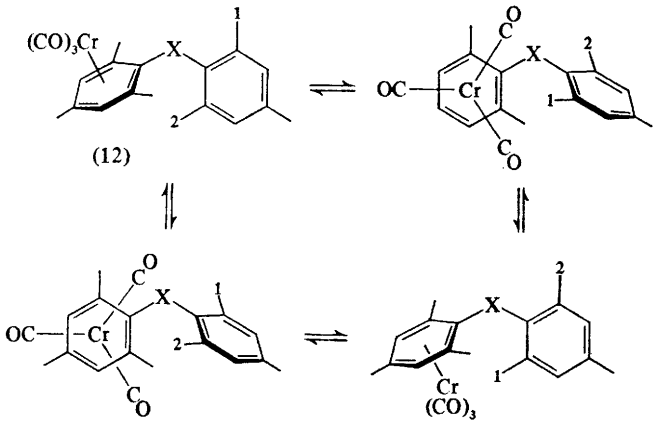
direct evidence from i.r. or variable-temperature n.m.r. for bridge–terminal interchange of nitrosyl ligands; an increase in barrier height compared with the manganese and iron compounds follows seemingly from the order established for *cis–trans* equilibration. Thermodynamic data are summarized in Table 3. The order of barrier heights for both exchange processes is Cr > Mn > Fe and may be correlated with the respective strengths of nitrosyl and carbonyl bridges. Stabilization of the *cis*-isomer in the order Fe > Mn > Cr was not expected, since the increased intramolecular contacts in the *cis*-form noted from crystallographic work might be expected to increase further as the M—M distance decreases. It is postulated that puckering of the four-membered ring $[M_2(CO)_x(NO)_{2-x}]$ in the *cis*-isomer relieves strain to a greater degree as the M—M distance decreases. The observation that the *trans*-isomer undergoes bridge–terminal interchange more readily than the *cis* follows from Cotton's mechanism (see below). Low-temperature n.m.r. and steric considerations indicate that the probable ground state of the dimesityl(tricarbonyl)chromium derivates (12; X = CH_2, CO, $\diagdown C{=}CH_2$, or $\diagdown CHOH$) and the similar compound

[11] R. M. Kirchner, T. J. Marks, J. S. Kristoff, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 6602.
[12] T. J. Marks and J. S. Kristoff, *J. Organometallic Chem.*, 1972, **42**, C91.
[13] J. G. Bullit, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 1972, **11**, 671.

Table 3 *Thermodynamic parameters for bridge–terminal ligand interchange and* cis ⇌ trans *equilibration in the complexes* $[(h^5\text{-}C_5H_5)ML_2]_2$ *(from ref.* 11)

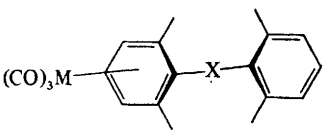
Compound	*Bridge–terminal* E_a/kcal mol^{-1}	*cis* ⇌ *trans* E_a/kcal mol^{-1}	*cis* ⇌ *trans* ΔH/kcal mol^{-1}	*cis* ⇌ *trans* ΔS/cal K^{-1} mol^{-1}	*cis* ⇌ *trans* ΔG_{298}/kcal mol^{-1}
$[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$					
cis	11.0±1.0	12.0±1.0	0.9±0.1	3.5±0.5	−0.15±0.1
trans	8.0±1.0	12.0±1.0			
$[(h^5\text{-}C_5H_5)Mn(CO)(NO)]_2$					
cis	13.8±0.6	19.1±2.4	−0.16±0.1	0.93±0.4	−0.44±0.3
trans	13.8±0.6	19.1±2.4			
$[(h^5\text{-}C_5H_5)Cr(NO)_2]_2$					
cis		21.5±1.3	−2.1±0.3	−1.7±1.0	−1.6±0.3
trans		23.4±1.2			

[$Cr(CO)_3$(2,6-dimethylphenyl mesityl ketone)] is as shown. The accepted rotation mechanism in uncomplexed diarylmethanes involves both rings rotating about the central group at the same rate and in such a manner as to be always mutually perpendicular, the so called 'cog-wheel' mechanism. As Scheme 3 shows this cannot



Scheme 3

explain the observed n.m.r. equivalences in the complexes, since methyl groups 1 and 2 clearly remain inequivalent. It is therefore proposed that equivalence is attained by rotation of just the uncomplexed ring with the intermediacy of a conformation such as (13). Rotational barriers when X = CO are *ca.* 5 kcal mol^{-1} higher than in other complexes. This is attributed to stabilization of the ground-state conformation in the former by conjugation between the carbonyl group and the uncomplexed ring.[14] Olefin rotation in [(h^5-C_5H_5)Cr(CO)(NO)(CH_2=CH_2)] takes place about the metal–olefin bond axis ($\Delta G^{\ddagger}_{238}$ = 11.4 ± 0.2 kcal mol^{-1}).[15]

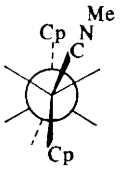


(13)

Molybdenum and Tungsten.—In the low-temperature limit [(h^5-C_5H_5)$(CO)_3$MoMo(CNMe)$(CO)_2$(h^5-C_5H_5)] exists as a mixture of isomers. At least four individual species were apparent in the n.m.r. out of five possible non-equivalent rotational permutations. However, only one could be unequivocally assigned as that noted in the solid state (14). Warming results in the eventual collapse of the cyclopentadienyl signals to one sharp line. It is immediately evident, therefore, that the equilibration process involves rapid transfer of the isocyanide between metal atoms. This particular process was recognized in the n.m.r. as that having the lowest energy and the

[14] W. S. Trahanovsky, D. J. Kowalski, and M. J. Avery, *J. Amer. Chem. Soc.*, 1974, **96**, 1502.
[15] H. Alt, M. Herberhold, C. G. Krieter, and H. Strack, *J. Organometallic Chem.*, 1974, **77**, 353.

parameters $E_a = 12.7 \pm 0.5$ kcal mol^{-1}, $\log A = 12.6 \pm 0.5$, $\Delta H^{\ddagger} = 12.3 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2.6 \pm 1.4$ cal K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298} = 13.0 \pm 0.5$ kcal mol^{-1} were calculated. These are very similar to those for bridge–terminal interchange of one carbonyl for one isocyanide in iron dimers (see ref. 23 later). The participation of bridged intermediates [μ-$(CO)_2$ or μ-(CO)-μ-(CNMe)] in the equilibration mechanism was therefore inferred.[16]



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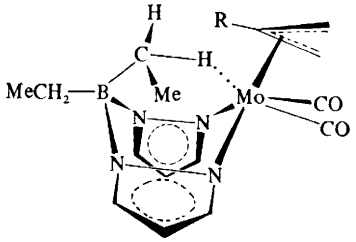
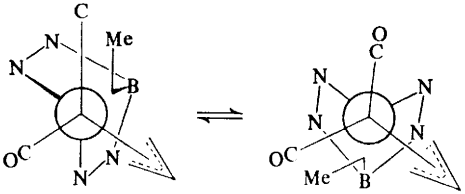


(15)

(Pyrazolyl)borato-complexes of molybdenum are no strangers to these Reports and in particular the interaction between the substituent on boron and molybdenum has been noted. The complex [{$Et_2B(pz)_2$}$Mo(CO)_2(h^3$-$CH_2CRCH_2)$] (15) (R = H or Ph) is in fact formally represented as containing a three-centre, two-electron C—H···Mo bond. Not surprisingly this interaction dominates the dynamics of the molecule in solution. The ground-state structure in solution is as noted in the solid state, *i.e.* (15). Warming results in the advent of two distinguishable fluxional processes in the variable-temperature n.m.r. The lower-energy process corresponds to the interconversion of (15) with its mirror image. This step is necessarily accompanied by an exchange of roles between bonding and non-bonding α-hydrogens. The second process is observed above ambient temperature and consists of scission of the Mo···H bond and a pyrazolyl–molybdenum ring flip. The ground-state structure is recovered but with an α-carbon of the other ethyl group now in a bonding role (Scheme 4). It is argued that $\Delta H^{\ddagger}$ for this process, 17 kcal mol^{-1} (R = H) or

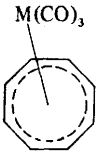


Scheme 4

19 kcal mol^{-1} (R = Ph), represents the strength of the C—H···Mo bond.[17] The ^{13}C n.m.r. spectrum of [(cyclo-octatetraene)$M(CO)_3$] (M = Mo[18] or W[19]) collapses

[16] R. D. Adams, M. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 6594.
[17] F. A. Cotton and A. G. Stanislowski, *J. Amer. Chem. Soc.*, 1974, **96**, 5074.
[18] F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Amer. Chem. Soc.*, 1974, **96**, 4723.
[19] E. W. Randall, E. Rosenberg, and L. Milone, *J.C.S. Dalton*, 1973, 1672.

symmetrically as the temperature is raised. This result argues against the familiar 1,2-shift mechanism previously held to explain the fluxional behaviour of the cyclo-octatetraene ligand. Instead a random rearrangement is proposed based on a common symmetrical intermediate (16) having an almost flat C_8H_8 ring.[18] The epimerization of the diastereoisomers of (17) follows a first-order rate law in toluene and DMF. The insensitivity of the rate constants to solvent effects may indicate a regular pentatopic rearrangement of the co-ordination skeleton.[20]



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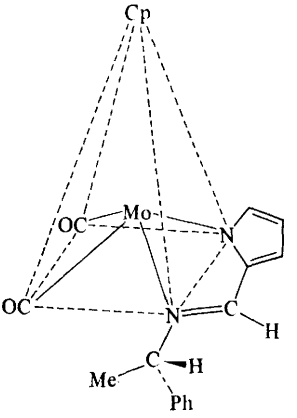
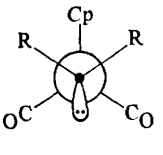


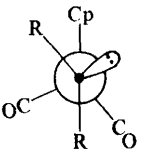
(17)

3 Group VII

The observation of four instead of two CO stretching vibrations in the i.r. spectra of $[(h^5\text{-}C_5H_5)Mn(CO)_2SR_2]$ (R = Me, Et, Pr^n, or Bu^n, or SR_2 = tetrahydrothiophen) is interpreted as indicative of the first known rotamers, (18) and (19), about an Mn—S bond. Exchange is evidently slow on the i.r. time-scale at normal temperatures. The spectra were insensitive to low temperature, and high-temperature experiments were not attempted.[21]



(18)



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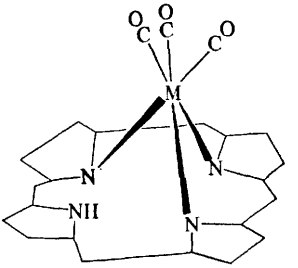


(20)

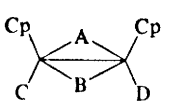
The complexes [(monohydrogen *meso*-tetraphenylporphinato)$Re(CO)_3$], [(HMP)-$Re(CO)_3$], and [(HMP)$Tc(CO)_3$] (HMP = monohydrogen mesoporphyrin IX

[20] H. Brunner and W. A. Herrmann, *J. Organometallic Chem.*, 1973, **63**, 339.
[21] I. S. Butler and T. Sawai, *Inorg. Chem.*, 1973, **12**, 1994.

dimethyl esterato), have ground-state structures based on (20). Above 299 K a fluxional process is evident from the n.m.r. which results in the collapse of the signals from the HMP bridge methine protons and from the β-pyrrole protons of the first compound. These observations are interpreted in terms of intramolecular movement of the $M(CO)_3$ moiety between the four available nitrogen donors with concomitant transfer of the N-proton.[22]

4 Group VIII: Iron Triad

Iron.—*Carbonyl and Isocyanide Complexes.* The question of the fluxional properties of polynuclear metal carbonyls is by no means a new one. In 1970 it received its most satisfactory explanation in terms of rapid bridge–terminal interchange of carbonyl groups. Although this model has been widely used, particularly with reference to dinuclear $[(h^5\text{-}C_5H_5)ML_2]_2$ species, several inconsistences and unexplained observations remained. In the current period Adams and Cotton have proposed a mechanism which fits fully and consistently the observed data for the series $[(h^5\text{-}C_5H_5)_2Fe_2(CO)_nL_{4-n}]$ [L = CO, CNR, or $P(OR)_3$].[23] From the joint points of view of convenience to the reader and limited space the experimental information available[23–25] is reviewed in tabular form (Table 4). The mechanism itself, however, will be dealt with here, whilst we have already mentioned its consistency in connection with fluxional molecules of Group VI metals.[11–13,16] Three hypotheses are necessary:



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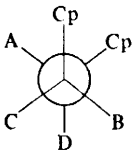

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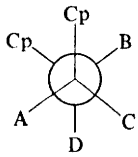

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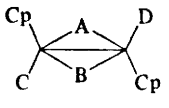

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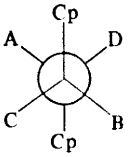

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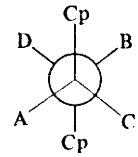

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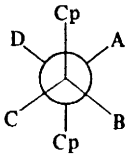

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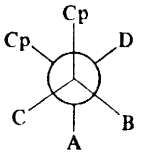

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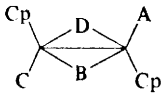
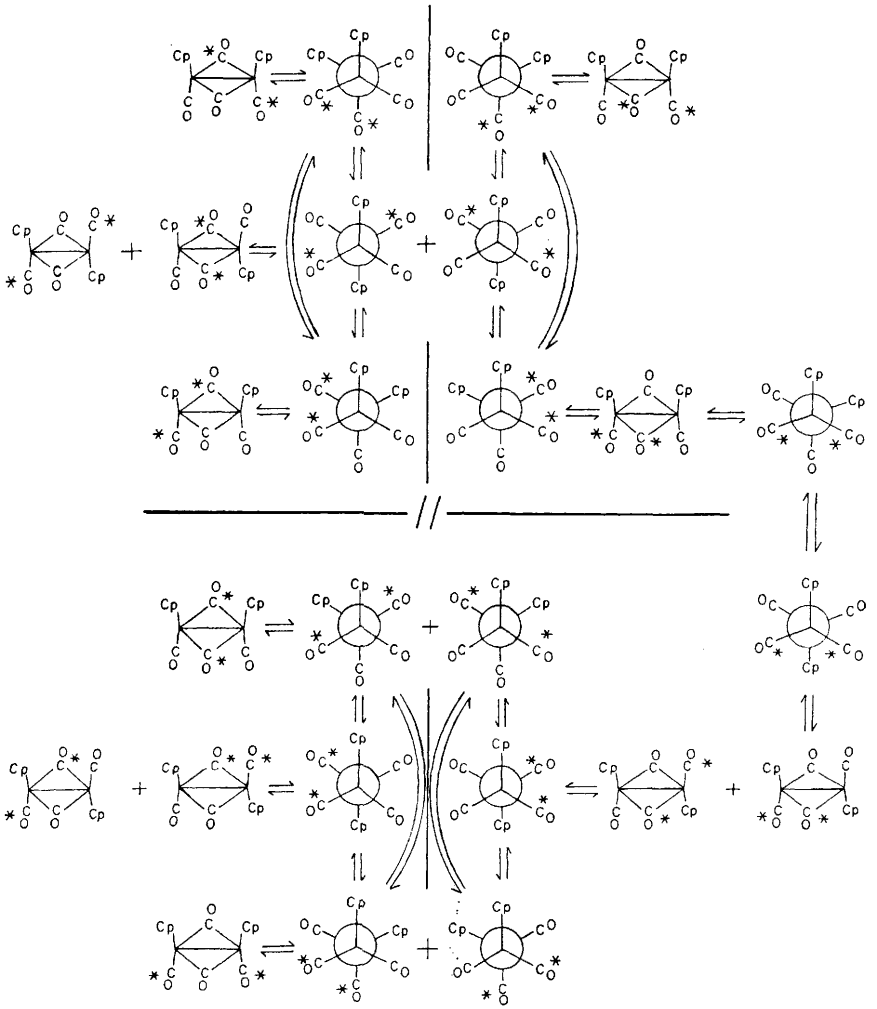


(29)

[22] M. Tsutsui and C. P. Hrung, *J. Amer. Chem. Soc.*, 1974, **96**, 2638.
[23] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 6589.
[24] F. A. Cotton, L. Kruczynski, and A. J. White, *Inorg. Chem.*, 1974, **13**, 1402.
[25] D. C. Harris, E. Rosenberg, and J. D. Roberts, *J.C.S. Dalton*, 1974, 2398.

(*a*) the two bridges open simultaneously and the unbridged species then rotates to the most easily accessible *staggered* conformation; thus a *cis*-isomer (21) must go to (22) or (23) whilst a *trans*-isomer (24) must go to (25) or (26); (*b*) rotations through $2\pi n/3$ (n = 1 or 2) are permitted and contribute significantly to the overall activation energy; thus (22) may give (27) or (28); (*c*) the resultant non-bridged rotamers close bridges simultaneously but with due observation of the principle of microscopic reversibility; thus since (21) goes directly to (22) or (23) [but not (27) or (28)] so (27) will generate, for example, (29) on closing bridges. These postulates are exemplified in the case of $[(h^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ in Scheme 5. Although there are many degeneracies here the Scheme may be used in other examples by substituting CO*



Scheme 5

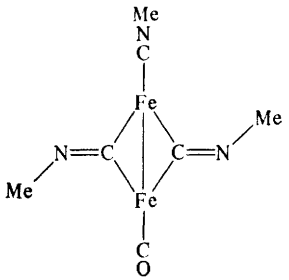
(Reprinted by permission from *J. Amer. Chem. Soc.*, 1973, **95**, 6589)

Table 4 *Examples of the consistency of the Adams–Cotton mechanism for the fluxional processes occuring in* $[(h^5\text{-}C_5H_5)_2Fe_2(CO)_nL_{4-n}]$[a]

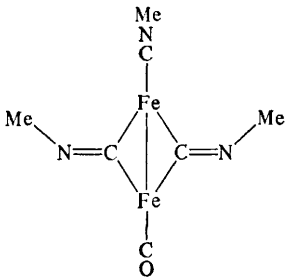
Complex	*Principal method used*	*Ground state*	*Processes occurring*	*Explanation offered specifically by Scheme 5*	*Ref.*
$[Cp_2Fe_2(CO)_4]$	^{1}H n.m.r.	(21) + (24) (A = B = C = D = CO)	Bridge–terminal CO interchange; *cis* ⇌ *trans* isomerization	Bridge–terminal interchange in the *trans*-isomer occurs uniquely and is the lowest-energy process. *cis* ⇌ *trans* conversion and bridge–terminal interchange in the *cis*-isomer occur in roughly the same temperature range	23
$[Cp_2Fe_2(CO)_2(CNMe)_2]$	^{1}H n.m.r.	(21) (A = B = CNMe; C = D = CO) + (24) (A = C = CO; B = D = CNMe)	(i)[b] Interconversion of Cp rings and simultaneous bridge–terminal interchange of CNMe groups in (24) (ii) (21) ⇌ (24) interconversion	(i) Analogous to bridge–terminal interchange in *trans*-isomer above (E_a = 19.8 kcal mol^{-1}; *cf.* E_a below) (ii) The mechanism shows that (21) and (24) (plus another 'unstable' isomer) form a specific closed set out of possibly 6 permutations (E_a = 23.0 kcal mol^{-1})	23
$[Cp_2Fe_2(CO)_3\{P(OR)_3\}]$ R = Ph R = Et	^{13}C n.m.r.	(21) [A = B = C = CO; D = P(OR)$_3$] + (24) [A = B = C = CO; D = P(OR)$_3$]	*cis–trans* isomerization and bridge–terminal CO scrambling occur with the same rate and activation parameters	In the presence of a non-bridging ligand the mechanism leads explicitly to the fact that isomerization and bridge–terminal interchange form a closed, cyclic process. This necessitates them having the same rate[24]	24 25

[a] See also comments on the $[Cp_2Mn_2(NO)_4]$, $[Cp_2Cr_2(NO)_2(CO)_2]$, and $[Cp_2Fe_2(CO)_4]$ series in the section on chromium.[11] [b] (i) is the lower-energy process; the explanations are then numbered accordingly.

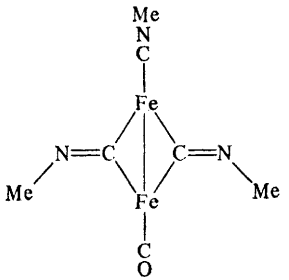
appropriately. Of particular note is that the *trans*-isomer may interchange terminal and bridging groups by opening bridges and reclosing *without* rotation as in (*b*), whereas for the *cis*-isomer rotation is necessary. In addition *cis–trans* isomerization must take place by internal rotation of the unbridged forms. The reader is now referred to Table 4. The dynamic processes occurring in $[(h^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNCMe_3)]$ contrast somewhat with those in Table 4. Although the exchange of isocyanide between metal atoms is arrested at 223 K ($\Delta G^{\ddagger}_{263}$ = 14 kcal mol^{-1}), *cis–trans* isomerization is still rapid even at 173 K and therefore has an upper-limit $\Delta G^{\ddagger}$ of 7 kcal mol^{-1} {*cf.* 10.5 kcal mol^{-1} for $[(h^5\text{-}C_5H_5)_2Fe_2(CO)_4]$}. However, in the absence of relative rates of bridge–terminal interchange for the *trans*- and *cis*-forms the $\Delta G^{\ddagger}$ results may be regarded as surprising without contradicting the Adams–Cotton mechanism.[26] An additional possibility in isocyanide complexes of this type is the occurrence of inversion about nitrogen. In the low-temperature limit the ^{1}H n.m.r. spectrum of $[(h^5\text{-}C_5H_5)_2Fe_2(CO)(CNMe)_3]$ clearly shows the *anti*-isomer (30) and one of either of two *syn*-forms (31) or (32). Warming results in the onset of



(30)



(31)

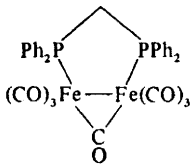


(32)

exchange between these forms, yielding $\Delta G^{\ddagger}_{193}$ = 10.4 ± 0.5 kcal mol^{-1} (*syn*) and $\Delta G^{\ddagger}_{193}$ = 10.0 ± 0.5 kcal mol^{-1} (*anti*). Interestingly there appears to be no bridge–terminal interchange in this complex. *syn*- and *anti*-Isomers were also characterized in the isomer (24; A = C = CO, B = D = CNMe) of $[(h^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)_2]$ and could be possible also in (21; A = B = CNMe, C = D = CO), where in addition the *anti*-isomer has been noted in the solid state.[27] Comparison of

[26] R. D. Adams, F. A. Cotton, and J. H. Troup, *Inorg. Chem.*, 1974, **13**, 257.
[27] F. A. Cotton and B. A. Frenz, *Inorg. Chem.*, 1974, **13**, 253.

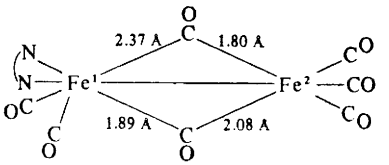
the bridge–terminal barriers for this complex (15—20 kcal mol^{-1}) with those for nitrogen inversion (*ca.* 10 kcal mol^{-1}) shows how little the latter will influence the rate of the former. No conclusion was reached on whether during bridge–terminal interchange a formerly terminal CNMe group bridges with the alkyl *syn* or *anti* to the metal to which it was terminally co-ordinated.[28] Room-temperature measurements on the i.r. time-scale indicate that the probable ground-state structure of $[Fe_2(CO)_7(Ph_2PCH_2PPh_2)]$ in solution is as found in the solid state (33). The ^{13}C n.m.r.



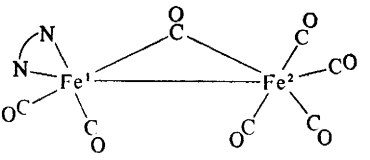
(33)

spectrum at the same temperature, however, consists of only a triplet (J_{P-C} = 5 Hz). It is deduced that scrambling of the carbonyl groups over all sites occurs in the fast-exchange limit. Cooling to 173 K does not arrest this process and, although detailed mechanistic conclusions were thus prevented, some kind of bridge–terminal interchange seems likely.[29]

Substituting the weakly π-acidic bipyridyl for two carbonyl groups in $[Fe_2(CO)_9]$ yields $[(bipy)Fe_2(CO)_7]$ (34) which is notable for the presence of a grossly unsymmetrical carbonyl bridge. Mechanistically this is interpreted in terms of a means of relieving the induced excess electron density on Fe-1. It is proposed that initially the intermediate (35) is formed. This would be more stable than the product arising



(34)



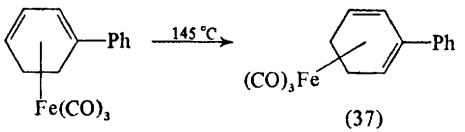
(35)

directly from simple substitution since the ensuing terminal carbonyl groups, being better π-acids than their bridging counterparts, would be better able to relieve excess electronic charge on Fe-1. Completion of an unsymmetrical bridge then leads to (34), whilst preserving the electron-density transfer pathway.[30]

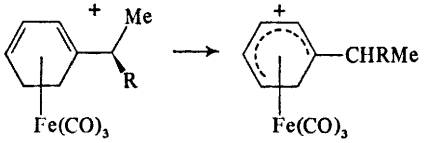
Diene Complexes. The fluxional behaviour of $[RFe(CO)_3]$ (R = 1,3-hexadiene, butadiene, or cycloheptatriene) results in a single ^{13}C n.m.r. CO signal in the high-temperature limit. The exchange, which probably involves carbonyl and/or diene rotation, can be arrested by cooling to give two signals corresponding to basal and apical sites in a square pyramid. Similar behaviour was noted for analogous PF_3

[28] R. D. Adams and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 249.
[29] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4422.
[30] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 1233.

complexes in Volume 3.[31] The hydrogen rearrangement reactions of (36) to give (37)[32] and of (38; R = H or Me) to give (39)[33] can both proceed *via* hydrogen abstraction by the metal to give a metal hydride intermediate. This route was well authenticated by deuterium isotope effects and trapping experiments in the case of (36), but the isomerization (38) to (39) does not occur *via* an *intramolecular* rearrangement of a stable hybride intermediate.

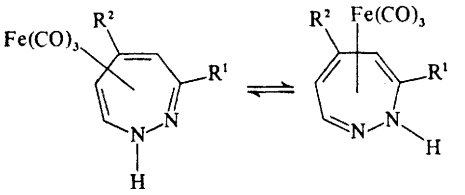


(36) (37)



(38) (39)

Large-ring Complexes. Variable-temperature n.m.r. studies of the 1(1*H*),2-diazepine complex (40; $R^1 = R^2 = H$) reveal the fluxional/tautomeric rearrangement shown in Scheme 6 ($\Delta G^{\ddagger}_{298} = 13.7 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.2 \pm 4.0$ cal K^{-1} mol^{-1}).



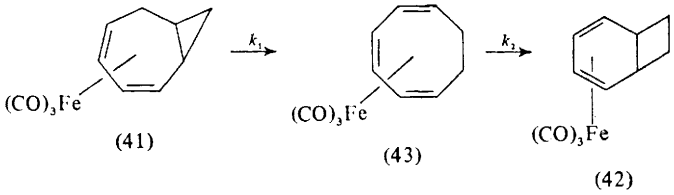
(40)

Scheme 6

The hydrogen shift is shown to be an essential prerequisite of the mechanism by the demonstration of the non-fluxional nature of molecules having N-substituents and also R^1 and $R^2 \neq H$. In these cases alternative sites give rise to isomers having differing energy contents, unlike those in Scheme 6. Concurrently with these observations it was found that the complex having $R^2 = Me$, $R^1 = H$ is fluxional whereas that having $R^2 = H$, $R^1 = Me$ is not, the latter having enforced stability of the structure shown in (40).[34]

[31] L. Kruczynski and J. Takats, *J. Amer. Chem. Soc.*, 1974, **96**, 932.
[32] T. H. Whitesides and J. P. Neilan, *J. Amer. Chem. Soc.*, 1973, **95**, 5811.
[33] C. R. Jablonski and T. S. Sorensen, *Canad. J. Chem.*, 1974, **52**, 2085.
[34] A. J. Carty, R. F. Hobson, H. A. Patel, and V. Snieckus, *J. Amer. Chem. Soc.*, 1973, **95**, 6835.

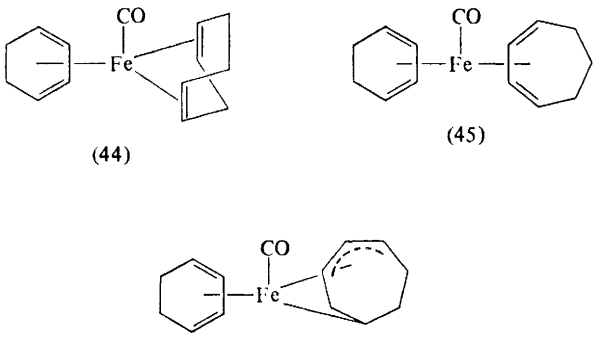
The thermal isomerization of (41) to (42) ($k_1 = 1.8 \times 10^{-5}$ s^{-1} at 393 K) proceeds *via* (43), production of which is rate controlling (Scheme 7). This is clearly shown by



(41) (43) (42)

Scheme 7

g.c. and by kinetic analysis of the data. Values of k_2 were previously known, thereby enabling time–concentration relationships to be calculated for (43) which agreed with the corresponding relationships for the peak postulated as arising from (43) in the g.c. The detailed mechanism can involve either a metal hydride intermediate or can proceed *via* oxidative addition of iron to the cyclopropane ring.[35] At 323 K the 1,4-diene complex (44) isomerizes to the 1,3-form (45) plus (46) ($k_{obs} = 3.6 \times 10^{-4}$ s^{-1}). At higher temperatures (363 K) complex (46) rearranges further to give a final equilibrium mixture consisting of 90% (45) and 10% (46).[36]



(44) (45) (46)

Five-co-ordinate Complexes. Fluxional rearrangements in compounds of this class, whose ground-state structures are expected to be trigonal bipyramidal, have been frequently noted. However, attempts to study these (probably Berry-type) processes have been repeatedly thwarted by their apparently very low activation energies. For example, the process which averages the axial and equatorial ^{13}C n.m.r. signals of [Fe(CO)$_5$] at ambient temperature has not been arrested even at *ca.* 100 K![37] It has recently been found, however, that for XPF_4 (X = R_2N or RS) compounds the barrier to rotation about the P—X bond makes a significant contribution to the

[35] M. Brookhart, R. E. Dedmond, and B. F. Lewis, *J. Organometallic Chem.*, 1974, **72**, 239.
[36] B. F. G. Johnson, J. Lewis, T. W. Matheson, I. E. Ryder, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1974, 269.
[37] P. Meakin and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 7272.

overall activation energy.[38] Two groups[39,40] have extended this rationale to encompass [(olefin)Fe(CO)$_4$] complexes, since the barriers to olefin rotation are known to be fairly substantial and might therefore contribute to the total barrier height to the extent of making the low-temperature limit accessible. This was indeed observed in the carbonyl ^{13}C n.m.r. spectra of a variety of complexes (Table 5), many of which, in

Table 5 *Data for fluxional* [(olefin)Fe(CO)$_4$] *molecules*

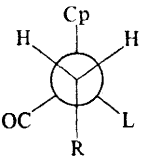
Olefin	*Temperature*/K *for limiting spectrum*	E_a/kcal mol^{-1}	*Ref.*
Styrene	148	—	39
CH_2=CHPh	< 193	'low'	39
Ethyl acrylate	193	11.1	40
Diethyl fumarate	243[40]	14.3,[40] ~13.0[39]	39,40
Dimethyl fumarate	*a*	~13.0	39
Diethyl maleate	243	14.1	40
F_2C=CClF	283	—	40
Cl_2C=CF_2	'ambient'	> 15	39

[a] Exchange barrier 'can be estimated . . . at 263 K'.

fact, have very moderate ground-state limiting temperatures, giving rise to spectra consistent with a trigonal bipyramid having equatorial olefin. In agreement with the theory the overall (Berry plus olefin rotation) activation energies were found to correlate well with the π-acceptor ability of the olefin (Table 5). Evidence was also presented[39] which clearly indicates that a Berry rearrangement and olefin rotation are interdependent and that the results are not simply due to carbonyl–olefin exchange. The ground-state structure of [M(NO)(diphos)$_2$]$^+$ (M = Fe or Ru) gives rise to an AA′BB′ proton-decoupled ^{31}P n.m.r. spectrum; T = 188 K (Fe) or 173 K (Ru). This is consistent with a trigonal bipyramid having equatorial NO. Averaging of equatorial and axial sites in the high-temperature limit is ascribed to a Berry turnstile rotation as opposed to a single twist mechanism. This information was deduced from the phosphorus-decoupled ^{1}H n.m.r. of the chelate 'backbone' in the region of fast exchange by comparison of the observed values of the vicinal coupling constants with those calculated from the Karplus equation and then averaged according to the respective mechanisms.[41]

General. Trends in J_{AX} and J_{BX} (A, B = methylene protons, X = ^{31}P) with the steric nature of R and L in [(h^5-C_5H_5)Fe(CO)L(CH_2R)] [R = $SiMe_3$, L = PPh_3 or $P(OMe)_3$; R = Ph, L = PPh_3, $PMePh_2$, or $P(OMe)_3$] suggest the presence of three rotamers (47)—(49) which at 'infinite' temperature are probably more or less equally populated. At low temperature the disparity between J_{AX} and J_{BX} would indicate preference for (47) or (49) as the most stable rotamer; in fact (47) receives most

[38] E. L. Muetterties, P. Meakin, and R. Hoffman, *J. Amer. Chem. Soc.*, 1972, **94**, 5674.
[39] S. T. Wilson, N. J. Coville, J. R. Shapely, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1974, **96**, 4038.
[40] L. Kruczynski, L. K. K. LiShingMan, and J. Takats, *J. Amer. Chem. Soc.*, 1974, **96**, 4006.
[41] P. R. Hoffman, J. S. Millar, C. B. Ungermann, and K. G. Caulton, *J. Amer. Chem. Soc.*, 1973, **95**, 7902.



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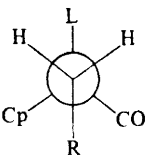

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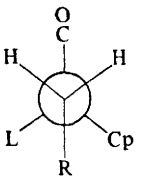
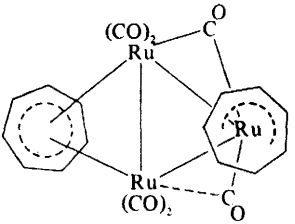


(49)

support. It was also found that at room temperature bulkier phosphines and the bulkier $SiMe_3$ group tend to favour population of (47).[42]

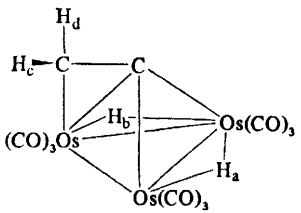
Ruthenium.—Takats *et al.* have extended their ^{13}C n.m.r. work on the [(diene)-$Fe(CO)_3$][31] and [(olefin)$Fe(CO)_4$][40] systems described above to include the analogous ruthenium complexes. Generally the same results were found for, and the same theories could be applied to the respective type of complex. Activation energies in the olefin complexes are higher for ruthenium than for iron and this is attributed to an increased metal-*d*–olefin-π^* interaction in the ruthenium–olefin bond. This, of course, supports the coupled olefin rotation–Berry rearrangement mechanism outlined above.[43] A preliminary report on $[(C_7H_7)(C_7H_9)Ru_3(CO)_6]$ (50) has tentatively



(50)

identified three fluxional processes. Rotation of the C_7H_9 ring relative to the Ru_3 triangle can be arrested at *ca.* 180 K ($\Delta G^{\ddagger}_{218} = 9.5 \pm 0.5$ kcal mol^{-1}) but that of the C_7H_7 ring is still apparent at this temperature. Carbonyl exchange is regarded as 'probable' but without any direct evidence.[44]

Osmium.—In the last volume of these Reports we examined an interesting series of reactions between $[Os_3(CO)_{12}]$ and ethylene or benzene. In the current period these



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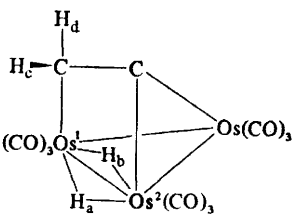
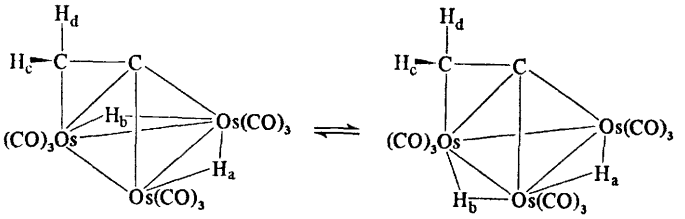


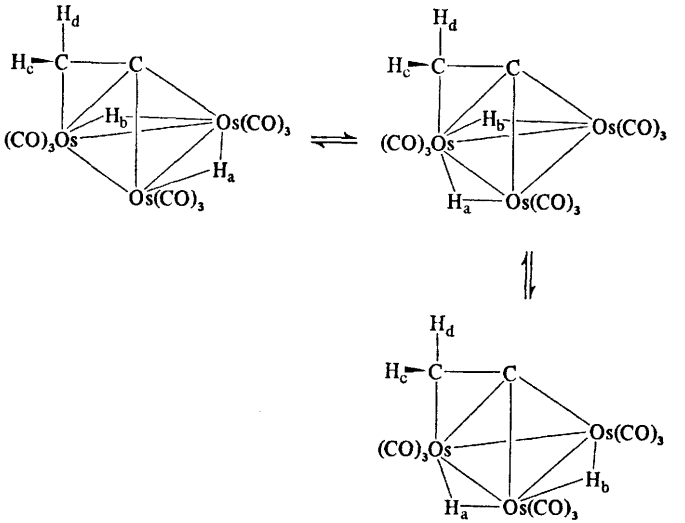
(52)

[42] K. Stanley and M. C. Baird, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 1111.
[43] L. Kruczynski, J. L. Martin, and J. Takats, *J. Organometallic Chem.*, 1974, **80**, C9.
[44] T. H. Whitesides and R. A. Budnik, *J.C.S. Chem. Comm.*, 1974, 302.

and similar reactions have been investigated in greater detail. In particular, the fluxional character of the product of the reaction with ethylene, $[H_2Os_3(C_2H_2)(CO)_9]$, has received most attention. A crystal structure determination supports the ground-state structures (51) or (52). In the high-temperature limit (345 K) H_c–H_d exchange occurs (E_a = 85.3 kJ mol^{-1}, $\Delta H^{\ddagger}$ = 82.4 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 32.4 J K^{-1} mol^{-1}), but only limited broadening of the H_a and H_b resonances could be observed even at 388 K. Faster H_c–H_d interconversion in (51) is accommodated by a probable combination of two mechanisms (Schemes 8a and 8b). Scheme 8a exchanges H_c and



Scheme 8a



Scheme 8b

H_d but not H_a and H_b, whereas Scheme 8b leads to simultaneous exchange of H_a with H_b and H_c with H_d. The equivalent to Scheme 8a for structure (52) would probably involve interchange of the CH_2 group between Os-1 and Os-2.[45]

5 Group VIII: Cobalt Triad

ML_5 Complexes.—Since their original report[46] on $[Rh\{P(OMe)_3\}_5]^+[BPh_4]^-$, the first fluxional C_{3v} ML_5 species to be observed in the slow exchange limit, Meakin

[45] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1974, 1415.

[46] J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, 1973, **95**, 1344 (see also Vol. 3 of these Reports).

and Jesson have proceeded to a thorough investigation of analogous systems using ^{31}P n.m.r. We include here, in fact, data on Ni, Pd, and Pt complexes.[47–49] The systems studied and activation parameters obtained are summarized in Table 6. The

Table 6 *Data for the intramolecular rearrangement in* d^8 ML_5 *cations (from ref.* 49)

Metal	L	$\Delta G^{\ddagger}$/kcal mol^{-1}	*Temperature*/K
Co^+	$P(OCH_2)_3CMe$	10.0	200
Rh^+	$P(OMe)_3$	7.5	200
	$P(OCH_2)_3CMe$	7.8	153
	$P(OCH_2)_3CEt$	7.8	150
	$P(OEt)_3$	9.9	208
	$P(OCH)_3(CH_2)_3$	10.3	210
	$P(OBu^n)_3$	11.1	228
Ir^+	$P(OMe)_3$	8.0	200
	$P(OCH_2)_3CMe$	8.4	200
	$P(OEt)_3$	10.4	215
	$P(OBu^n)_3$	11.5	231
Ni^{2+}	$P(OCH_2)_3CMe$	~8.3	200
	$P(OCH_2)_3CEt$	8.3	200
	$P(OCH)_3(CH_2)_3$	10.9	220
Pd^{2+}	$P(OCH_2)_3CMe$	5.7	127
	$P(OMe)_3$	6.2	138
	$P(OEt)_3$	8.0	200
Pt^{2+}	$P(OMe)_3$	6.5	143
	$P(OCH_2)_3CMe$	7.0	147
	$P(OEt)_3$	9.2	199

intramolecular rearrangement, which is characterized as such by the retention of ^{31}P–^{103}Rh coupling in the region of fast exchange, takes place in all cases *via* exchange of a pair of equatorial ligands with the axial groups. As might be expected, barriers increase with the size of the phosphine. Variation of anion in several cases (M = Co,[49] Rh,[47] or Ni[49]) produces negligible differences in exchange rates and leads to the probably general conclusion that ion-pairing is not responsible for induced rigidity at low temperatures. For a given L barriers are fairly insensitive to the metal. However, members of the cobalt triad do each have a higher barrier than the corresponding member of the nickel triad. Above 273 K the ^{31}P n.m.r. doublet observed for $[Rh\{P(OMe)_3\}_5]^+[BPh_4]^-$ in the fast intramolecular exchange limit collapses to a singlet. Addition of free phosphite does not affect the exchange rate. These observations indicate a dissociative intermolecular process, but whether this involves an axial or an equatorial group could not be determined.[48] These results are worth contrasting with those for $[Rh_2\{P(OMe)_3\}_8]$ (each rhodium atom has local C_{3v} symmetry) where intermolecular exchange uniquely of equatorial phosphites has been characterized (see ref. 55 later).

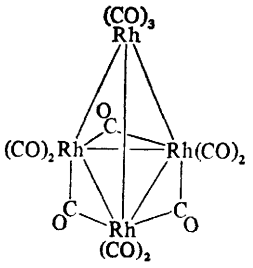
Cobalt.—Thermal rearrangement of cobaltaboranes involves migration of carbon atoms over the cobalt–boron polyhedra. Kinetic data on a series of non-icosohedral cobaltaboranes and the parent carbaboranes reveal that inclusion of the cobalt atom

[47] P. Meakin and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 7272.
[48] P. Meakin and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 5751.
[49] J. P. Jesson and P. Meakin, *J. Amer. Chem. Soc.*, 1974, **96**, 5760.

lowers the barriers to rearrangement. Thus, [2-(h^5-C_5H_5)-2-Co-1,6-$C_2B_7H_9$] rearranges more easily than 1,6-$C_2B_8H_{10}$. In addition it was found that ΔH^+ and ΔS^+ for B_6—B_8 and B_{10} systems were very similar, thereby suggesting similar mechanisms in each case. Like the parent twelve-atom compounds $[B_{12}H_{12}]^{2-}$ and $C_2B_{10}H_{12}$, [(h^5-C_5H_5)$CoC_2B_9H_{11}$], however, has a higher rearrangement barrier.[50] Variable-temperature ^{19}F and ^1H n.m.r. studies of complexes of the type [(h^5-C_5H_5)-CoI(L)R_F] (L = tertiary phosphine, R_F = perfluoroalkyl) indicate hindered rotation about the cobalt–carbon bond. The results are consistent with others from the same authors, *i.e.* that the large phosphines, notably PPh_3, favour population of the rotamer analogous to (47) (for CO read I, for H read F, and for R read CF_3).[51]

Rhodium.—The study of the type of molecular behaviour dealt with in this chapter has been facilitated in recent years by the increasing commercial availability of ^{13}C n.m.r. facilities. The attractiveness of rhodium compounds (^{103}Rh, 100% abundant, $I = \frac{1}{2}$) for study by this technique is obvious and has stimulated work on a variety of systems. Although fascinating from the chemist's point of view this has made the reviewer's task of classification rather difficult. Apart from one obvious category we have been forced into the use of a (very) miscellaneous section.

Cluster Compounds. The ^{13}C n.m.r. spectrum of $[Rh_4(CO)_{12}]$ at 188 K is consistent with the C_{3v} structure (53) determined by *X*-ray analysis. Above *ca.* 273 K bridge–terminal carbonyl scrambling occurs rapidly and by a single process.[52,53] Two processes, however, were identified in the case of $[RhCo_3(CO)_{12}]$. That of lower energy involves exchange of bridging carbonyl sites within the triangular faces $RhCo^1Co^2$, $RhCo^2Co^3$, and $RhCo^3Co^1$ in (54) such that the carbonyls on rhodium remain



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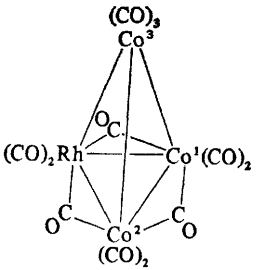
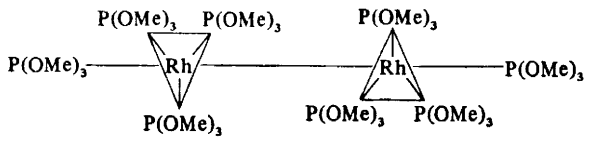


(54)

associated with that metal but exchange with each other. At higher energies the mechanism is extended to the $Co^1Co^2Co^3$ face, thereby scrambling carbonyls over all sites.[53] In contrast to these complexes $[Rh_{12}(CO)_{20}(\mu_2\text{-}CO)_2(\mu_3\text{-}CO)_8]^{2-}$ remains rigid at 385 K.[54] $[Rh_2\{P(OMe)_3\}_8]$ (55) is rigid at room temperature as shown by an

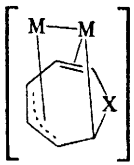
[50] D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1974, **96**, 3085.
[51] R. J. Burns, P. B. Bulkowski, S. C. V. Stevens, and M. C. Baird, *J.C.S. Dalton*, 1974, 415.
[52] J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J.C.S. Chem. Comm.*, 1973, 807.
[53] B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J.C.S. Chem. Comm.*, 1974, 441.
[54] P. Chini, S. Martinengo, D. J. A. McCaffrey, and B. T. Heaton, *J.C.S. Chem. Comm.*, 1974, 310.



(55)

A_3BX (A, B = ^{31}P, X = ^{103}Rh) ^{31}P n.m.r. spectrum. At *ca.* 373 K the A part of the spectrum has collapsed to a singlet whereas the B part retains ^{103}Rh coupling. These changes are reversible. Addition of $P(OMe)_3$ causes no change in the spectrum at room temperature but the free-ligand and bound-A $P(OMe)_3$ signals coalesce at 373 K. These results indicate reversible intermolecular exchange specifically of the equatorial phosphites.[55] Since each rhodium atom has local C_{3v} symmetry it is worth contrasting these results with those for $[Rh\{P(OMe)_3\}_5]^+$ where intra- and intermolecular exchange have been characterized.[47,48] Unfortunately, in the intermolecular process in this complex it was indeterminate whether axial or equatorial ligands exchanged.[48]

Miscellaneous. High-temperature ^1H and ^{13}C n.m.r. of [56; M = (Cp)Rh or M_2 = (Cp)Rh(μ-H)Rh(Cp), X = CH_2CH_2; M = (Cp)Rh, X = CH_2] are consistent with one rearrangement process whereby only the metal–metal axis oscillates relative to the dienyl ring. The cyclopentadienyl signals, for instance, remain inequivalent at all temperatures. These results may be contrasted with those from similar iron complexes (56; M = $Fe(CO)_3$, X = CH_2CH_2) where in the high-temperature limit all the carbonyls become equivalent. Thus at least one other



(56)

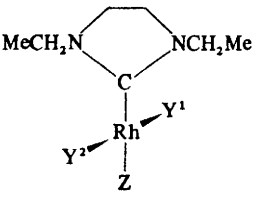
process must occur.[56] Variable-temperature ^1H n.m.r. studies of cationic and neutral complexes $[M(all)_2L_2][BF_4]$ and $[M(all)_2(X^1X^2)]$ (all = h^3-allyl or 2-methylallyl, L = Group V donors or MeCN, X^1X^2 = tropolonate or pyridine-2-carboxylate) indicate slightly different fluxional characteristics. The cationic compounds undergo 'left–right' (*syn–syn* plus *anti–anti*) exchange *via* dissociation of one L followed by a Berry pseudorotation of the resulting formally five-co-ordinate species. In the neutral compounds both this (*via* X^1–X^2 dissociative exchange) and concomitant *syn–anti* exchange were noted.[57]

The compounds of general formula $[Rh(RNC)_4(tcne)]^+X^-$ exhibit temperature-dependent ^1H n.m.r. spectra that can be interpreted in terms of restricted olefin rotation about the rhodium–olefin bond in what was decided was a 'time-averaged'

[55] R. Mathieu and J. F. Nixon, *J.C.S. Chem. Comm.*, 1974, 147.
[56] J. Evans, B. F. G. Johnson, J. Lewis, and R. Watt, *J.C.S. Dalton*, 1974, 2368.
[57] M. Green and G. J. Parker, *J.C.S. Dalton*, 1974, 333.

square pyramid ($\Delta G^{\ddagger}_{306}$ = 16.6 kcal mol^{-1} for R = Me, X = BPh_4). Substitution by PPh_3 to give $[Rh(RCN)_2(PPh_3)_2(tcne)]^+X^-$ induces rigidity in the metal–olefin bond, as shown by a static spectrum in the range 198—322 K. However, in analogous phosphine compounds containing fumaronitrile instead of tcne olefin rotation can once more be recognized. A stronger metal–olefin π-interaction is known to oppose olefin rotation. These results were therefore ascribed to the overall π-characteristic of the metal–olefin bond resulting from the combined influences of the π-acidity of the olefin and the basicity of the transition-metal moiety.[58]

Rotation about the metal–carbon bond of the carbene complexes $[Rh(L^{Et})Y^1(Y^2)Z]$ (57; L^{Et} = $\overline{CN(Et)CH_2CH_2NEt}$; Y^1 = Y^2 or $Y^1 \neq Y^2$; Y^1, Y^2, Z are

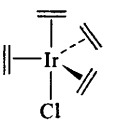


(57)

many combinations of L^{Et}, CO, PPh_3, cod, and Cl) can be induced at high temperatures (*ca.* 353 K). In the case of *trans*-$[Rh(L^{Et})_2(CO)Cl]$, $E_a \leqslant 10$ kcal mol^{-1}, $\Delta G^{\ddagger}_{363} \approx 16$ kcal mol^{-1}, $\Delta H^{\ddagger} < 9$ kcal mol^{-1}, and $\Delta S^{\ddagger} \approx 20$ cal K^{-1} mol^{-1}. The results support evidence from crystal structure determinations that the metal–carbon bond in such complexes does not have substantial double-bond character.[59]

Variable-temperature ^1H n.m.r. studies of [(cod)Rh(mnt-Me)] (mnt-Me = *S*-methylmaleonitriledithiolate) are diagnostic of two rearrangement processes. Loss of ^{103}Rh coupling to the *S*-methyl protons at *ca.* 273 K means that one process is almost certainly cleavage of the Rh—S bond before recombination. The other process could not be slowed down on the n.m.r. time-scale at 193 K and is probably inversion about sulphur.[60]

Iridium.—Proton T_1 measurements on solid $[IrCl(C_2H_4)_4]$ (58) show two minima in T_1 *vs.* $1/T$ plots. Thus two processes by which relaxation is facilitated are arrested as the temperature is raised. These are ascribed to rotation of axial and equatorial ethylene by 180° flips. Values of E_a are $< 1.6 \pm 0.1$ kcal mol^{-1} (axial C_2H_4) and 5.3 ± 0.2 kcal mol^{-1} (equatorial C_2H_4). These agree with earlier solution work (see Volume 3) where axial olefin rotation could not be arrested at low temperatures.[61]



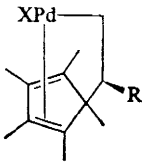
(58)

[58] T. Kaneshima, K. Kawakami, and T. Tanaka, *Inorg. Chem.*, 1974, **13**, 2198.
[59] M. J. Doyle and M. F. Lappert, *J.C.S. Chem. Comm.*, 1974, 679.
[60] D. G. VanDerveer and R. Eisenberg, *J. Amer. Chem. Soc.*, 1974, **96**, 4994.
[61] K. van Putte and A. van der Ent, *Inorg. Chim. Acta*, 1973, **7**, 497.

6 Group VIII: Nickel Triad

General.—Details of $[ML_5]^+X^-$ (M = Ni, Pd, or Pt; L = tertiary phosphites) systems can be found under the appropriate heading in Section 5.[48,49]

Palladium.—The complexes [59; X = acac, Cl_2-(59)(dimer), R = Ph or *p*-tolyl] formed by reaction of α-butyne, arylmercury, and palladium dichloride (followed appropriately by metathesis with $acac^-$) exhibit a fluxional process which can be arrested on the n.m.r. time-scale at 273 K. ^1H N.m.r. results are consistent with alternating co-ordination of palladium between the two double bonds in the *dihapto*-cyclopentadienyl ring. At higher temperatures (343 K) irreversible conversion of (59; R = Ph) into (60) occurs. This was shown to proceed *via* the intermediacy of (for instance) (61).[62] A rather similar type of compound to (59) has been shown to



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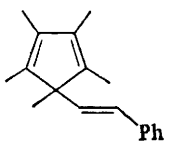

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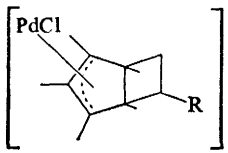
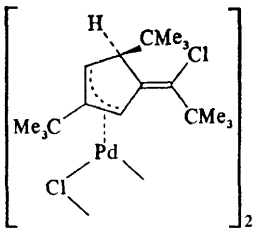


(61)

undergo intramolecular interchange of palladium between endo- and exo-cyclic h^3-allylic systems, *i.e.* in (62) and (63). The process can be arrested at 243 K and has



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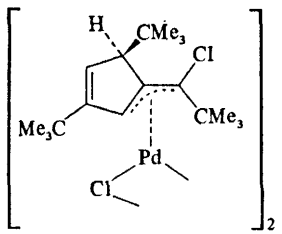
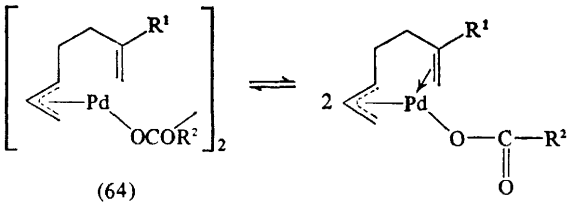


(63)

E_a = 41.5 kJ mol^{-1}.[63] The palladium(II) hepta-2,6-dienyl complexes (64) exist in solution at normal temperatures as a rapidly equilibrating mixture of the h^3-dimer and h^5-monomer forms (Scheme 9). The position of equilibrium is seen to be affected



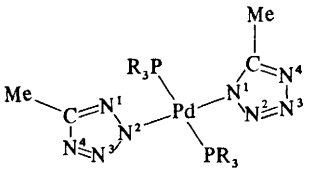
(64)

Scheme 9

[62] T. Hosakawa, C. Calvo, H. B. Lee, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1973, **95**, 4914.
[63] P. M. Bailey, B. E. Mann, A. Segnitz, K. L. Kaiser, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1974, 567.

by the substituents R^1 and R^2 and by the solvent.[64] Low-temperature ^1H n.m.r. measurements on $[Pd(PBu^t_2Ph)_2]$ show two signals for the phenyl *ortho* protons at 213 K, thereby indicating restricted rotation about the P—Ph bond. Similar effects were noted in the case of the P—Bu^t bond. Whilst interesting in themselves these results did not contribute favourably to the authors' main quandary, *i.e.* a large disparity in PPdP bond angles of 176° and 158° in the above compound and in $[Pd\{P(C_6H_{12})_3\}_2]$ respectively.[65]

$[(R_3P)_2PdX_2]$ (R_3P = a large range of tertiary phosphines, X = 5-methyl- or 5-trifluoromethyl-tetrazolate) exhibits *cis–trans* and linkage isomerization in solution. The latter depends on which combination of N-1 and N-2 is bound, for example (65). It was found that linkage isomerization is faster than phosphine exchange in the

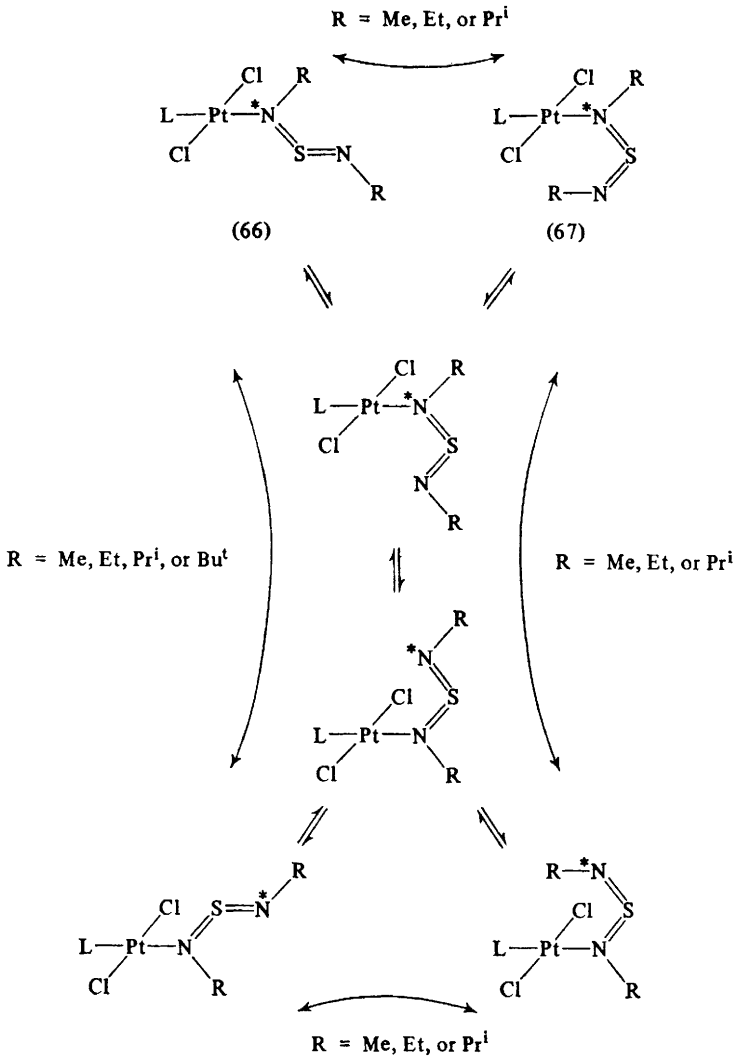


(65)

presence of free phosphine and that the opposite pertains in the absence of catalyst. The principle aim of the work, however, was elucidation of the uncatalysed and phosphine-catalysed *cis* $\rightleftharpoons$ *trans* mechanisms with the use of the 5-substituent on tetrazole as an n.m.r. probe. In this respect conductimetric measurements confirmed ionic species in solution but only in the presence of added phosphine. Thus in the catalysed pathway consecutive displacement of X^- by phosphine (see the platinum section below) seems feasible, whereas in the uncatalysed pathway phosphine is displaced by solvent to give the intermediate. The results appear compatible with others from the same laboratory (see ref. 71 below) which propose consecutive displacement of anion *and* phosphine in the isomerization of analogous $[(R_3P)_2MX_2]$ species.[66]

Platinum.—^1H and ^{13}C n.m.r. studies of the dialkylsulphurdi-imine complexes $[PtCl_2L(R{-}N{=}S{=}N{-}R)]$ (L = Group IV or V donors) reveal the presence of two isomers (66) and (67) for R = Me, Et, or Pr^i, but only one (66) for R = Bu^t. At temperatures between 253 and 303 K the former complexes undergo fast exchange between the two forms. Retention of coupling to ^{195}Pt confirms that the mechanism is intramolecular, and double-resonance experiments show that the same nitrogen remains co-ordinated, *i.e.* that each R retains a separate identity. On heating the complex having R = Bu^t (> 333 K) all the methyl signals broaden. These results indicate exchange between nitrogens. In fact this 'nitrogen-jump' process also gets under way on heating the other complexes. The mechanism is summarized in Scheme 10.[67]

[64] R. P. Hughes, T. Jack, and J. Powell, *J. Organometallic Chem.*, 1973, **63**, 451.
[65] A. Immirzi and A. Musco, *J.C.S. Chem. Comm.*, 1974, 400.
[66] D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1974, **96**, 6298.
[67] J. Kuyper and K. Vrieze, *J. Organometallic Chem.*, 1974, **74**, 289.



Scheme 10

A thorough study of olefin rotation barriers in [PtCl(acac)(olefin)] and [$PtCl_2$L-(olefin)] (the olefins are monosubstituted, 1,1- or *cis*- or *trans*-disubstituted, or tri-substituted) reveal the expected upward trend with increasing bulk and also with electronegativity of the substituent. The orientation of the olefin in the ground state does not follow strictly the same trends, the most populated isomers being found for relatively small but electronegative substituents.[68]

There exists some ambiguity concerning the nature of the *cis–trans* isomerization of square-planar [L_2MX_2] (M = Pd or Pt) species in the presence of a catalyst L′.

[68] J. Ashley-Smith, Z. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 128.

Two mechanisms have been proposed: (*a*) consecutive displacement of X (Scheme 11), which should provide for mixing of L and L′, and (*b*) fluxional rotation of a

$$cis\text{-}[MX_2L_2] \underset{X}{\overset{L'}{\rightleftharpoons}} [MXL_2L']^+ \underset{L}{\overset{X}{\rightleftharpoons}} trans\text{-}[MX_2LL']$$

Scheme 11

distorted five-co-ordinate intermediate $[L_2L'MX_2]$ in which the M—L′ bond is unique. Criticism of (*a*) during the current period is based upon the failure to observe phosphine mixing by the addition of PEt_3 to *cis*-$[PtCl_2(PPh_3)_2]$ and also the failure of Cl^- to react rapidly with $[PtCl(PEt_3)_3]^+$. Since the *cis–trans* isomerization of $[PtCl_2(PEt_3)_2]$ in the presence of PEt_3 is very fast, theoretically so too should be the latter reaction.[69] However, the validity of these criticisms has in turn been criticized.[70] The position of the equilibrium

$$[PtCl(PR_3)_3]^+ + Cl^- \rightleftharpoons cis\text{-}[PtCl_2(PR_3)_2] + PR_3$$

has been shown to depend strongly on the thermodynamic stability of the complexes on either side rather than on the kinetic effect of displacement by Cl^-. Thus, in the case of R = Et, the left-hand side is highly favoured. Solutions of *cis*-$[PtCl_2(PEt_3)_2]$ and PPh_3, on the other hand, favour the right-hand side. Concerning the apparent failure of PEt_3 to displace PPh_3 from *cis*-$[PtCl_2(PPh_3)_2]$, the equilibrium

$$cis\text{-}[PtCl_2(PPh_3)_2] + 3PEt_3 \qquad [PtCl(PEt_3)_3]^+Cl^- + 2PPh_3$$

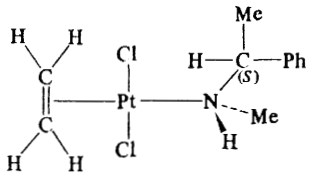
lies in fact well to the right, yet addition of methanol causes precipitation of *cis*-$[PtCl_2(PPh_3)_2]$ since *this is the least soluble complex*. These particular criticisms of consecutive displacement of X are therefore certainly unfounded. In cases where there is evidently less disparity in solubility or thermodynamic properties, *i.e.* on mixing 1 : 1 molar ratios of *cis*-$[\{(MeO)_3P\}_2MCl_2]$ and *cis*- plus *trans*-$[(MePPh_2)_2MCl_2]$ (M = Pd or Pt) or various ratios of $(MeO)_3P$ and $[(MePPh_2)_2PdCl_2]$, the mixed product *cis*-$[\{(MeO)_3P\}(MePPh_2)MCl_2]$ is indeed found.[71] The authors of this paper consider that all the available data in this field still do not indicate a unique mechanism. Rather, as well as (*a*) and (*b*), a third mechanism (*c*), involving consecutive displacement of L by L′, is feasible. Mechanism (*a*) should dominate in polar media when L′ is a strong base and (*c*) in non-polar media when X^- is strongly basic. The remaining pathway (*b*) may be taken in non-polar solvents when L and L′ are roughly equal in basic properties. Intuitively, at least, one feels satisfied with these conclusions. Finally it has been shown that the reaction

$$cis\text{- or } trans\text{-}[PtCl_2(PEt_3)_2] + L + NaClO_4 \longrightarrow [PtClL(PEt_3)_2]^+ClO_4^- + NaCl$$

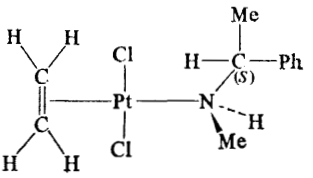
proceeds with retention of configuration. This is quite certain in the case of the *trans*-complex and probably so also for the *cis*, although in this case isomerization to the *trans*-isomer occurs rapidly. Thus it may be seen that isomerization in mechanism (*a*) can take place in the intermediate or in the final step of Scheme 11.[72]

[69] W. J. Louw, *J.C.S. Chem. Comm.*, 1974, 353.
[70] J. Powell and D. G. Cooper, *J.C.S. Chem. Comm.*, 1974, 749.
[71] D. A. Redfield and J. H. Nelson, *J. Amer. Chem. Soc.*, 1974, **96**, 6219.
[72] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Canad. J. Chem.*, 1974, **52**, 692.

Co-ordination of (*S*)-*N*-methyl-α-methylbenzylamine to platinum(II) produces an 85 : 15 mixture of epimers (68) and (69). Equilibration between these forms occurs very rapidly at room temperature, but at 223 K 15% of (68) was converted into (69) over a period of one hour.[73]



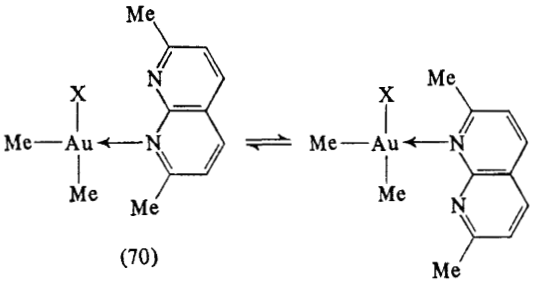
(68)



(69)

7 Gold

At room temperature in CH_2Cl_2 or $CHCl_3$ solution the complexes $[Me_2AuX(dmn)]$ (dmn = 2,7-dimethyl-1,8-naphthyridine, X = Cl, Br, I, OCN, SCN, or SeCN) (70) exhibit ^1H n.m.r. spectra which consist of a methyl singlet and an AB quartet from the dmn ligand and two Au–Me singlets. At low temperatures (*ca.* 183 K) the dmn signals split into two AB patterns and two methyl singlets. This is consistent with the slowing down of the exchange process shown in Scheme 12. The authors do not



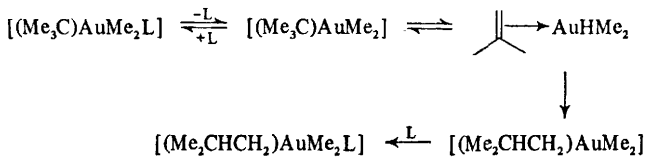
(70)

Scheme 12

indicate with certainty the relative orientation of the dmn and Me_2AuX units although, as far as the ligands X and Me influence the chemical shift of the dmn methyl signals, only a perpendicular orientation can explain the results.[74]

Trialkylgold compounds of the type $[RMe_2Au(PPh_3)]$ undergo three rearrangement reactions: alkyl isomerization (*e.g.* R = $Bu^t \rightarrow R = Bu^i$), reductive elimination of two alkyls, and *cis–trans* isomerization. Kinetic and n.m.r. studies indicate that the first two processes are dissociative in nature and occur by a common trigonal intermediate $[RMe_2Au]$ formed by loss of phosphine. The complex $[Bu^tMe_2Au(PPh_3)]$, for instance, undergoes β-hydrogen elimination before re-addition to give the different alkyl isomer (Scheme 13) or *cis*-reductive elimination (as dealt with in

[73] P. Salvadori, R. Lazzaroni, and S. Merlino, *J.C.S. Chem. Comm.*, 1974, 435.
[74] H. Schmidbaur and K. C. Dash, *J. Amer. Chem. Soc.*, 1973, **95**, 4855.



Scheme 13

detail in Chapter 6). In comparison, *cis–trans* isomerization is considered to proceed *via* a unimolecular mechanism involving spontaneous inversion of configuration about gold.[75]

We are most grateful to Professor F. A. Cotton for supplying his original copy of Scheme 5.

[75] A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 6140.

ERRATA

Vol. 3, 1974

Pages 13—15. Reference 33 (p. 13) to the study by Sutin *et al.* of the reaction of horse-heart ferricytochrome *c* with Cr^{II} is incorrect. The correct reference is in fact given in the legend to Figure 1 on p. 14. Ref. 33 deals with the outer-sphere reduction of *trans*-$[Co(N)_4(NH_3)_2]^{3+}$ complexes (p. 15).

Pages 193, 198—199. The complexes used in the investigations reported in references 157 and 177 contained the ligand tmd, not pn as erroneously stated in the text and in Tables 8, 11, and 12. Of the two lines devoted to *trans*-$[Cr(pn)_2Br_2]^+$ in Table 12 the upper (ref. 157) in fact refers to *trans*-$[Cr(tmd)_2Br_2]^+$, the lower (ref. 179) to *trans*-$[Cr(pn)_2Br_2]^+$ as stated.

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