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A Specialist Periodical Report

Inorganic Reaction Mechanisms

Volume 2

A Review of the Literature Published between September 1970 and November 1971

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Organic formulae composed by Wright's Symbolset method

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Foreword

The format and coverage of this second volume dealing with Inorganic Reaction Mechanisms are very similar to those of the first volume. There is a little less on mechanisms of reactions of organic derivatives of the non-metals, and we have less often permitted ourselves the luxury of dealing with references in more than one context.

The nominal period of coverage of the literature is September 1970 to November 1971, inclusive. Unfortunately towards the end of this period there were considerable delays in the delivery of some periodicals, especially from the United States. Some journal issues have therefore had to be held over for consideration in the third volume of this Report.

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

SI units have made extremely rare appearances in the literature which we have scanned. We have therefore not felt that the time is ripe for their general adoption in this volume. We have usually reported activation parameters in the form, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ or E_a, $\log A$, used by the authors, except where conversion is required to maintain consistency, especially within tables.

The Reporters are grateful to many of their colleagues for advice and comments. In particular we would like to thank Drs. J. S. Coe, P. Moore, D. R. Rosseinsky, G. Stedman, and A. G. Sykes for reading parts of the manuscript and making many valuable remarks.

J. B.

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Abbreviations for Ligands and Solvents

General

R	alkyl, aryl
L	unidentate ligand
LL	bidentate ligand
LLL	terdentate ligand
LLLL	quadridentate ligand

Specific

ac	acetoin
acac	acetylacetonate
addo	acetylacetonedioximate
ATP	adenosine triphosphate
bd	benzildioximate
big	biguanide
bipy	2,2′-bipyridyl
bn	2,3-diaminobutane
bpha	benzoylphenylhydroxylamine
but	buta-1,3-diene
bzac	benzoylacetonate
bzbz	dibenzoylmethane
cal	calmagite [1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonate]
cd	cyclohexanedione
chdd	cyclohexanedionedioximate
cod	cyclo-octadiene
cot	cyclo-octatetraene
cyclam	1,4,8,11-tetra-azacyclotetradecane
cydta	cyclohexane-1,2-diaminetetra-acetate
dam	bis(diphenylarsino)methane
diars	*o*-phenylenebisdimethylarsine
dien	diethylenetriamine
dimedta	2,3-diaminobutanetetra-acetate
diphos	1,2-bisdiphenylphosphinoethane
DMF	dimethylformamide
dmg	dimethylglyoximate
DMSO	dimethyl sulphoxide
dopa	dihydroxyphenylalanine

dtpa	diethylenetriaminepenta-acetate
edda	ethylenediaminediacetate
edma	ethylenediaminemonoacetate
edta	ethylenediaminetetra-acetate
egta	ethylene glycol bis-(2-aminoethyl ether)-tetra-acetate
en	ethylenediamine
α-fd	α-furildioximate
gly	glycine
hedta	*N*-(2-hydroxyethyl)ethylenediamine
heida	*N*-(2-hydroxyethyl)iminodiacetate
hfac	hexafluoroacetylacetonate
ida	iminodiacetate
ma	mandelate
mal	malonate
mg	methylglyoximate
mhd	5-methylhexane-2,4-dionate
mn	malononitrile
mnt	maleonitriledithiolate
niox	nioxime
nor	norbornadiene
npo	2-nitrosopent-2-ene-4-one oxime
nta	nitrilotriacetate
ox	oxalate
oxs	8-hydroxyquinoline-5-sulphonic acid
par	4-(2-pyridylazo)resorcinol
pdta	propylenediaminetetra-acetate
phen	1,10-phenanthroline
pic	picoline [methylpyridine]
pmhd	1-phenyl-5-methylhexane-2,4-dionate
pn	propylenediamine
ppd	*p*-phenylenediamine
py	pyridine
qd	quinonedi-imine
salen	*NN'*-bis-(salicylaldehydo)ethylenediamine
tcne	tetracyanoethylene
tet	*NNN'N'*-tetramethylethylenediamine
2,3,2-tet	1,4,8,11-tetra-azaundecane
3,2,3-tet	1,5,8,12-tetra-azadodecane
tet-a, tet-b	5,7,7,12,14,14-hexamethyl-1,4,8,11-cyclotetra-azatetradecane
tetren	tetraethylenepentamine
tfac	1,1,1-trifluoroacetylacetonate
THF	tetrahydrofuran
tma	thiomalic acid
tn	trimethylenediamine

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
ttha	triethylenetetraminehexa-acetic acid
tu	thiourea
xyl	xylenol orange

Part I

ELECTRON TRANSFER PROCESSES

By
A. McAULEY

Introduction

BY A. McAULEY

The format of this Part closely follows that in Volume 1. Although a degree of selection has had to be imposed owing to the large number of papers involving electron transfer processes, an attempt has been made to cover as comprehensively as possible all the areas in which studies are currently being undertaken. Compilations of data have also been assembled to allow easier comparison of the rate constants and thermodynamic parameters of reactions of a similar type.

Electron transfer processes between two metal ions continue to be examined, and a recent monograph [1] sets out clearly the various modes of interaction between the reactant species. The effects of non-bridging ligands on these processes have been discussed,[2] the main influence of such groups, both on oxidant and reductant, being to change the activation free energy by altering the overall free energy of the reaction. Although the donor ligands involving either N- or O-co-ordination have been most utilized, the effects of thioether ligands as non-bridging ligands have also been studied.[3] In the reactions of chromium(VI), the three-unit change in oxidation state contrasts with the (usually) single electron transfer step in most metal ion reactions. The reactions of this ion with both aquo-metal ions and complex species have been reviewed.[4]

Several other useful reviews of reactions involving metal ions have also been published. Redox reactions of chromium(III)–amine species have been described[5] and a survey has been made of the solution chemistry together with reaction paths involved in the redox reactions of various plutonium species.[6] Oxidation reactions of thallium(III) have also been described.[7] Developments in the redox chemistry of peroxides have been reviewed,[8] the nature of the reactions which involve iron(III) in various complexed forms providing a fascinating example of the manner in which geometry and co-ordination to the metal centre greatly affect the reactivity of the system. Redox properties of cobalt chelates, with delocalized

[1] H. Taube, 'Electron Transfer Processes in Solution', Academic Press, New York 1971.
[2] J. E. Earley in *Progr. Inorg. Chem.*, 1970, **13**, 243.
[3] J. H. Worrell and T. A. Jackman, *J. Amer. Chem. Soc.*, 1971, **93**, 1045.
[4] J. H. Espenson, *Accounts Chem. Res.*, 1970, **3**, 347.
[5] C. S. Garner and D. A. House, in 'Transition Metal Chemistry', ed. R. L. Carlin, Marcel Dekker, New York, 1970, vol. 6, p. 226.
[6] J. M. Cleveland, 'The Chemistry of Plutonium', Gordon and Breach, New York, 1970, p. 47.
[7] A. G. Lee, 'The Chemistry of Thallium', Elsevier, Amsterdam, 1971, p. 295.
[8] S. B. Brown, P. Jones, and A. Suggett, *Progr. Inorg. Chem.*, 1970, **13**, 159.

electronic structure have been described,[9] and transfer processes involving metalloporphyrins have been reviewed.[10] In the case of dithiolene complexes of transition metals,[11] the mode of reaction is influenced by solvent, the extent of conjugation of the ligands, and substituents on the donor atoms.

The oxidation of organic substrates by metal-ion species continues to be a fruitful source of study. The question of bonded and non-bonded interactions in one-electron transfer processes has been explored,[12] and several papers have been devoted to the nature of possible metal ion–substrate intermediates.[13–15] The question of covalent bond formation between oxidant and reductant as a pre-requisite to the electron transfer step has also been investigated for a large number of reactions.[16] The mechanisms of reactions of lead(IV) with organic species have been reviewed[17] and the reactions of oxygen-containing radicals and hydrogen atoms with metal ions in various oxidation states have been surveyed.[18] The introduction of such ions into a system where radical polymerization is occurring results in retardation of the chain polymerization, both oxidizing and reducing ions being involved in the termination processes. The role of electrons in radical systems has been examined,[19] and heterolytic oxidation reactions of hydrogen peroxide in acid solutions have also been reviewed.[20]

[9] G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc.* (*A*), 1970, 2870.
[10] P. Hambright, *Co-ordination Chem. Rev.*, 1971, **6**, 249.
[11] J. A. McCleverty, in 'Reactions of Molecules at Electrodes', ed. N. S. Hush, J. Wiley and Sons, London, 1971.
[12] J. S. Littler in 'Essays on Free-Radical Chemistry', Chemical Society Special Publication No. 24, p. 383.
[13] C. F. Wells and C. Barnes, *J. Chem. Soc.* (*A*), 1971, 380.
[14] K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, 1971, **93**, 2543.
[15] C. M. Bell, E. D. McKenzie, and J. Orton, *Inorg. Chim. Acta*, 1971, **5**, 109.
[16] E. Chaffee and J. O. Edwards, ref. 2, p. 205.
[17] J. B. Aylward, *Quart. Rev.*, 1971, **25**, 407.
[18] E. T. Denisov, *Uspekhi Khim.*, 1971, **40**, 43.
[19] T. J. Kemp and T. J. Stone, ref. 12, p. 365.
[20] T. A. Turney, *New Zealand J. Sci.*, 1971 **14**, 299.

1

Reactions Between Two Metal Complexes

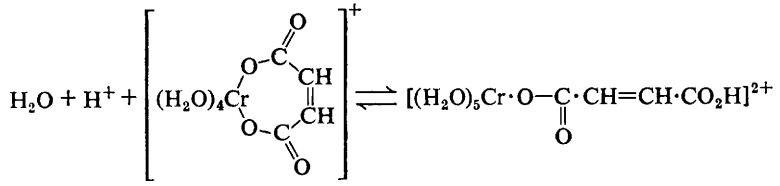
BY A. McAULEY

1 Reducing Agents

Chromium(II).—Quantitative data for this and the other reducing agents are tabulated in Table 1, p. 19.

Many reactions have been studied using this reductant, and with inert oxidants, such as the ammine complexes of cobalt(III), there is the possibility of characterizing more fully the inner-sphere route in redox systems.

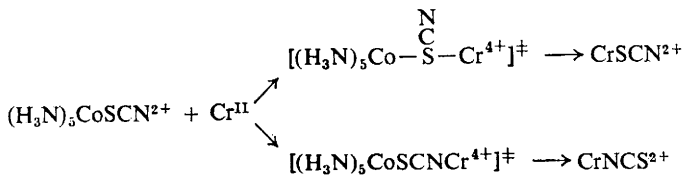
In the reduction of maleatopenta-amminecobalt(III), the (quantitatively) inner-sphere process yields an initial ratio of 4 : 1 of chelated to unidentate complexes of chromium(III).[21] The amounts of the two maleato-complexes formed are however dependent on acidity, and it has been shown that the interconversion of the two species,



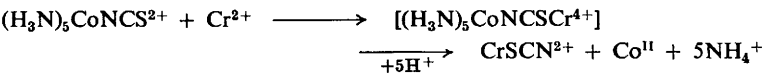
is catalysed by chromium(II). The nature of the activated complexes in both the cobalt(III) and isomerization reactions is considered to be similar, with a chelated chromium(II) environment. The rate of reduction of the methylmaleato-complex does not differ substantially from that of the maleato-species. In the chromium(II) reductions of thiocyanato- and isothiocyanatopenta-amminecobalt(III) complexes,[22] both adjacent and remote inner-sphere attack is observed. In an excess of chromium(II), two reactions with $(H_3N)_5CoSCN^{2+}$ are detected, the first yielding a mixture of $CrSCN^{2+}$ and $CrNCS^{2+}$. In the second stage, the species $CrSCN^{2+}$ is isomerized [chromium(II)-catalysed] to $CrNCS^{2+}$. The initial step is considered to

[21] M. V. Olson and H. Taube, *Inorg. Chem.*, 1970, **9**, 2072.
[22] C. Shea and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 3055.

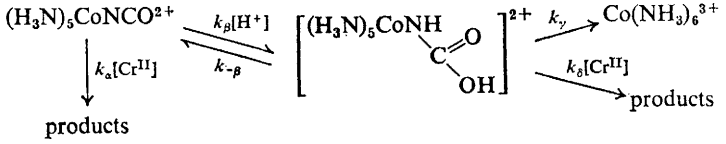
involve the parallel reactions



the fraction of the S-bonded complex produced being 0.29. In the case of the reaction with $(H_3N)_5CoNCS^{2+}$, it is considered that the mechanism involves quantitative remote attack,



The reaction is substantially slower than that involving the sulphur-bonded penta-ammine complex, a factor which is in part accounted for by the high electron-mediating ability of a sulphur atom bound to the oxidizing centre for reaction *via* an inner-sphere mechanism. Kinetic studies on the Cr^{II} reduction of isocyanopenta-amminecobalt(III) have also been carried out,[23] the redox reaction being accompanied by a parallel hydrolysis step. The expected hydrolysis product $[Co(NH_3)_6^{3+}]$ is not, however, found under the experimental conditions, and it is suggested that an intermediate is formed (Scheme 1). This might either decompose in an acid-catalysed



Scheme 1

reaction to yield $Co(NH_3)_6^{3+}$, or the N-bonded complex could act as a bridging ligand in an electron transfer. The latter reaction is considered to be at least 60 times faster than the former. The predominantly inner-sphere reductions of a series of carboxylatopenta-amminecobalt(III) complexes have been re-examined at high acidities,[24] where for the acetato-complex the decrease in the reduction rate on increasing the hydrogen-ion concentration is suggestive of association between the complex and H^+. Although inductive effects are small, steric influences could be important. The reduction of the trimethylacetato-complex is much slower than that of the other complexes, reflecting the strong hindrance, but the reaction is nevertheless considered to proceed *via* an inner-sphere route for at least 70% of the reaction.

It has been proposed that the groups in the bridging molecule attached to the oxidizing and reducing agents in these reactions should have a lone pair available for bonding and must also form part of a conjugated system.

[23] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 198.
[24] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1983.

Such criteria cannot be simultaneously satisfied in the case of the NH_2 group. Studies have thus been undertaken to examine the mode of interaction of complexes where such a group is the potential bridging site.[25] The reductions of penta-ammine cobalt complexes of urea, carbamate, *N*-cyanoguanidine [$N{\equiv}C{-}N{=}C(NH_2)_2$], and cyanamide ($N{\equiv}C{-}NH_2$), by chromium(II) involve an outer-sphere path with the exception of the carbamato-species, where, however, there is no evidence of a nitrogen-bonded chromium(III) species as product. The cyanamide-complex reaction follows the rate law

$$-\mathrm{d}\ln[(H_3N)_5CoNCNH_2^{3+}]/\mathrm{d}t = k'[Cr^{II}][H^+]^{-1}$$

which is consistent with the reaction scheme involving a rapid pre-equilibrium:

$$(H_3N)_5CoNCNH_2^{3+} \rightleftharpoons (H_3N)_5CoNCNH^{2+} + H^+$$

$$(H_3N)_5CoNCNH^{2+} + Cr^{II} \xrightarrow{k_1} \text{products}$$

In this case, bridged electron-transfer occurs. The fact that urea and *N*-cyanoguanidine complexes are reduced with low rate constants, and that only when the conjugate base of the cyanamide complex is formed does the inner-sphere route become operative confirms the suggestion that two non-σ-bonding electron pairs are required on the ligand attaching to the reducing agent in the transition state.

The relative rates of reduction of cobalt(III) complexes containing groups bridging in the activated complex have been determined by the method of competing reactions,[26] where two potential bridging groups (in the same or in separate ions) may react with the chromium(II). For the systems $Co(NH_3)_5L^{2+} + Cr^{2+}$, where L = I, Br, Cl, F, and N_3, the relative rates are 2.75 : 1.89 : 1.51 : 1.00 : 0.88. These ratios are, however, dependent on ionic strength. If the two halides are present in the same complex, as in *cis*- and *trans*-$Co(en)_2ClBr^+$, the relative rate parameters are decreased to 1.14 and 1.00 respectively. For a series of *trans* substituted chloro-bis(ethylenediamine)cobalt(III) complexes, it would appear that the activating effect of the group *trans* to the bridging ligand is in the order

$$Br^- > NO_2^- > H_2O > Cl^- > NCS^- > NH_3$$

A possible *cis* effect may also be operative. It is of interest to note that these reductions are susceptible to free-ligand effects, the order in anions decreasing in the sequence

$$P_2O_7^{4-} > N_3^- > NCS^- > SO_4^{2-} > Cl^-$$

Sykes and his co-workers have made a detailed study of the metal-ion reduction of μ-amido-μ-(ligand)-bis[tetra-amminecobalt(III)] complexes where ligand = sulphato,[27] selenato,[27] phosphato,[28] oxalato,[29] and

[25] R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, 1971, **93**, 625.
[26] M. C. Moore and R. N. Keller, *Inorg. Chem.*, 1971, **10**, 747.
[27] R. S. Taylor, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 277.
[28] M. Green, R. S. Taylor, and A. G. Sykes, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2157.
[29] K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

hydroxo.[30] In the reaction between Cr^{II} and the μ-amido-μ-sulphato-complex,[27] there is a two-stage reaction (Co^{III}_2 = dimer),

$$2Cr^{2+} + Co^{III}_2 \longrightarrow 2Co^{III} + Cr^{III}_2$$

with an attack of a chromium(II) on the cobalt(III) centre in each case. The intermediate Cr^{III}—Co^{III} (Figure 1), formed at the end of the first stage, has

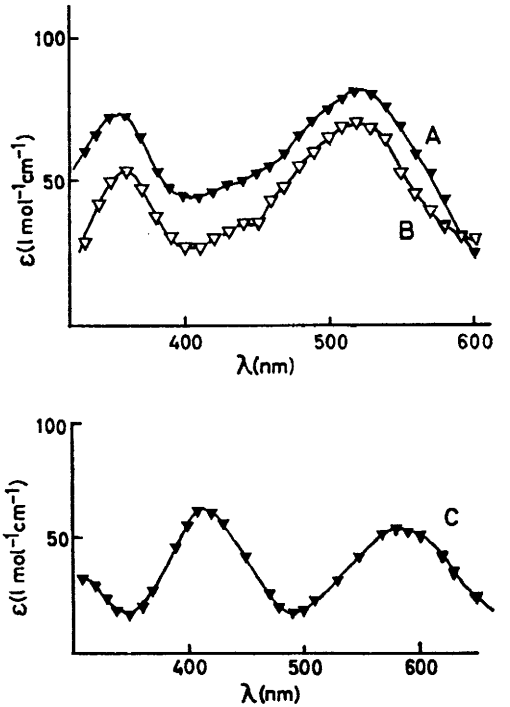


Figure 1 *The spectrum* (A) *of the product of the first stage of the reaction of the* μ*-amido-*μ*-sulphato-complex, believed to be* $(NH_3)_5Co\cdot SO_4\cdot Cr(H_2O)_5^{4+}$, *and* (B) *the spectrum which would be observed for a solution containing equivalent amounts of* $Co(NH_3)_5SO_4^+$ *and* $Cr(H_2O)_5SO_4^+$. (C) *The spectrum of the dichromium*(III) *product of the second stage of the reaction*
[Reproduced by permission from *J. Chem. Soc.* (*A*), 1971, 277]

been characterized spectroscopically using the stopped-flow method, and is considered to be the complex ion μ-sulphato-[penta-amminecobalt(III)]-[penta-aquochromium(III)]. The rate law for this reaction may be expressed as

$$-\mathrm{d}\ln[Co^{III}_2]/\mathrm{d}t = k_1[Cr^{2+}]$$

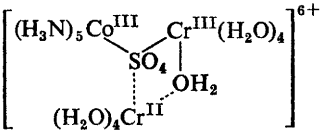
The second stage of the reduction is substantially slower and is hydrogen-ion

[30] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1991.

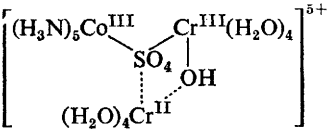
dependent, the rate law being

$$-\mathrm{d}\ln[\mathrm{Co^{III}\cdot Cr^{III}}]/\mathrm{d}t = (k_2 + k_3[\mathrm{H^+}]^{-1})[\mathrm{Cr^{2+}}]$$

The hydrogen-ion inverse dependence has been taken as consistent with hydroxy-bridging, and the transition states (1) and (2) for the reaction paths k_2 and k_3 respectively may be described as shown. In the corresponding



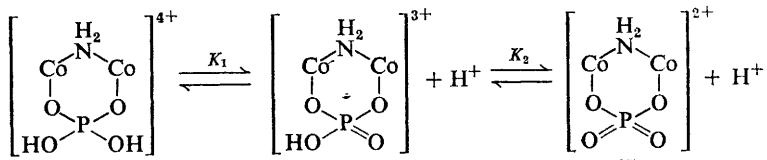
(1)



(2)

μ-selenato reaction only the first step could be investigated, but in this case the reduction is faster by a factor of 50 than that for the μ-sulphato-system, a result which is explicable in terms of the ease with which the free oxoanions are reduced.

The μ-phosphato-complex [28] reacts in rather a similar manner to the sulphato-species, the two-stage reaction again involving intermediate formation. The μ-amido-μ-phosphato-species may however undergo protonation at low pH (the ammonia groups have been omitted for clarity). K_1 and K_2 represent the acid dissociation constants. Studies on the first stage indicate that the species (4) is the reactant although complex (3) is the form predominating in solution. In the second reaction, the rate of disappearance of the cobalt(III)–chromium(III) intermediate is dependent



(3) (4) (5)

on acidity and it may be that in this case the activated complex involves deprotonation and multiple bridging. In the reaction of the corresponding μ-amido-μ-oxalato-species, two stages of reduction are observed,[29] of which the first involves both a protonated and a deprotonated form of the bridged complex ion. The second path, however, is acid independent.

The reduction of the μ-amido-μ-hydroxo-complex is further complicated by aquation and hydroxo-bridge cleavage reactions which are rate determining.[30] The rate law

$$-\mathrm{d}\ln[\mathrm{Co^{III}}]_2/\mathrm{d}t = k_1 + k_2[\mathrm{H^+}] + (k_3 + k_4[\mathrm{H^+}])[\mathrm{Cr^{II}}]$$

involves the reactions (k_1), the displacement of a co-ordinated ammonia by a water molecule, and (k_2), the composite rate constant for the formation of the singly bridged μ-amido-bis-aquo-dimer. Both the mono- and bis-aquo-complexes are considered to react rapidly with the reductant. The

attack of Cr^{II} on the doubly bridged μ-amido-μ-hydroxo-species is negligible. A further pathway involving the protonated μ-amido-μ-aquo-complex has been detected, and this must be outer-sphere.

A two-electron inner-sphere reduction of chloropenta-ammineplatinum(IV) has been described,[31] the final products in the pH range 0—2 being $CrCl^{2+}$, $Cr(H_2O)_6^{3+}$, and $Pt(NH_3)_4^{2+}$. In the presence of excess reductant, an intermediate is observed with a subsequent rapid decay. Since the chloride ion is incorporated into the chromium(III) product, it is suggested that the initial two-electron process

$$Cr^{II} + Pt^{IV} \longrightarrow Pt^{II} + Cr^{IV}Cl$$
$$Cr^{IV}Cl + Cr^{II} \longrightarrow Cr^{III}Cl + Cr^{III}$$

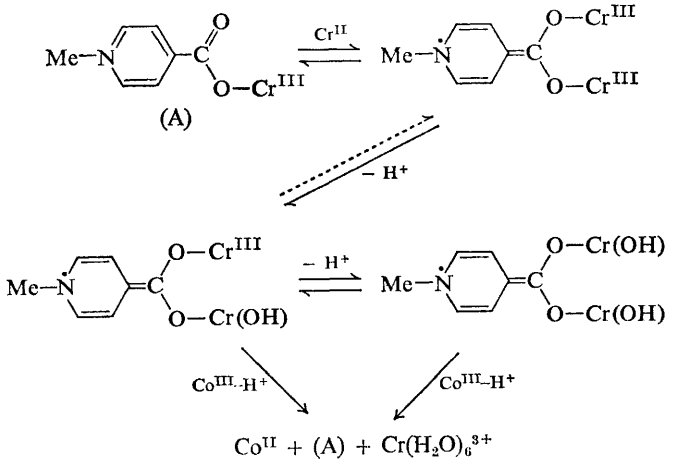
is followed by a slower reaction of the chromium(IV) species with the reductant to yield the products. Transfer of a ligand in an inner-sphere process is also observed in the rapid reaction between chromium(II) and $Co(en)_2(SCH_2CO_2)^+$ where the mercaptoacetate is found in the oxidized product.[32]

The outer-sphere reductions of slowly reacting species such as $Co(NH_3)_6^{3+}$, $(NH_3)_5Co(DMF)^{3+}$, and $(NH_3)_5Co(py)^{3+}$ are greatly accelerated by certain pyridine derivatives [33] which possess an alkenyl or carbonyl substituent γ to the nitrogen. The increase in rate is most pronounced when 4-pyridine-carboxylic acid and its carboxy-bound-penta-aquochromium(III) derivative are present. The corresponding β-derivatives show no catalytic action, and that of the α-analogues is only marginal. In the presence of the (γ-) chromium(III) complex (1.8×10^{-3} M) the reduction rate of $Co(NH_3)_6^{3+}$ is increased by a factor of 2.6×10^4. The mechanism is considered to involve two hydrogen-ion-related highly reactive dinuclear radical ions (Scheme 2). The high reactivity of the dinuclear radicals may be promoted by the fact that electron loss from an extended conjugated complex-ion involves less bond distortion and solvent reorganization than that from a small hydrated cation.

The kinetics of oxidation of mixed 2,2′- and 4,4′-bipy–chromium(II) complexes by cobalt(III) species have also been investigated.[34] Addition of 4,4′-bipy to acidic aqueous solutions of $Cr(2,2'\text{-bipy})_3^{2+}$ produces the mono-protonated complex $[Cr(2,2'\text{-bipy})_2(4,4'\text{-bipy-H})(H_2O)]^{3+}$, which is found to react 20—40 times faster than the tris-(2,2′-bipy)-Cr^{II} species. The factors governing the rates include solvation differences between the reactants and the activated complexes, and the excitation energy of the cobalt(III) complexes from the t_{2g}^6 ground state to the $t_{2g}^5e_g^1$ configuration. Although there is no direct proof of the geometry of the activated complex involved in the reaction of the mixed (2,2′-4,4′-H) species, the considerably more negative

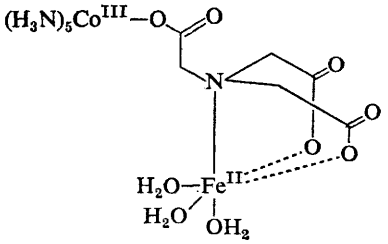
[31] J. K. Beattie and F. Basolo, *Inorg. Chem.*, 1971, **10**, 486.
[32] R. H. Lane and L. E. Bennett, *Chem. Comm.*, 1971, 491.
[33] J. R. Barber and E. S. Gould, *J. Amer. Chem. Soc.*, 1971, **93**, 4045.
[34] J. Ulstrup, *Trans. Faraday Soc.*, 1971, **67**, 2645.

value for $\Delta S^{\ddagger}$ in comparison with those for $Cr(2,2'\text{-bipy})_3^{2+}$ suggests that specific orientation of the reactants is required for the attack by the oxidant at one of the heteroligands of the chromium(II), probably the 4,4'-bipy-H centre.



Scheme 2

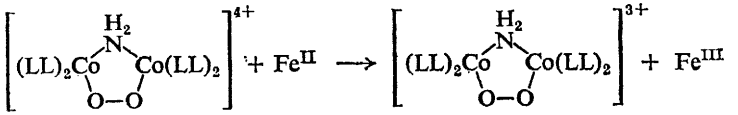
Iron(II).—Evidence has been established[35] for a dinuclear intermediate preceding the electron-transfer process in the oxidation of iron(II) by pentaamminecobalt(III)nitrilotriacetate, in which only one of the carboxylates in the latter ligand is bound to the cobalt centre. In acid solution, the predominating form of the oxidant is $(H_3N)_5CoLH_2$ [where L = $N(CH_2CO\text{-}O)_3^{3-}$], but in the pH range 1.3—3.4, the kinetics are consistent with a bridged mechanism involving the chelation of the reductant prior to electron transfer, the precursor complex being considered to be of the form (6) and having a life-time of the order of 10 s, and an equilibrium quotient of $\sim 10^6$ mol^{-1}.



(6)

[35] R. D. Cannon and J. Gardiner, *J. Amer. Chem. Soc.*, 1970, **92**, 3800.
[36] K. M. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1414.

The 1 : 1 reductions of μ-amido-μ-superoxo-cobalt(III) complexes involving bipyridyl and 1,10-phenanthroline (LL) have been shown to be first order in reductant and in metal complex but independent of acidity in the range 0.05—0.20 M.[36] The products of the reactions are the corresponding μ-peroxo-species,



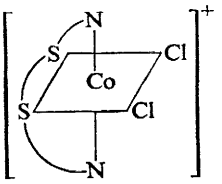
the net reaction being an electron transfer from the metal ion to the superoxo-bridge of the dicobalt complex. In the case of the ligands quoted compared with NH_3 or en, the rates are considerably faster, the effect being associated with the delocalization of the electron into the bipy and phen ligand systems.

Superoxo-bridged dinuclear complexes of rhodium(III) with pyridine or γ-picoline ligands (L), $[(H_2O)L_4Rh \cdot O_2 \cdot RhL_4(H_2O)]^{5+}$, have been prepared,[37] in which acid–base equilibria involving the complex water molecules have been demonstrated. The corresponding dichloro-complex has been shown to be a strong oxidant, the reaction

$$[Rh_2L_8Cl_2O_2]^{3+} + Fe^{II} \longrightarrow [Rh_2L_8Cl_2O_2]^{2+} + Fe^{III}$$

yielding the peroxo-bridged analogue which may in acid media be re-oxidized using Ce^{IV} or MnO_4^- to the original superoxo-ion. Iron(II) salts also interfere with the method of detection of peroxocobalt(III) complexes by means of the chemiluminescent oxidation of luminol,[38] the iron(II) being oxidized by atmospheric oxygen.

The effect of thioether donor-atoms as non-bridging ligands in the reduction of cobalt(III) complexes has been investigated,[3] the reaction of iron(II) with *S-cis*-dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) being 10^3 times more rapid than that for *cis*-$Co(en)_2Cl_2^+$ under comparable conditions. The geometry of the ion (7) has been shown to involve two *cis* thioether donor-atoms, and the chloride participation in the bridging mechanism is evidenced by the lack of reaction with complexes with the corresponding 1,10-phenanthroline and 2,2′-bipyridyl groupings in the inner co-ordination sphere.



(7)

[37] A. W. Addison and R. D. Gillard, *J. Chem. Soc.* (*A*), 1970, 2523.
[38] R. D. Gillard and A. Spencer, *J. Chem. Soc.* (*A*), 1970, 1761.

The reduction of $Co(NH_3)_5Cl^{2+}$, and *cis*- and *trans*-$Co(NH_3)_4(N_3)_2^+$ is accelerated by several orders of magnitude in the presence of catalytic amounts of poly(vinylsulphonate) (PVS).[39] As the iron(II) concentration is increased, the reaction rate increases but passes through a maximum, decreasing on further additions of reductant. The activation energy increases with increasing concentrations of catalyst, suggesting that long-range electrostatic interactions do not account for the increases in rate. In the reduction of multidentate cobalt(III) complexes of the type *cis*-α-$Co(trien)Cl_2^+$, and *cis*-α- and *cis*-β-$Co(trien)OH_2Cl^{2+}$, the rate decreases with an increase in the number of chelate rings in the metal complex.[40] This effect may be ascribed to the role of the non-bridging ligands in these reactions, and it has been suggested that the electron transfer into the unoccupied d_{z^2} of the cobalt will take place more readily on lowering the energy of this orbital. Such a result would be obtained if the ligand *trans* to the bridging group had a low ligand-field strength. This effect together with the removal of the *trans* ligand in the *z* direction away from the metal atom accounts for the decreasing rate in the series NH_3 > en > trien, where the ligand field increases in the reverse order.

A two-stage reduction of $PtCl_6^{2-}$ has been described [41] in which a fast complex formation is followed by a slower intramolecular redox step. Potentiometric evidence has been obtained for Pt^{IV}–Fe^{II} and $(Fe^{II})_2$–Pt^{IV} complexes which differ only slightly in stability constant.

The kinetics of the reduction of the hydrated cobalt(III) ion have been re-examined [42] over a large temperature range, the rates being first order with respect to each reactant,

$$-\mathrm{d}\ln[Co^{III}]/\mathrm{d}t = \{k_0 + k_1'/[H^+]\}[Fe^{II}]$$

A marked acidity dependence is attributable to hydrolysis of the oxidant, the mechanism being described in terms of the reactions

$$Co(H_2O)_6^{3+} + Fe^{II} \xrightarrow{k_0} Co^{2+} + Fe^{III}$$

$$(H_2O)_5CoOH^{2+} + Fe^{II} \xrightarrow{k_1} Co^{2+} + Fe^{III}$$

Both reaction rates are sensitive to the nature of the medium, and the rate constants are considered too large for a rate-determining substitution on the Co_{aq}^{3+} or $CoOH^{2+}$ ions. The overall free-energy change for the reaction (ΔG^0_{est}) has been calculated together with those for the reaction of a series of other iron(II)-containing reactants with cobalt(III). The plot of the activation free-energy $\Delta G_0^{\ddagger}$ against ΔG^0_{est} is approximately linear (Figure 2) suggesting that the reactions might proceed *via* an outer-sphere pathway,

[39] H. Morawetz and G. Gordimer, *J. Amer. Chem. Soc.*, 1970, **92**, 7536.
[40] Y. Kurimura, K. Ohashi, T. Ohtsuki, and K. Yamamoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 1293.
[41] R. I. Novoselov, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1970, **4**, 66 (*Chem. Abs.*, 1971, **74**, 80 276k).
[42] G. Davies, *Inorg. Chem.*, 1971, **10**, 1155.

although the slope (0.23) deviates from that of 0.50 predicted using the Marcus theory. The activation entropies are also more negative for $CoOH^{2+}$ reactions than for the corresponding Co^{3+} systems, which is counter to the effect anticipated from increased entropy due to liberation of a water molecule on formation of a bridged transition state. The reactions of $CoOH^{2+}$ may have some S_N2 character in their mechanism. The fact that the reaction between Fe^{II} and $CoOH^{2+}$ is about two orders of magnitude slower than would be predicted on the basis of free-energy considerations does tend to suggest that an additional activation parameter may involve the conversion of the Co^{III}_{aq} (t_{2g}^6) to some high-spin configuration.

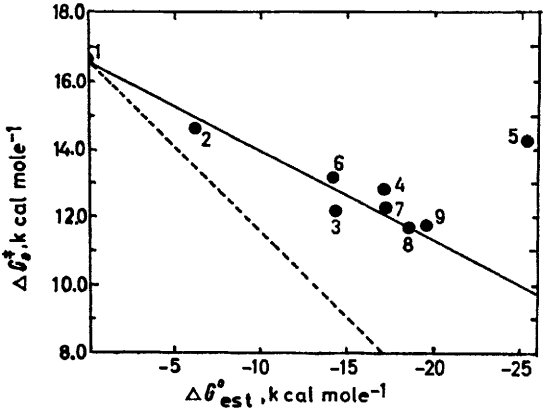


Figure 2 *Plot of* $\Delta G_0^{\ddagger}$ *against* ΔG^0_{est} *at* 25 °C *and* 3M *ionic strength for reactions of* Co^{3+}_{aq}. *Reductants shown are* 1, Co^{2+}_{aq}; 2, Mn^{2+}_{aq}; 3, I^-; 4, p-*hydroquinone*; 5, Fe^{2+}_{aq}; 6, *tris-(5-nitro-phen)iron*(II); 7, *tris-(5-chloro-phen)iron*(II); 8, *tris-(phen)-iron*(II); 9, *tris-(5-methyl-phen)iron*(II). *A line of theoretical slope* 0.5 *is shown for comparison. See ref.* 42 *for details of rate parameters*
(Reproduced by permission from *Inorg. Chem.*, 1971, **10**, 1155)

The reaction between permanganate and tris-(1,10-phenanthroline)iron(II) has been examined [43] using fast-reaction techniques:

$$5Fe(phen)_3^{2+} + MnO_4^- \xrightarrow{+8H^+} 5Fe(phen)_3^{3+} + Mn^{II} + 4H_2O$$

the empirical rate law

$$-0.2\frac{d[Fe(phen)_3^{2+}]}{dt} = \frac{k_0 k_1[Mn^{VII}][Fe(phen)_3^{2+}]^2}{k_1[Fe(phen)_3^{2+}] + k_2[Fe(phen)_3^{3+}]}$$

being derived, where k_0 represents the observed rate constant, which is linearly dependent on the hydrogen-ion concentration. No evidence for an intermediate was obtained, and the role of the proton may be to overcome the thermodynamically unfavoured one-electron reaction between the

reactants. The mechanism may be described in terms of the formation of Mn^{VI}:

$$MnO_4^- + Fe(phen)_3^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MnO_4^{2-} + Fe(phen)_3^{3+}$$

$$HMnO_4 + Fe(phen)_3^{2+} \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} HMnO_4^- + Fe(phen)_3^{3+}$$

$$MnO_4^{2-} + Fe(phen)_3^{2+} \longrightarrow MnO_4^{3-} + Fe(phen)_3^{3+}$$

$$HMnO_4^- + Fe(phen)_3^{2+} \longrightarrow HMnO_4^{2-} + Fe(phen)_3^{3+}$$

Rate constants of 6×10^3 l mol^{-1} s^{-1} for k_1 and $\sim 1.2 \times 10^{11}$ l mol^{-1} s^{-1} for k_2 suggest that the former step proceeds *via* an outer-sphere path with a minimum of inner-sphere reorganization, whereas the latter reaction is diffusion controlled. The comparable constants for k_1' and k_2' are, however, 2.4×10^8 l mol^{-1} s^{-1} and 4.5×10^3 l mol^{-1} s^{-1}, requiring the half-cell

$$HMnO_4 + e \longrightarrow HMnO_4^-$$

to have a potential of $\sim$ 1.3 V. The positive $\Delta S^{\ddagger}$ associated with k_2 may be interpreted as deriving from the attack of the oxygen of the $HMnO_4$ between the planes of the phenanthrolines with accompanying release of associated water molecules.

Vanadium(II).—A number of kinetic data for reactions involving vanadium(II) as reductant have been interpreted in terms of the substitution on $V(H_2O)_6^{2+}$ being rate determining. Reactions with penta-amminecobalt(III) carboxylato-complexes have been examined [24] and show a first-order rate dependence on the reducing ion. Although the specific rates agree with previous studies under comparable conditions, the activation parameters differ considerably. The latter data, however, conform well to an electron-transfer reaction which is substitution-controlled although the mechanism may not be conclusively inner-sphere. In the case of the benzoato-complex, for example, the rate is much lower than for the inner-sphere bi-oxalato-complex. For the corresponding N-co-ordinated nicotinic acid [44] and isonicotinic acid complexes, however, there is a rate dependence on hydrogen-ion concentration, the overall rate law being

$$-\mathrm{d}[Co^{III}]/\mathrm{d}t = \{a + b/(c + [H^+])\}[Co^{III}][V^{II}]$$

The data are consistent with the mechanism in which the undissociated forms of the complexes react *via* two pathways:

$$(H_3N)_5CoLH^{3+} + V^{II} \xrightarrow{k_a} \text{products}$$

$$(H_3N)_5CoLH^{3+} + V^{II} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} (H_3N)_5CoLV^{4+} + H^+$$

$$(H_3N)_5CoLV^{4+} \xrightarrow{k_c} \text{products}$$

[43] K. W. Hicks and J. R. Sutter, *J. Phys. Chem.*, 1971, **75**, 1107.
[44] C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, 1971, **10**, 1235.

whence

$$k_{obs} = k_a + \frac{k_b\, k_c/k_{-b}}{(k_c/k_{-b} + [H^+])}$$

The k_0 value of $\sim$ 1 l mol^{-1} s^{-1} suggests that this pathway may involve an outer-sphere transfer by comparison with the acid-independent rate constant for $(H_3N)_5Co\ py^{3+}$ (0.24 l mol^{-1} s^{-1}) where such a mechanism is required owing to lack of a suitable bridging group. At low acidities, however, there is a substantial inner-sphere contribution, in which there is remote attack by the reductant at the carboxylic acid group with the formation of the dinuclear intermediate which is in steady-state equilibrium with the reactants.

The reductions of μ-amido-μ-sulphato- and μ-amido-μ-selenato-bis[tetraamminecobalt(III)] proceed *via* two stages [45] each involving the reaction of a cobalt(III) centre with a vanadium(II) ion. The kinetics are complicated by the fact that the second stage of the reduction is the more rapid and required to be investigated separately. Unlike the nicotinic acid complexes, however, no acidity dependence was observed. Rate constants and activation parameters are consistent with a vanadium(II)-substitution controlled reaction. Unlike the corresponding chromium(II) reaction where the reduction of the selenato-complex takes place $\sim$ 50 times faster than that of the sulphato-species, in the present system the increase is only two-fold. In the reduction of the analogous μ-amido-μ-phosphato-complex, only the first stage is directly measurable, the rate law being of the form [28]

$$-\,\mathrm{d}\ln[Co^{III}{}_2]/\mathrm{d}t = (k_a + k_b[H^+])[V^{II}]/(K_1 + [H^+])$$

where k_a and k_b represent the rate constants for the reactions of the $\mu(NH_2, HPO_4)$ and $\mu(NH_2,H_2PO_4)$ species respectively and K_1 represents the equilibrium constant for the first ionization of the bound phosphate group. No evidence was obtained for a cobalt(III)–vanadium(III) intermediate. In comparison with the chromous-ion reduction, where there is no reduction involving the diprotonated (k_b) form, the possibility of an outer-sphere mechanism for vanadium(II) in this case may not be excluded. Protonated and un-ionized forms of the μ-amido-μ-oxalato-complex have been shown to be reactive, where, like the phosphato-system, only the first stage of the vanadium(II) reduction is measurable:[29]

$$V^{II} + (H_3N)_4Co\begin{matrix}NH_2\\ \diagdown\ \diagup\\ C_2O_4\end{matrix}Co(NH_3)_4^{3+} \xrightarrow{H^+} V^{III} + Co(NH_3)_5C_2O_4^{+} + Co^{III} + 4NH_4^{+}$$

$$V^{II} + (H_3N)_5CoC_2O_4^{+} \xrightarrow{H^+} V^{III} + 5NH_4^{+} + C_2O_4^{2-} + Co^{II}$$

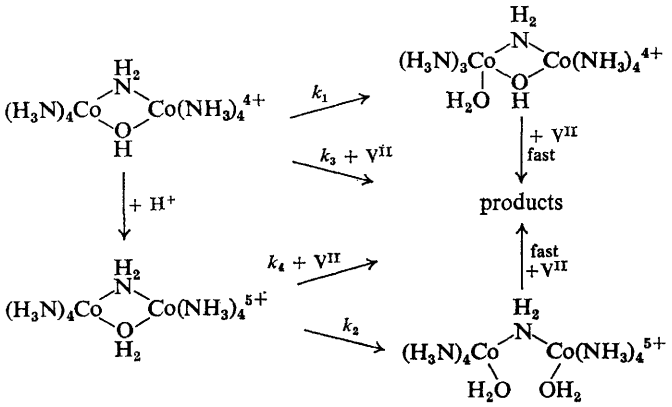
Although the bonding of the oxalate in $(H_3N)_5CoC_2O_4^{+}$, $(H_3N)_4CoC_2O_4^{+}$, and the dinuclear complex varies considerably, the reaction rates are in good agreement, the common rate-determining step being associated with substitution into the inner co-ordination sphere of the vanadium(II) ion.

[45] M. Green, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 509.

The kinetics of the reaction with μ-amido-μ-hydroxo-bis[tetra-ammine-cobalt(III)] follows a rate law of the type

$$-\mathrm{d}\ln[\mathrm{Co^{III}}_2]/\mathrm{d}t = k_1 + k_2[\mathrm{H^+}] + k_3[\mathrm{V^{II}}] + k_4[\mathrm{H^+}][\mathrm{V^{II}}]$$

where, as in the reaction with chromium(II) as reductant, one of the steps (k_1) involves the replacement of a co-ordinated ammonia by water. Also, the rate of aquo-bridge cleavage (formed on protonation of the hydroxy-group) is comparable with that of reduction. Such reactions result in the formation of four bridged complexes which are capable of reduction (Scheme 3).



Scheme 3

Kinetic parameters for the oxidation of vanadium(II) by mercury(II) which involve both one-electron and two-electron paths have been re-examined.[46, 47] In an excess of mercury(II) the reaction may be described by the mechanisms

$$\mathrm{V^{II}} + \mathrm{Hg^{II}} \xrightarrow{k_a} \mathrm{V^{III}} + \mathrm{Hg^{I}}$$

$$\mathrm{V^{II}} + \mathrm{Hg^{I}} \xrightarrow{\text{rapid}} \mathrm{V^{III}} + \mathrm{Hg^{0}}$$

$$\mathrm{Hg^{0}} + \mathrm{Hg^{II}} \xrightarrow{\text{rapid}} [\mathrm{Hg^{I}}]_2$$

and

$$\mathrm{V^{II}} + \mathrm{Hg^{II}} \xrightarrow{k_b} \mathrm{V^{IV}} + \mathrm{Hg^{0}}$$

with subsequent fast removal of Hg^0 by Hg^{II}. Whereas the one-electron reaction is probably outer-sphere, the inverse hydrogen-ion dependence in the two-electron path is suggestive of the reactants V^{II} and $HgOH^+$ with an activated complex involving a hydroxy-bridge.*

[46] M. Green and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 3221.
[47] M. Green and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3067.

* D. L. Toppen and R. G. Linck (*Inorg. Chem.*, 1971, **10**, 2635) have recently discussed the role of co-ordinated water as a bridging ligand in redox systems and have compared the relative rates of reduction of various complex ions with Cr^{II} and V^{II}. For outer-sphere reactions, it appears that $k(Cr^{II})^1/k(V^{II}) \approx 0.02$.

Uranium(III), Ytterbium(II), Europium(II), and Copper(I).—Several studies have been made using the strongly reducing uranium(III) ion

$$U^{IV} + e \rightleftharpoons U^{III}, \quad E^0 = -0.63 \text{ V}$$

where although the ion is capable of converting water into hydrogen, no significant deterioration of such solutions was noted over a period of several hours. In an extensive investigation [48] four types of cobalt(III) complexes have been used as oxidants involving (*a*) the hexa-amine species $Co(en)_3^{3+}$ and $Co(NH_3)_6^{3+}$, which react *via* outer-sphere routes, (*b*) aquo-ammine complexes of the type $(H_3N)_5Co(H_2O)^{3+}$, (*c*) acido-penta-ammine complexes with halides or pseudo-halides, and (*d*) species with ligands capable themselves of reduction, *e.g.* $(H_3N)_5CoONO_2^{2+}$.

The outer-sphere reactions are second order overall, and hydrogen-ion independent although strongly accelerated by anions, the observed rate constant being expressed in the form

$$k_{obs} = k_1 + k_2[X^-]$$

where k_1 represents the rate constant in perchlorate media. The catalytic rates k_2 fall in the order $Cl^- > Br^- > I^-$, the effect of fluoride ion being very considerable ($\sim 10^5$ greater). In the case of the aquo-penta-ammine reactions, a hydrogen-ion dependence is observed which is suggestive of a hydroxide-bridged intermediate being formed which has a marked effect on the reaction rates. In this system, the role of the hydroxide ion may be to lower the energy of the transition state during which the precursor complex reacts *via* electron transfer. The complexes of the type $(H_3N)_5CoX^{2+}$, however, show no hydrogen-ion dependence, and relatively small effects of added anions. The relative rates (Table 1) are strongly suggestive of an inner-sphere mechanism on the basis of the extents to which the differing X groups can stabilize the transition states. In the reaction with $(H_3N)_5CoNO_2^{2+}$ and $(H_3N)_4CoNO_3^{2+}$, there is interference from ligand reduction, although this is less marked in the case of the corresponding nitrito- and bi-oxalato-species.

The reduction of the tetra-amminediaquocobalt(III) ion, *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ has been examined

$$U^{3+} + Co(NH_3)_4(H_2O)_2^{3+} \xrightarrow{+4H^+} U^{4+} + Co^{2+} + 4NH_4^+ + 2H_2O$$

in acid solutions at various ionic strengths.[49] Considerable care was taken in the purification of the cobalt complex and the variations in spectral characteristics of samples from various preparations have been noted. The overall rate data conform to the law

$$-d[U^{III}]/dt = \{k_a + k_b/[H^+]\}[U^{III}][Co^{III}]$$

the first term predominating. No complex hydrogen-ion dependence of the type described in the previous study was observed, although the chloride-ion catalysis of the reaction has been noted. As in the previous investigation,

[48] R. T. Wang and J. H. Espenson, *J. Amer. Chem. Soc.*, 1971, **93**, 380.
[49] J. D. White and T. W. Newton, *J. Phys. Chem.*, 1971, **75**, 2117.

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

Oxidant	k (25 °C)	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Chromium(II)					
$Co(NH_3)_5(mal)^{2+}$	2.0×10^2	1.00	2.9	− 38	21[a]
$Co(NH_3)_5(Me\ mal)^{2+}$	1.5×10^2	1.0	—	—	21[b]
$Co(NH_3)_5SCN^{2+}$	1.9×10^5	1.0	—	—	22[c]
$Co(NH_3)_5SCN^{2+}$	8×10^4	1.0	—	—	22[d]
$Co(NH_3)_5NCS^{2+}$	19	1.0	—	—	22
$Co(NH_3)_5NCO^{2+}$	0.5	1.0	8.8	− 30.4	23
$Co(NH_3)_5(O_2CH)^{2+}$	7.2	1.0	8.3	− 27	24
$Co(NH_3)_5(O_2CMe)^{2+}$	0.35	1.0	8.2	− 33	24
$Co(NH_3)_5(O_2CPh)^{2+}$	0.15	1.0	9.0	− 32	24
$Co(NH_3)_5(O_2C\cdot CH_2Cl)^{2+}$	0.12	1.0	8.9	− 33	24
$Co(NH_3)_5(O_2C\cdot CHCl_2)^{2+}$	7.5×10^{-2}	1.0	8.1	− 36	24
$Co(NH_3)_5(O_2C\cdot CMe_3)^{2+}$	7.0×10^{-3}	1.0	11.1	− 31	24
$Co(NH_3)_5(O_2C\cdot CCl_3)^{2+}$	1.7×10^{-2}	1.0	9.3	− 35	24
$[(H_3N)_4Co\cdot\mu(NH_2,SO_4)\cdot Co(NH_3)_4]^{3+}$	7.4	2.0	8.7	− 25.3	27
$[(H_3N)_5Co\cdot\mu(SO_4)\cdot Cr(H_2O)_5]^{4+}$	0.26	2.0	14.6	− 12.2	27
$[(H_3N)_5Co\cdot\mu(SO_4)\cdot Cr(H_2O)_5]^{4+}$	0.19	2.0	13.9	− 15.3	27[e]
$[(H_3N)_4Co\cdot\mu(NH_2,SeO_4)\cdot Co(NH_3)_4]^{3+}$	372	2.0	7.2	− 22.6	27
$[(H_3N)_4Co\cdot\mu(NH_2,HPO_4)\cdot Co(NH_3)_4]^{3+}$	31.6	2.0	9.16	− 21.0	28
$[(H_3N)_4Co\cdot\mu(NH_2,H_2O)\cdot Co(NH_3)_4]^{5+}$	1.12×10^3	2.0	19.9	− 7.5	30[f, g]
$Pt(NH_3)_5Cl^{3+}$	5×10^4	0.1	—	—	31
$Co(en)_3^{3+}$	25	0.1	11.0	− 14.8	34[h]
$Co(NH_3)_6^{3+}$	215	0.1	10.2	− 13.8	34[h]
$Co(tn)_3^{3+}$	2.9×10^3	0.1	6.7	− 19.5	34[h, i]
racemic $[Co(pn)_3^{3+}]$	18	0.1	11.4	− 14.7	34[h]
racemic $[Co(2,3\text{-}bn)_3^{3+}]$	635	0.1	8.6	− 16.7	34[h, j]
$Co(dien)_2^{3+}$	245	0.1	10.2	− 12.0	34[h, k]
$(H_3N)_5Co(OAc)^{2+}$	500	0.1	8.5	− 17.6	34[h]

Table 1 (*cont.*)

Oxidant	k (25 °C)	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$Co(en)_3^{3+}$	9.1×10^2	0.1	3.3	− 34	34[l]
$Co(NH_3)_6^{3+}$	5.5×10^3	0.1	2.9	− 32	34[l]
$Co(tn)_3^{3+}$	7.85×10^4	0.1	1.3	− 31.5	34[l, i]
racemic $[Co(pn)_3^{3+}]$	600	0.1	4.6	− 33	34[l]
racemic $[Co(2,3\text{-bn})_3^{3+}]$	1.28×10^4	0.1	5.3	− 22	34[l, j]
$Co(dien)_2^{3+}$	6.60×10^3	0.1	2.4	− 33	34[l, k]
$(H_3N)_5Co(OAc)^{2+}$	8.05×10^3	0.1	1.6	− 31	34[l]
Iron(II)					
$(H_3N)_5CoL$	9.4×10^{-2}	1.0	—	—	35[m, n]
$[(H_3N)_5Co \cdot O_2 \cdot Co(NH_3)_5]^{5+}$	2.8×10^{-2}	2.0	6.9	− 41.5	36[o]
$[(H_3N)_4Co \cdot \mu(NH_2,O_2) \cdot Co(NH_3)_4]^{4+}$	25.2	2.0	6.54	− 29.6	36[o]
$[(H_3N)_3Co \cdot \mu(NH_2,OH,O_2) \cdot Co(NH_3)_3]^{3+}$	1.52	2.0	6.95	− 38.5	36[o]
$[(en)_2Co \cdot \mu(NH_2,O_2) \cdot Co(en)_2]^{4+}$	21.1	2.0	6.9	− 28.2	36[o]
$[(bipy)_2Co \cdot \mu(NH_2,O_2) \cdot Co(bipy)_2]^{4+}$	7.06×10^3	0.25	2.67	− 31.4	36[o]
$[(phen)_2Co \cdot \mu(NH_2,O_2) \cdot Co(phen)_2]^{4+}$	1.07×10^4	0.25	2.21	− 32.2	36[o]
$(H_3N)_5CoCl^{2+}$	1.35×10^{-3}	1.0	12.5	− 30	3
cis-$Co(en)_2Cl_2^+$	1.6×10^{-3}	1.0	—	—	3
cis-$Co(SSNN)Cl_2^+$	1.35	1.0	9.25	− 36.6	3[p]
cis-α-$Co(trien)Cl_2^+$	4×10^{-4}	1.0	—	—	40[q]
cis-α-$Co(trien)OH_2Cl^{2+}$	1.6×10^{-4}	1.0	—	—	40[q]
cis-β-$Co(trien)OH_2Cl^{2+}$	9.8×10^{-5}	1.0	—	—	40[q]
$Co(H_2O)_6^{3+}$	2.25×10^2	3.0	15.2	4.7	42
$(H_2O)_5CoOH^{2+}$	3.85×10^2	3.0	15.8	8.2	42
MnO_4^-	6×10^3	0.456	—	—	43
$HMnO_4$	2.4×10^8	0.456	—	—	43
Vanadium(II)					
$(H_3N)_5Co(O_2CH)^{2+}$	3.63	1.0	13.9	− 13	24[r]
$(H_3N)_5Co(O_2CPh)^{2+}$	0.63	1.0	12.4	− 18	24[r]

Table 1 (*cont.*)

Oxidant	k (25 °C)	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$(H_3N)_5Co(O_2CMe)^{2+}$	1.15	1.0	11.6	− 19	24[r]
$(H_3N)_5Co(nic)^{3+}$	1.0	1.0	—	—	44[s]
$(H_3N)_5Co(isonic)^{3+}$	1.4	1.0	—	—	44[s]
$(H_3N)_5Co(nic)^{3+}$	7.1	1.0	—	—	44[s, t]
$(H_3N)_5Co(isonic)^{3+}$	5.3	1.0	—	—	44[s, t]
$(H_3N)_5CoSO_4^{+}$	25.5	2.0	11.6	− 13.1	45
$(H_3N)_4Co\cdot\mu(NH_2,SO_4)\cdot Co(NH_3)_4^{3+}$	7.94	2.0	11.2	− 16.8	46
$(H_3N)_4Co\cdot\mu(NH_2,SeO_4)\cdot Co(NH_3)_4^{3+}$	15.3	2.0	11.7	− 14.1	46
$(H_3N)_4Co\cdot\mu(NH_2,HPO_4)\cdot Co(NH_3)_4^{3+}$	2.91	2.0	13.3	− 11.9	28
$(H_3N)_4Co\cdot\mu(NH_2,H_2PO_4)\cdot Co(NH_3)_4^{4+}$	0.64	2.0	11.0	− 22.8	28
$(H_3N)_4Co\cdot\mu(NH_2,C_2O_4)\cdot Co(NH_3)_4^{3+}$	3.51	2.0	11.2	− 18.6	29
$(H_3N)_4Co\cdot\mu(NH_2\cdot HC_2O_4)\cdot Co(NH_3)_4^{4+}$	22.7	2.0	12.0	− 11.2	29
Hg^{II}	1.04	2.0	15.8	− 5.6	47[u]
Hg^{II}	8.69	2.0	14.8	− 4.6	47[v]
Uranium(III)					
$Co(NH_3)_6^{3+}$	1.32	0.2	—	—	48
$Co(en)_3^{3+}$	0.13	0.2	—	—	48
$(H_3N)_5CoBr^{2+}$	1.42×10^4	0.20	2.0	− 32.7	48
$(H_3N)_5CoCl^{2+}$	3.24×10^4	0.20	2.7	− 29.0	48
$(H_3N)_5CoN_3^{2+}$	1.08×10^6	0.20	—	—	48
$(H_3N)_5CoF^{2+}$	5.40×10^5	0.20	—	—	48
$(H_3N)_5CoCN^{2+}$	3.45×10^3	0.20	—	—	48
$(H_3N)_5CoNCS^{2+}$	1.8×10^1	0.2	—	—	48
$(H_3N)_5(O_2CMe)^{2+}$	1.5×10^4	0.2	—	—	48
cis-$Co(en)_2Cl_2^{+}$	2.15×10^4	0.2	—	—	48
trans-$Co(en)_2Cl_2^{+}$	2.15×10^5	0.2	—	—	48
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	1.64×10^3	2.0	3.67	− 31.5	49
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	0.2	2.0	—	—	49[w]
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	4.4×10^{-3}	2.0	—	—	49[x]

Table 1 (*cont.*)

Oxidant	*k* (25 °C)	*I* (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$(H_2O)_5CrF^{2+}$	1.7×10^{1}	0.20	—	—	50
$(H_2O)_5CrN_3^{2+}$	4.0×10^{1}	0.20	—	—	50
$(H_2O)_5CrSCN^{2+}$	9.0×10^{3}	0.20	—	—	50
cis-$Cr(H_2O)_4Cl_2^{+}$	5.1×10^{1}	0.2	—	—	50
trans-$Cr(H_2O)_4Cl_2^{+}$	4.4×10^{1}	0.2	—	—	50
Ytterbium(II)					
$Co(en)_3^{3+}$	4.5×10^{2}	0.20	—	—	51
$Co(NH_3)_6^{3+}$	2.28×10^{3}	0.20	—	—	51
$(H_3N)_5Co(H_2O)^{3+}$	3.15×10^{4}	0.20	—	—	51
$(H_3N)_5CrCl^{2+}$	9.5	0.20	—	—	51
$(H_3N)_5CrBr^{2+}$	14.2	0.20	—	—	51
$(N_3N)_5CrF^{2+}$	40.2	0.20	—	—	51
Copper(I)					
$(H_3N)_5Co(O_2CMe)^{2+}$	$< 4 \times 10^{-3}$	1.1	—	—	53
$(H_3N)_5Co(O_2CPh)^{2+}$	$< 2 \times 10^{-3}$	1.1	—	—	53
$(H_3N)_5Co(O_2C \cdot CH_2OH)^{2+}$	$< 6 \times 10^{-3}$	1.1	—	—	53
$(H_3N)_5Co$(2,3-py-dicarb)	3.6	1.1	—	—	53[v]
$(H_3N)_5Co$(2,6-py-dicarb)	25	1.2	—	—	53[v]
$(H_3N)_5Co$(4-cin-carb)	12	1.1	—	—	53[z]

[a] mal = maleato. [b] MeMal = methylmaleato. [c] Remote inner-sphere attack. [d] Adjacent inner-sphere reaction. [e] Hydrogen-ion independent path. [f] $T = 35$ °C. [g] Composite rate constant involving protonation of bridging ligand. [h] Reductant is $Cr(2,2'\text{-dipy})_3^{2+}$. [i] tn = trimethylenediamine. [j] 2,3-bn = *meso*-2,3-butanediamine. [k] dien = diethylenetriamine [l] Reductant is $[Cr(2,2'\text{-dipy})_2(4,4'\text{-dipy-H})(H_2O)]^{3+}$. [m] First-order rate decay (s^{-1}). [n] L is nitrilotriacetate. [o] $T = 9.0$ °C. [p] SSNN is *S-cis*-dichloro(1,8-diamino-3,6-dithiaoctane). [q] $[H^+] = 0.1$M. [r] $[H^+] = 0.50$M. [s] nic = nicotinic acid, isonic = isonicotinic acid. [t] Formation reaction for dinuclear intermediate. [u] One-electron path. [v] Two-electron path. Assuming $HgOH^+$ as reactant, the rate constant becomes 3.2×10^4 l mol^{-1} s^{-1}. [w] Inverse hydrogen-ion dependent path. [z] Reductant is Np^{III}. [y] py-dicarb = pyridine-carboxylate. [z] 4-cinnolinecarboxylate [compound (8), p. 25].

adherence to a Debye–Hückel equation is described in the variation of rate with ionic strength. The minor pathway (k_b) involves loss of hydrogen ion prior to the formation of the activated complex. Several runs were performed using Np^{3+} instead of U^{3+} as reductant, a similar rate law being observed although the reactions were considerably slower. This is probably due to the better reducing properties of U^{III}.

In the reduction of the chromium(III) complexes $(H_2O)_5Cr^{III}X$ where X = H_2O, F, Cl, Br, NCS, N_3, and SCN,[50] the second-order reactions are markedly dependent on acidity, in contrast with the reactions of the penta-ammine cobalt analogues where there are no sufficiently acidic protons. The rate law is of the form

$$+ d[U^{IV}]/dt = - d[Cr^{III}]/dt = \{k_1 + k_2/[H^+] + k_3/[H^+]^2\}[Cr^{III}][U^{III}]$$

Involvement of the complexed hydroxo-group has been suggested in accord with a mechanism of the type

$$(H_2O)_5CrCl^{2+} \rightleftharpoons (H_2O)_4Cr(OH)Cl^+ + H^+$$

$$(H_2O)_4Cr(OH)Cl^+ + U^{III} \rightleftharpoons (H_2O)_4Cr(OH)(Cl)U^{III} \longrightarrow U^{IV} + Cr^{II}$$

Ligand equilibration of the uranium(IV) product is rapid, and use has been made of kinetic parameters in the interpretation of the rate effects.

Solutions of the strongly reducing ytterbium(II) ion have been prepared electrolytically in acid media and studies made of the fast redox reactions with cobalt(III) and chromium(III) complexes.[51] The outer-sphere reductions of $Co(en)_3^{3+}$ and $Co(NH_3)_6^{3+}$ are considerably faster than for other reductants, the second-order rate constants being 1.34×10^6 greater than that for the corresponding europium(II) reduction, the factor for chromium(II) being 2.6×10^7. As with the uranium(III) systems, however, the reactions are strongly catalysed by halide ions, the rate law in the presence of Cl^- being

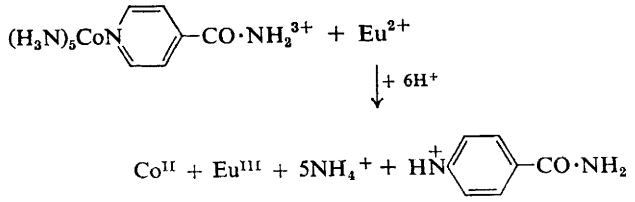
$$- d[Yb^{2+}]/dt = (k_\alpha + k_\beta[Cl^-])[Yb^{II}][CoL_6^{3+}]$$

where the role of the anion is considered to be that of a pseudo-bridging ligand between oxidant and reductant.

The rate constants for the Yb^{II} reduction of the penta-ammine chromium(III) halide complexes follow the unusual order $F^- > Br^- > Cl^-$, which is also observed in the inner-sphere reactions of the reductant with $Cr(H_2O)_4X^{2+}$ ions. The reduced catalytic activity of anions in the penta-ammine complexes would be in keeping with an inner-sphere route.

Further studies of electron-transfer reactions involving europium(II) have also been performed,[52] and in contrast to studies where the organic functional groups act as bridging ligands, evidence has been described of a pathway *via* radical formation. In the reaction involving the complexed

[50] R. T. Wang and J. H. Espenson, *J. Amer. Chem. Soc.*, 1971, **93**, 1629.
[51] R. J. Christensen and J. H. Espenson, *Chem. Comm.*, 1970, 756.
[52] C. Norris and F. R. Nordmeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 4044.



isonicotinamide ligand observed absorbance changes deviate markedly from those expected for a first-order reaction in cobalt complex and reductant. It has been found that the presence of free nicotinamide affects the reaction rate although ammonium and cobalt(II) ions do not. The mechanism consistent with the acceleration may be written as (L = isonicotinamide):

$$H^+ + (H_3N)_5CoL^{3+} + Eu^{2+} \xrightarrow{k_a} Co^{II} + Eu^{III} + HL^+$$

$$HL^+ + Eu^{II} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} HL^{\bullet} + Eu^{III}$$

$$H^+ + HL^{\bullet} + (H_3N)_5CoL^{3+} \xrightarrow[k_c]{} Co^{II} + 2HL^+ + 5NH_4^+$$

Assuming a steady-state concentration for the radical HL the rate law

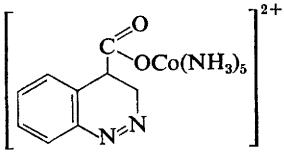
$$\frac{-\,d[Co^{III}]}{dt} = k_a[Co^{III}][Eu^{II}] + \frac{k_b k_c[Co^{III}][Eu^{II}][HL^+]}{k_{-b}[Eu^{III}] + k_c[Co^{III}]}$$

may be derived. It is of interest that no comparable behaviour is observed in the reduction of the corresponding $(H_3N)_5Co(py)^{3+}$ and $(H_3N)_5Co(nicotinamide)^{3+}$ complexes where there is adherence to second-order behaviour. The presence of free isonicotinamide in these systems does, however, promote the acceleration described above. The reduction of cobalt(III) complexes by europium(II) is also catalysed by 4-pyridinecarboxylic acid [33] and other chromium(III) complexes.

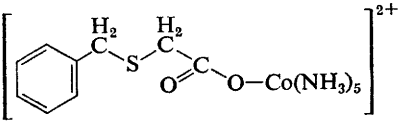
The use of copper(I) as a reducing agent has been examined in a series of reactions and comparison made with chromium(II).[53] Although the redox potential of this ion is lower than that of chromium(II), the (presumably) tetrahedral nature of the hydrated ion together with its lower overall charge reduce the steric and electrostatic barriers to reaction with an oxidant of positive charge. The rates of reaction with carboxylatopenta-ammine cobalt(III) complexes are less than those for the corresponding Cr^{II} systems, in keeping with the lower redox potential. Several types of cobalt(III) complex have been examined, very slow reactions being observed between the reductant and $(H_3N)_5CoL^{2+}$ where L = benzoate, salicylate, maleate, glycolate, or acetate. Pyridinecarboxylato-complexes however react much more rapidly, and in these systems where the $COOCo^{III}(NH_3)_5$ grouping is found to be α to a basic nitrogen atom, the mechanism is considered to be

[53] E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Amer. Chem. Soc.*, 1971, **93**, 5661.

of the inner-sphere type with a chelated transition state which is lost on protonation of the nitrogen. The only reduction which would appear to proceed *via* a remote attack involves the 4-cinnolinecarboxylate-complex (8) where the possibility of chelation in the activated complex is configurationally excluded. Neighbouring-group participation is observed in the rate increase with the *S*-benzylthioglycollato-complex (9) where there is again the possibility of ring formation.



(8)



(9)

2 Oxidizing Agents

Chromium(VI).—Quantitative data for Cr^{VI} and the other oxidizing agents will be found in Table 2. The use of chromium(VI) as an oxidant has recently been reviewed [4] in its reactions with transition-metal complexes. Kinetic studies of the equilibrium

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Table 2 *Rate constants and thermodynamic parameters for oxidation reactions involving metal ions. Units and conditions are as quoted in Table* 1

Reaction	k(25 °C)	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$Cr^{VI} + Ta_6Br_{12}^{2+}$	9.5×10^3	1.00	—	—	55
$Cr^{VI} + Ta_6Cl_{12}^{2+}$	2.8×10^4	1.00	—	—	55
$Fe^{III} + In^{I}$	1.1×10^3	0.70	6.2	− 23.2	60[a]
$Ce^{IV} + Co(C_2O_4)_3^{3-}$	1.2×10^{-3}	~ 3.0	—	—	66[b]
$Ce^{IV} + Cr(C_2O_4)_3^{3-}$	4.0×10^{-2}	~ 3.0	—	—	66[b]
$Ce^{IV} + Rh(C_2O_4)_3^{3-}$	6.1×10^{-4}	~ 3.0	—	—	66[b]

[a] Oxidant is $FeOH^{2+}$. [b] 1.0M sulphuric acid.

have been made in the pH range 2—4, where the rate law is of the form [54]

$$-d[Cr_2O_7^{2-}]/dt = k_\alpha[Cr_2O_7^{2-}][H^+] - k_\beta[HCrO_4^-]^2[H^+]$$

the reactions being acid-catalysed under the prevailing acidity conditions. The multi-step oxidation of the tantalum cluster-ion $Ta_6Br_{12}^{2+}$ has been examined,[55] in which the initial process might involve the single-electron transfer

$$Ta_6Br_{12}^{2+} + H^+ + HCrO_4^- \xrightarrow{k_\alpha} Ta_6Br_{12}^{3+} + H_2CrO_4^-$$

with formation of the chromium(v) intermediate, and two subsequent rapid

[54] J. R. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, 1971, **10**, 635.
[55] J. H. Espenson and R. J. Kinney, *Inorg. Chem.*, 1971, **10**, 376.

steps to yield the octahedral $Cr(H_2O)_6^{3+}$ ion. The rate law is observed to be

$$-\,d[Ta_6Br_{12}^{2+}]/dt = \{k_\alpha + k_\beta[HCrO_4^-]\}[Ta_6Br_{12}^{2+}][H^+][HCrO_4^-]$$

the second pathway (k_β), second order in chromium(VI), being considered to involve the dichromate anion in the activated complex. The possibility of a two-electron transfer to Cr^{IV} cannot however be completely excluded. In the case of the analogous chloro-complex, $Ta_6Cl_{12}^{2+}$, there is a rate increase by a factor of ~ 3 which is consistent with the stronger (by 0.1 V) reducing properties of the chloro-species. The reaction with hexachloroiridate(III) has been investigated,[56] the overall stoicheiometry being

$$HCrO_4^- + 3IrCl_6^{3-} + 7H^+ \longrightarrow Cr^{III} + 3IrCl_6^{4-} + 4H_2O$$

the sole chromium(III) product being the $Cr(H_2O)_6^{3+}$ ion. Under conditions of a 30-fold excess of reductant being present initially, it was found that first-order plots showed curvature, and a complex dependence on $IrCl_6^{3-}$ was suggested. The reaction follows the rate equation

$$\frac{-\,d\,[HCrO_4^-]}{dt} = \left\{k_1[IrCl_6^{3-}] + \frac{k_2[IrCl_6^{3-}]^2}{(1 + k_3[IrCl_6^{3-}])}\right\}\frac{[HCrO_4^-]}{[IrCl_6^{4-}]}$$

where k_1, k_2, and k_3 are composite terms. The form of the rate law is suggestive of a dinuclear intermediate of the type Cr^{VI}–Ir^{III}, but no spectral evidence for a complex of this type was found. An interesting feature of the study, however, is the interpretation that the first rate-law term derives from a rate-determining conversion of a Cr^V intermediate into a more reactive form. There are several indistinguishable mechanisms; the most favoured involves the steps

$$Cr^{VI} + IrCl_6^{3-} \underset{\text{fast}}{\rightleftharpoons} Cr^V + IrCl_6^{2-} \quad (K_1 \ll 1)$$

$$Cr^V \underset{k_b}{\overset{k_a}{\rightleftharpoons}} Cr^{V*}$$

$$Cr^{V*} + IrCl_6^{3-} \xrightarrow{k_c} Cr^{IV} + IrCl_6^{2-}$$

$$Cr^{V*} \xrightarrow{k_d} Cr^{V**}$$

$$Cr^{V**} + IrCl_6^{3-} \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} Cr^{IV} + IrCl_6^{2-}$$

where $k_1 = k_a K_1$, $k_2 = k_a k_c K_1/k_b$, and $k_3 = k_c/k_b$. The various forms of the chromium(V) intermediates are considered to involve differing configurations, since Cr^V complexes are generally four-co-ordinate and those of Cr^{IV} six-co-ordinate, and the change in co-ordination number in oxidations of this type may occur at the Cr^V–Cr^{IV} redox step.

The oxidation of cobalt(II) complexes with nitrilopolyacetic acid ligands, Y (edta, diethylenetriaminepenta-acetic acid, *trans*-1,2-cyclohexanediaminetetra-acetic acid),

$$3Co^{II}Y + Cr^{VI} \longrightarrow 3Co^{III}Y + Cr^{III}$$

[56] J. P. Birk and J. W. Gasiewski, *Inorg. Chem.*, 1971, **10**, 1586.

has been investigated,[57] pathways involving the protonated [$Co^{II}HY$] complexes also being described in some instances.

Chromium(IV) has also been postulated as an intermediate in oxidations using chromium(VI). Several types of reactions involving this species have been described [58] including disproportionation and oxidation–reduction, *e.g.*

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

and

$$Cr^{IV} + Mn^{II} \longrightarrow Cr^{III} + Mn^{III}$$

or

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

Evidence for such processes has been derived from studies on the stoicheiometries of Cr^{VI} oxidations of ligands which will be dealt with more fully in the next chapter.

Iron(III).—The mechanism of the non-complementary redox reaction

$$trans\text{-}[Pt(NH_2Me)_2Br_2] + 2Fe^{III} + 2Br^- \underset{k_\beta}{\overset{k_\alpha}{\rightleftharpoons}} trans\text{-}[Pt(NH_2Me)_2Br_4] + 2Fe^{II}$$

has been described.[59] Under experimental conditions where the oxidant and bromide ion are in considerable excess, the pseudo-first-order rate constant may be expressed as

$$k_{obs} = k_\alpha[Fe^{III}][Br^-]$$

although in the presence of differing concentrations of iron(II) ($\leqslant$ 40-fold excess of this reagent) the forward reaction did not go to completion, the approach to equilibrium being retarded. There is, however, no effect of the square-planar platinum(II) species on the second-order reduction of the octahedral Pt^{IV} complex in the reverse reaction. The mechanism consistent with the data

$$Fe^{III} + Br^- \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} FeBr^{2+}$$

$$[(H_2NMe)_2PtBr_2] + FeBr^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (H_2NMe)_2PtBr_3 + Fe^{II}$$

$$[(H_2NMe)_2PtBr_3] + FeBr^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(H_2NMe)_2PtBr_4] + Fe^{II}$$

involves the formation of a five-co-ordinate platinum(III) intermediate with two one-electron-transfer steps.

[57] K. Ohashi, A. Ohnuma, K. Yamamoto, and Y. Kurimura, *Nippon Kagaku Zasshi*, 1971, 51 (*Chem. Abs.*, 1971, **74**, 130 972g).

[58] G. P. Haight, T. J. Huang, and B. Z. Shakashiri, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2169.

[59] A. Peloso and M. Basato, *J. Chem. Soc.* (*A*), 1971, 725.

In the reaction with indium(I),[60]

$$In^{I} + 2Fe^{III} \longrightarrow 2Fe^{II} + In^{III}$$

the rate law may be expressed in the form

$$-d[Fe^{III}]/dt = 2k_a[In^{I}][Fe^{III}]/[H^{+}]$$

where k_a is a composite term involving both the rate constant and the hydrolysis constant for the aquated ferric ion. Under conditions of hydrogen-ion concentration > 0.1M the stoicheiometry falls from that expected according to the reaction described to lower values, and consistency of behaviour was obtained using an ethylene atmosphere. Unlike the previous example of a non-complementary process, the presence of iron(II) in large excess has no effect on the rate which is again considered to proceed *via* two single-electron-transfer steps with the intermediate formation of indium(II). From the hydrogen-ion dependence, it is considered that the principal reaction pathway involves the iron(III) species $FeOH^{2+}$, but it is not certain whether or not the mechanism is inner-sphere.

In the reaction with tin(II) chloride, in hydrochloric acid,[61]

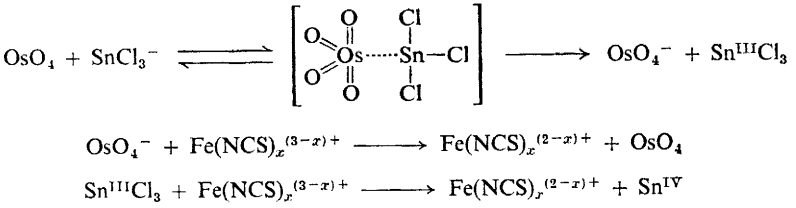
$$2Fe^{III} + SnCl_2 + 2Cl^{-} \longrightarrow 2Fe^{II} + SnCl_4$$

a complex dependence on chloride ion has been observed due to the formation of various tin(II)–chloro-complexes, the reaction rate being greater than for the corresponding reaction in perchlorate and nitrate[62] media. In the presence of thiocyanate, and high $[Cl^{-}]$, the mechanism involves the formation of an intermediate tin(III) species:

$$Fe(NCS)_x^{(3-x)+} + SnCl_4^{2-} \rightleftharpoons Fe(NCS)_x^{(2-x)+} + SnCl_4^{-}$$

$$SnCl_4^{-} + Fe(NCS)_x^{(3-x)+} \longrightarrow Fe(NCS)_x^{(2-x)+} + SnCl_4$$

The reactions are catalysed by osmium(VIII), the proposed route involving the additional sequence shown in Scheme 4.



Scheme 4

In the catalytic reaction, however, the dependence on reductant concentration differs from that previously, with retardation of the rate after an optimum value. The evidence for an initial osmium(VIII)–tin(II)-chloro-complex has been substantiated by spectrophotometric studies.

[60] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1628.
[61] I. I. Alekseeva and L. N. Zhir-Lebed, *Zhur. neorg. Khim.*, 1971, **16**, 1108.
[62] I. I. Alekseeva and L. N. Zhir-Lebed, *Izvest. Vyssh. Uchebn. Zaved. Khim. i khim Technol.*, 1970, **13**, 1260 (*Chem. Abs.*, 1971, **74**, 46 016r).

The aquated molybdenum(III) ion has recently been prepared with the trifluoromethylsulphonate counter ion, and the dimeric Mo_2^{4+} ion has also been observed.[63] This latter ion may be oxidized to molybdenum(VI) using excess of iron(III) as oxidant. Anhydrous iron(III) perchlorate has been used to oxidize bis(π-cyclopentadienyldicarbonyliron) [64] in acetonitrile or acetone, two moles of Fe^{III} being rapidly consumed, the products being the solvent-bound complexes (π-C_5H_5)$Fe(CO)_2NCMe^+$ and (π-C_5H_5)$Fe(CO)_2(OCMe_2)^+$. In the latter case, the weakly co-ordinating solvent molecule may be replaced by a variety of ligands. The cationic product in the reaction of nitrous oxide and $(H_3N)_5Ru(H_2O)^{2+}$ has been shown to be the pentaammine(dinitrogenoxide)ruthenium(II) species.[65] Oxidation of an aqueous solution of this ion with iron(III) gives a quantitative conversion to the $[(H_3N)_5Ru^{III}OH]^{2+}$ complex.

Cerium(IV).—The acid-promoted redox decomposition and cerium(IV) oxidation of the tris(oxalato)cobaltate(III) ion have been studied in aqueous acid media.[66] In 1M sulphuric acid, in the absence of oxidant, there occurs an induction period prior to the internal redox decomposition of the anion. On addition of the cerium(IV), however, there results an *increased* rate of reduction of the cobalt(III) centre in contrast to the behaviour of this oxidant to $M(C_2O_4)_3^{3-}$ complexes where M = Cr, Rh, or Ir. The induction in the acid-catalysed decomposition is consistent with the formation of a unidentate oxalato-complex-ion which may be the main route towards the stepwise reduction to yield Co^{II} and CO_2. From spectral studies on the total expected absorbance values on mixing, it would appear that the cerium(IV) ion is involved in the pre-equilibrium formation of a dinuclear species which might undergo internal electron transfer with reduction to cerium(III). A possible mechanism in this system may then be written as shown in Scheme 5 ($ox^{2-} = C_2O_4^{2-}$). The variations in rate of the one-electron redox reactions of this type are dependent on the nature of the activated complex, which may differ from one metal centre to another in respect of the number of protons and sulphate anions incorporated.

The oxidation of plutonium(IV) has been studied [67] in both acid sulphate and nitrate media, the reaction being inhibited by SO_4^{2-} with a complex reaction order. The rate is, however, independent of nitrate-ion concentration in the range 0.001—0.1M, suggesting that, under these conditions, nitrate-ion complexing is negligible and that the medium is similar to that of perchlorate. The rate is inversely dependent on $[H^+]^2$ and the main reaction path is considered to involve

$$PuOH^{3+} + CeOH^{3+} \longrightarrow Pu^{V} + Ce^{III}$$

$$Pu^{V} + Ce^{IV} \longrightarrow Pu^{VI} + Ce^{III}$$

[63] A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 3287.
[64] E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, 1971, **10**, 1673.
[65] A. A. Diamantis and G. J. Sparrow, *Chem. Comm.*, 1970, 819.
[66] H. G. Kruszyna and R. M. Milburn, *Inorg. Chem.*, 1971, **10**, 1578.
[67] A. Ekstrom and A. B. McLaren, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3511.

although paths involving the dihydroxo-complex-ion may also be taken into account.

$$Co^{III}(ox)_3^{3-} + Ce^{IV} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} [Co^{III}(ox)_3Ce^{IV}]$$

$$[Co^{III}(ox)_3Ce^{IV}] \overset{\text{slow}}{\rightleftharpoons} [Co(ox)_3\text{–}Ce^{III}]$$

$$[Co(ox)_3\text{–}Ce^{III}] \xrightarrow{\text{rapid}} Co(ox)_3^{4-} + Ce^{III}$$

$$[Co(ox)_3\text{–}Ce^{III}] \xrightarrow{\text{rapid}} Co^{II} + 2ox^{2-} + 2CO_2 + Ce^{III}$$

$$Co(ox)_3^{4-} \xrightarrow{\text{rapid}} Co^{II} + 2ox^{2-} + 2CO_2$$

Scheme 5

Although the redox potentials favour electron transfer between cerium(IV) and thallium(I), the reaction is very slow. Catalysis by osmium(VIII) has, however, been observed in both sulphate [68] and perchloric acid media.[69] In the latter system, although perchlorate complexing is not completely ruled out, the reactive species is considered to be the hydrolysed cerium(IV) ion, the mechanism

$$Ce(OH)^{3+} + Tl^{I} \overset{\text{rapid}}{\rightleftharpoons} [Ce(OH)Tl]^{4+}$$

$$[Ce(OH)Tl]^{4+} + Os^{VIII} \xrightarrow{\text{slow}} Ce^{III} + Tl^{III} + Os^{VI}$$

$$Ce^{IV} + Os^{VI} \xrightarrow{\text{rapid}} Ce^{III} + Os^{VII}$$

$$Ce^{IV} + Os^{VII} \xrightarrow{\text{rapid}} Ce^{III} + Os^{VIII}$$

being postulated with rapid regeneration of the osmium(VIII) catalyst. It may be that the rate-determining process as written involves a series of steps incorporating as it does two two-electron transfers. The scheme, however, does account for the observed rate law:

$$\text{Rate} = k_a[Ce^{IV}][Tl^{I}][Os^{VIII}]/[H^+]$$

A similar rate law is observed with sulphate[68] present, although in this case sulphato-cerium(IV) complexes are considered reactive. No effect on the rate is observed in the presence of Tl^{III} and Ce^{III} ions. Kinetic and analytical applications have been described in the iodine-catalysed cerium(IV)–arsenic(III) reaction in 0.5M sulphuric acid.[70]

[68] B. P. Sinha and H. P. Mathur, *Z. phys. Chem.* (*Leipzig*), 1971, **246**, 342.
[69] B. P. Sinha and H. P. Mathur, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1673.
[70] P. A. R. Reggeti, *Chem. Abs.*, 1971, **74**, 25 436n.

3 Miscellaneous Redox Reactions

Quantitative data for the reactions discussed here will be found in Table 3. The reaction between hexachloroiridate(IV) and pentacyanocobaltate(II) has been investigated, the process involving two stages,[71] the rapid first step yielding a dinuclear intermediate which disappears in the slower second reaction. Under the experimental conditions used (~ 10^{-4}M reagent concentrations), the rate of formation of the intermediate was too fast for measurement in the flow apparatus, the second-order rate constant being estimated at 10^7 l mol^{-1} s^{-1}. The metastable intermediate is considered to be the complex $Cl_5IrClCo(CN)_5^{5-}$ formed by an inner-sphere reaction.

Table 3 *Rate constants and thermodynamic parameters for redox reactions involving metal ions. Units and conditions are as quoted in Table* 1

Reaction	k (25 °C)	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$IrCl_6^{2-} + Co(CN)_5^{3-}$	$> 10^7$	0.10	—	—	71
$IrCl_6^{2-} + Co(CN)_5^{3-}$	4.0	0.10	15.4	− 4.2	71[a]
$HO^- + HCo(CN)_5^{3-}$	9.6×10^{-2}	0.50	—	—	73[b]
$V^V + Sn^{II}$	0.46	2.0	6.0	39.2	76[c]
$V^{III} + Hg^{II}$	1.6×10^{-2}	2.0	—	—	78[d]

[a] First-order decay (s^{-1}) of dinuclear intermediate. [b] $T = 24$ °C. [c] Hydrogen-ion dependent pathway. [d] $T = 35$ °C.

The overall reaction products, hexachloroiridate(III) and hydroxopentacyanocobaltate(III), are found after the second stage where there is a Co—Cl bond fission:

$$[Cl_5IrClCo(CN)_5]^{5-} + OH^- \longrightarrow IrCl_6^{3-} + (HO)Co(CN)_5^{3-}$$

It is of interest that on dissociation of the dinuclear species the bridging ligand remains in the primary co-ordination sphere of the reduced form of the oxidant. In this respect, therefore, the dissociation of this complex may be seen as a metal-catalysed aquation of the parent complex. The affinity of mercury(II) for cobalt(III)-bound thiocyanate ion has been discussed[72] where complexes of the type $[(H_3N)_5CoNCS\ Hg]^{4+}$ and $[(H_3N)_5CoNCS]_2$-Hg^{6+} have been encountered, the data being used to analyse mercury(II)-induced aquations and the role of dinuclear-complex formation in inner-sphere electron-transfer systems. The stoicheiometry and kinetics of the reactions between pentacyanocobaltate(II) and hydridopentacyanocobaltate(III) with mercury(II) have been described.[73] In the case of the $Co(CN)_5H^{3-}$ ion, two complexes $(NC)_5CoHg(CN)^{3-}$ and $(NC)_5CoHgCo$-$(CN)_5^{6-}$, are formed, the latter species being formed *via* the redox steps

$$Co(CN)_5H^{3-} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(CN)_5^{4-} + H_2O$$

$$Co(CN)_5^{4-} + Hg(CN)_2 \xrightarrow{k_2} NCHgCo(CN)_5^{3-} + CN^-$$

[71] B. Grossman and A. Haim, *J. Amer. Chem. Soc.*, 1970, **92**, 4835.
[72] L. C. Falk and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 215.
[73] H. S. Lim and F. C. Anson, *Inorg. Chem.*, 1971, **10**, 103.

At high concentrations of mercury(II), however, a second pathway must be invoked, in which the hydrido-complex may react directly with the $Hg(CN)_2$. The same reaction products are given with $Co(CN)_5^{3-}$, although here the reaction is slower, possibly owing to the requirement of the initial dismutation

$$2Co(CN)_5^{3-} + H_2O \longrightarrow Co(CN)_5H^{3-} + Co(CN)_5OH^{3-}$$

Disproportionation of ammine(pyridine)ruthenium(III) complexes has been observed in alkaline media.[74] At pH $\geqslant$ 8 solutions of the complex $(H_3N)_5Ru\,py^{3+}$, which are almost colourless in more acidic conditions, show a marked colour which resembles that of the corresponding ruthenium(II) complexes, the effect

$$2(H_3N)_5Ru^{III}L \rightleftharpoons (H_3N)_5Ru^{II}L + Ru^{IV}$$

being partially reversible. The rate law in various buffer mixtures conforms to the equation

$$-\,d[(H_3N)_5RuL^{3+}]/dt = k[(H_3N)_5RuL^{3+}]^2$$

where L = pyridine, pyrazine, iso-nicotinate, or 4-pyridinecarboxaldehyde. The ruthenium(IV) product has the pyridine nucleus attached, and may initially be derived from the loss of protons from the co-ordinated ammonia, a process which would be consistent with the pH dependence of the equilibrium. In the presence of arsenate and carbonate (buffers) there may be evidence for Ru^{IV} complexes with these ligands.

The reduction reactions of *trans*-PtL_2Cl_4 (where L = PEt_3, piperidine, or SEt_2) and of *trans*-$PtLBr_4$ with bis-(*o*-phenylene)-bis(dimethylarsine) [= (diars)] -nickel(II) and -palladium(II) have been examined [75] in methanol. In the presence of halide ions (Y^- = Cl^- or Br^-) in solution, the nickel complex reacts,

$$trans\text{-}[PtL_2Cl_4] + [Ni(diars)_2Y]^+ \xrightarrow{+Y^-} trans\text{-}[PtL_2Cl_2] + [Ni(diars)_2Y_2]^+$$

the reaction order being unity with respect to both reagents. In the case of the palladium(II) reaction, although the platinum complex is reduced, there is no oxidation of the palladium detected. The rates are ligand dependent, following the sequence in k_2 of PEt_3 < pip < SEt_2, the tetrabromo-derivatives reacting 50—200 times as fast as the tetrachloro-derivatives when the reductant is $[Ni(diars)_2Y]^+$, whereas they react 5×10^3 faster when the reductant is $[Pt(diars)_2Y]^+$. This difference in behaviour is consistent with a more pronounced class 'b' character in Pt^{II} complexes compared with Ni^{II} species.

In the oxidation of tin(II) by vanadium(V) in perchlorate media,[76] the rate law

$$-\,d[V^V]/dt = k_\alpha[Sn^{II}][V^V]^2 + k_\beta[Sn^{II}][V^V]$$

[74] De F. P. Rudd and H. Taube, *Inorg. Chem.*, 1971, **10**, 1543.
[75] A. Peloso, *Gazzetta*, 1970, **100**, 851.
[76] B. Schiefelbein and N. A. Daughtery, *Inorg. Chem.*, 1970, **9**, 1716.

is observed where k_α and k_β are acidity dependent. The rapid reduction of molybdenum(VI) by tin(II) in chloride media has been described.[77] The reaction involves the formation of an intensely brown-coloured Mo^{V} species with a concentration ratio of Sn : Mo of 1 : 2. The two-stage reaction was investigated using the stopped-flow technique, the formation involving a chain or consecutive process, whereas the subsequent decay is independent of reductant concentration.

In the reaction of vanadium(III) with mercury(II) in perchlorate media,[78]

$$2V^{III} + 2Hg^{II} \longrightarrow 2V^{IV} + [Hg^{I}]_2$$

the rate law may be expressed as

$$\frac{-\,d[V^{III}]}{dt} = \frac{2k_1 k_2[V^{III}]^2[Hg^{II}]}{(k_{-1} + k_3)[V^{IV}] + k_2[V^{III}]} + \frac{2k_1 k_3[V^{III}][Hg^{II}][V^{IV}]}{(k_{-1} + k_3)[V^{IV}] + k_2[V^{III}]}$$

although at low initial vanadium(IV) concentrations, the second step is negligible. The reaction is considered to involve two consecutive one-electron steps *viz.* $V^{3+} \rightarrow VO^{2+} \rightarrow VO_2^{+}$, *i.e.*,

$$V^{III} + Hg^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V^{IV} + Hg^{I}$$

$$V^{III} + Hg^{I} \xrightarrow{k_2} V^{IV} + Hg^{0}$$

$$V^{IV} + Hg^{I} \xrightarrow{k_3} V^{V} + Hg^{0}$$

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

$$Hg^{0} + Hg^{II} \longrightarrow [Hg^{I}]_2$$

A direct two-electron transfer from $V^{III} \rightarrow V^{V}$ is considered unlikely, since it would require drastic changes in the inner co-ordination sphere of the vanadium(III) reactant which are energetically unfavourable.

A study has been made of the reaction between rhenium(VII) and electrolytically generated titanium(III),[79] the rate law in high sulphuric acid concentrations (~ 8M) being

$$-\,d[Re^{VII}]/dt = k[H_2SO_4][Re^{VII}][Ti^{III}]^2$$

Chloride ion catalyses the reaction and has an effect on the final product which is considered to be a dinuclear Ti^{IV}–Re^{IV} complex. It is of interest that on preparation of rhenium(V) and reaction with Ti^{III}, there is an instantaneous reduction to yield the same dinuclear product. The use of non-aqueous media for investigating electron-transfer reactions is increasing and a review of solvent effects of systems involving metal complexes in homogeneous and heterogeneous phases has recently been published.[80]

[77] A. P. Filippov, *Zhur. neorg. Khim.*, 1970, **15**, 3019.
[78] M. Green, W. C. E. Higginson, J. B. Stead, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3069.
[79] K. Sheitanov and R. Chavdarova, *Izv. Otd. khim. Nauki, Bulg. Akad. Nauk*, 1970, **3**, 183 (*Chem. Abs.*, 1971, **74**, 25 462t).
[80] N. Tanaka, *Kogyo Kagaku Zasshi*, 1970, **73**, 2231 (*Chem. Abs.*, 1971, **74**, 91 649k).

The reduction of uranyl ion by titanium(III) has been investigated in various solvents.[81] In acetonitrile or DMF, at ambient temperature, there is a rapid reaction involving the chloro-complexes of the reductant and the complexed uranyl ion to yield $TiOCl_2$ and UCl_6^{2-}, whereas in acetone or $(BuO)_3PO$ the uranium product is UCl_5^-. The uncharged UCl_5 complex predominates in methanol. The mechanism of the reaction is however attributed to direct electron- and oxygen-atom-transfer between the inner co-ordination spheres of the titanium(III) and uranium.

4 Electron Exchange Reactions

Quantitative data for these reactions will be found in Table 4. The reactions between $Cr(H_2O)_6^{2+}$ and $(H_2O)_3(NH_3)_2CrCl^{2+}$, $(H_2O)_2(NH_3)_3CrCl^{2+}$, and $(H_2O)_4(NH_3)CrCl^{2+}$ have been examined [82] in an attempt to identify the factors, particularly the non-bridging ligand effects, which contribute to the overall activation energy. All three complexes are considered to have a chloro- and an aquo-ligand in positions *trans* to each other and with the complex ion *trans*-$(H_2O)(NH_3)_4CrCl^{2+}$, they give four examples of species where the only variable may be seen to be the change in the strength of the ligand field in positions *cis* to the chloro-ligand. An inner-sphere reaction mechanism is operative with chloride transfer and the data strongly suggest a correlation between activation energies and the ligand-field strength of the chromium(III) oxidant.

The chromium(II) reduction of azidopenta-amminechromium(III) has been studied,[83] and for reactions of complexes of the type $(H_3N)_5CrX^{2+}$, the reactivity order for varying ligands X is $I^- > Br^- > Cl^- > N_3^- > F^-$, which is the same for the analogous reaction with $(H_3N)_5CoX^{2+}$ complexes. In the reaction with the corresponding chloropenta-amminechromium(III) complex,[84] in the presence of ethylenediamine, it has been shown that complexes formed by the reductant also react with a regular increase in rate with increasing nitrogen co-ordination. These effects have been discussed in terms of increased ligand-field strength. In the chromium(II)-catalysed aquation of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$, the rate law

$$\text{Rate} = k_2[Cr^{II}][\text{complex}]$$

is observed,[85] with resultant formation of $(H_2O)_5CrI^{2+}$. Again it is considered that the non-bridging ligands in this inner-sphere redox reaction undergo rearrangement in the formation of the activated complex, and that for chromium this is more easily achieved with oxygen than with nitrogen donor atoms, the reduction of both isomers being more rapid that that of the complex $Cr(NH_3)_5I^{2+}$. The reaction rate for the aquo-iodo-species is

[81] Y. I. Belyaev, V. M. Vdovenko, A. I. Skoblo, and D. N. Suglobov, *Radiokhimiya*, 1971, **13**, 140 (*Chem. Abs.*, 1971, **74**, 130 887h).
[82] T. J. Williams and C. S. Garner, *Inorg. Chem.*, 1970, **9**, 2058.
[83] R. Davies and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 1102.
[84] T. J. Williams and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 975.
[85] D. W. Hoppenjans, G. Gordon, and J. B. Hunt, *Inorg. Chem.*, 1971, **10**, 754.

Table 4 *Electron-exchange reactions. Rate constants and thermodynamic parameters for redox reactions involving metal ions. Units and conditions are as quoted in Table* 1

Reaction	k (25 °C)	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$Cr^{II} + Cr(NH_3)_4(H_2O)Cl^{2+}$	1.27	1.5	9.8	− 28.1	82[a]
$Cr^{II} + Cr(NH_3)_3(H_2O)Cl^{2+}$	2.19	1.5	9.9	− 26.1	82[a]
$Cr^{II} + Cr(NH_3)_2(H_2O)_3Cl^{2+}$	6.9	1.5	9.1	− 27	82[a]
$Cr^{II} + Cr(NH_3)(H_2O)_4Cl^{2+}$	19.1	1.5	8.4	− 27	82[a]
$Cr^{II} + (H_3N)_5CrN_3^{2+}$	1.8×10^{-2}	1.0	12.4	− 24.9	83
$Cr^{II} + (H_3N)_5CrCl^{2+}$	2.2×10^{6}	1.4	—	—	84
$Cr(en)^{2+} + (H_3N)_5CrCl^{2+}$	4.0×10^{7}	1.4	—	—	84
$Cr(en)_2^{2+} + (H_3N)_5CrCl^{2+}$	1.6×10^{8}	1.4	—	—	84
Cr^{II} + *cis*-$Cr(NH_3)_4(H_2O)I^{2+}$	14.6	1.0	8.7	− 24	85
Cr^{II} + *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$	165	1.0	7.1	− 24	85
$Cr^{II} + (H_2O)_4Crmal^{+}$	63	1.0	6.0	− 31	21[b]
$Cr^{II} + (H_2O)_5CrHmal^{2+}$	4	1.0	9.0	—	21[c]
$Cr^{II} + (H_2O)_5CrSCN^{2+}$	40	1.0	—	—	22
$Cr^{II} + (H_2O)_5CrNCS^{2+}$	1.4×10^{-4}	1.0	—	—	22
$Fe^{II}L_6 + Fe^{III}L_6$	34.4	0.1	9.4	− 19	91[d]
$Fe^{II} + FeCl^{2+}$	130	0.1	5.2	− 27	91[d]
$Fe^{II} + FeNCS^{2+}$	224	0.1	8.9	− 17	91[d]
$Fe^{II} + FeCl_2^{+}$	1.02×10^{3}	0.1	—	—	91[d]
$Fe^{II} + Fe(NCS)_2^{+}$	2.96×10^{3}	0.1	—	—	91[d]
$\alpha + (H_3N)_5Co(O_2)Co(NH_3)_5^{5+}$	0.170	0.245	13.2	− 18	95[e]
$\alpha + (H_3N)_4Co\cdot\mu(NH_2,O_2)\cdot Co(NH_3)_4^{4+}$	12	0.245	—	—	95[e]
$\alpha + (bipy)_2Co\cdot\mu(NH_2,O_2)\cdot Co(bipy)_2^{4+}$	2.35×10^{3}	0.245	—	—	95[e]
$\alpha + (phen)_2Co\cdot\mu(NH_2,O_2)\cdot Co(phen)_2^{4+}$	6.17×10^{3}	0.245	—	—	95[e]
$RuX^{+} + Ru^{3+}$	$> 10^{2}$	0.3m	—	—	99

[a] $[H^+] = 1.5M$ $HClO_4$. [b] mal = maleate; acid-dependent path, $[H^+] = 1.0M$. Hmal = monodentate maleate. [d] Solvent = dimethylsulphoxide. [e] α = α-form of $[(en)_2Co\cdot\mu(NH_2,O_2)\cdot Co(en)_2]^{3+}$; see text.

substantially greater, however, than that for the corresponding aquo-chloro-complex,[82] suggesting participation of the bridging group in the mechanism. Rates of reduction of chromium-ammine complexes *via* iodo- and chloro-bridging are also dependent on ligand effects.[85] The reduced-metal-ion-catalysed aquation of hexacyanochromate(III) to pentacyano-hydroxochromate(III) has been investigated [86] in aqueous alkaline media. In concentrations of cyanide and hydroxide greater than 0.1M and a ratio $[OH^-] : [CN^-] < 2$, an equilibrium is established between the species $Cr(CN)_6^{3-}$ and $Cr(CN)_5OH^{3-}$. A first-order dependence on both Cr^{II} and Cr^{III} species is observed and two reactions are considered, the initial electron transfer

$$Cr(CN)_6^{3-} + Cr(CN)_5OH^{4-} \rightleftharpoons Cr(CN)_6^{4-} + Cr(CN)_5OH^{3-}$$

followed by the rapid equilibrium

$$Cr(CN)_6^{4-} + HO^- \rightleftharpoons Cr(CN)_5OH^{4-} + CN^-$$

Although the question of mechanism cannot be unambiguously resolved, an outer-sphere route is favoured. Electron-transfer reactions have also been utilized in the synthesis of alkylenediaminetetra-acetatochromate(III) complexes,[87] $Cr(ata)H_2O^-$, the mechanism involving the rapid formation of the chromium(II) complexes

$$Cr^{II} + ata^{4-} \overset{\text{fast}}{\rightleftharpoons} Cr(ata)^{2-}$$
$$Cr(ata)^{2-} + Cr^{III} \longrightarrow Cr^{III}(ata)H_2O + Cr^{II}$$

being followed by the rate-determining electron-exchange reaction.

Medium effects in the iron(II)–(III) exchange, measured [88] at low temperature in lithium and sodium perchlorate solutions at differing ionic strengths, have been interpreted in terms of displacement of the hydrolysis equilibrium by protons present, the variation in activity coefficients, and the participation of hydrolysed iron complexes in the reactions. Attempts have also been made to examine the exchange rates at various hydrogen-ion concentrations using the Mössbauer effect.[89] Unfortunately, however, with the high concentrations of reagents used, the electron transfer is too rapid in the $FeOH^{2+}$–Fe^{2+} reaction, although there is no evidence for rapid exchange of more highly hydrolysed species. The electron-transfer reaction has also been studied in non-aqueous media and in mixed water–solvent solutions. The rate of reaction is found [90] to increase at constant hydrogen-ion concentration in the presence of increasing amounts of *N*-methylacetamide and *NN'*-dimethylacetamide (L), the order in hydrogen ion in a constant solvent–water mixture being − 1. Four reactions are considered to occur, those

[86] L. Jeftic and S. W. Feldberg, *J. Phys. Chem.*, 1971, **75**, 2381.
[87] H. Ogino, J. J. Chung, and N. Tanaka, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 125.
[88] W. J. Gelsema and H. A. Vink, *Rec. Trav. chim.*, 1971, **90**, 165.
[89] M. Komov, A. Vertes, I. Dezsi, and I. Ruff, *Acta Chim. Acad. Sci. Hung.*, 1970, **66**, 285 (*Chem. Abs.*, 1971, **74**, 68 384m; *Chem. Abs.*, 1971, **75**, 10 861u).
[90] G. Wada and R. Yoshihara, *Kogyo Kagaku Zasshi*, 1970, **73**, 2309 (*Chem. Abs.*, 1971, **75**, 10 843q).

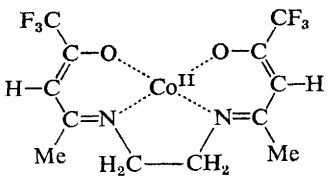
involving Fe^{2+} with FeL^{3+} and $Fe(OH)L^{2+}$ being similar in rate to the primary aquo-complex systems, suggesting that the solvating role of L is much less pronounced than its complexing role. The suggested mechanism is one involving hydrogen-atom transfer in a Grotthus scheme. The iron(II)–iron(III) reaction has been investigated in DMSO in the presence of thiocyanate ions, the rate constants for the reactions involving $FeNCS^{2+}$ and $Fe(NCS)_2^+$ being determined.[91] The observed rate is, however, almost independent of acidity. A comparison of the data for the acceleration of the reaction by Cl^- and NCS^- in water and DMSO suggests that in the systems studied an inner-sphere route is operative with the thiocyanate group acting as a bridging ligand, there being no hydrogen atoms in the solvent which would play an important part in a hydrogen-atom-transfer mechanism.

The transfer reaction in the redox system $Co(NH_3)_6^{2+}/Co(NH_3)_6^{3+}$ has been studied using polarization-resistance measurements at platinum electrodes,[92] although hydrolysis and ion-pair formation influence the exchange. The redox behaviour of complexes with macrocyclic ligands (L) has been examined for first-row transition-metal ions.[93] Using cyclic voltammetry, it has been shown that although the $M^{II}L$–$M^{I}L$ couples are quasi-reversible, those involving the $M^{III}L$–$M^{II}L$ configurations are irreversible. The behaviour is dependent on solvent and electrode and for cobalt(III) complexes, half-wave potentials for the reductions

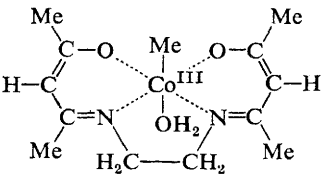
$$Co^{III}LX_2 \longrightarrow Co^{II}LX_2$$

vary with the ligand-field strength of group X. Electron-transfer reactions involving alkyl-group transfer between cobalt ions have been examined with quadridentate Schiff bases as the co-ordinating ligands.[94] The complex *NN'*-ethylenebis-(4,4,4-trifluoro-1-methyl-3-oxobutylideneiminato)cobalt(II), Co^{II}(fmbo), (10) reacts readily ($t_{\frac{1}{2}} < 2$ min) in DMSO with *NN'*-ethylenebis-(1-methyl-3-oxobutylideneiminato)methylaquocobalt(III), $Co^{III}Me(H_2O)$(mob), (11) according to the equation

$$Co^{III}Me(H_2O)(mob) + Co^{II}(fmbo) \rightleftharpoons Co^{II}(mob) + Me(H_2O)Co^{III}(fmbo)$$



(10)

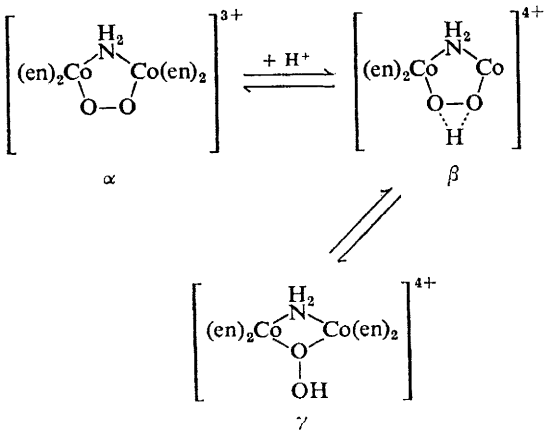


(11)

[91] G. Wada, N. Yoshizawa, and Y. Sakamoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 1018.
[92] H. Bartelt, *Electrochim. Acta*, 1971, **16**, 307.
[93] D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, 1971, **10**, 1739.
[94] A. Van den Bergen and B. O. West, *Chem. Comm.*, 1971, 52.

The corresponding ethyl-cobalt(III) complex reacts in a similar manner, although the analogous perfluoro-derivative shows no reaction.

Factors affecting the electron-transfer reactions between O_2^- and O_2^{2-} bridging ligands in dinuclear complexes of cobalt(III) have been investigated.[95] The μ-amido-μ-peroxo-complex $[(en)_2Co\cdot\mu(NH_2,O_2)\cdot Co(en)_2]^{3+}$ has been shown to exist in the protonated and unprotonated forms although the γ-complex is formed only in strongly acidic media (Scheme 6).



Scheme 6

In the reaction with superoxo-complexes of the type $[LCo\cdot\mu(NH_2,O_2)Co\text{-}L]^{4+}$ where L = $(NH_3)_4$, $(bipy)_2$, or $(phen)_2$ and with $[(H_3N)_5Co\cdot O_2\cdot Co(NH_3)_5]^{5+}$, the 1 : 1 redox reactions take place *via* the α-form, the β-complex accounting for less than 5% of the rate constant, although the proton in the latter form might have been expected to help in the bridging of the O_2^- to the O_2^{2-} in the electron-transfer step. Where there is the possibility of electron delocalization in the ligand system, the rate of transfer is substantially faster than in the ammine complexes, an order which parallels the iron(II) reductions of these superoxo-complexes.

A tetrahedral copper(I)–copper(II) redox system has been described involving dodecatungstocuprate complexes.[96] The copper(II) species, $CuW_{12}O_{40}^{6-}$, may be reversibly reduced at a dropping-mercury electrode to the corresponding copper(I) complex with two further reduction steps involving the tungsten atoms. The copper(I) ion is stable with respect to disproportionation and represents the first example of a complex of this type with a univalent ion. The co-ordination of the copper atoms is through oxygen, and it is considered that the facile reduction takes place owing to the fact that only small stereochemical changes are involved with no prior

[95] D. R. Wexell and M. T. Pope, *Chem. Comm.*, 1971, 886.
[96] K. M. Davies and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1418.

dissociation of the multidentate ligand being required. In the electron-exchange reaction between gold(I) and gold(III)[97] in the presence of *cis*-1,2-dicyanoethylenedithiolate (edt^{2-}) there occurs the formation of the gold(II) species $Au(edt)_2^{2-}$, the reaction apparently being specific for this ligand. Homogeneous electron-transfer reactions may be studied using internal-reflection spectroscopy[98] and the theoretical aspects of the technique have been described. Among systems studied is the reaction

$$Ta_6Br_{12}^{2+} + Ta_6Br_{12}^{4+} \rightleftharpoons 2Ta_6Br_{12}^{3+}$$

The substitution of halide ions into $Ru(H_2O)_6^{3+}$ has been investigated and been found to be catalysed by aquoruthenium(II) ions.[99] The mechanism is considered to involve a rate-determining substitution of the halide ion on the Ru^{II} complex, with a subsequent rapid electron-transfer process (X^- = halide)

$$Ru^{2+} + X^- \underset{k_\beta}{\overset{k_\alpha}{\rightleftharpoons}} RuX^+$$

$$RuX^+ + Ru(H_2O)_6^{3+} \underset{k_\delta}{\overset{k_\gamma}{\rightleftharpoons}} RuX^{2+} + Ru(H_2O)_6^{2+}$$

with $k_\gamma[Ru^{III}]$ at least an order of magnitude greater than k_β. A lower limit of the electron-transfer rate is considered to be $\sim 10^2$ l mol^{-1} s^{-1}.

An ^{18}O tracer study of the uranium(IV)–(VI) electron exchange has been made.[100] The half-life of the oxygen exchange between UO_2^{2+} and H_2O in the absence of uranium(IV) is $\sim 2.3 \times 10^3$ h, whereas with the reduced form of the metal present this value falls to $\sim$ 50—60 h. The ^{18}O exchange is thus considered to take place *via* an activated complex in the reaction

$$U^{VI} + U^{IV} \rightleftharpoons [U^{IV} \cdot U^{VI}]^{\ddagger} \longrightarrow U^{IV} + U^{VI}$$

$$\downarrow$$

$$U^{18}O_2^{2+} + U^{4+} + 2H_2O$$

[97] J. H. Waters, T. J. Bergendahl, and S. R. Lewis, *Chem. Comm.*, 1971, 834.
[98] N. Winograd and T. Kuwana, *J. Amer. Chem. Soc.*, 1971, **93**, 4343.
[99] T. W. Kallen and J. E. Earley, *Inorg. Chem.*, 1971, **10**, 1149.
[100] Y. Kato, K. Suzuki, H. Fukutomi, H. Tomigasu, and G. Gordon, *Bull. Tokyo Inst. Technol.*, 1970, **96**, 133 (*Chem. Abs.*, 1971, **74**, 16 094x).

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. Such investigations have provided much mechanistic data and an increasingly important aspect is the evidence for inner-sphere reactions with the formation of metal-ion complex intermediates. The question of replacement as a prerequisite to redox reactions has been discussed[16] and the role of the intermediate defined. It is of interest to note that identification of an intermediate does not necessarily infer its involvement in the rate-determining process, in that, for the reactions

$$M^{n+} + L \underset{}{\overset{K_1}{\rightleftharpoons}} ML^{n+} \qquad (1)$$

$$ML^{n+} \overset{k_1}{\rightleftharpoons} \begin{bmatrix}\text{activated}\\ \text{complex}\end{bmatrix}^{\ddagger} \xrightarrow{\text{fast}} \text{products} \qquad (2)$$

and

$$M^{n+} + L \overset{K_2}{\rightleftharpoons} ML^{n+} \qquad (3)$$

$$M^{n+} + L \overset{k_2}{\rightleftharpoons} \begin{bmatrix}\text{activated}\\ \text{complex}\end{bmatrix}^{\ddagger} \xrightarrow{\text{fast}} \text{products} \qquad (4)$$

the forms of the experimental rate law will be identical under conditions of $[L] \gg [M^{n+}]$. Where $[M^{n+}]_{tot}$ represents the total initial concentration of M^{n+} $(= [M^{n+}] + [ML^{n+}])$, the rate laws corresponding to (1) and (2), and (3) and (4), may be expressed as

$$\frac{-\,d[ML^{n+}]}{dt} = k_1 K_1 [M^{n+}]_{tot}[L]/(1 + K_1[L])$$

and

$$\frac{-\,d[ML^{n+}]}{dt} = k_2 K_2 [M^{n+}]_{tot}[L]/(1 + K_2[L])$$

respectively, and assignment of the role of the complex ion cannot be made unambiguously on the basis of rate law alone if the equilibria (1) and (3) are very rapidly established. Where it is possible to identify the formation of an intermediate in a sequential process, then characterization is possible. In many redox reactions there is covalent bond formation between the oxidant and reductant, and from analysis of several types of system it would appear that such a process provides a low-energy pathway for electron transfer. Mechanistic implications and the possible ambiguities of rate laws have recently been discussed by Birk.[101] Inner-sphere redox reactions

[101] J. P. Birk, *J. Chem. Educ.*, 1970, **47**, 805.

of this type occur more frequently when neutral or negatively charged ligands are involved, rather than with cationic reducing species and in this section the modes of interaction of various metal-ion oxidants are described. In general, systems involving cationic species have been more thoroughly investigated, but the nature of the reactions of anionic oxidants is increasingly under examination and where possible reference has been made to reactions of this type. Quantitative data for some of the reactions discussed are presented in the Table on p. 86.

1 Cobalt(III)

The nature of the species present in acidic aqueous solutions containing cobalt(III) has been reinvestigated in an attempt to characterize any dinuclear aquocobalt(III) complexes. The ^{18}O studies, where the evidence for bridged dinuclear complex ions is based on the partial liberation of oxygen from the decomposition of the inner co-ordination sphere of the cobalt(III), have been re-examined [102] and it would appear that there is no 'hold-back' of oxygen in 0.3—0.6 mol l^{-1} Co^{III} in 1.5—6M-$HClO_4$, the molecular oxygen released on dilution of such solutions with ^{18}O-enriched water having a composition identical to that of the solvent. Very considerable precautions were taken in the preparation of the cobalt(III) [and cobalt(II)] stock solutions, which were used within a few minutes of completion of their preparation.

The stoicheiometries and kinetics of the oxidations of H_2O_2, HNO_2, Br^-, I^-, SCN^-, and hydroquinone have been reported,[103] the reactions being first order with respect to both oxidant and reductant with no kinetic or spectrophotometric evidence for intermediate complex formation. In the case of hydrogen peroxide, under the experimental conditions used, the reaction

$$2Co^{III} + H_2O_2 \longrightarrow 2Co^{II} + O_2 + 2H^+$$

takes place and a general reaction scheme for the substrates (S) may be expressed as

$$\begin{aligned}
Co^{III} + H_2O &\underset{}{\overset{K_h}{\rightleftharpoons}} CoOH^{2+} + H^+ \qquad (5)\\
Co^{III} + S &\xrightarrow{k_1} Co^{II} + S^\bullet\\
CoOH^{2+} + S &\xrightarrow{k_2} Co^{II} + S^\bullet\\
Co^{III} + S^\bullet &\xrightarrow{\text{rapid}} \text{products}\\
S^\bullet + S^\bullet &\xrightarrow{\text{fast}} S_2
\end{aligned}$$

From the data available, it appears that for Br^-, Cl^-, HN_3, and SCN^-, the rates of reaction with Co^{3+}(aq) are influenced by the water-exchange rate on the oxidant, whereas those for I^- and hydroquinone occur too rapidly ($\approx 2 \times 10^3$ and $\approx 8 \times 10^3$ faster) for this to be a rate-determining factor. The results on the hydrogen peroxide system appear to contrast markedly with those in another study,[104] in which evidence is suggested from stopped-flow traces for two intermediate complexes of the type $CoH_2O_2^{3+}$ and (Co^{III},-HO_2^-). Studies of the halide ion oxidations have also been carried out in

[102] R. K. Murmann, *Inorg. Chem.*, 1971, **10**, 2070.
[103] G. Davies and K. O. Watkins, *J. Phys. Chem.*, 1970, **74**, 3388.
[104] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1971, **67**, 760.

very strongly acidic media [105] (3—7M-$HClO_4$). Although the order with respect to reactants is still unity (in the case of bromide ion even in an excess of oxidant), the overall rate of reaction increases with acidity, in contrast to the other studies where a linear dependence on $[H^+]^{-1}$ has been observed in accordance with equilibrium (5). In the reaction with iodide, after the equivalence point a secondary (reversible) process has been detected involving either complex formation

$$I_2 + Co^{III} \rightleftharpoons CoI^{2+} + I^+$$

or the formation of iodate

$$I_2 + 10Co^{III} \rightleftharpoons 2IO_3^- + 10Co^{II}$$

In the reaction with hydroxylamine,[106] under the same highly acidic conditions, the oxidation has been found to be first order in cobalt(III) and zero order in substrate, with a rate dependence on cobalt(II). Addition of bisulphate ions increases the rate, with the possibility of another reaction path involving the complex ion $CoSO_4^+$.

The oxidation of organic dicarboxylic (oxalic, malonic, and succinic) acids has been examined [107] in sulphuric acid media, and up to *ca.* 3M-H_2SO_4 there is an inverse acid dependence, whereas in solutions > 3M the reaction rate increases with increasing acid concentration. Complex formation has been invoked and the rates decrease in the order oxalic > malonic > succinic. The inner sphere reaction with oxalic acid has also been studied in perchlorate media:[108]

$$2Co^{III} + H_2C_2O_4 \longrightarrow 2Co^{II} + 2CO_2 + 2H^+$$

Any intermediate complexes formed could not be detected by spectrophotometric or kinetic means. Under the acidity conditions used (0.1—3.0M) various protonated forms of the reducing agent are present and the mechanism has been proposed with reactions (6)—(11) rate determining:

$$Co^{3+} + H_2O \overset{K_h}{\rightleftharpoons} CoOH^{2+} + H^+ \quad (5)$$

$$Co^{3+} + H_2C_2O_4 \xrightarrow{k_1} Co^{II} + ox^{\bullet} \quad (6)$$

$$CoOH^{2+} + H_2C_2O_4 \xrightarrow{k_2} Co^{II} + ox^{\bullet} \quad (7)$$

$$Co^{3+} + HC_2O_4^- \xrightarrow{k_3} Co^{II} + ox^{\bullet} \quad (8)$$

$$CoOH^{2+} + HC_2O_4^- \xrightarrow{k_4} Co^{II} + ox^{\bullet} \quad (9)$$

$$Co^{3+} + C_2O_4^{2-} \xrightarrow{k_5} Co^{II} + ox^{\bullet} \quad (10)$$

$$CoOH^{2+} + C_2O_4^{2-} \xrightarrow{k_6} Co^{II} + ox^{\bullet} \quad (11)$$

$$Co^{III} + ox^{\bullet} \xrightarrow{\text{rapid}} Co^{II} + CO_2$$

[105] B. Šrámková, J. Zýka, and J. Doležal, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **30**, 177, 185.
[106] B. Šrámková, J. Zýka, and J. Doležal, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **30**, 169.
[107] J. K. Sthapak and S. Ghosh, *Indian J. Chem.*, 1971, **9**, 331.
[108] G. Davies and K. O. Watkins, *Inorg. Chem.*, 1970, **9**, 2735.

The observed rate constant (k_{obs}) may be best represented by an expression of the type

$$k_{obs} = \frac{A + B[H^+]^{-1} + C[H^+]^{-2}}{1 + K_{1a}[H^+]^{-1}}$$

where $A = 2k_1$, $B = 2(k_2 K_h + k_3 K_{1a})$ and $C = 2K_{1a}(k_4 K_h + k_5 K_{2a})$, in which K_h is the hydrolysis constant for the aquated cobalt(III) ion and K_{1a} and K_{2a} represent the first and second acid dissociation constants for the organic substrate. On consideration of the data available, the assumptions $k_2 K_h \gg k_3 K_{1a}$ and $k_4 K_h \gg k_5 K_{2a}$ are believed to hold, so that rate parameters corresponding to reactions (6), (7), and (9) have been evaluated. Several other data involving the reactions of $CoOH^{2+}$ have been obtained and an examination (see Table) indicates that the rate increases with increasing negative charge product, as is found in complex formation reactions which are considered to proceed *via* a dissociative (S_N1) mechanism.

The effects of H^+, Co^{II}, F^-, and Ag^+ on the reaction of cobalt(III) with water have been examined,[109] and in the oxidation of diacetone alcohol [110] there is indirect evidence for an intermediate complex from Michaelis–Menten plots.

Whereas the mono-oxalatocobalt(III) complexes undergo rapid redox reactions,[108] the corresponding bis- and tris-oxalato-species are much less readily decomposed. In the hydrolysis of di-μ-hydroxo-bis{dioxalatocobaltate(III)},[111] in aqueous solution at pH 3.5—4.6, the initial product is the bisoxalatodiaquocobaltate(III) which decomposes to yield cobalt (II), no divalent metal ion being derived directly from the dimeric complex. The spontaneous reduction of the 1,2,3-triaquodiethylenetriaminecobalt(III) cation in aqueous perchloric acid (0.1—2.0M) has been shown to follow the rate law [112]

$$\frac{-\,d[Co(dien)^{3+}]}{dt} = \{k_1 + k_2'[H^+]^{-1}\}[Co(dien)^{3+}]$$

the acid dependence being accounted for by reaction of the hydroxo-complex

$$(H_2O)_3Co(dien)^{3+} \rightleftharpoons (H_2O)_2Co(dien)OH^{2+} + H^+$$

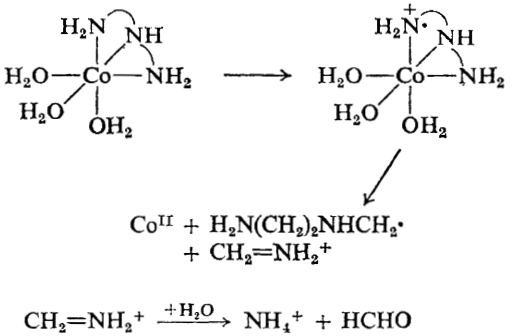
k_1 $\qquad$ k_2

Co^{II} + oxidized dien products

The mechanism may involve the electron transfer from a co-ordinated nitrogen to the cobalt centre with the formation of a radical, which then

[109] J. K. Sthapak and S. Ghosh, *J. Indian Chem. Soc.*, 1971, **48**, 231.
[110] A. Meenakshi and M. Santappa, *Indian J. Chem.*, 1970, **8**, 467.
[111] L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1971, 2589.
[112] C. S. Garner and P. Wilairat, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1833.

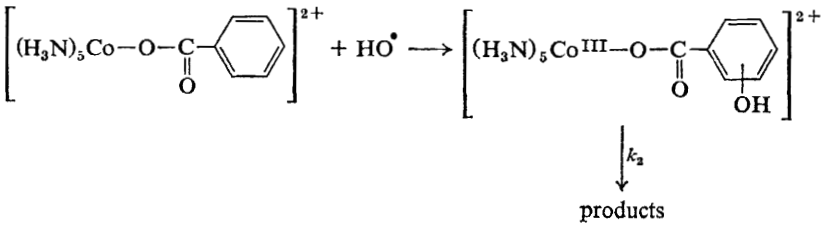
decomposes to yield the methyliminium cation, $CH_2{=}NH_2^+$, which on further reaction gives formaldehyde and ammonia, *i.e.*



$$Co^{II} + H_2N(CH_2)_2NHCH_2^{\bullet} + CH_2{=}NH_2^+$$

$$CH_2{=}NH_2^+ \xrightarrow{+H_2O} NH_4^+ + HCHO$$

The reaction of the benzoatopenta-amminecobalt(III) complex with hydroxyl radicals has been studied,[113] the radical formed decomposing in a second-order reaction:



where $k_2 = 3 \times 10^7$ l mol^{-1} s^{-1}, and no intramolecular redox reaction of the intermediate radicals with the cobalt(III) takes place. Although the site of hydroxyl addition to the ring is not constant, all the radicals formed are conjugated to the cobalt centre through π-electron delocalization and their spectra are similar to that of the uncomplexed benzoate–radical adduct. Under high-dose conditions no cobalt(II) is formed, and from dose-rate studies it is considered that the rate of inner electron transfer to yield cobalt(II) is slower than 10^2 s^{-1}.

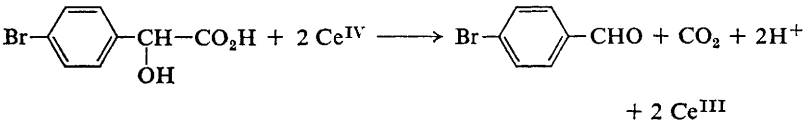
2 Cerium(IV)

The oxidation of formic acid in perchloric acid media has been investigated spectrophotometrically,[114] the reaction being so slow that it was not followed to completion. There is, however, evidence for an inner-sphere reaction, in that in the presence of increasing concentrations of formic acid the optical density increases progressively, the effect being confirmed by extrapolation of the plots to zero time. The rate of disappearance of oxidant

[113] H. Cohen and D. Meyerstein, *Israel J. Chem.*, 1970, **8**, suppl., 95 pp; *J. Amer. Chem. Soc.*, 1971, **93**, 4179.

[114] C. F. Wells and M. Husain, *J. Chem. Soc.* (*A*), 1971, 380.

is first order, the pseudo-first-order rate constant increasing with $[HCO_2H]$ to a value independent of substrate concentration. In this region the rate constant is dependent on perchloric acid concentration. On the basis of these observations, it is considered that both $Ce^{IV}(HCO_2H)$ and $Ce^{IV}(HCO_2^-)$ complexes are formed with only the latter acting as an oxidizing agent. The mechanism of oxidation of this ion has also been compared with those for other metal ion reagents.[115] The oxidation of *p*-bromomandelic acid in sulphate media [116] occurs according to the equation



$$+ 2\ Ce^{III}$$

and although no spectroscopic evidence is available for complex formation, the kinetic data may be interpreted in terms of such a species. Complexes are also involved in the reaction with DMF,[117] the inner-sphere oxidation yielding free radicals as intermediates. The stoicheiometry and kinetics of the oxidation of hydrazine [118] have been investigated in sulphuric acid, at low acidities the stoicheiometry being $Ce^{IV} : N_2H_4 = 1 : 1$, but this ratio increases at higher acid concentrations to a limiting value of 4 : 1 at *ca.* 10M-$[H^+]$. There is no kinetic or spectrophotometric evidence for an intermediate complex, the mechanism being described as

$$\begin{aligned}
N_2H_5^+ &\rightleftharpoons N_2H_4 + H^+ \\
Ce^{IV} + N_2H_5^+ &\rightleftharpoons [Ce^{IV},N_2H_4] + H^+ \\
Ce^{IV} + N_2H_5^+ &\longrightarrow Ce^{III} + N_2H_3^{\bullet} + 2\,H^+ \\
Ce^{IV} + N_2H_4 &\longrightarrow Ce^{III} + N_2H_3^{\bullet} + H^+ \\
[Ce^{IV},N_2H_4] &\longrightarrow Ce^{III} + N_2H_3^{\bullet} + H^+ \\
N_2H_3^{\bullet} &\xrightarrow{\text{fast}} \tfrac{1}{2}N_4H_6 \xrightarrow{\text{fast}} \tfrac{1}{2}N_2 + NH_3
\end{aligned}$$

where $Ce^{IV} \equiv Ce(SO_4)_2$. Considerable catalytic activity is noted in the presence of manganese(II), probably owing to the rapid oxidation of the substrate by Mn^{III} which could be generated as an oxidizing intermediate. The reaction is also catalysed by ruthenium(III) [119] the mechanism involving the additional steps

$$\begin{aligned}
Ru^{III} + Ce^{IV} &\rightleftharpoons Ru^{IV} + Ce^{III} \\
Ru^{IV} + N_2H_4 &\longrightarrow Ru^{III} + N_2H_3^{\bullet}
\end{aligned}$$

with decomposition of the $N_2H_3^{\bullet}$ intermediate as described previously.

[115] C. F. Wells, 'Proceedings of the 3rd Symposium on Co-ordination Chemistry', ed. M. T. Beck, Hungarian Chemical Society, Budapest, 1971.
[116] V. K. Grover, S. K. Mishra, and Y. K. Gupta, *Indian J. Chem.*, 1970, **8**, 247.
[117] S. S. Krishnamurthy and S. Sundarajan, 'Proceedings of the 1st Chemistry Symposium', A.E.C., Bombay, 1969, vol. 2, p. 261 (*Chem. Abs.*, 1971, **74**, 35 136*d*).
[118] S. K. Mishra and Y. K. Gupta, *J. Chem. Soc.* (*A*), 1970, 2918.
[119] V. F. Romanov, *Zhur. neorg. Khim.*, 1971, **16**, 1119.

The dependence of the rate of reduction of cerium(IV) by H_2O_2 on the Hammett acidity function has been described,[120] the reaction being carried out in sulphate media, the rate law

$$\frac{-\,d[Ce^{IV}]}{dt} = 2k_{obs}\frac{[Ce^{IV}]^2[H_2O_2]}{[Ce^{III}]}$$

being observed at constant acidity. On increasing the sulphuric acid concentration from 2.0 to 8.0M, however, the decrease in the rate is consistent with an equilibrium between $HO_2^{\bullet}$ and $H_2O_2^{+}$, whereas from 8.0 to 13.0M the involvement of H_2O_2 and $H_3O_2^{+}$ must be considered. The mechanism may be described as

$$\begin{aligned}
Ce^{IV} + H_2O_2 &\rightleftharpoons Ce^{III} + H_2O_2^{+}\\
H_2O_2^{+} &\rightleftharpoons H^{+} + HO_2^{\bullet}\\
Ce^{IV} + HO_2^{\bullet} &\longrightarrow Ce^{III} + HO_2^{+}\\
HO_2^{+} &\longrightarrow H^{+} + O_2\\
Ce^{IV} + H_2O_2^{+} &\longrightarrow Ce^{III} + H_2O_2^{2+}\\
H_2O_2^{2+} &\longrightarrow H^{+} + HO_2^{+}
\end{aligned}$$

The 'oscillating' redox reaction between bromate, cerium(IV), and a dicarboxylic (malonic) acid has also been investigated.[121]

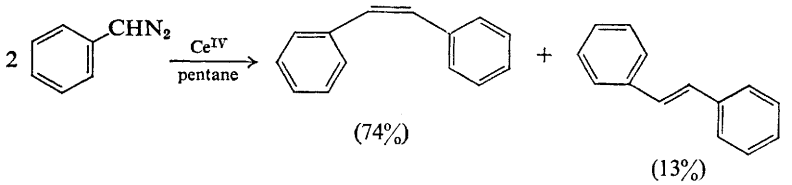
Several studies have been made using the reactions with aminopolycarboxylate ions in order to identify cerium(IV) complexes. The complex formation and oxidation of diethylenetriaminepenta-acetic acid (dtpa) have been investigated[122] in sulphuric acid using the stopped-flow technique, this being the first instance of identification of a complex formed between cerium(IV) and a ligand of this type. For complexation to occur, the acidity of the medium requires to be less than 1.3M, the rate being faster with decreasing hydrogen ion concentrations, probably owing to the deprotonation of the amino-N atoms. Second-order reactions are observed under similar conditions with edta and its analogues,[123] although in this study the extent of complexing is considered to be less. For the ligands of this type, the rate constant is dependent on the nature of the amino-group, the order decreasing in the sequence tertiary > secondary > primary, which is also observed in the oxidations by other one-electron reagents such as $Fe(CN)_6^{3-}$. A stable cerium(IV) species has been prepared[124] with 2,2′-bipyridine-1,1′-dioxide (LL) and found to be insoluble in polar and non-polar solvents. From a consideration of the spectra, it is suggested that in the eight-co-ordinate diamagnetic species $[Ce(LL)_3(NO_3)_2](ClO_4)_2$, both LL and NO_3 are co-ordinated *via* oxygen atoms.

The relative oxidation potentials of the Ce^{IV}/Ce^{III} and Bk^{IV}/Bk^{III} couples have been measured[125] in varying concentrations of perchloric and nitric

[120] H. A. Mahlman, R. W. Matthews, and T. J. Sworski, *J. Phys. Chem.*, 1971, **75**, 250.
[121] G. J. Kasperek and T. C. Bruice, *Inorg. Chem.*, 1971, **10**, 382.
[122] S. B. Hanna and R. K. Hessley, *Inorg. Nuclear Letters*, 1971, **7**, 83.
[123] G. N. Rao, *Indian J. Chem.*, 1970, **8**, 328.
[124] M. V. Warren and S. K. Madan, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3710.
[125] B. Weaver and J. N. Stevenson, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1877.

acids, cerium(IV) being the stronger oxidant in the latter medium. Studies have been made of oxidations in the presence of platinum surfaces in perchloric acid,[126] catalysis of the reaction with water being observed.

Metal complexes have been proposed in the oxidation of organic compounds. In the oxidative cleavage[127] of 1,2-diarylethanols in 75% acetonitrile and 85% aqueous acetic acid, the reactions proceed *via* one-electron transfer. The cerium(IV)-catalysed decomposition of aryldiazomethanes to *cis*- and *trans*-stilbenes[128] has been investigated. With phenyldiazomethane, the reaction



takes place and it is of interest to note that such reactions do not proceed with cerium(IV) which has previously been reduced with acetone. The mechanism proposed involves an oxidative chain reaction:

$$PhCHN_2 + Ce^{IV} \longrightarrow Ce^{III} + PhCHN_2^{+\bullet}$$

$$PhCHN_2^{+\bullet} + PhCHN_2 \longrightarrow PhCHCHPh^{+\bullet} + 2N_2$$

$$PhCHCHPh^{+\bullet} + PhCHN_2 \longrightarrow PhCHN_2^{+\bullet} + PhCH{=}CHPh$$

The selective ability of higher-valent metal ions to oxidize organic free radicals has been examined[129] and two mechanisms[130] have been proposed for the decomposition of cerium(IV) carboxylates in the presence of olefins and aromatic hydrocarbons: (*i*) involving a non-decarboxylative route with the generation of carboxyalkyl radicals *via* thermal decomposition, and (*ii*) the formation of alkyl radicals and CO_2 in the decarboxylation reaction. E.s.r. studies using cerium(IV) have been used to provide evidence for the formation of the sulphite radical anion $SO_3^{-\bullet}$ in the oxidation of sulphite.[131]

3 Chromium(VI)

The kinetics and mechanism of the oxidation of thiosulphate have been studied,[132] the reaction proceeding with variable stoicheiometry to SO_4^{2-} and $S_4O_6^{2-}$. Spectroscopic evidence for the formation of a complex

$$HCrO_4^- + H^+ + S_2O_3^{2-} \underset{}{\overset{K}{\rightleftharpoons}} H_2O + CrS_2O_6^{2-}$$

[126] J. Casado, A. Arrizabalaga, and F. Andres-Ordax, *Anales de Quim.*, 1971, **67**, 217 (*Chem. Abs.*, 1971, **75**, 53 759*j*).
[127] P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, 1971, **93**, 4536.
[128] W. S. Trahanovsky, M. D. Robbins, and D. Smick, *J. Amer. Chem. Soc.*, 1971, **93**, 2086.
[129] E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 1971, **93**, 524.
[130] E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 1971, **93**, 995.
[131] R. O. C. Norman and P. M. Storey, *J. Chem. Soc.* (*B*), 1971, 1009.
[132] M. I. Edmonds, K. E. Howlett, and B. L. Wedzicha, *J. Chem. Soc.* (*A*), 1970, 2866.

is presented with $K = 2.4 \times 10^5$ and $\Delta H^\circ \approx -3$ kcal mol^{-1}. At pH 4 the main reaction involves attack of a thiosulphate ion on the intermediate complex, the rate expression being

$$\text{Rate} = k_1[CrS_2O_6^{2-}][S_2O_3^{2-}](1 + k_2[H^+])$$

It is of interest that unsubstituted chromium(III) species are the metal-ion products of the reaction. In the reaction with hydrazine,[133] the rate is first order with respect to both Cr^{VI} and substrate, with a complex dependence on acidity. Michaelis–Menten kinetics are suggestive of intermediate complex formation and the rate-determining process involves a two-electron reaction. The rate law differs somewhat from that derived previously:[134]

$$\frac{-\,d[Cr^{VI}]}{dt} = [HCrO_4^-][N_2H_5^+](k_1[H^+] + k_2[HCrO_4^-])$$

where the reaction products in the pH range 1.9—3.0 are elemental nitrogen and the hexa-aquochromium(III) ion. The products have been confirmed in a separate investigation [58] where the differing modes of reaction of hydrazine with (*a*) one- and (*b*) two-equivalent oxidizing agents have been taken into account, *i.e.*

$$(a)\quad N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^-$$
$$(b)\quad 2N_2H_4 \longrightarrow N_2 + NH_4^+ + 2e^-$$

Although the addition of manganese(II) to the reacting system in conditions of an excess of chromium(VI) over hydrazine causes a retardation of the rate of disappearance of the oxidant, the effect of the divalent cation is to provide a reaction pathway where one half of the hydrazine is oxidized to yield ammonia. A similar observation has been made on the reaction in excess reductant in the absence of Mn^{II}. In the presence of edta,[135] however, where the chromium(VI) oxidation of the aminopolycarboxylate is very slow, the reaction rate increases—the product now being the substitution-inert Cr^{III}–edta complex ion. Experimentally, half the chromium(VI) is converted to this product and this is considered to derive from a dimeric chromium(VI) species involving both edta and hydrazine as ligands. In the reaction with hydroxylamine,[136] the stoicheiometry is dependent on the reagent in excess, *i.e.* in the presence of excess oxidant

$$2Cr_2O_7^{2-} + 3NH_3OH^+ + 10H^+ \longrightarrow 4Cr^{3+} + 3NO_2^- + 11H_2O$$

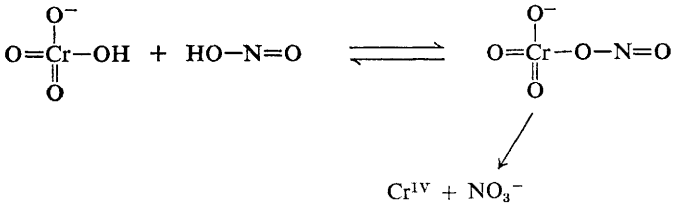
whereas with larger concentrations of substrate present the reaction

$$2Cr_2O_7^{2-} + 6NH_3OH^+ + 10H^+ \longrightarrow 4Cr^{3+} + 3N_2O + 17H_2O$$

prevails. The reaction order under all conditions for NH_3OH^+ is, however, always unity, whereas only at low $[Cr^{VI}]$ is the same value observed. There is no dependence on acidity, and complex formation is postulated. The

[133] V. M. S. Ramanujam and N. Ventakasubramanian, *Indian J. Chem.*, 1970, **8**, 948.
[134] M. T. Beck and D. A. Durham, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1971.
[135] M. T. Beck and D. A. Durham, *J. Inorg. Nuclear Chem.*, 1971, **33**, 461.
[136] N. Hlasivcova and I. Novak, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2027.

rate law exhibited in the oxidation of nitrous acid in the pH range 0.4—1.3 is complex, suggesting the existence of dimeric metal-ion intermediates.[137] One pathway in the mechanism involves the fast equilibrium condensation of two monoprotonated species



The resultant complex undergoes an intramolecular two-electron transfer, with rapid conversion of the chromium(IV) produced to a less-reactive form.

A preliminary report of the oxidation of oxalic acid has been presented,[58] the favoured rate law being

$$\frac{d[Cr^{VI}]}{dt} = k_1[Cr^{VI}][H_2C_2O_4][HC_2O_4^-]$$

E.s.r. analysis of reacting systems gives strong evidence of the formation of both Cr^V and a radical in frozen reaction mixtures at − 178 °C, but only Cr^V in flow systems at ambient temperatures. From a product investigation it has been shown that if the Westheimer mechanism were operative, the chromium(III) formed would result directly from Cr^V, and only $(H_2O)_6Cr^{3+}$ and possibly a small amount of $CrC_2O_4^+$ might result since oxalate co-ordinated to the intermediate Cr^V would be oxidized to CO_2. The products observed are $Cr(H_2O)_6^{3+}$, 55%; $CrC_2O_4^+$, 22%; $Cr(C_2O_4)_2^-$, 14%; and $Cr(C_2O_4)_3^{3-}$, 7%. If Cr^{IV} can co-ordinate to oxalate and oxidize oxalic acid to a radical intermediate which reduces Cr^{VI} to Cr^V, then the mechanism

$$\begin{aligned}
Cr^{IV} + nH_2C_2O_4 &\rightleftharpoons Cr(C_2O_4)_n^{4-2n} \\
Cr(C_2O_4)_n^{4-2n} &\longrightarrow Cr(C_2O_4)_{n-1}^{3-2(n-1)} + C_2O_4^{\bullet-} \\
C_2O_4^{\bullet-} + HCrO_4^- &\longrightarrow Cr^V + 2CO_2 \\
Cr^V + H_2C_2O_4 &\longrightarrow Cr(H_2O)_6^{3+} + 2CO_2
\end{aligned}$$

may be postulated. To account for all the products, however, some disproportionation of the Cr^{IV} is required, and the radical observed at low temperatures may be due to the oxidation of oxalate bound to the Cr^{IV}. Pure chromium(VI) oxidations have been examined in the reaction with propan-2-ol.[138] Both cerium(IV) and cerium(III) affect the rate of oxidation. In the reaction with phenyl-t-butylmethanol, in the absence of cerium(IV), the reaction products are 64% pivalophenone and 36% cleavage products, benzaldehyde and t-butyl alcohol. When cerium(IV) is present in concentration 50 times less than that of the chromium(VI), the amount of cleavage

[137] D. A. Durham, L. Dozsa, and M. T. Beck, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2971.
[138] M. P. Doyle, R. J. Swedo, and J. Rocek, *J. Amer. Chem. Soc.*, 1970, **92**, 7599.

is reduced to about 5% of the reaction product. Under such conditions it is considered that the only form of the oxidant reacting with the organic substrate (L^1) is the Cr^{VI}, the lower (intermediate) oxidation states being involved in electron-transfer reactions with the cerium, *i.e.*

$$Cr^{VI} + L^1 \xrightarrow[\text{rate determining}]{\text{slow}} Cr^{IV} + L^2$$
$$Cr^{IV} + Ce^{IV} \longrightarrow Cr^{V} + Ce^{III}$$
$$Cr^{V} + Ce^{IV} \longrightarrow Cr^{VI} + Ce^{III}$$
$$Cr^{IV} + Ce^{III} \longrightarrow Cr^{III} + Ce^{IV}$$

The stoicheiometry of the oxidation of isopropyl alcohol as a function of time has been used to test the role of chromium(V) as an intermediate in such reactions. The rates of disappearance of both Cr^{VI} and Cr^{V} in 97% acetic acid were examined spectrophotometrically,[139] and the concentration of product acetone was calculated as a function of time based on two model-reaction schemes. The data may be best represented by the scheme

$$R_2CHOH + HCrO_4^- + H^+ \rightleftharpoons R_2CHO,CrO_3H + H_2O$$
$$R_2CHO,CrO_3H \longrightarrow R_2C{=}O + Cr^{IV}$$
$$R_2CHOH + Cr^{IV} \longrightarrow R_2\dot{C}OH + Cr^{III}$$
$$R_2\dot{C}OH + Cr^{VI} \longrightarrow R_2C{=}O + Cr^{V}$$
$$R_2CHOH + Cr^{V} \longrightarrow R_2C{=}O + Cr^{III}$$

where the formation of one equivalent of Cr^{V} is accompanied by the formation of two equivalents of acetone. A free-radical mechanism has been postulated to describe oxidation of arenes,[140] in weakly acidic conditions. In the reaction with *p*-alkylbenzenesulphonates, the reactive oxidant is considered to be $HCrO_4^-$, the rate law

$$\frac{-\,d[Cr^{VI}]}{dt} = k[Cr^{VI}]_{tot}[\text{substrate}]\left\{\frac{[H^+]}{[H^+] + K}\right\}$$

involving the equilibrium constant (K) for the reaction

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$$

Differences in the oxidation rates of polycyclic alcohols (together with isotope effects) have been considered in terms of the variations of the ground-state non-bonded interactions between isomeric forms.[141]

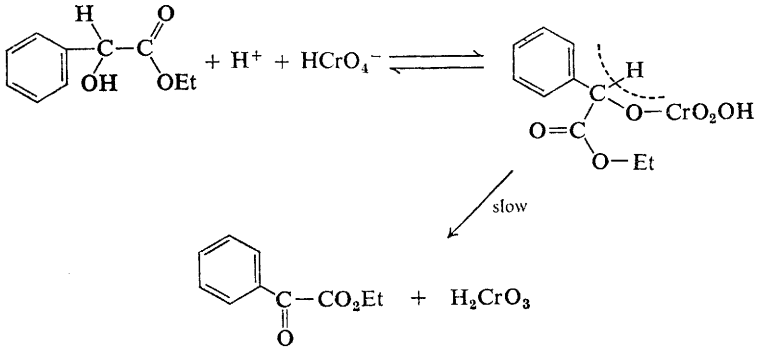
The reactions with organic acids have been investigated: in the case of the lower saturated fatty acids [142] the oxidations are first order with respect to $[Cr^{VI}]$ and substrate, and second order in acid. The final product (acetic acid) accelerates the rate, which also increases with increasing chain length in the substrate. Two electron exchanges are postulated as the rate-determining steps in the reaction with aldehydes in 90% acetic acid in the presence of N-donor chelating agents.[143] Spectral and magnetic data have

[139] K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, 1971, **93**, 2543.
[140] D. G. Lee and U. A. Spitzer, *Canad. J. Chem.*, 1971, **49**, 2763.
[141] R. Baker and T. J. Mason, *J. Chem. Soc.* (*B*), 1971, 988.
[142] S. M. Khan, A. A. Khan, and M. A. Beg, *Z. phys. Chem.* (*Leipzig*), 1970, **245**, 17.
[143] S. K. Anantakrishnan and R. Varadarajan, *Indian J. Chem.*, 1970, **8**, 423.

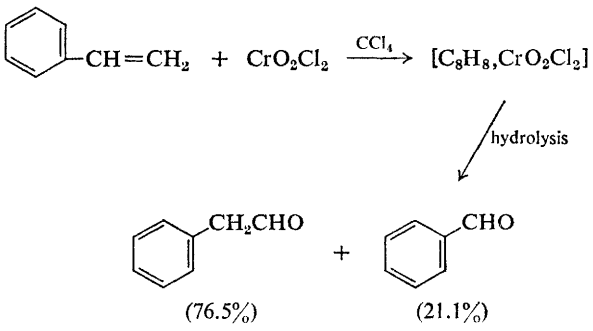
been used in an attempt to characterize the intermediate of undetermined oxidation state in the reaction with mandelic acid,[144] where catalyses by Mn^{II}, Ce^{III}, and Co^{II} are considered to derive from the interactions of these metal ions with the transient complex. The oxidation of organic esters follows the rate law [145, 146]

$$\text{Rate} = k_1[HCrO_4^-][\text{ester}][H^+]$$

the rates in general being less than for the corresponding acid. In the case of ethyl mandelate [145] the C—H bond rupture is considered to be the rate-determining process:



The kinetics of the chromyl chloride oxidation of the carbon–carbon double bond of styrene have been examined using stopped-flow spectrophotometry,[147] the product being a chromyl chloride–styrene adduct. The rate is first order with respect to each reactant and a linear free-energy relationship (Hammett correlation) has been shown to hold for a variety of substituted groups. The data are consistent with a mechanism involving electrophilic attack by the chromium(VI) species on the double bond to yield the adduct, which decomposes on hydrolysis to give phenylacetaldehyde and benzaldehyde as the major reaction products:



[144] K. H. Heckner, K. H. Grupe, and R. Landsberg, *Z. phys. Chem.* (*Leipzig*), 1971, **247**, 91.
[145] G. V. Bakore and C. L. Jain, *Z. phys. Chem.* (*Leipzig*), 1970, **245**, 1.
[146] D. S. Jha and G. V. Bakore, *J. Chem. Soc.* (*B*), 1971, 1166.
[147] F. Freeman and N. J. Yamachika, *J. Amer. Chem. Soc.*, 1970, **92**, 3730.

The oxidation of the azidopenta-aquochromium(III) ion by nitrous acid has been studied in perchlorate and chloride media in an attempt to generate the five-co-ordinate intermediate $Cr(H_2O)_5^{3+}$.[148] The rapid reactions in the presence of such scavenger ions as Cl^-, Br^-, HSO_4^-, or NCS^- indicate that the active intermediate has only a limited discriminating ability, the suggested mechanism being (X = Cl^-)

$$H^+ + HNO_2 \overset{\text{fast}}{\rightleftharpoons} H_2NO_2^+$$

$$H_2NO_2^+ + X^- \overset{\text{fast}}{\rightleftharpoons} NOX + H_2O$$

$$Cr(H_2O)_5N_3^{2+} + H_2NO_2^+ \rightleftharpoons Cr(H_2O)_5N_4O^{3+} + H_2O$$

$$Cr(H_2O)_5N_3^{2+} + NOX \rightleftharpoons Cr(H_2O)_5N_4O^{3+} + Cl^-$$

$$Cr(H_2O)_5N_4O^{3+} \longrightarrow Cr(H_2O)_5^{3+} + N_2 + N_2O$$

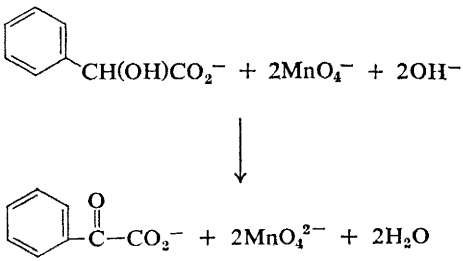
$$Cr(H_2O)_5^{3+} \xrightarrow[+H_2O]{\text{fast}} Cr(H_2O)_6^{3+}$$

$$Cr(H_2O)_5^{3+} \xrightarrow[+X^-]{\text{fast}} Cr(H_2O)_5X^{2+}$$

No incorporation of perchlorate into the primary co-ordination sphere of the chromium(III) was observed.

4 Manganese(VII) and Manganese(III)

Although the mechanisms of the Mn^{VII} oxidations of organic mono- and di-carboxylic acids have been much examined under acidic conditions, the faster reactions in alkaline media have only recently been investigated.[149] In contrast to the reaction in acidic solution where, with mandelic acid as substrate, oxidative decarboxylation occurs to yield benzaldehyde and CO_2, at the higher pH the product is phenylglyoxylic acid:

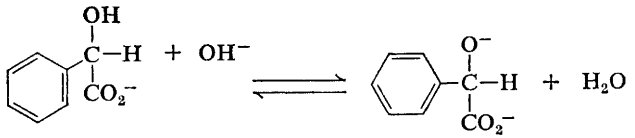


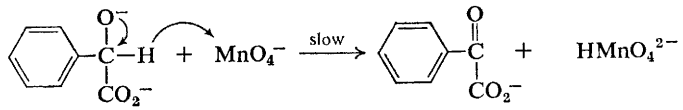
There is a single electron exchange in the metal ion. Using a stopped-flow device, a two-term rate law is operative (ma^- = mandelate anion).

$$\frac{-\,d[MnO_4^-]}{dt} = k_1[MnO_4^-][ma^-] + k_2[MnO_4^-][ma^-][OH^-]$$

although at lower pH a term involving the undissociated acid must be incorporated. In the pH range 12.7—13.6, however, the mechanism

[148] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1970, 2819.
[149] F. Freeman and M. A. H. Scott, *J. Org. Chem.*, 1970, **35**, 2989.





$$HMnO_4^{2-} + MnO_4^- + OH^- \xrightarrow{\text{fast}} 2MnO_4^{2-} + H_2O$$

accounts for the major reaction pathway. In the reaction with hydroxycyclohexanecarboxylic acids,[150] a complex pH dependence is observed, the mechanism involving complex formation between the neutral hydroxy-acid and the permanganate. The intermediate complex is, however, considered to undergo a (reversible) deprotonation prior to the rate-determining electron transfer step. Acid-dependent and -independent paths have also been described in the oxidation of ethyl acetate in perchloric acid.[151] The mechanism of the fast reaction between Mn^{VII} and nitrite[152] has been investigated in glycine and phthalic acid buffers. The rate law may be expressed as

$$\text{Rate} = k_1[HNO_2] + k_2[HNO_2]^2 + k_3[HNO_2]^3[H^+]^3$$

being independent of the MnO_4^- concentration. The rate-determining steps involve the formation of NO^+, N_2O_3, and $N_3O_3^{3+}$ species. In contrast, the oxidation of phenylmethanenitronate anions[153] is first order with respect to MnO_4^- and to nitronate ion, and zeroth order in hydroxide, the activated complex being either a partly bridged resonance stabilized species or a cyclic manganese(v) ester.

The manganese(III) oxidation of methanol[154] has been reported. The reaction, which takes place *via* an inner-sphere mechanism, is first order in both oxidant and substrate. The effects of other cations have been examined, catalysis by cobalt(II) and aluminium(III) being exhibited with retardation of the reaction specific to manganese(II). Inner-sphere complexes have also been detected in the corresponding reaction with pinacol in acidic perchlorate media.[155] The oxidation of α-hydroxyisobutyric acid,[156] however,

[150] R. Stewart and J. A. MacPhee, *J. Amer. Chem. Soc.*, 1971, **93**, 4271.
[151] P. V. S. Rao, *Z. phys. Chem.* (*Leipzig*), 1971, **246**, 352.
[152] L. Dozsa and M. T. Beck, *Magyar Kém. Folyóirat*, 1970, **76**, 557 (*Chem. Abs.*, 1971, **74**, *68 231j*).
[153] F. Freeman and A. Yeramyan, *J. Org. Chem.*, 1970, **35**, 2061.
[154] C. F. Wells and C. Barnes, *J. Chem. Soc.* (*A*), 1971, 430.
[155] C. F. Wells and C. Barnes, *J. Chem. Soc.* (*A*), 1971, 1405.
[156] C. F. Wells and C. Barnes, *Trans. Faraday Soc.*, 1971, **67**, 3297.

is sufficiently slow to be investigated by conventional techniques. The initial part of the reaction has been studied using a flow device, and the increase in optical density in this time scale is consistent with complex formation. Several systems have been described with manganese(III) sulphate as oxidant. In the reaction with acetophenone,[157]

$$CH_3COC_6H_5 + Mn^{III} \rightleftharpoons [Mn^{III}OC(CH_3)C_6H_5]$$

$$\downarrow$$

$$C_6H_5CO_2H + HCHO \xleftarrow[Mn^{III}]{fast} [C_6H_5COCH_2]^{\bullet} + H^+ + Mn^{II}$$

the rate is first order in each reactant, although independent of acidity and of solvent composition. A similar observation has been made in the corresponding reaction with methyl ethyl ketone.[158] The product of the oxidation (in 20% acetic acid) of acetone is formaldehyde,[159] and a polymeric species is obtained in the reaction with dimethyl sulphoxide,[160] where the rates decrease at high substrate concentrations. In the reaction with thiocyanate[161] there is a second-order dependence on manganese(III) concentration, the mechanism being expressed as

$$2Mn^{III} + SCN^- \rightleftharpoons [Mn_2SCN]^{5+} \xrightarrow{slow} 2Mn^{II} + SCN^+$$
$$SCN^+ + SCN^- \rightleftharpoons (SCN)_2$$

The decreasing rate at higher ligand concentrations is ascribed to consecutive complex formation.

The oxidations of thiols to disulphides by manganese(III) trisacetylacetonate are relatively slow[162] compared to their rates of reaction by other metal ions. The use of manganese(III) acetate in oxidations using free radicals has been reported.[129] When a solution of oct-1-ene, acetone, and manganese(III) acetate in acetic acid is heated, three major products are reported, the initial step involving the oxidation of acetone

$$Mn^{III}(OAc)_3 + CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow {}^{\bullet}CH_2\overset{O}{\overset{\|}{C}}CH_3 + H^+ + Mn^{II}$$

to yield an α-keto-radical which can then add to an unsaturated centre to form a secondary alkyl radical. The latter species is selectively and rapidly oxidized by the manganese(III), which accounts for the absence of any significant polymerization during the reaction.

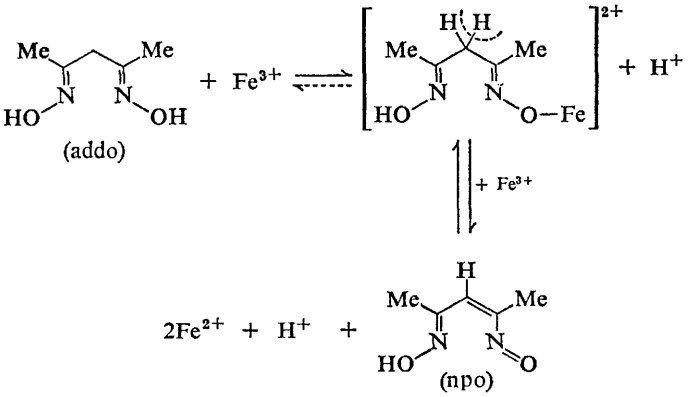
[157] P. Nath and K. K. Banerji, *Canad. J. Chem.*, 1970, **48**, 2414.
[158] K. K. Banerji, P. Nath, and G. V. Bakore, *Bull. Chem. Soc., Japan*, 1970, **43**, 2027.
[159] K. K. Banerji, P. Nath, and G. V. Bakore, *Indian J. Chem.*, 1970, **8**, 337.
[160] N. G. Devi and V. Mahadevan, *Chem. Comm.*, 1970, 797.
[161] L. Treindl and H. Dubrabova, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2022.
[162] T. Nakaya, H. Arabori, and M. Imoto, *Bull. Chem. Soc. Japan*, 1970, **43**, 1888.

5 Iron(III)

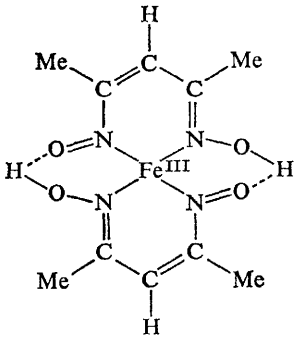
The oxydo-reduction and complex formation between iron(III) and acetylacetone dioxime (addo),

$$2Fe^{III} + addo \rightleftharpoons 2Fe^{2+} + npo$$
$$Fe^{3+} + 2npo \longrightarrow Fe(npo)_2^{3+}$$

where npo = 2-nitrosopent-2-en-4-one oxime, have been investigated [163] and have been shown to involve a multistep reaction where in the redox stage there is the formal removal of two protons, one from the oxime group, the second from the symmetrical methine bridge:



The nitroso-product is formed *via* an electron transfer in the second stage. The reduced form of the ligand may dimerize, the resulting substrate forming a complex with the excess iron(III) present:



The complex formation step has a rate constant a factor of three slower than the oxidation reaction.

[163] I. Adato, A. H. I. Ben-Bassar, and S. Sarel, *Israel J. Chem.*, 1970, **8**, 889.

Unlike the iron(III)–cysteine complex, which undergoes ready intramolecular oxidation–reduction, the ferric–thiol chromophores in penicillamine and cysteamine-*N*-acetic acid are considerably longer lived and may be investigated using conventional spectrophotometric techniques.[164] Two iron(III) complexes, one red and one violet, have been described for cysteamine-*N*-acetic acid, the red species being much less robust than the violet. The formation of the iron(III)–penicillamine chromophore has been studied in aqueous media at pH *ca.* 9, the slow decomposition

$$2Fe^{3+} + RS^- \longrightarrow 2Fe^{2+} + RS{-}SR$$

being retarded in the absence of oxygen. The coloration persists in DMSO and DMF solutions, where the redox reaction is faster in the former solvent than in the latter, although this decomposition reaction has a half-life of *ca.* 7 h compared with the stopped-flow time-scale reaction in the corresponding cysteine complex. The process parallels in the case of the penicillamine the observed lack of catabolism of the amino-acids in living systems and is probably due to steric effects of the ligands involved.

Two studies have been reported of the ferricyanide–sulphite reaction.[165, 166] The rapid spectral changes observed on mixing the reagents [165] are considered to result from the formation of intermediates, the reaction proceeding according to the mechanism:

$$Fe(CN)_6^{3-} + SO_3^{2-} \rightleftharpoons [(NC)_5Fe(CNSO_3)]^{5-} \quad (12)$$

$$[(NC)_5Fe(CNSO_3)]^{5-} + Fe(CN)_6^{3-} \rightleftharpoons [(NC)_5Fe(CNSO_3)]^{4-} + Fe(CN)_6^{4-} \quad (13)$$

$$[(NC)_5Fe(CNSO_3)]^{4-} + H_2O \longrightarrow Fe(CN)_6^{4-} + SO_4^{2-} + 2H^+ \quad (14)$$

where reactions (12) and (14) are slower than (13). The oxidized form of the product in (13) may exist as a Fe^{II}–S^{VI} complex and radiotracer studies indicate the formation of some dithionate. Attempts to characterize intermediates in similar reactions have not proved successful. In the presence of catalytic amounts of copper(II) or animal charcoal, however, there is a reduction in the extent of intermediate complex formation. These catalytic effects have been ascribed to two-electron transfer redox reactions,[166] and the rate of the uncatalysed system is controlled by the probability of such a transfer in the ternary complex SO_3^{2-}–$[Fe(CN)_6^{3-}]_2$. With the copper(II) present, however, complex formation of the type Cu^{II}–SO_3^{2-}–$Fe(CN)_6^{3-}$ might be possible. The oxidation kinetics of 2-mercaptoethylamine hydrochloride have been studied in aqueous hydrochloric acid.[167] A reaction order of unity with respect to both thiol and oxidant is observed and the

[164] C. M. Bell, E. D. McKenzie, and J. Orton, *Inorg. Chim. Acta*, 1971, **5**, 109.
[165] J. M. Lancaster and R. S. Murray, *J. Chem. Soc.* (*A*), 1971, 2755.
[166] M. Solc and J. Veprek-Siska, *Naturwiss.*, 1970, **57**, 671.
[167] R. C. Kapoor, R. K. Chohan, and B. P. Sinha, *J. Phys. Chem.*, 1971, **75**, 2036.

ferrocyanide formed acts as an autocatalyst ($\overset{+}{R}SH$ = thiol):

$$Fe(CN)_6^{3-} + \overset{+}{R}SH \xrightarrow{k_1} HFe(CN)_6^{3-} + \overset{+}{R}S^{\bullet}$$

$$HFe(CN)_6^{3-} + \overset{+}{R}SH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{HFe(CN)_5\overset{+}{S}R\}^{3-} + HCN$$

$$\{HFe(CN)_5\overset{+}{S}R\}^{3-} + Fe(CN)_6^{3-} + HCN \xrightarrow{k_3} 2HFe(CN)_6^{3-} + \overset{+}{R}S$$

$$2\overset{+}{R}S \longrightarrow R{-}S{-}S{-}R^{2+}$$

Radical ions are also involved[168] in the oxidation of hydroxamic acids, RCONHOH, in alkaline media

$$RCONH{\cdot}OH \rightleftharpoons RCO{\cdot}\bar{N}{\cdot}OH + H^+$$

$$RCO{\cdot}\bar{N}{\cdot}OH + Fe(CN)_6^{3-} \xrightarrow{-H^+} RCO{\cdot}\dot{N}{\cdot}O^- + H^+ + Fe(CN)_6^{4-}$$

One equivalent of oxidant reacts stoicheiometrically (in the presence of H_4edta to remove trace metal ions) at pH $\geqslant$ 9.5 and the radical-anion was identified using e.s.r. The reaction products, *NO*-diacylhydroxylamines, are formed on dimerization, rearrangement, and subsequent hydrolysis of the radical-anion. The reaction with cerium(IV) as oxidant yields, in a multi-step process, the corresponding carboxylic acid and $NH(OH)_2$; the latter is further oxidized to nitrate

$$RCONHOH \xrightarrow{+2Ce^{IV}} RCO_2H + HN(OH)_2$$

$$HN(OH)_2 + 4Ce^{IV} \longrightarrow HNO_3 + 4Ce^{III}$$

The mechanism of the ferricyanide oxidation of hydroxylamine has been examined in weakly acidic solutions,[169] 4.2 < pH < 5.7, where the reactive form of the substrate is the unprotonated NH_2OH, the reaction mechanism being described by the equations

$$NH_2OH + Fe(CN)_6^{3-} \longrightarrow NH_2O^{\bullet} + Fe(CN)_6^{4-} + H^+$$

$$2NH_2O^{\bullet} \longrightarrow N_2 + 2H_2O$$

Several studies have been made of the catalysis of oxidations of this type by osmium(VIII). In the reaction with selenium(IV),[170] the rate law indicates a first-order dependence in [Se^{IV}], [$Fe(CN)_6^{3-}$], [HO^-], and [Os^{VIII}], the rate increasing with increasing ionic strength. The mechanism proposed involves the formation of an unstable $HSeO_4^{2-}$ intermediate which then undergoes attack by the osmium(VIII) to yield the oxidized product:

$$SeO_3^{2-} + OH^- \underset{\text{fast}}{\rightleftharpoons} HSeO_4^{3-}$$

$$HSeO_4^{3-} + Fe(CN)_6^{3-} \underset{\text{slow}}{\rightleftharpoons} HSeO_4^{2-} + Fe(CN)_6^{4-}$$

$$HSeO_4^{2-} + Os^{VIII} \xrightarrow{\text{fast}} HSeO_4^{-} + Os^{VII}$$

$$Os^{VII} + Fe(CN)_6^{3-} \xrightarrow{\text{fast}} Os^{VIII} + Fe(CN)_6^{4-}$$

[168] T. R. Oliver and W. A. Waters, *J. Chem. Soc.* (*B*), 1971, 677.
[169] V. K. Jindal, M. C. Agrawal, and S. P. Mushran, *J. Chem. Soc.* (*A*), 1970, 2060.
[170] V. K. Jindal, M. C. Agrawal, and S. P. Mushran, *J. Chem. Soc.* (*A*), 1971, 622.

the catalyst being regenerated by reaction with a further mole of oxidant. In contrast, however, the corresponding reaction with tellurium(IV) [171] has the observed rate law

$$\frac{-\,d[Fe(CN)_6^{3-}]}{dt} = k[Fe(CN)_6^{3-}][Os^{VIII}][OH^-]$$

with no dependence on the tellurium(IV) concentration. In this system an initial rapid reaction is followed by a slower first-order process:

$$OsO_4 + OH^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} HOsO_5^-$$

$$HOsO_5^- + Fe(CN)_6^{3-} \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \text{complex}$$

$$\text{complex} + Te^{IV} \xrightarrow{\text{fast}} Te^{V} + Fe(CN)_6^{4-} + HOsO_5^-$$

$$Te^{V} + Fe(CN)_6^{3-} \xrightarrow{\text{fast}} Te^{VI} + Fe(CN)_6^{4-}$$

The product of the corresponding reaction [172] with acetaldehyde is oxalate, the rate-determining process in this instance being considered to derive from the reaction of an osmium(VIII)–enolate complex in a two-electron step, the resulting Os^{VI} being re-oxidized to its original oxidation state by reaction with $Fe(CN)_6^{3-}$.

The kinetics of redox reactions of oxidized *p*-phenylenediamine derivatives (ppd) have been investigated.[173] The photolysis of *p*-azidoaniline in water rapidly yields quinonedi-imine (qd) and the reaction

$$\text{ppd} + \text{qd} \rightleftharpoons 2\ \text{semiquinone}$$

has been examined. The semiquinone is also produced in the reaction with ferricyanide:

$$\text{qd} + H^+ + Fe(CN)_6^{3-} \rightleftharpoons \text{semiquinone} + Fe(CN)_6^{4-}$$

$$\text{semiquinone} + Fe(CN)_6^{4-} \rightleftharpoons \text{ppd} + Fe(CN)_6^{3-}$$

but it itself further reduced by ferrocyanide to yield the diamine. Kinetic isotope effects in normal and heavy water are consistent with a mechanism involving hydrogen atom transfer in the second stage of the reaction, the transition state probably involving a protonated form of the ferrocyanide.

6 Vanadium(V)

Two studies have been made of the oxidation of hypophosphorous acid. In perchlorate media [174] the rate law of the redox reaction is indicative of several vanadium(V)–phosphorous(I) complexes being kinetically

[171] V. K. Jindal, M. C. Agrawal, and S. P. Mushran, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2469.
[172] P. C. Pandey, V. N. Singh, and M. P. Singh, *Indian J. Chem.*, 1971, **9**, 430.
[173] R. C. Baetzold and L. K. J. Tong, *J. Amer. Chem. Soc.*, 1971, **93**, 1347.
[174] J. N. Cooper, H. L. Hoyt, C. W. Buffington, and C. A. Holmes, *J. Phys. Chem.*, 1971, **75**, 891.

significant:

$$\text{Rate} = \{k_0 + k_1[H_3PO_2] + k_2[H_3PO_2]^2\}[VO_2^+][H_2PO_2^-][H^+]$$

The k_0 term corresponds to the direct protonation of the vanadium(V)–phosphorus(I) species followed by a tautomerization step in which water abstracts a phosphinic proton, whereas the second and third terms correspond to the protonation of the complexes $VO_2(H_2PO_2)(H_3PO_2)$ and $VO_2(H_2PO_2)(H_3PO_2)_2$. The reaction is slightly retarded by Cl^- but accelerated by silver(I), probably owing to the reaction sequence

$$Ag^I + H_3PO_2 \longrightarrow Ag^0 + H_3PO_3$$
$$Ag^0 + V^V \xrightarrow{\text{fast}} Ag^I + V^{IV}$$

since the rate order in vanadium(V) in the presence of the catalyst falls to almost zero. In sulphuric acid,[175] the stoicheiometry may be represented by the equation

$$H_3PO_2 + 2V^V + H_2O \longrightarrow H_3PO_3 + 2V^{IV} + 2H^+$$

The reaction rates are greater in sulphate media, possibly owing to the reactions of complexes of the type $V(OH)_3HSO_4^+$, and it is considered that the mechanism involves free radical formation since polymerization of an added olefinic derivative such as acrylamide has been observed. Vanadium(V) complexes have also been described in reactions with *p*-phenetidine [176] and whereas the rates for VO_2^+ are slow, those for the higher polymeric aggregates are faster.

The oxidation of butane-1,3-diol has been investigated in both perchlorate and sulphuric acid media,[177] the reaction proceeding faster in the latter. The rate under these conditions is proportional to the square of the sulphuric acid, bisulphate, and hydrogen ion concentrations, whereas in perchloric acid a plot of log k_{obs} against $-H_0$ is linear with a slope of less than unity. The mechanism may be interpreted by the scheme in which there is a slow attack of a water molecule on an intermediate complex (RCH_2OH = diol):

$$RCH_2OH + V^V \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} [RCH_2O\cdot V^V]$$
$$\Big|_{H}$$
$$\Big\downarrow \text{slow}+H_2O$$
$$RCHO + V^{IV} \xleftarrow[+V^V]{\text{fast}} RCHOH + H_3\overset{+}{O} + V^{IV}$$

[175] K. K. Sengupta, B. B. Pal, and D. C. Mukherjee, *Z. phys. Chem.* (*Frankfurt*), 1970, **72**, 230.
[176] P. R. Boutcher, M. Mitewa, and B. G. Jeliazkowa, *Inorg. Chim. Acta*, 1971, **5**, 75.
[177] R. N. Mehrota, *J. Chem. Soc.* (*B*), 1970, 1722.

In such a mechanism, Michaelis–Menten kinetics are observed only if the initial equilibrium constant is greater than that for the rate-determining process, conditions which are observed experimentally in *ca.* 4M-H_2SO_4.

7 Thallium(III)

The kinetics and mechanism of the oxidation of phosphorous acid

$$Tl^{III} + H_3PO_3 + H_2O \longrightarrow Tl^{I} + H_3PO_4 + 2H^+$$

have been examined,[178] the observed rate law being expressed in the form

$$\frac{-\,d[Tl^{III}]}{dt} = \frac{k_1 K[Tl^{III}][H_3PO_3]}{([H^+] + K[H_3PO_3])}$$

the reaction proceeding *via* the formation of an intermediate Tl^{III}–H_3PO_3 complex ($K = 29$, $T = 60$ °C, $I = 3.15$ mol l^{-1}). The inverse acid dependence has been ascribed to the reaction of the hydrolysed species $TlOH^{2+}$. Several mechanisms consistent with the rate law are described, involving both the reactions of Tl^{3+} and $TlOH^{2+}$, *e.g.*

$$Tl^{3+} + H_3PO_3 \underset{}{\overset{K}{\rightleftharpoons}} [Tl(H_2PO_3)]^{2+} + H^+$$

$$TlOH^{2+} + H_3PO_3 \overset{K'}{\rightleftharpoons} [Tl(H_2PO_3)]^{2+} + H_2O$$

and

$$[Tl(H_2PO_3)]^{2+} \xrightarrow[+H_2O]{k} Tl^{I} + H_3PO_4 + H^+$$

although both systems yield the same intermediate complex. The absence of general acid catalysis, which has been observed in other oxidations of H_3PO_3, is noted and it may be that the high charge on the oxidant induces P—H bond rupture more readily than attack of H^+ on the unprotonated —P—H oxygen.

The rate of oxidation of cyclohexane-1,2-dione has been investigated [179] and the effects of various anions Cl^-, Br^-, SO_4^{2-}, and OAc^- were noted. Generally the introduction of a ligand into the inner co-ordination sphere of the oxidant causes an increase in the reaction rate. In the case of acetate, the results have been interpreted using the rate equation

$$\text{Rate} = [S]\{k_1[Tl^{3+}] + k_2[TlOH^{2+}] + k_3[TlOAc^{2+}] + k_4[Tl(OAc)_2] + k_5[Tl(OAc)_3] + k_6[Tl(OAc)_2(OH)]\}$$

where [S] = substrate concentration. From a knowledge of the equilibrium constants for the various acetate complexes formed under differing concentrations of acetate, it has been possible to construct a rate profile

[178] K. S. Gupta and Y. K. Gupta, *J. Chem. Soc.* (*A*), 1971, 1180.
[179] R. Favier and M. Zador, *Canad. J. Chem.*, 1970, **48**, 2407.

(Figure 1) where the theoretical and experimental curves have been compared. Methylcyclobutene is rapidly oxidized by metal ions Tl^{III}, Hg^{II}, or Pd^{II} in aqueous solution to yield cyclopropyl methyl ketone,[180] the mechanism in the case of Tl^{III} involving the formation of an oxo-thallium adduct which

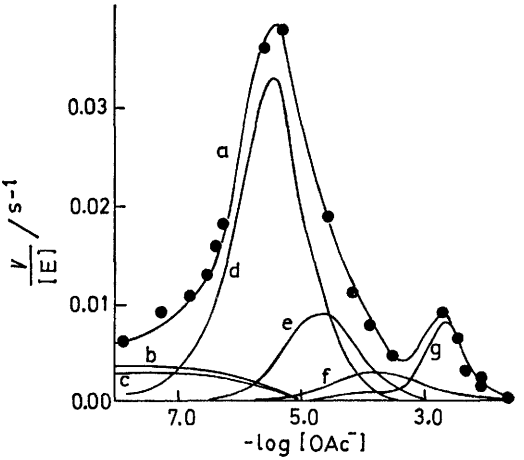
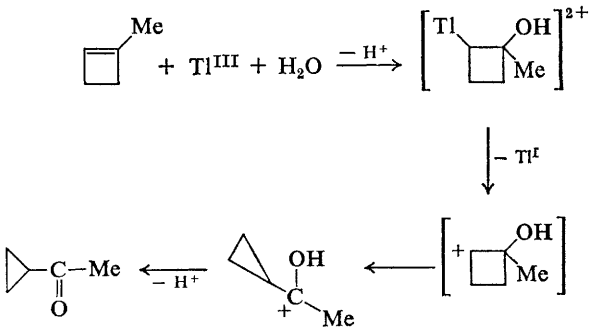


Figure 1 *Influence of acetate ion on the rate of oxidation of cyclohexane-1,2-dione; T = 25 °C, $[Tl^{III}]$ = 2.5 × 10^{-4}, [1,2-cd] = 1 × 10^{-4}, and I = 0.5M = $[H^+]$. Curve* (a) *represents the fit of calculated and experimental points for the overall reaction whereas curves* (b), (c), (d), (e), (f), *and* (g) *represent contributions from the reactions of the species* Tl^{III}, $TlOH^{2+}$, $TlOAc^{2+}$, $Tl(OAc)_2^+$, $Tl(OAc)_3$, *and* $Tl(OAc)_2OH$, *respectively. V is the rate of reaction and* [E] *is the concentration of the enol form of the dione*

(Reproduced by permission from *Canad. J. Chem.*, 1970, **48**, 2407)

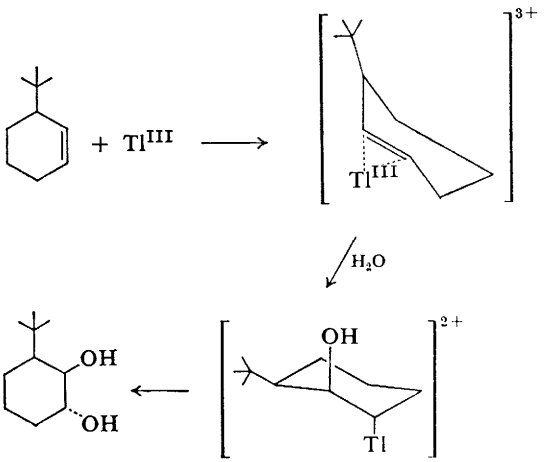
loses Tl^I to give an intermediate carbonium ion:



The oxidation of cyclohexenes in sulphate media yields diols as products,[181] the stereochemistry of which suggests that the α-hydroxy-group participates

[180] J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Comm.*, 1971, 40.
[181] C. Freppel, R. Favier, J.-C. Richer, and M. Zador, *Canad. J. Chem.*, 1971, **49**, 2586.

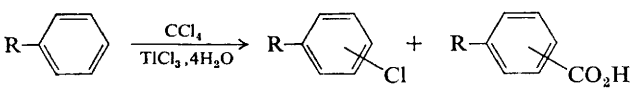
in the breaking of the C—Tl bond in the organothallium intermediate, *e.g.* for t-butylcyclohexene the reaction path may be written as



and the fact that only *trans* diols are produced indicates the exclusion of an S_N2 substitution of the thallium. Thallium(III) ions have also been shown to catalyse the electrochemical oxidations of alkenes:[182]

$$Tl^{I} \longrightarrow Tl^{III} \text{ (anodic reaction)}$$
$$Tl^{III} + \text{alkene} \longrightarrow Tl^{I} + \text{products}$$

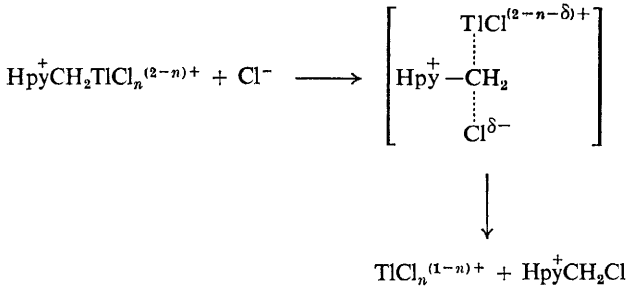
In the study of radiation-induced oxidation of alcohols by thallium(III) in aqueous media, the formation of Tl^{II} intermediates has been invoked, which react with the alcohol.[183] Carboxylation of aromatic hydrocarbons with thallium(III) chloride in CCl_4 has been described:[184]



the thallium salt being reduced to the + 1 oxidation state. In the reactions with porphyrins, however,[185,186] trifluoroacetate ion gives thallium(III) complexes which in the presence of excess trifluoroacetic acid undergo demetallation and oxidation of the porphyrin at the *meso*-position. In the case of *trans*-octaethylchlorin,[186] oxidative rupture of the macrocycle results, yielding analogues of bile pigments.

[182] R. Favier, C. Freppel, J.-C. Richer, and M. Zador, *Canad. J. Chem.*, 1971, **49**, 2590.
[183] C. E. Burchill and G. C. Hickling, *Canad. J. Chem.*, 1970, **48**, 2466.
[184] S. Uemura, O. Sakasi, and M. Okamo, *Chem. Comm.*, 1970, 1139.
[185] K. M. Smith, *Chem. Comm.*, 1971, 540.
[186] J. A. S. Cavaleiro and K. M. Smith, *Chem. Comm.*, 1971, 1384.

The kinetics and mechanism of the decomposition of pyridiniomethylthallium(III) species in aqueous solution have been described.[187] The presence of small amounts of chloride ion markedly decreases the rate of the first-order decomposition, but in high chloride ion concentrations, the rate again increases. In all cases the inorganic product is Tl^{I}, the organic species being either the hydroxymethylpyridinium ion or, as the chloride ion concentration increases, chloromethylpyridinium ion. Complex formation between the organothallium(III) species and chloride ion has been identified, the rate data being interpreted in terms of an S_N2 mechanism in which the thallium(I) ion is displaced by attack of the appropriate nucleophile on the pyridiniomethyl group, *e.g.*



The observed order of the leaving group ($Tl^+ > TlCl > TlCl_2^- > TlCl_3^{2-}$) is consistent with the stabilization by Cl^- ion of thallium(III) relative to thallium(I).

8 Other Metal-ion Oxidants

The kinetics and mechanism of the silver(II) oxidation of phosphorous acid have been examined,[188] the reaction proceeding *via* two independent paths, the rate law at constant acidity having the form

$$\frac{-0.5\mathrm{d}[Ag^{II}]}{\mathrm{d}t} = k_\alpha[H_3PO_3] + k_\beta\frac{[Ag^{II}]^2[H_3PO_3]}{[Ag^{I}]}$$

The first term shows a dependence on acidity, the rate increasing slightly in more acidic conditions and is considered to involve the rate-determining dissociation of a proton from a P—H bond, generating a reactive intermediate with an electron pair on the phosphorus atom which reacts rapidly in the redox step:

$$H_3PO_3 + H^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} H_4PO_3^+$$

$$H_4PO_3^+ \overset{\text{slow}}{\rightleftharpoons} :P(OH)_3 + H^+$$

$$:P(OH)_3 + Ag^{II} \xrightarrow{\text{fast}} \text{products}$$

[187] M. D. Johnson and D. Vamplew, *J. Chem. Soc.* (*B*), 1971, 507.
[188] A. Viste, D. A. Holm, P. L. Wang, and G. D. Veith, *Inorg. Chem.*, 1971, **10**, 631.

In the second reaction the preferred mechanism may be represented by the equations

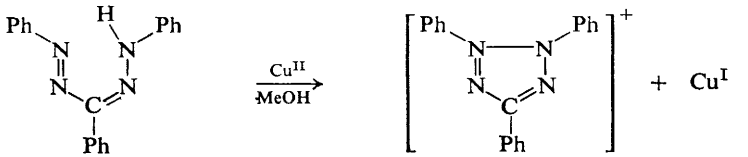
$$2Ag^{II} \underset{\leftarrow}{\overset{\text{rapid}}{\rightleftharpoons}} Ag^{I} + Ag^{III}$$

$$Ag^{III} + H_3PO_3 + H_2O \longrightarrow Ag^{I} + H_3PO_4 + 2H^+$$

where a two-electron transfer involving silver(III) is invoked.

The redox disproportionation of silver(I) sulphite complexes has been described.[189] The species $Ag(SO_3)^-$ and $Ag(SO_3)_2^{3-}$ and higher complexes react in a rate law which is second order with respect to sulphite, the rates being greatest for the 1 : 1 complexes and decreasing with increasing concentrations of the higher complex ions. The silver(I) ion-assisted dimethyl sulphoxide oxidation of organic halides has been reported.[190]

The bidentate ligand 1,3,5-triphenylformazan (A) is stoicheiometrically oxidized by copper(II) to the corresponding tetrazolium ion (B) in methanolic solution:[191]



(A) (B)

The oxidation is catalytic in the presence of air and both the chloro and acetate complexes of the metal ion react. In the case of the corresponding cobalt(II) solutions, three products are observed, with evidence for complex formation between the metal ion and formazan with a secondary oxidation step. Surprisingly, however, the activity of the cobalt salts is promoted by the absence of air. E.s.r. evidence has been presented for a short-lived intermediate in the adduct formation between dibutyldithiocarbamatocopper(II) and N-containing bases of the pyridine and piperidine type.[192]

The kinetics of formation and decomposition of a copper(III) periodate complex in alkaline media have been studied,[193] the reaction

$$Cu^{II} + IO_4^- \xrightarrow{HO^-} [Cu^{III}IO_4]^{2+}$$

being first order with respect to copper(II) in KOH solution. The rate of reduction of the complex formed is dependent on its concentration and is inhibited by periodate ions, which are involved in a reverse reaction with the copper(II) produced to yield the initial complex. The reactions of tervalent copper ions (formed in radiolysed solutions $Cu^{2+} + OH^{\bullet} \rightarrow Cu^{III} + OH^-$)

[189] E. Danilczuk, *Roczniki Chem.*, 1970, **44**, 1657 (*Chem. Abs.*, 1971, **74**, 80 245*z*).
[190] W. W. Epstein and J. Ollinger, *Chem. Comm.*, 1970, 1338.
[191] R. Price, *J. Chem. Soc.* (*A*), 1971, 3379.
[192] B. J. Corden and P. H. Rieger, *Inorg. Chem.*, 1971, **10**, 263.
[193] G. Rosovskis, A. Y. Prokopchik, and R. Jankanskas, *Kinetika i Kataliz*, 1971, **12**, 82.

have been investigated in neutral and acidic media.[194] At pH 6.0, the disappearance of copper(III) was found to involve two steps: an initial minor rapid process, the proportion of which increased with increasing copper(II) present, followed by a second-order decomposition which is independent of ClO_4^- or SO_4^{2-}. In N_2O-saturated solutions, small concentrations of Cu^I are formed and the Cu^{II}-dependent rapid first reaction may be explained by the process

$$Cu^{III} + Cu^I \xrightarrow{k_1} 2Cu^{II}$$

where $k_1 = 3.6 \times 10^9$ l mol^{-1} s^{-1}, followed by the slower reaction

$$Cu^{III} + Cu^{III} \xrightarrow{k_2} 2Cu^{II} + H_2O_2$$

where $k_2 = 2.3 \times 10^7$ l mol^{-1} s^{-1}. Hydroxyl radicals are not seen as intermediates in the decomposition of copper(III) in neutral solutions, and in the reaction of this ion under these conditions with NO_2^- a copper(II) dependence is again observed, owing to the formation of a nitrocopper(II) complex

$$\begin{aligned} Cu^{II} + NO_2^- &\rightleftharpoons CuNO_2^+ \\ Cu^{III} + CuNO_2^+ &\longrightarrow Cu^{II} + CuNO_2^{2+} \\ CuNO_2^{2+} &\longrightarrow Cu^{II} + NO_2^\bullet \end{aligned}$$

In acidic media, however, the *relative* rates of reaction of copper(III) with NO_2^-, Br^-, CH_3OH, or H_2O_2 are broadly similar to those for the corresponding oxidations by hydroxyl radicals, although the former reactions are an order of magnitude slower. The mechanism at pH *ca.* 3 is considered to involve the formation of hydroxyl radicals *via* the reaction

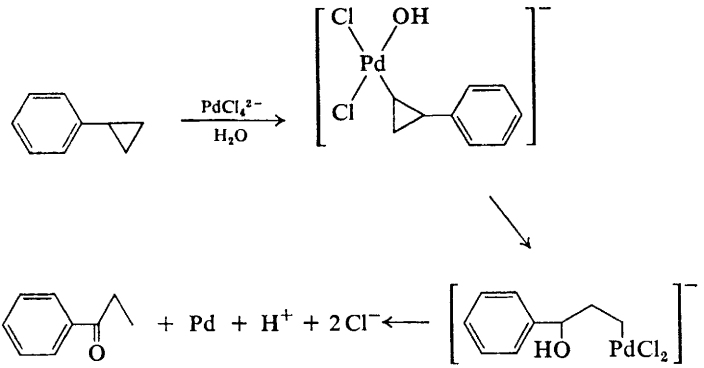
$$Cu^{III}(aq) \rightleftharpoons Cu^{II} + OH^\bullet$$

with a subsequent redox reaction of the hydroxyl radical with the reductant to yield the products. It is suggested that copper(III) may be formed by different oxidants in the presence of ligands which lower the redox potential of the Cu^{III}/Cu^{II} couple, but that copper(III) oxidizes only slowly, if at all, reductants which are not ligands complexed within its inner co-ordination sphere.

The oxidation of methylcyclobutene by Hg^{II} and Pd^{II} in 1M perchloric and hydrochloric acids has been described,[180] and whereas the thallium(III) reaction involves an intermediate complex, the corresponding oxomercurial species is relatively stable. The products of oxidation and isomerization of phenylcyclopropane by palladium(II) have been reported.[195] In 2 : 1 glyme–H_2O (v/v) using $PdCl_4^{2-}$ as oxidant, propiophenone and phenylacetone are the major products, the reaction proceeding *via* an oxypalladium complex,

[194] D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 638.
[195] R. J. Ouellette and C. Levin, *J. Amer. Chem. Soc.*, 1971, **93**, 471.

e.g. in the formation of propiophenone,



The rate-determining process is considered to involve the conversion of the initial intermediate complex into a σ-bonded 1,3-oxypalladium adduct which undergoes further rapid reactions possibly involving two specific, consecutive 1,2-hydride shifts. In the reaction with cyclohexene and other unsaturated hydrocarbons of this type [196] under acidic conditions (1.5M-$HClO_4$), a fast oxidation with palladium acetate is observed, the products being cyclohexanone and other acetate-containing species. A slower oxidation is reported, however, in the presence of oxygen.

The oxidation of cysteine and glutathione by molybdenum(VI) has been reported [196] in phosphate buffer at pH 7.50. No evidence was found for complex formation between the oxidant and either substrate although molybdenum(V) forms a strong 1 : 2 species with cysteine, the stoicheiometric reaction being written as

$$2MoO_4^{2-} + 6\text{cysteine} \longrightarrow [Mo^{V}_2O_3(\text{cysteine})_4]^{4-} + \text{cystine}$$

where cystine is the reduced (R—S—S—R) form. The rate law for the redox reaction may be expressed as

$$\frac{-\,d[Mo^{VI}]}{dt} = k_3[Mo^{VI}][\text{cysteine}]^2$$

A mechanism consistent with these findings may be written as (RSH = cysteine)

$$MoO_4^{2-} + RSH \rightleftharpoons [Mo^{VI}O_3,RSH]^{2-}$$

$$[Mo^{VI}O_3,RSH]^{2-} + RSH \xrightarrow{\text{slow}} [Mo^{V}O_3,RSH]^{3-} + RS^{\bullet}$$

$$[Mo^{V}O_3,RSH]^{3-} + RSH \rightleftharpoons [Mo^{V}O_2(RSH)_2]^{3-}$$

$$2[Mo^{V}O_2(RSH)_2]^{3-} \rightleftharpoons [Mo^{V}_2O_3(RSH)_4]^{4-}$$

$$2RS^{\bullet} \xrightarrow{\text{fast}} RS—SR$$

[196] J. F. Martin and J. T. Spence, *J. Phys. Chem.*, 1970, **74**, 2863.

the rate-determining redox step involving a 1 : 1 complex. In contrast, in the reaction with glutathione there is no rate dependence on oxidant, the rate law being

$$\frac{-\,d[Mo^{VI}]}{dt} = k_1[\text{glutathione}]$$

and in this case it is considered that two forms of the substrate exist, one of which is possibly a cyclic thioether and that the rate-controlling step is the formation of a secondary reactive glutathione molecule which can interact with the oxidant. The product of the reaction is considered to be a weak monomeric, e.s.r.-active Mo^{V}-containing complex. Characterization and triplet state e.s.r. spectra of a dinuclear $[Mo^{V}]_2$–glutathione complex has, however, been described in a separate study.[197] The preparations of mono- and di-nuclear dinitrogen complexes of molybdenum(I) have been described,[198] $MoOCl_3$(diphos) (where diphos = $Ph_2PCH_2CH_2PPh_2$) being reduced by $LiAlH_4$ in THF to yield initially a green unstable complex of the type $MoOCl_2$(diphos)THF, which on reaction with zinc dust in the presence of excess diphos gives an air-stable yellow Mo^{I} complex $MoCl(N_2)$-$(diphos)_2$. The N—N bond strengths in dinitrogen complexes of this type are markedly affected by the different oxidation states of the molybdenum.

Redox interchange reactions of *trans*-dihalogenotetra-amineplatinum(IV) complexes have been investigated.[199] In the reaction of iodide ion with [*trans*-Pt(en)(tet)Br_2]$^{2+}$ (en = ethylenediamine, tet = *NNN'N'*-tetramethylethylenediamine) there is complete reduction to [Pt(en)(tet)]$^{2+}$ and no evidence for di-iodoplatinum(IV) complexes. In the reaction with [*trans*-$Pt(en)_2Cl_2$]$^{2+}$, however, the product is [$Pt(en)_2I_2$]$^{2+}$. In the former system, where the complex is sterically hindered, there is no dependence on added [Pt(en)(tet)]$^{2+}$, the mechanism probably involving the direct reductive attack of the halide ion on the co-ordinated halide to yield the product. In the latter reaction, however, the presence of [$Pt(en)_2$]$^{2+}$ results in an increase in the reaction rate consistent with the formation of a bridged transition state of the form

$$X\cdots Pt^{IV}\cdots X\cdots Pt^{II}\cdots Y$$

The data for a series of reactions involving the attack of an anion on the halide co-ordinated to platinum(IV) are given, and in all cases there is consistency with a redox mechanism of the type

$$X{-}Pt^{IV}{-}X + Y^- \xrightarrow{\text{slow}} X^- + Pt^{II} + XY$$

Linear free energy relationships have been observed between the free energies of activation and the standard free energies of the reduction reactions. From the gradients of such correlations it is suggested that the transition states are similar in character to the products.

[197] T. J. Huang and G. P. Haight, *J. Amer. Chem. Soc.*, 1971, **93**, 611.
[198] L. K. Atkinson, A. H. Mawby, and D. C. Smith, *Chem. Comm.*, 1971, 157.
[199] A. J. Poe and D. H. Vaughan, *J. Amer. Chem. Soc.*, 1970, **92**, 7537.

The oxidations of organic nitrogen compounds by lead tetra-acetate have been reviewed,[200] and the need stressed for mechanistic studies, especially in the area of characterization of intermediates formed. Use has been made of this reagent in the oxidation of substituted phenols [201] in acetic acid. The reactions are first order with respect to both oxidant and reductant and a free-radical mechanism has been postulated with a rate order in terms of substituents

$$H > o\text{-}Cl > p\text{-}Cl > m\text{-}NO_2 > o\text{-}NO_2 > p\text{-}NO_2$$

there being a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the systems studied.

Mechanistic implications in the role of phenol in the uranium(IV)–chlorine(III)–phenol reaction have been described.[202] In the reaction between U^{IV} and Cl^{III} in aqueous media, there is evidence of a reactive chlorine intermediate which is scavenged on addition of the phenol. The reactive intermediates have been shown to be chlorine and $[Cl_2O_2]$, the fact that neither Cl^{V} nor ClO_2 is formed implying that direct reaction between the latter reagent and phenol must occur. At pH $\geqslant$ 1, the scavenged species is almost entirely the $[Cl_2O_2]$ intermediate, the reactions being consistent with the mechanism

$$U^{IV} + Cl^{III} \xrightarrow{\text{slow}} U^{VI} + Cl^{I}$$

$$Cl^{I} + Cl^{III} \xrightarrow{k_1} Cl_2O_2$$

$$Cl^{I} + Cl^{-} \xrightarrow{k_2} Cl_2$$

$$Cl_2O_2 + C_6H_5OH \xrightarrow{\text{fast}} ClC_6H_4OH + H^+ + Cl^{III}$$

$$Cl_2 + C_6H_5OH \xrightarrow{\text{fast}} ClC_6H_4OH + H^+ + Cl^-$$

where $k_1 \geqslant 10\,k_2$. The reactivity order of chlorine oxidants with phenol has been shown to be

$$Cl_2O_2 \approx Cl_2 \gg HOCl \approx ClO_2 > HClO_2 > ClO_2^- \approx ClO_3^- > ClO_4^-$$

The oxidation of tetraphenylborate by hexachloroiridate(IV) [203]

$$BPh_4^- + 2IrCl_6^{2-} + H_2O \longrightarrow Ph_2BOH + Ph_2 + IrCl_6^{3-} + H^+$$

proceeds quantitatively in aqueous media, the rate law

$$\frac{-\,d[BPh_4^-]}{dt} = k_2[BPh_4^-][IrCl_6^{2-}]$$

showing no acid dependence. A radical mechanism is postulated, and it is suggested that iridium(IV) may act as a one-electron outer sphere transfer

[200] J. B. Aylward, *Quart. Rev.*, 1971, **25**, 407.
[201] S. Das, K. K. Satpathy, P. L. Nayak, and M. K. Rout, *J. Indian Chem. Soc.*, 1971, **48**, 62.
[202] E. B. Grimley, R. Buchacek, and G. Gordon, *Inorg. Chem.*, 1971, **10**, 873.
[203] P. Abley and J. Halpern, *Chem. Comm.*, 1971, 1238.

reagent with the mechanism

$$BPh_4^- + IrCl_6^{2-} \xrightarrow{k_2} BPh_4^{\bullet} + IrCl_6^{3-}$$
$$BPh_4^{\bullet} + IrCl_6^{2-} \xrightarrow{\text{rapid}} BPh_4^{+} + IrCl_6^{3-}$$
$$BPh_4^{+} \xrightarrow{\text{rapid}} [BPh_2^{+}] + (Ph)_2$$
$$BPh_2^{+} + H_2O \xrightarrow{\text{rapid}} Ph_2BOH + H^+$$

9 Peroxodisulphate

The kinetics of the oxidation of iodine [204] in aqueous solutions

$$5S_2O_8^{2-} + I_2 + 6H_2O \longrightarrow 2IO_3^- + 10SO_4^{2-} + 12H^+$$

have been studied spectrophotometrically, the rate law being expressed as

$$\frac{-\,d[I_2]}{dt} = k_\alpha[S_2O_8^{2-}]^{\frac{1}{2}}[I_2]^{\frac{1}{2}} + k_\beta[S_2O_8^{2-}][I_2]^{\frac{1}{2}}$$

At low persulphate concentrations, the order of 0.5 observed with respect to oxidant may be accounted for by the mechanism

$$I_2 \rightleftharpoons 2I^{\bullet}$$
$$S_2O_8^{2-} \overset{k_1}{\rightleftharpoons} 2SO_4^-$$
$$SO_4^- + I^{\bullet} \xrightarrow{k_2} SO_4^{2-} + I^+$$
$$I^{\bullet} + S_2O_8^{2-} \xrightarrow{k_3} SO_4^{2-} + SO_4^- + I^+$$

with subsequent rapid oxidation of the I^+ by peroxodisulphate. Both Cu^{II} and Ag^{I} catalyse the reaction, and in these the possibility of Cu^{III} and Ag^{II} or Ag^{III} intermediates being involved in cyclic redox reactions is considered. The reaction is, however, retarded by oxygen, owing to a more rapid interaction of the SO_4^- radical with O_2 than with the iodine atom such that pathway k_2 is suppressed.

The oxidation of the copper(II)–hydrazine complex has been investigated,[205] the rate law being of the form

$$\frac{-\,d[S_2O_8^{2-}]}{dt} = \left(\frac{K_h[Cu^{II}]^2}{[H^+]}\right)\left(k_\alpha + \frac{k_\beta K_h}{[H^+]}\right)$$

where K_h is the hydrolysis constant for the copper(II) ion and k_α and k_β are rate constants. At high acidities, (up to 0.1M-H^+) the reactive species are considered to be the Cu^{2+} ion and the complex $Cu(N_2H_4)^{2+}$, whereas at lower acid concentrations the hydroxo-complexes of the metal ion are involved in the activated complexes.

The silver(I)-catalysed oxidation of americium(III) by $S_2O_8^{2-}$ has been studied using ^{241}Am tracer techniques,[206] coprecipitation with lanthanum trifluoride representing a good method of monitoring the micromolar

[204] F. Secco and S. Celsi, *J. Chem. Soc.* (*A*), 1971, 1092.
[205] R. Swaroop and Y. K. Gupta, *Indian J. Chem.*, 1971, **9**, 361.
[206] A. Ohyoshi, A. Jyo, T. Shinohara, and E. Ohyoshi, *Radiochem. Radioanalyt. Letters*, 1971, **6**, 121.

concentrations of reductants used. A first-order dependence on Am^{III} is observed, the product being Am^{IV}. In the reaction with neptunium(VI), however,[207] in 0.2M-NaOH, the reaction order with respect to reductant is zero. At 60 °C, the rate is almost independent of $S_2O_8^{2-}$ concentration, the rate-controlling process being determined by the decomposition of peroxodisulphate. Silver(I) catalysis is also observed as is that due to nickel(II) and cobalt(II). The reaction product is Np^{VII}, but at higher hydroxide ion concentrations (*ca.* 8M) a different mechanism may be operative.

Osmometric measurements on the nature of the interaction with ferrocyanides[208] have been made in the presence of different counter ions, extensive ion-pairing being observed, although the extent of interaction varies from one cation to another. In all, four reaction paths have been identified:

$$2Fe(CN)_6^{4-} + S_2O_8^{2-} \xrightarrow{k_1} 2Fe(CN)_6^{3-} + 2SO_4^{2-}$$

$$2MFe(CN)_6^{3-} + S_2O_8^{2-} \xrightarrow{k_2} 2Fe(CN)_6^{3-} + 2SO_4^{2-} + 2M^+$$

$$2Fe(CN)_6^{4-} + MS_2O_8^{-} \xrightarrow{k_3} 2Fe(CN)_6^{3-} + 2SO_4^{2-} + M^+$$

$$2MFe(CN)_6^{3-} + MS_2O_8^{-} \xrightarrow{k_4} 2Fe(CN)_6^{3-} + 2SO_4^{2-} + 3M^+$$

Using a Brønsted equation in which the ionic strength term has been derived from an extended Debye–Hückel correlation, it has been shown that for the ions $M^+ = Li^+$, Na^+, K^+, Rb^+, or Cs^+ the first (k_1) pathway is operative but only in the case of Li^+ to an appreciable extent. For the cations Li^+ or Na^+, the k_2 route is operative whereas for K^+, Rb^+, or Cs^+ the reaction proceeds *via* the k_4 mechanism, the rate constants extrapolated to zero ionic strength being remarkably similar.

The oxidations of ethanol and glycerol have been studied, the reactions being zeroth order with respect to peroxodisulphate.[209] Methanol inhibits the reaction and it is suggested that C_2H_5OH–$S_2O_8^{2-}$ complexes are formed in the reaction, which is inhibited by increasing concentrations of sulphate ion. Peroxodisulphate has been shown to induce the reduction of mercuric chloride by glycine,[210] although the reaction proceeds much more rapidly in the presence of copper(II). The rate law is complex, the role of the copper ion being to complex the glycine and to act as a chain initiator in the redox reaction of the copper(II)–glycine complex with peroxodisulphate to yield SO_4^- radicals and an unstable Cu^{III}–glycinate species. $S_2O_8^{2-}$ has also been used as an oxidant in the reaction with *N*-methylbiphenyl-2-carboxamides.[211]

[207] V. P. Shilov, N. N. Krot, and A. D. Gel'man, *Radiokhimiya*, 1971, **13**, 9 (*Chem. Abs.*, 1971, **74**, 130 929*h*).
[208] R. W. Chlebek and M. W. Lister, *Canad. J. Chem.*, 1971, **49**, 2943.
[209] A. L. Samvelyan, N. M. Beileryan, and O. A. Chaltykyan, *Doklady Akad. Nauk Armyan* S.S.R., 1970, **50**, 283 (*Chem. Abs.*, 1971, **74**, 46 035*w*).
[210] K. Kumar and L. X. Saxena, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2491.
[211] D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Comm.*, 1971, 889.

Evidence has been obtained for an inner-sphere mechanism in the isoelectronic peroxodiphosphate ($P_2O_8^{4-}$) ion oxidation of metal complexes.[212] For a series of reactants of the type $Fe(LL)_3^{2+}$ and $Fe(LLL)_2^{2+}$ (where LL = bipyridyl or phenanthroline and LLL = terpyridyl), there is no parallel to the outer sphere path observed in the $S_2O_8^{2-}$ oxidation of the same complexes. The mechanism is considered to involve the rate-determining partial dissociation of one of the ligands, with $P_2O_8^{4-}$ (or PO_4^{2-}) approaching the vacant position, followed by a subsequent fast oxidation reaction. An exception may be in the case of the complex $[Ru^{II}(phen)_2pyCl]^+$. In the case of osmium(II) complexes, however, no reaction takes place in the absence of catalysts since no prior dissociation occurs.

10 Halogens and Halogen-containing Derivatives

The oxidation of halates to perhalates by xenon difluoride in aqueous solution has been investigated,[213] although whereas maximum yield of ClO_4^- and IO_4^- are *ca.* 93% based on XeF_2, those of perbromate are significantly lower (*ca.* 12%). The maximum yields are also dependent on concentration of halate present. In the reaction with ClO_3^- and IO_3^-, the oxidant is considered to be a hydrolysed xenonoxy-compound, since at high halate concentrations the rate of disappearance of XeF_2 from solutions is not markedly increased. The mechanism is considered to involve a rate-determining oxidation of water by XeF_2, *e.g.* (HO_3^- = halate)

$$XeF_2 + H_2O \longrightarrow XeO + 2HF$$
$$XeO + H_2O \longrightarrow Xe + H_2O_2$$
$$XeO + HO_3^- \longrightarrow Xe + HO_4^{-*}$$
$$HO_4^{-*} \longrightarrow HO_4^-$$
$$HO_4^{-*} + H_2O \longrightarrow HO_3^- + H_2O_2$$
$$H_2O_2 + XeF_2 \longrightarrow Xe + O_2 + 2HF$$

where HO_4^{-*} is an intermediate which can either proceed to form a stable perhalate ion or it may react with water to yield a halate species. In the case of BrO_3^-, it is considered that the low oxidation yields are consistent with the latter as the predominating process. In the oxidation of iodate, at low concentrations a mechanism similar to that indicated is postulated, but at higher substrate concentrations ($> 2 \times 10^{-3}$ mol l^{-1}) the direct reaction

$$XeF_2 + IO_3^- + H_2O \longrightarrow Xe + 2HF + IO_4^-$$

is operative, where the formation of an intermediate iodate-ester of xenon might be important. Experiments with ClO_3^-, in the presence of ^{18}O-enriched solvent, however, indicate that during the course of the reaction there is no gross exchange of oxygen between solvent oxygen and ClO_3^- or ClO_4^-. In the case of the bromate, some enrichment of the unreacted BrO_3^- is observed, in keeping with the mechanism postulated.

[212] E. Chaffee, I. I. Creaser, and J. O. Edwards, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1.
[213] E. H. Appelman, *Inorg. Chem.*, 1971, **10**, 1881.

The kinetics and mechanism of the Cl^-–ClO_3^- reaction in moderately concentrated (2.5—5.8M) perchloric and sulphuric acid media [214] have been studied, the overall reaction being represented by the equation

$$2H^+ + ClO_3^- + Cl^- \longrightarrow ClO_2 + \tfrac{1}{2}Cl_2 + H_2O$$

The reaction order with respect to Cl^- falls from 2.0 at lower acidities to 1.1 at 5.6M-$HClO_4$. The order with respect to stoicheiometric acid concentration is high and may be accounted for by the reaction

$$H^+,4H_2O \rightleftharpoons H^+ + 4H_2O$$

The mechanism is postulated as involving the steps

$$3H^+ + 2Cl^- + ClO_3^- \rightleftharpoons HClO_2 + Cl_2 + H_2O$$
$$HClO_2 + H^+ + ClO_3^- \longrightarrow 2ClO_2 + H_2O$$

where the formation of chlorine has an inhibiting effect on the reaction rate. The oxidation of phosphite and selenite by hypochlorite [215] has been examined as a function of pH, the maximum reaction rate being observed at pH *ca.* 7. The initial rates of thermal decomposition of aqueous perchloric acid (1.1—6.6M) at high temperature (295—322 °C) have been investigated,[216] using a perchlorate ion activity electrode, there being a 3.5 order dependence on the stoicheiometric perchloric acid concentration. The mechanism is considered to involve the rate-determining reaction of two undissociated substrate molecules:

$$H^+ + ClO_4^- \rightleftharpoons HClO_4$$
$$2HClO_4 \xrightarrow{\text{slow}} \text{intermediates} \xrightarrow{\text{rapid}} H_2O + Cl_2 + \tfrac{7}{2}O_2$$

Chloride ion is found to have an accelerating effect on the reaction rate, and it is considered that if sufficient chloride ion is present the reaction

$$4H^+ + 3Cl^- + ClO_4^- \longrightarrow 2Cl_2 + 2H_2O + O_2$$

may also occur. No thermal decomposition of perchloric acid is observed at lower temperatures. The ion $Nb_6Cl_{12}^{2+}$ is extremely inert to chloride ion exchange [217] as measured by $^{36}Cl^-$ at 90 °C. Under these conditions, however, the solutions undergo decomposition to yield H_2, HCl, and Nb^V.

Chlorine(I) species react with the tris-(1,10-phenanthroline)iron(II) ion in two ways, one of which is dependent on the dissociation of the complex cation [218] and involves a one-electron oxidation to yield $Fe(phen)_3^{3+}$ as product. The observed rate constant in conditions of excess oxidant may be described in terms of the expression

$$k_{obs} = k_\alpha + \left[\frac{k_\beta[H^+]/K + k_\gamma}{[H^+]/K + 1}\right][Cl^I]$$

[214] P. Crisci and F. Lenzi, *Canad. J. Chem.*, 1971, **49**, 2552.
[215] V. P. Tolstikov, *Zhur. obshchei Khim.*, 1971, **41**, 301 (*Chem. Abs.*, 1971, **75**, 40 890*v*).
[216] M. P. Henderson, V. I. Miasek, and T. W. Swaddle, *Canad. J. Chem.*, 1971, **49**, 317.
[217] J. E. Land, H. H. Musgrove, and J. E. Teggins, *J. Less-Common Metals*, 1971, **23**, 207.
[218] M. G. Ondrus and G. Gordon, *Inorg. Chem.*, 1971, **10**, 474.

where k_α represents the rate constant for the rate-determining dissociation, which may be followed by a rapid two-electron oxidation, *e.g.*

$$[Fe(phen)_3]^{2+} \underset{}{\overset{k_\alpha}{\rightleftharpoons}} [Fe(phen)_2]^{2+} + phen$$

$$[Fe(phen)_2]^{2+} + HOCl \xrightarrow{rapid} [Fe(phen)_2]^{4+} + OH^- + Cl^-$$

$$[Fe(phen)_2]^{2+} + OCl^- + H_2O \xrightarrow{rapid} [Fe(phen)_2]^{4+} + 2OH^- + Cl^-$$

$$[Fe(phen)_2]^{4+} + [Fe(phen)_2]^{2+} + 2H_2O \xrightarrow{rapid} [(phen)_2Fe(OH)_2Fe(phen)_2]^{4+} + 2H^+$$

to yield the dimeric hydroxo-bridged species. The rate constants k_β and k_γ represent the reactions involving the direct oxidation of the complex ion by HOCl and ClO^-, respectively. In this case the product $[Fe(phen)_3]^{3+}$ is unstable under the hydrogen ion conditions used (pH 7.2) and it decomposes to the dimeric form. From a comparison of activation parameters it appears that this route, which involves a one-electron pathway with a two-electron oxidant (Cl^I), is less favoured. Two-electron redox reactions of this ion are apparently only observed when the primary co-ordination sphere of the metal ion is penetrated by the oxidant. The oxidation of organic substrates by hypochlorite is catalysed by ruthenium(III) chloride.[219] The production of cyclohexanone from cyclohexanol is virtually quantitative in the presence of Ru^{III}, whereas this product is not observed in the absence of the metal ion, suggesting that the regeneration of high oxidation states of ruthenium are involved in the overall reaction. The oxidation of bipyridinium quaternary salts by Cl_2, ClO_2, and MnO_4^- have been examined.[220] There is a fast reaction with ClO_2, which is considered the oxidant of choice for the removal of bipyridinium salts of this type, whereas the slower reactions with Cl_2 and MnO_4^- conform to second-order kinetics. In the case of permanganate a considerable variation in rate with pH is noted, the reaction increasing with increasing pH, whereas little effect of acidity was noted with Cl_2 as reactant. In general with Mn^{VII} and Cl_2, the rates of reaction with paraquat are less than for diquat under the same experimental conditions. The kinetics of the oxidation of bromide ions by Cl_2 in molten $ZnCl_2$–KCl mixtures have been described.[221]

The mechanism of reduction of IrX_6^{2-} (X = Cl or Br) by iodide and other reductants has been investigated.[222] A study of the reaction products indicates that the mechanism involves an outer-sphere redox process. The reaction between $IrCl_6^{2-}$ and I^- is second-order overall, being first-order with respect to each reactant. The outer-sphere reactions of $IrCl_6^{3-}$, $IrBr_6^{3-}$, and $Ir(H_2O)Cl_5^{2-}$ with Br_2 and Cl_2 have been studied in acidic

[219] S. Wolfe, S. K. Hasan, and J. R. Campbell, *Chem. Comm.*, 1970, 1420.
[220] H. M. Gomaa and S. D. Fanst, *J. Agric. Food Chem.*, 1971, **19**, 302 (*Chem. Abs.*, 1971, **74**, 10 3545*p*).
[221] I. Slama and J. Mala, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2686.
[222] R. I. Novoselov and Z. A. Muzykantova, *Zhur. neorg. Khim.*, 1970, **15**, 3084.

media, with a direct interaction between the t_{2g} orbitals of the metal and the orbitals of the halogen. The reactions of hypobromite ions or of hypobromous acid with iodate, nitrite, or formate,[223] together with the decomposition of hypobromite in aqueous solution, have been described. The mechanism of the latter reaction may be described as

$$2BrO^- \xrightarrow{k_0} BrO_2^- + Br^-$$

$$BrO_2^- + BrO^- \xrightarrow{k_1} BrO_3^- + Br^-$$

with k_1 somewhat greater than k_0. In the reaction with nitrite (or formate) ions, the rate law may be represented by the equation

$$\frac{-\,d[BrO^-]}{dt} = 3k_0[BrO^-]^2 + \frac{k_2[BrO^-][NO_2^-]}{[HO^-]}$$

the reaction product being NO_3^- (or CO_3^{2-}). In the case of iodate, however, the product of the reaction is the ion $H_2IO_6^{3-}$. From a comparison of the corresponding reactions with ClO^-, the reactions of the hypobromite ion are in general more rapid. A kinetic investigation of the decomposition of bromite has been described:[224] the order of reaction with respect to hydrogen ion is dependent on the pH, the value being close to 2 in the range pH 6.6—8.25 and at pH 3.56—6.26 the order is unity. In the presence of bromide ions which act as a catalyst, the reaction orders with respect to this ion and to BrO_2^- are close to unity. At pH values below 6.26, bromine is observed as one of the reaction products (the others being bromate, bromide, and hypobromite) and under these conditions the reaction mechanism may be described as

$$2HBrO_2 \longrightarrow HBrO_3 + HBrO$$

$$HBrO_2 + Br^- \longrightarrow HBrO + BrO^-$$

$$H^+ + HBrO + Br^- \longrightarrow H_2O + Br_2$$

The subsequent reaction between hypobromite and bromite has been shown to be rapid, requiring fast reaction techniques for its characterization. The oxidation of neptunium(VI) by hypobromite has been studied in alkaline media,[225] stable neptunium(VII) salts being formed. There is a rate dependence on hydroxide ion concentration, and nickel(II), cobalt(II), or copper(II) ions increase the reaction rate whereas silver(I) or iron(II) have no effect.

Studies of the oxidations of oxovanadium(IV) by halate ions have been reported. In the reaction with bromate [226]

$$BrO_3^- + 5VO^{2+} + 2H_2O \longrightarrow \tfrac{1}{2}Br_2 + 5V^V + 4H^+$$

[223] M. W. Lister and P. E. McLeod, *Canad. J. Chem.*, 1971, **49**, 1987.
[224] A. Massagli, A. Indelli, and F. Pergola, *Inorg. Chim. Acta*, 1970, **4**, 593.
[225] V. P. Shilov, N. N. Krot, and A. D. Gel'man, *Radiokhimiya*, 1970, **12**, 896 (*Chem. Abs.*, 1971, **74**, 130 893*g*).
[226] R. C. Thompson, *Inorg. Chem.*, 1971, **10**, 1892.

the rate law in perchloric acid may be expressed as

$$\frac{-\,d[BrO_3^-]}{dt} = k_\alpha[BrO_3^-][V^{IV}]$$

for up to three half-lives, deviations past this stage being associated with an additional reaction parameter dependent on the intial Br^V/V^V ratios. At low hydrogen ion concentrations and in the presence of excess vanadium(IV), further oxidation by the bromine product may be observed, but this secondary process becomes competitive with the reaction only in the latter stages. In the presence of large initial bromate ion concentrations, the data are consistent with the rate scheme

$$VO^{2+} + BrO_3^- \xrightarrow{k} VO_2^+ + BrO_2$$

$$VO^{2+} + BrO_2 + H_2O \xrightarrow{\text{rapid}} VO_2^+ + HBrO_2 + H^+$$

$$2HBrO_2 \xrightarrow{\text{rapid}} BrO_3^- + HOBr + H^+$$

$$VO^{2+} + HOBr \xrightarrow{\text{rapid}} \tfrac{1}{2}Br_2 + VO_2^+ + H^+$$

Bromide ion and allyl alcohol act as scavengers in the reaction, the former reacting effectively with the bromous acid formed whereas the latter is considered to interact with lower intermediates such as hypobromous acid. In the corresponding reaction with chlorate and iodate,[227] differing mechanisms are observed. In the presence of excess chlorate, the rate law may be expressed as

$$\frac{-\,d[V^{IV}]}{dt} = \frac{k_1[ClO_3^-][V^{IV}]}{1 + K_1[ClO_3^-]}$$

The mechanism involves the formation of an adduct which decomposes in the rate-determining step:

$$ClO_3^- + V^{IV} \underset{\text{rapid}}{\rightleftharpoons} [VO^{2+},ClO_3^-]\ (K_1)$$

$$[VO^{2+},ClO_3^-] \xrightarrow{k_0} \text{products}$$

In the case of the iodate, however, a 1 : 2 complex is formed,

$$IO_3^- + VO^{2+} \underset{\text{rapid}}{\rightleftharpoons} [VO^{2+},IO_3^-]$$

$$[VO^{2+},IO_3^-] + IO_3^- \underset{\text{rapid}}{\rightleftharpoons} [VO^{2+},(IO_3^-)_2]$$

$$[VO^{2+},(IO_3^-)_2] \xrightarrow{k_0} \text{products}$$

The structures of the intermediates may involve bonding between the vanadium atom and one of the oxygens of the halate ion, with subsequent fission of this halogen–oxygen bond.

[227] C. W. Fuller and J. M. Ottaway, *Analyst*, 1970, **95**, 791.

Molybdate ions have been shown [228] to catalyse the reaction between bromate and iodide in aqueous solutions at pH 2—3, with the rate law of the form

$$\text{Rate} = k_0[BrO_3^-][I^-][H^+]^2 + k_1[BrO_3^-][I^-][H^+][Mo^{VI}]$$

The first term is the law observed in the absence of catalyst. The effect is dramatic, however, with associated rate constants k_0 and k_1 being 50.3 l mol^{-3} s^{-1} and 3.43 × 10^4 l mol^{-3} s^{-1} respectively, and may be ascribed to the formation of a Mo^{VI}–BrO_3^- complex with no evidence for any change in the oxidation state of the catalyst during the course of the reaction. The kinetics and mechanism of the bromate–ascorbic acid reaction have also been reported,[229] and the effects of phosphate on the oxidation of iodide by chlorate in the presence of catalytic concentrations of vanadium(IV) have been described,[230] the latter systems being considered to involve vanadium(IV)–phosphate complexes.

The mechanism of the oxidation of tetracyanoplatinate(II) and tetraammineplatinum(II) by bromine has been investigated.[231] In the presence of bromide ion, the products are [*trans*-$Pt(CN)_4Br_2]^{2-}$ and [*trans*-$Pt(NH_3)_4Br_2]^{2+}$, respectively, the reactions proceeding *via* a two-step mechanism. The first reaction involves the rapid oxidation of the platinum(II) species to a monobromoaquoplatinum(IV) complex which subsequently undergoes a slower displacement of the co-ordinated water by bromide, *e.g.*

$$Br_2 + [Pt(CN)_4]^{2-} \xrightarrow{\text{rapid}} Br^- + [Br{-}Pt(CN)_4{-}OH_2]^-$$

$$Br^- + [Br{-}Pt(CN)_4{-}OH_2]^- \xrightarrow{\text{rapid}} [Br{-}Br{-}Pt(CN)_4{-}OH_2]^{2-}$$

$$[Br{-}Br{-}Pt(CN)_4{-}OH_2]^{2-} + Br^- \xrightarrow{\text{slow}} Br^- + [Br{-}Pt(CN)_4{-}Br]^{2-} + H_2O$$

The rate law, however, shows an order of 2 with respect to bromide ion concentration, requiring the intermediate bromide association process shown prior to the secondary step.

The formation of iodine bromide in concentrated sulphuric acid has been shown to be a concerted termolecular process,[232] the rate law for the reaction

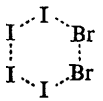
$$I_2 + Br_2 \rightleftharpoons 2IBr$$

being described by the expression

$$\text{Rate} = k_\alpha[I_2]_0[I_2][Br_2]$$

where $[I_2]_0$ respresents the initial iodine concentration, the other concentrations being instantaneous values. It is suggested that three halogen molecules are involved in a concerted process with a transition state of the type

[228] A. F. M. Barton and B. H. Loo, *J. Chem. Soc.* (*A*), 1971, 3032.
[229] J. Bognar and O. Jellinek, *Mickrochim. Acta*, 1970, 1017 (*Chem. Abs.*, 1971, **74**, 80 278*n*).
[230] E. E. Kriss and K. B. Yatsimirskii, *Zhur. neorg. Khim.*, 1971, **16**, 386.
[231] W. R. Mason, *Inorg. Chem.*, 1971, **10**, 1914.
[232] P. Schweitzer, and R. M. Noyes, *J. Amer. Chem. Soc.*, 1971, **93**, 3561.



Bromine is less effective than iodine as a catalyst for the reaction, with the molecule IBr intermediate in catalytic efficiency. The reaction of iodate with bromide in the presence of phenol may be represented as [233]

$$IO_3^- + 2Br^- + 2H^+ \longrightarrow IO_2^- + Br_2 + H_2O$$

where, under the conditions employed, no reaction between phenol and iodate is observed, although it reacts with the product bromine and iodite. The rate law

$$\frac{-\,d[IO_3^-]}{dt} = \frac{[IO_3^-][Br^-]^2[H^+]^2(k_1 + k_2[H^+]^2)}{1 + K[H^+]}$$

holds, where K represents the association constant for the HIO_3 species. A possible mechanism involves the formation of IO_2^+ with its subsequent reaction with both Br^- and HBr:

$$IO_2^+ + 2Br^- \longrightarrow IO_2^- + Br_2$$
$$IO_2^+ + 2HBr \longrightarrow HIO_2 + Br_2 + H^+$$

although both processes are considered to be multi-step in character.

Ruthenium(III) and ruthenium(IV) complexes have been described as catalysts in the redox reactions of periodate,[234] in strongly acidic media (1—5M-HCl). In the oxidation of amines, *e.g.* benzidine, the mechanism involved may be described as

$$H_2N(C_6H_5)_2\overset{+}{N}H_3 + [Ru(OH)Cl_5]^{2-} \rightleftharpoons [H_2N(C_6H_5)_2\overset{+}{N}H_3Ru(OH)Cl_5]^-$$

$$[H_2N(C_6H_5)_2\overset{+}{N}H_3Ru(OH)Cl_5]^- \longrightarrow H_3\overset{+}{N}(C_6H_5)_2NH + [Ru(OH)Cl_5]^{3-} + H^+ \quad \text{slow}$$

$$[Ru(OH)Cl_5]^{3-} + H_6IO_6^+ \xrightarrow{\text{rapid}} [Ru(OH)Cl_5]^{2-} + 3H_2O + IO_3^\bullet$$

where the rate-determining step is the reduction of ruthenium(IV) by the amine with rapid re-oxidation of the metal complex by the oxidant. The oxidation of iodide by isopolymolybdic acids in the presence of germanium(IV) and phosphorus(V) has been reported,[235] the two-stage reactions involving the formation of a Ge^{IV} (or P^V) complex with the molybdate, followed by a secondary reaction of this intermediate with I^- to yield the blue heteropolyacid. The two-electron reaction of indium(I) with tri-iodide ions,

$$In^I + I_3^- \xrightarrow{k_2} In^{III} + 3I^-$$

[233] D. N. Sharma and Y. K. Gupta, *J. Phys. Chem.*, 1971, **75**, 2516.
[234] V. E. Kalinina, R. P. Morozova, K. B. Yarsimisskii, and O. G. Ignat'eva, *Zhur. neorg. Khim.*, 1971, **16**, 1097.
[235] I. I. Alekseeva, I. I. Nemzer, and A. P. Ryser, *Izvest. V.U.Z. Khim. i khim. Tekhnol.*, 1970, **13**, 1423.

has been shown [60] to be too rapid for measurement by stopped-flow spectrophotometry, the value of k_2 being $\geqslant 2 \times 10^8$ l mol^{-1} s^{-1} at 10 °C. The oxidation of sulphydryl groups of cysteine peptides by iodine has been described,[236] the products in some instances being cyclic cystines. In the reaction between iodine and azide,[237] thiocyanato-complexes of Rh^{III}, Cr^{III}, and Co^{III} are found to act as catalysts; the effect is less marked for free NCS^-. The increases in rate are most marked in the case of the N-bonded thiocyanate complexes.

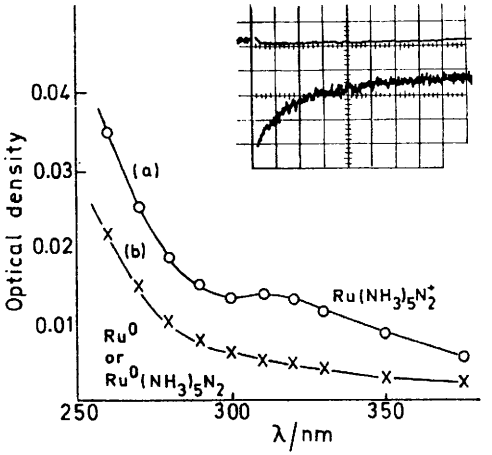


Figure 2 *Absorption spectra of the products of the reduction of* $Ru(NH_3)_5N_2^{2+}$ *by* e^-_{aq} (~ 10 μM). (a) $Ru(NH_3)_5N_2^+$ *produced immediately and* (b) *the products after* ~ 500 μs. *The inset shows the oscilloscope trace (at* 330 nm) *indicating immediate formation and decay of the ruthenium*(I) *species*

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11 Reactions of the Hydrated Electron

Spectroscopic and kinetic aspects of reduction reactions involving solvated electrons have been reviewed [19] together with those of radical anions. The dinitrogenruthenium(II) complex $Ru(NH_3)_5N_2^{2+}$ has been shown [238] to be rapidly reduced by e^-_{aq} in aqueous media to yield the corresponding ruthenium(I) complex, which has been characterized spectrally (Figure 2). This intermediate, however, decays to a species with a lower absorption *via* a second-order reaction

$$2Ru(NH_3)_5N_2^+ \longrightarrow Ru(NH_3)_5N_2^{2+} + Ru^0(NH_3)_5N_2$$

with the formation of the zero-valent ruthenium state, and slower absorption changes are considered to be due to the deposition of ruthenium metal.

[236] B. Kamber, *Helv. Chim. Acta*, 1971, **54**, 927.
[237] L. Dozsa, D. A. Durham, and M. T. Beck, *Magyar Kém. Folyóirat*, 1970, **76**, 555 (*Chem. Abs.*, 1971, **74**, 68 192*x*).
[238] J. H. Baxendale and Q. G. Mulazzani, *J. Inorg. Nuclear Chem.*, 1971, **33**, 823.

It is not clear, at present, whether the spectrum (Figure 2) may be attributed to the penta-ammino-complex or to the ruthenium atoms formed by the rapid dissociation of the complex. There is no evidence, however, for the reduction of the ligand nitrogen under these conditions. Hydrated electrons generated in the pulse radiolysis of aqueous solutions containing cobalt(III) cyanide complexes react very rapidly ($k_2 \sim 10^9$—10^{10} l mol^{-1} s^{-1}) with the cobalt solutes.[239] Reactions of the type

$$Co(CN)_5X^{3-} + e^-_{aq} \longrightarrow Co(CN)_5^{3-} + X^-$$

conform to the rate law of the type

$$-d[e^-_{aq}]/dt = k_2[Co(CN)_5X^{3-}][e^-_{aq}]$$

By variation of ligand X (= CN, H, NO_2, NCS, OH, N_3, Cl, or I) a uniform variation of the rate of reaction with the energy of the $d \rightarrow d$ electronic transition has been observed, and it may be that the electron is reacting *via* an outer-sphere mechanism, the primary co-ordination shell of the aquated reductant being considered to involve four tetrahedrally disposed water molecules. In the corresponding reaction with the pentacyanocobaltate(II) ion,[240] the transient cobalt(I) complex ion $Co(CN)_5^{4-}$ has been identified. This ion further reacts with water to yield the hydridopentacyanocobaltate(III) species:

$$Co(CN)_5^{2-} + e^-_{aq} \xrightarrow{k_1} Co(CN)_5^{4-}$$

$$Co(CN)_5^{4-} + H_2O \xrightarrow{k_2} Co(CN)_5H^{3-} + HO^-$$

The ion $Co(CN)_5^{4-}$ is isoelectronic with $Fe(CO)_5$ and $Mn(CO)_5^-$ and is considered to have a trigonal-bipyrimidal structure, so that both reactions involve considerable configurational changes. The reactions of complexes of the type $M(CN)_5NO^{3-}$ (where M = Mn, Ni, or Co) and of $Fe(CN)_5NO^{2-}$ have been investigated,[241] together with the corresponding reaction with hydroxyl radicals. The cobalt and iron complexes show high reactivity with e^-_{aq} but relatively low interaction with OH$^\bullet$, whereas the opposite behaviour is observed with manganese and nickel species. A correlation between the redox rates and the stretching frequencies for the NO bond is, however, observed for the pentacyanonitrosyl complexes. Using pulse radiolysis, it has been demonstrated that the O^-_{aq} radical ion is an intermediate in the reaction of e^-_{aq} with nitrous oxide.[242] The rapid reactions with various reducing substrates have been examined in high solute concentrations using competition experiments between two solutes, one of which was a one-electron reducing agent [$Fe(CN)_6^{4-}$, I^-, Br^-, Fe^{II}, or Ce^{III}].

In the reaction of sodium with alcohols, the electron is generated without the formation of other reactive species, thus providing a means of examining

[239] G. D. Venerable, *Inorg. Chem.*, 1971, **10**, 1999.
[240] G. D. Venerable and J. Halpern, *J. Amer. Chem. Soc.*, 1971, **93**, 2176.
[241] B. Jezowska-Trzebiatowska, E. Kalecinska, and J. Kalecinska, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1971, **19**, 265 (*Chem. Abs.*, 1971, **75**, 25 927*u*).
[242] D. Zehavi and J. Rabani, *J. Phys. Chem.*, 1971, **75**, 1738.

the reactions of these species.[243] In the reaction with ethan[^{2}H]ol or methan[^{2}H]ol, there is evidence for a bimolecular reaction involving the formation of D_2:

$$e^-_{ROD} + e^-_{ROD} \longrightarrow D_2 + 2RO^-$$

where RO^- = OMe^- or OEt^-. An electron dimer may, however, be formed prior to the production of the hydrogen. The existence of dielectrons $(e_2^{2-})_{aq}$ in aqueous solution has been discussed,[244] although their existence as long-lived species has been questioned.

12 Metal-ion Reductions

The acceleration of the rate of reduction of hydroxylamine by chromium(II) in the presence of sulphate ions has been investigated,[244] the rate enhancement being due to the greater reactivity of the Cr^{II}–SO_4^{2-} ion pair compared with the hexa-aquochromium(II) ion. The reduction of organic radicals derived from propan-2-ol or ether results in chromium(III) complexes.[245] Neither Cr^{II} nor hydrogen peroxide reacts with substrates of this type, but on addition of a solution of chromium(II) perchlorate to a solution containing either the alcohol or the ether and hydrogen peroxide, carbon-bonded complexes of the type $(H_2O)_5CrL^{2+}$ are formed where L = substrate. The mechanism is considered to involve the abstraction of a hydrogen atom from the organic molecule and the rapid capture of the radical formed by the aquochromium(II) ion. There is no evidence for dimer formation, and the rates of aquation of the chromium(III) complexes have been studied. The reduction of benzaldehyde in aqueous acidic ethanol has been investigated,[246] there being several reaction pathways. From acid-dependence studies it is suggested that the reactive form of the substrate is a protonated hydrate or hemiacetal, *e.g.*

$$\begin{array}{l} \mathrm{OH} \\ | \\ \mathrm{PhCH} \\ | \\ \mathrm{OH_2^+} \end{array} + Cr^{II} \longrightarrow PhCH(OH) + Cr(H_2O)_6^{3+}$$

the reduction proceeding *via* ligand transfer of water to form an α-hydroxybenzyl radical. This species can now interact further to yield the reductive-coupling product. Several forms of benzaldehyde have been described in the solvent mixture, and in the presence of chloride ions a further reaction pathway is observed.

The vanadium(II) reduction of nitrate ion has been investigated [247, 248] using the time dependence of polarographic diffusion currents. At pH < 2

[243] J. W. Fletcher and P. J. Richards, *Canad. J. Chem.*, 1971, **49**, 2275.
[244] P. A. Jones and C. B. Monk, *J. Chem. Soc.* (*A*), 1971, 971.
[245] W. Schmidt, J. H. Swinehart, and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 1117.
[246] D. D. Davis and W. B. Bigelow, *J. Amer. Chem. Soc.*, 1970, **92**, 5127.
[247] K. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 2030.
[248] K. Tanaka, K. Morinaga, and K. Nakano, *Bull. Chem. Soc. Japan*, 1970, **43**, 2778.

there is a linear dependence on hydrogen-ion concentration, and in the presence of sulphate, complexing is observed. The mechanism may be described as

$$V^{II} + NO_3^- + H^+ \longrightarrow V^{III} + NO_2 + HO^-$$
$$V^{II} + NO_3^- \longrightarrow VO^{2+} + NO_2^-$$
$$V^{II} + VO^{2+} \longrightarrow [VOV]^{4+}$$
$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$
$$V^{II} + NO^+ \longrightarrow V^{III} + NO$$
$$V^{II} + NO_2^- + 2H^+ \longrightarrow V^{III} + NO + H_2O$$
$$2V^{II} + 2NO + 2H^+ \longrightarrow 2V^{III} + N_2O + H_2O$$

where the first reaction predominates in acid solutions. The corresponding reduction of malic and fumaric acids has been reported,[249] the general rate expression

$$\text{Rate} = \{k_1[A] + k_2[A][H^+] + k_3[A]^2 + k_4[A]^2[H^+]\}[V^{II}]^2$$

being observed, where [A] is the organic acid concentration. At low acidities, the (absorbance–time) rate profiles show a decrease followed by a slower increase, which is consistent not with complex formation but with further slower reactions of the vanadium(III) produced. In some instances, *e.g.* with maleic acid, there is evidence for *cis–trans* isomerization, the pathway involving vanadium(II) complex formation. Potentiometric studies have been made on the vanadium(II) [and vanadium(III)] reactions with hydroxylamine.[250] In chloride and sulphate media in acid (0.1—3M), the reaction may be expressed in terms of a two-electron process

$$V^{II} + NH_2OH + H^+ \longrightarrow NH_4^+ + VO^{2+}$$

whereas at higher acidities, > 5M, a two-stage process may occur with the intermediate formation of vanadium(III)

$$2V^{2+} + NH_2OH + 3H^+ \longrightarrow 2V^{III} + NH_4^+ + H_2O$$
$$2V^{III} + NH_2OH + H_2O \longrightarrow 2VO^{2+} + NH_4^+ + H^+$$

The reduction of water by the hexacyanonickelate(I) anion has been described [251]

$$[Ni_2(CN)_6]^{4-} + 2CN^- + H_2O \longrightarrow 2Ni(CN)_4^{2-} + 2OH^- + H_2$$

The kinetics obey the rate law

$$-d[Ni_2(CN)_6^{4-}]/dt = \{k_1[CN^-] + k_2[HCN]\}[Ni_2(CN)_6^{4-}]$$

From a linear dependence of the rate function on the hydrogen-ion concentration, a mechanism has been postulated involving two rate-determining

[249] E. Vrachnou-Astra, P. Sakellaridis, and K. Katakis, *J. Amer. Chem. Soc.*, 1970, **92**, 3936.
[250] R. Benes and J. Novak, *Coll. Czech. Chem. Comm.*, 1970, **35**, 3788.
[251] D. Bingham and M. G. Burnett, *J. Chem. Soc.* (*A*), 1970, 2165.

steps

$$Ni_2(CN)_6^{4-} + CN^- \longrightarrow Ni(CN)_3^{3-} + Ni(CN)_4^{2-}$$
$$Ni_2(CN)_6^{4-} + HCN \longrightarrow HNi(CN)_3^{2-} + Ni(CN)_4^{2-}$$

the second reaction being operative at a pH of 10.3. These reactions may be followed by fast attack on solvent molecules to yield hydrogen and hydroxide. In the corresponding reduction of buta-1,3-diene,[252] the slow step is the bimolecular reaction

$$Ni_2(CN)_6^{4-} + C_4H_6 \longrightarrow (\pi\text{-}C_4H_6)Ni_2(CN)_6^{4-}$$

although the overall stoicheiometry indicates that this process is rapidly followed by further elimination of cyanide in the reaction

$$(\pi\text{-}C_4H_6)Ni_2(CN)_6^{4-} + C_4H_6 \longrightarrow (\pi\text{-}C_4H_6)_2Ni_2(CN)_4^{2-} + 2CN^-$$

The formation of *trans*-but-2-ene and *cis*-but-2-ene is interpreted in terms of the reduction of two cyanonickel intermediates α_1 and α_2 which contain a π-methylallyl and a π-buta-1,3-diene ligand respectively, the α_1 species yielding predominantly the *trans*-isomer whereas α_2 gives the *cis*-form.

The reduction of chloramine T (*N*-chlorotoluene-*p*-sulphonamide) by hexacyanoferrate(II) has been studied [253] in the pH range 6.2—7.1, where the rate is measurable using conventional techniques. In more acidic media the rate increases sharply. The first-order reaction plots show a rapid reaction followed by a slower process, the discussion being based on this second step. The initial stages are considered to derive from the disproportionation of the substrate into toluene-*p*-sulphonamide and dichloramine T, although, under the reaction conditions where this more rapid reaction accounts for as much as 30% of the total reaction, it would appear that other reactions may be involved. Voltammetric studies of the anodic catalytic current of the oxidation of hexacyanoferrate(II) at a platinum electrode [254] indicate that the oxidation current of the iron(II) complex is increased markedly in the presence of amidopyridine, there being a reaction of the oxidized iron species with the amine, which is first order with respect to both amine and hydroxide ion. With histidine and histamine, however, the orders deviate from unity, the overall reactions being slower. The reaction between pentacyanonitrosylferrate(II) and thiocyanate has been investigated.[255] On irradiation of a solution containing $(NC)_5FeNO^{2-}$ and thiocyanate, a blue colour develops (λ_{max} = 580—590 nm), a similar spectrum being given if the mixture is made basic and then acidified. In basic media, the equilibria involved may be represented as

$$(NC)_5FeNO^{2-} + 2OH^- \rightleftharpoons (NC)_5FeNO_2^{4-} + H_2O$$

and

$$(NC)_5FeNO_2^{4-} + H_2O \rightleftharpoons (NC)_5FeH_2O^{3-} + NO_2^-$$

In the presence of thiocyanate, however, displacement of the co-ordinated

[252] D. Bingham and M. G. Burnett, *J. Chem. Soc.* (*A*), 1971, 1782.
[253] M. C. Agrawal, S. P. Mushran, *J. Phys. Chem.*, 1971, **75**, 838.
[254] A. Rashid and R. Kalvoda, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1970, **28**, 245.
[255] C. Andrade and J. H. Swinehart, *Inorg. Chim. Acta*, 1971, **5**, 207.

nitro- and aquo-groups may occur, with the formation of the complex ion $(NC)_5Fe(NCS)^{4-}$, which on acidification is oxidized by nitrous acid to the blue-coloured iron(III) complex:

$$(NC)_5Fe(NCS)^{4-} + HNO_2 \longrightarrow (NC)_5Fe(NCS)^{3-}$$

Rate studies on the formation of the iron(III) complex in the presence of nitrite ion confirm that the iron(II)–thiocyanate complex is a precursor to the oxidized species. In the corresponding reaction with thiourea [256] in basic solution the order with respect to the thiol is complex, and plots of log k_{obs} (observed rate constant) against pH pass through a maximum at pH $\approx$ 11.5. The violet-coloured adduct formed in the reaction is considered to incorporate two pentacyanoferrate(II) groups and one mole of thiourea, but on addition of acid the reversible formation of a blue colour is observed.

The reduction of plutonium(VII) in alkaline media has been described,[257] the reaction with $Fe(CN)_6^{4-}$, N_2H_4, SO_3^{2-}, or HCO_2^- occurring very rapidly in the range 1.5—2.5M-KOH. The rate of reduction with iodide ion decreases with increasing hydroxide-ion concentration, and the corresponding reaction with iodate under identical conditions proceeds at a rate about six times slower, multi-step reactions being considered important in this system. The anions NO_3^-, oxalate, and acetate, however, are less effective reducing agents than water.

The reduction of perchlorate ion by titanium(III) in sulphate media has been investigated,[258] use being made of the rate measurement for analysis of low concentrations of ClO_4^- ion. The kinetic rate law in the presence of sulphate is less complex than that in chloride media, although whereas the order in reductant and hydrogen ion is unity, fractional order is observed for perchlorate ion. In the corresponding reaction with aquoruthenium(II) as reductant,[259] the products are ClO_3^- and $Ru(H_2O)_6^{3+}$. Some $RuCl^{2+}$ is also observed, consistent with reduction of the chlorate ion formed by ruthenium(II) and the rapid interaction of chlorine intermediates of lower oxidation states with the reducing ion. The rate law may be expressed in the form

$$\frac{d[Ru^{III}]}{dt} = \frac{2k_1[ClO_4^-][Ru^{II}]}{1 + K[Cl^-]}$$

the redox mechanism involving a rate-determining substitution step

$$Ru^{II} + ClO_4^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [RuOClO_3]^+$$

$$Ru^{II} + Cl^- \overset{K}{\rightleftharpoons} [Ru,Cl]^+$$

$$[RuOClO_3]^+ \xrightarrow{\text{rapid}} I_1 + I_2$$

$$Ru^{II} + I_1 + I_2 \xrightarrow{\text{rapid}} 2Ru^{III} + ClO_3^-$$

where I_1 and I_2 are intermediates which have not yet been identified,

[256] J. R. Bellinger, K. L. Lindfors, and D. X. West, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3837.
[257] Y. A. Komkov, N. N. Krot, and A. D. Gel'man, *Radiokhimiya*, 1970, **12**, 692 (*Chem. Abs.*, 1971, **74**, 91 696*y*).
[258] E. Bishop and N. Evans, *Talanta*, 1970, **17**, 1125.
[259] T. W. Kallen and J. E. Earley, *Inorg. Chem.*, 1971, **10**, 1152.

although if Ru^{IV} were formed, an outer-sphere reaction with Ru^{II} would be required to produce the monomeric $Ru(H_2O)_6^{3+}$ product. The substitution-controlled mechanism is given confirmation by the good correlation of the kinetic parameters for the perchlorate reduction and the substitutions of halide ions on the ruthenium(II) ion.

Evidence has been presented for an electron-transfer mechanism in the reduction of organic halides by cobalt(II)–Schiff-base complexes.[260] In the reaction between *NN'*-bis(salicylidene)ethylenediamino-1-methylimidazole-cobalt(II) [Co(salen)(MeIMD)] and *p*-nitrobenzyl bromide (RX) in methylene dichloride there is a quantitative transfer according to the equation

$$2Co(salen)(MeIMD) + RX + MeIMD \longrightarrow Co(salen)(MeIMD)_2^+ + Co(salen)(MeIMD)R + X^-$$

The observed rate law

$$-d[Co(salen)(MeIMD)]/dt = k[Co(salen)(MeIMD)][MeIMD][RX]$$

may be derived using a mechanism in which the rate-determining step is an outer-sphere reaction between the $Co(salen)(MeIMD)_2$ complex and the organic halide:

$$Co(salen)(MeIMD) + MeIMD \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} Co(salen)(MeIMD)_2$$

$$Co(salen)(MeIMD)_2 + RX \xrightarrow{k_1} [Co(salen)(MeIMD)_2^+] + RX^-$$

$$\downarrow$$

$$[Co(salen)(MeIMD)_2^+] + R^\bullet + X^-$$

$$Co(salen)(MeIMD) + R^\bullet \xrightarrow{\text{rapid}} Co(salen)(MeIMD)R$$

No co-ordination of the halide ion is observed. In contrast to these five-co-ordinate complexes, when high-spin six-co-ordinate cobalt(II) species react with substrates of this type, there is no inclusion of the radical into the primary co-ordination sphere of the metal ion, the observed products for nitrobenzyl halides being the corresponding dibenzyls. The carbonylation of pentacyanocobaltate(II) has been described,[261] the reaction

$$2Co(CN)_5^{3-} + 2CO \longrightarrow Co(CN)_6^{3-} + Co(CN)_3(CO)_2^{2-} + CN^-$$

proceeding *via* the mechanism

$$Co(CN)_5^{3-} + CO \underset{}{\overset{K_\alpha}{\rightleftharpoons}} Co(CN)_4CO^{2-} + CN^-$$

$$Co(CN)_4CO^{2-} + Co(CN)_5^{3-} \xrightarrow[\text{slow}]{k_1} [(OC)(NC)_3Co{-}CN{-}Co(CN)_5^{5-}]^{\ddagger}$$

$$\downarrow$$

$$Co(CN)_3(CO)_2 \xleftarrow[+CO]{\text{rapid}} [(OC)Co(CN)_3^{2-} + Co(CN)_6^{3-}]$$

the suggested structure for $Co(CN)_3(CO)_2^{2-}$ being trigonal bipyrimidal.

[260] L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 5752.
[261] J. Halpern and M. Pribanic, *J. Amer. Chem. Soc.*, 1971, **93**, 96.

Hydroxide has been shown to act [262] as a reducing agent for mixed-valence trimeric ruthenium complexes. The one-electron reaction of the brown complex

$$[(H_3N)_5RuORu(NH_3)_4ORu(NH_3)_5]^{7+} \xrightarrow{+e^-} [(H_3N)_5)RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$$

to the red-coloured reduced species takes place according to the equation

$$\text{brown} + OH^- \longrightarrow \text{red} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O$$

the rate law in buffered solutions in the range pH = 6.6—9.8 being

$$d[\text{red}]/dt = k[\text{brown}][HO^-]$$

The initial product of the reaction is an O^I species which is rapidly converted to O_2. The mechanism may involve the rate-determining attack of the hydroxide ion on the oxidized species to yield a μ-peroxo-intermediate. The reduced complex may be re-oxidized by cerium(IV) or hydrogen peroxide to the starting ion. The nature of the blue ruthenium(II) chloride solutions has been re-investigated,[263] with the identification of the anion cluster $Ru_5Cl_{12}^{2-}$. In dilute hydrochloric acid, these solutions reduce water, to yield hydrogen and the yellow complex ion *trans*-$[Ru(H_2O)_4Cl_2]^+$. Redox reactions of dinitrogen-containing dimeric ruthenium ammine complexes have also been described.[264]

The redox potential of the Np^{VII}/Np^{VI} couple has been measured in alkaline media,[265] the neptunium(VI) species in 0.1—1.5M sodium hydroxide being present as the ion $NpO_2(OH)_4^{2-}$; oxidation to Np^{VII} is considered to involve the loss of two hydroxide groups. Neptunium(VI) is also formed in the reaction of Np^V with nitrate ion in aqueous nitric acid:[266]

$$NpO_2^+ + \tfrac{1}{2}NO_3^- + \tfrac{3}{2}H^+ \rightleftharpoons NpO_2^{2+} + \tfrac{1}{2}HNO_2 + \tfrac{1}{2}H_2O$$

the nitrous acid produced being removed in the two-phase system used. The oxidation of uranium(III) in deoxygenated acid (0.05M-H_2SO_4) media has been described,[267] the rate being first order with respect to metal ion, with the formation of an equivalent amount of hydrogen. The mechanism is considered to involve the reaction

$$U^{III} + H_3O^+ \longrightarrow U^{IV} + H^\bullet + H_2O$$

there being no evidence for any interaction of the hydrogen atoms with the uranium(IV). The corresponding reaction with protoactinium(IV) has been investigated [268] in the acid range $0.1 < [H^+] < 0.8$M in nitric, hydrochloric,

[262] J. E. Earley and T. Fealey, *Chem. Comm.*, 1971, 331.
[263] D. Rose and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1791.
[264] C. M. Elson, J. Gulens, I. J. Itzkovitch, and J. A. Page, *Chem. Comm.*, 1970, 875.
[265] V. P. Shilov, N. N. Krot, and A. D. Gel'man, *Radiokhimiya*, 1970, **12**, 697.
[266] D. Gourisse, *J. Inorg. Nuclear Chem.*, 1971, **33**, 831.
[267] C. Avrain and M. Duflo-Plissonnier, *Rev. Chim. minérale*, 1970, **7**, 701 (*Chem. Abs.*, 1971, **74**, 46 066).
[268] M. Manier and M. Genet, *Rev. Chim. minérale*, 1970, **7**, 1087 (*Chem. Abs.*, 1971, **74**, 80 241v).

and perchloric acids. In this case, however, no effect of dissolved oxygen is observed and the rates are independent of ionic strength. The reaction rate decreases when the dielectric constant is lowered in ethanol and methanol solutions, and there is evidence for metal-ion-complex formation at high acid concentrations.

The reduction of molybdovanadic acid by hydrazine and ascorbic acid has been reported,[269] two electrons participating in the reduction of each mole of the polynuclear complex with the formation of the molybdenum 'blue'. In the reduced species, two of the molybdenum atoms have a quinquevalent oxidation state, the central vanadium(v) ion remaining unchanged. Using these reducing agents, however, the formation of the colour is limited to a fairly narrow acidity range (0.004—0.01M-H_2SO_4 for ascorbic acid).

The mechanism of per-rhenate reduction at a dropping-mercury electrode in a sodium sulphite solution has been described,[270] the multi-step process resulting in the formation of the rhenide ion, which is considered to react rapidly with the sulphite present to yield an intermediate Re^{I} species, which reacts further in the electrochemical process.

Table *Rate constants and thermodynamic parameters for metal-ion–ligand redox reactions. Second-order rate constants are in* l mol^{-1} s^{-1}. *The units of* $\Delta H^{\ddagger}$ *are* kcal mol^{-1} *and of* $\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}

Reaction	*k* (25 °C)	*I* (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$Co^{III} + H_2O_2$	$\leqslant 2$	3.0	—	—	103
$CoOH^{2+} + H_2O_2$	23.0	3.0	23.5	25	103[a]
$Co^{III} + HNO_2$	18	3.0	18.3	9	103
$CoOH^{2+} + HNO_2$	17.2	3.0	21.7	19	103[a]
$Co^{III} + Br^-$	$\leqslant 5$	3.0	—	—	103
$CoOH^{2+} + Br^-$	30.4	3.0	26.1	37	103[a]
$Co^{III} + SCN^-$	86.5	3.0	20.6	20	103
$CoOH^{2+} + SCN^-$	79.6	3.0	25.6	37	103[a]
Co^{III} + hydroquinone	2.2×10^3	3.0	18.2	18	103
$CoOH^{2+}$ + hydroquinone	1.28×10^3	3.0	18.6	17	103[a]
$Co^{III} + I^-$	8×10^3	3.0	19.4	25	103
$CoOH^{2+} + I^-$	2.86×10^3	3.0	21.5	30	103[a]
$Co^{III} + H_2C_2O_4$	~ 2	3.0	—	—	108
$CoOH^{2+} + H_2C_2O_4$	10.6	3.0	24.0	28	108[a]
$CoOH^{2+} + HC_2O_4^-$	81.5	3.0	25.9	39	108[a]
$CoOH^{2+} + NH_3OH^+$	3.2	2.1	22.5	20	[b, c]
$CoOH^{2+} + NH_2NH_3^+$	1.06	2.1	23.8	22	[b, c]
Tl^{3+} + 1,2-cd	0.12×10^2	0.50	—	—	179[d]
$TlOH^{2+}$ + 1,2-cd	0.93×10^2	0.50	—	—	179[d]
$TlOAc^{2+}$ + 1,2-cd	3.3×10^2	0.50	—	—	179[d]
$Tl(OAc)_2^+$ + 1,2-cd	0.67×10^2	0.50	—	—	179[d]
$Tl(OAc)_3$ + 1,2-cd	0.18×10^2	0.50	—	—	179[d]
$Tl(OAc)_2(OH)$ + 1,2-cd	1.67×10^2	0.50	—	—	179[d]
$TlBr^{2+}$ + 1,2-cd	1.6×10^{-2}	1.00	5	− 30	179[d]

[269] E. F. Tkach and N. A. Polotebnova, *Zhur. neorg. Khim.*, 1971, **16**, 210.

[270] K. S. Pakhomova and L. P. Volkova, *Zhur. analit. Khim.*, 1970, **25**, 2382 (*Chem. Abs.*, 1971, **74**, 682 218*k*).

Reaction	k (25 °C)	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
$Ag^{III} + H_3PO_3$	1.6	4.2	4	− 43	188[e]
$Cu^{II} + HO^{\bullet}$	3.1×10^8	—	—	—	194
$Cu^{III} + Cu^{I}$	3.6×10^9	—	—	—	194
$Cu^{III} + Cu^{III}$	2.3×10^7	—	—	—	194
$Fe(CN)_6^{3-} + S_2O_8^{2-}$	5.1×10^{-5}	→ 0	15.1	− 27.5	208
$LiFe(CN)_6^{3-} + S_2O_8^{2-}$	2.3×10^{-4}	→ 0	13.9	− 28.5	208
$NaFe(CN)_6^{3-} + S_2O_8^{2-}$	5.6×10^{-4}	→ 0	13.7	− 25.0	208
$RbFe(CN)_6^{3-}$ + $RbS_2O_8^{-}$	3.7×10^{-2}	→ 0	9.4	− 32	208
$CsFe(CN)_6^{3-}$ + $CsS_2O_8^{-}$	3.7×10^{-2}	→ 0	10.4	− 28.5	208
$HOCl + Fe(phen)_3^{2+}$	2.2×10^{-2}	1.0	16.2	− 11.6	218
$OCl^- + Fe(phen)_3^{2+}$	2.0×10^{-3}	1.0	25.3	14.1	218
$BrO^- + IO_3^-$	1.78×10^{-4}	1.11	25.2	4	223[f]
$HOBr + NO_2^-$	1.29	~ 1.0	2.5	− 49	223[g]
$HOBr + HCO_2^-$	6.9	~ 1.0	6.7	− 34	223[h]
$BrO_3^- + V^{IV}$	4.93	2.0	15.4	− 3.6	226
$e_{aq}^- + Ru(NH_3)_5N_2^{2+}$	4.2×10^9	—	—	—	238
$e_{aq}^- + Co(CN)_5^{2-}$	1.2×10^{10}	0.10	—	—	240[i]

[a] Units refer to product $k_2 K_h$ and are uncorrected for the enthalpy and entropy of dissociation of the Co_{aq}^{3+} ion. [b] Nitrate media. [c] K. Jijie and M. Santappa, *Proc. Indian Acad. Sci., Sect. A*, 1969, **69**, 117. [d] 1,2-cd = cyclohexane-1,2-dione. [e] H^+ = 3.1M. [f] T = 50 °C. [g] T = 48 °C. [h] T = 49.7 °C. [i] 0.1M-NaOH.

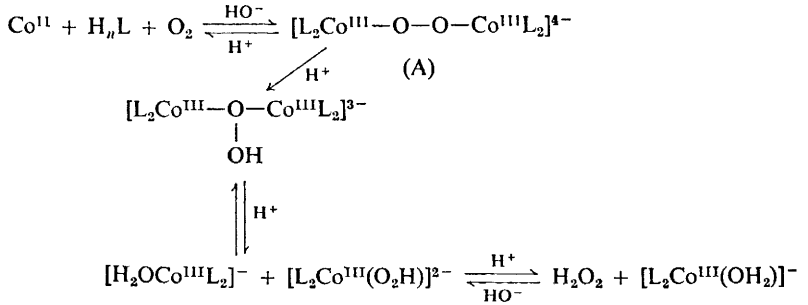
3

Reactions involving Oxygen and Hydrogen Peroxide

BY A. McAULEY

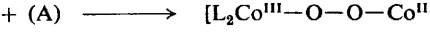
1 Cobalt(II) Complexes

The oxygenation of cobalt(II)–tripeptide complexes has been investigated,[271] the binding sites of glycyl-glycyl-glycine (triglycine) with the divalent metal ion in neutral and alkaline media being shown to involve nitrogen- (*via* the amino-group) and (probably) oxygen- (*via* the adjacent amide linkage) co-ordination. Oxygen uptake yields dimeric cobalt(III) species, and the reaction involves two oxygen-carrying intermediates with one reversible and one irreversible reaction stage. The second species contains a hydroperoxo-bridge, from which hydrogen peroxide may be liberated by titration with acid. A reaction scheme consistent with the data may be written as in Scheme 1 (L = tripeptide anion). Complex (A) is considered to be the



Scheme 1

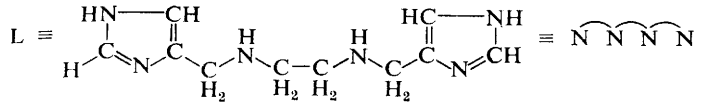
reversible oxygen carrier. This species may also undergo one-electron oxidation by metal ions, *e.g.* with cerium(IV); the corresponding superoxo-bridged complex is formed:



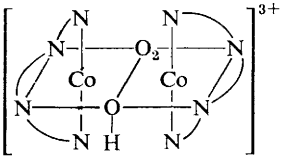
The uptake of oxygen in aqueous solutions of *NN'*-bis-[4-(5-imidazolyl)-methyl]ethylenediaminecobalt(II) is considered to result in the formation of the μ-dioxygen-μ-hydroxo-bis-*NN'*-[4-(5-imidazolyl)methyl]ethylene-diaminedicobalt(II) ion,[272] the complex ion being exceptionally stable in

[271] R. D. Gillard and D. A. Phipps, *J. Chem. Soc.* (*A*), 1971, 1074.
[272] A. Zuberbühler, Th. Kaden, and F. Koechlin, *Helv. Chim. Acta*, 1971, **54**, 1502.

basic media with respect to irreversible auto-oxidation to the dinuclear cobalt(III) complex. Representing the ligand (L)



in the manner shown, the structure of the product ion is



The mechanism is considered to involve the reaction of hydroxylated and non-dissociated intermediates (Scheme 2), the observed rate law for formation of the adduct being

$$CoL^{2+} \rightleftharpoons CoL(OH)^{+} + H^{+}$$
$$CoL(OH)^{+} + O_2 \rightleftharpoons Co^{II}L(OH)O_2^{+}$$
$$Co^{II}L(OH)O_2^{+} + CoL^{2+} \longrightarrow CoL_2O_2(OH)^{3+}$$
$$CoL^{2+} + O_2 \rightleftharpoons CoLO_2^{2+}$$
$$CoLO_2^{2+} + CoL^{2+} \rightleftharpoons CoL_2O_2(OH)^{3+} + H^{+}$$

Scheme 2

$$\text{Rate} = [CoL^{2+}]^2[O_2]\{k_\alpha + k_\beta[OH^-]\}$$

Dissociation of the complex is preceded by protonation, the rate being independent of acid concentration in the pH range 1—2.

The kinetics of formation of cobalt(III) products from cobalt L-histidine and L-lysine oxygen carriers have been described.[273] Basic solutions of the cobalt(II) complexes in the presence of excess ligand absorbed molecular oxygen, not all of which could be recovered. Some decomposition to dimeric cobalt(III) complexes occurred, and on acidification the presence of hydrogen peroxide was observed. The only product in the slow, quantitative oxidation of $CoCl_2(PEt_3)_2$ in organic solvents[274] is the corresponding phosphine oxide complex:

$$CoCl_2(PEt_3)_2 + O_2 \longrightarrow CoCl_2(OPEt_3)_2$$

The initial stages of the reaction conform to a reaction order of unity both in oxygen and in complex, and although there is no physical evidence for intermediate oxygen-adduct formation the proposed mechanism may be described as

$$CoCl_2(PEt_3)_2 + O_2 \rightleftharpoons O_2CoCl_2(PEt_3)_2$$
$$O_2CoCl_2(PEt_3)_2 \longrightarrow CoCl_2(OPEt_3)_2$$

[273] C. S. Sokol, H. Lausseger, L. J. Zompa, and C. H. Brubaker, jun., *J. Inorg. Nuclear Chem.*, 1971, **33**, 3581.

[274] D. D. Schmidt and J. T. Yoke, *J. Amer. Chem. Soc.*, 1971, **93**, 637.

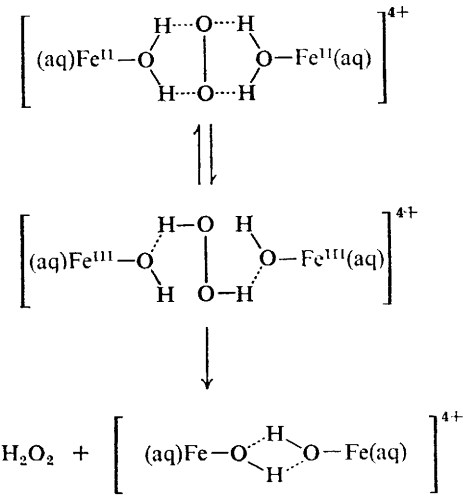
with rearrangement of the oxygenated complex. An alternative pathway, however, might involve the formation of an oxygen-bridged dinuclear complex.

2 Iron(II)–Iron(III) Complexes

A kinetic study has been made of the oxidation in aqueous media of iron(II) sulphate.[275] No reaction is observed at solute concentrations below 0.09M, and in the range 0.1—0.5M increasing temperature markedly increases the reaction rate. Over the range 20—80 °C, the hydroxide FeO(OH) and soluble hydroxoaquo-iron(III) complexes are found as reaction products. The mechanism proposed is of the form

$$A + O_2 \rightleftharpoons B$$
$$B + A \rightleftharpoons C \longrightarrow H_2O_2 + D$$

the overall last step in the reaction being represented as the multistep intramolecular redox reaction of the dimeric complex (Scheme 3). The



Scheme 3

oxidation may thus be viewed as the transfer of a hydrogen atom from the hydrated ferrous species to the oxygen molecule. The reaction has also been investigated in the presence of mineral and mono- and di-carboxylic acids.[276] Inhibition of the reaction was observed with HCl, HNO_3, H_2SO_4, and HCO_2H, but acids which readily form complexes with the metal ion markedly increased the rate. The mechanism proposed is similar to that suggested above with complexed iron(II) species involved, the high activity

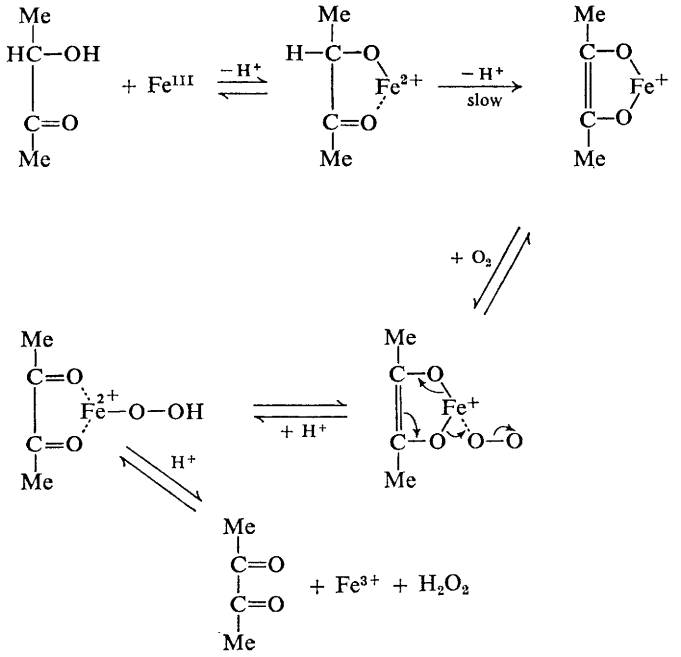
[275] A. N. Astanina and A. P. Rudenko, *Zhur. fiz. Khim.*, 1971, **45**, 345.
[276] A. N. Astanina and A. P. Rudenko, *Zhur. fiz. Khim.*, 1971, **45**, 352.

for oxalic and phosphoric acids being ascribed to the formation of stable iron(III) complexes which may assist in the breakdown of the intermediate species.

The iron(III)-catalysed oxidation of acetoin by molecular oxygen has been described,[277] the product being butane-2,3-dione. The rate law may be expressed as

$$-\,d[O_2]/dt = k_1[Fe^{III}][ac]/[H^+]$$

where ac = acetoin (3-hydroxybutan-2-one), although the rate of oxygen uptake is inhibited by the presence of the anions SO_4^{2-}, Cl^-, PO_4^{3-}, and acetate, which complex strongly with the iron(III). The mechanism involves the formation of an iron(III) complex which in the rate-determining step undergoes loss of a proton to yield an ene-diol complex (Scheme 4). The



Scheme 4

oxidation state of the iron in the reaction is not yet completely determined, but neither the reduced metal ion nor organic free-radicals are postulated as reactive intermediates. The role of the metal ion is seen to be one of catalysing the conversion of the substrate to the ene-diol, and by complexing both oxidant and reductant it provides a mechanism for electron transfer and allows the oxygen to interact *via* an ionic mechanism.

[277] P. K. Adolf and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1971, **93**, 3420.

3 Other Transition-metal Ion Complexes

The copper-ion-catalysed oxidation of thiomalic acid (tma) to the corresponding disulphide is considered to occur *via* the formation of a copper(II)–tma complex.[278] In 0.1M sodium hydroxide, in the presence of excess ligand, the complex $Cu(tma)_2$ has been characterized (λ_{max} = 340 nm), and in an oxygen-saturated solution the peak at 340 nm remains unchanged until all the thiol has been consumed, and then rapidly falls off to a minimum value. In oxygen-free conditions, the optical density at this wavelength decreases more slowly in a first-order reaction, the effect being due to reduction of the metal ion, confirmation of the change in oxidation state being given by decreases in the e.s.r. signal which parallel the reaction course. On mixing the solution of reduced complex ion with an oxygenated solution, immediate re-oxidation of the copper occurs. During the course of the reaction hydrogen peroxide is produced, which accumulates in the solution. When the thiol has been quantitatively oxidized, free copper(II) ions are released, which catalyse the immediate decomposition of the peroxide under these conditions. The tetrahedral copper(II)–copper(I) redox system [96] in dodecatungstocuprates has been described (Chapter 1), the copper(I) complex ion being shown to be stable with respect to disproportionation. In the presence of oxygen, however, rapid aerial oxidation takes place, with the quantitative regeneration of the copper(II) complex.

The reactions of nickel(II)–peptide complexes with oxygen have been discussed,[279] the tetra- and penta-peptides consuming oxygen in neutral solution to yield the amides of amino-acids and of peptides. With nickel(II)-tetraglycine at pH ~ 8, the consumption of oxygen occurs only after an induction period, during which a spectral change occurs with an increase in optical density at 350 nm. This absorbance, which is also observed in copper(II)– and cobalt(II)–O_2 reactions, diminishes with the formation of peroxide, and it may be that the transient intermediate initiates other reactions of O_2. The main reactant is considered to involve the doubly deprotonated ligand (L^{2-}) complexed to the metal ion, which forms small concentrations of an Ni^{II}–L^{2-}–O_2 complex. After a hydrogen-atom or electron transfer to the co-ordinated oxygen, a peptide radical is formed which is involved in an autocatalytic reaction. Evidence for a vanadium(III)–oxygen adduct has been described in the reaction of the *NN*-ethylenebis(salicylaldiminato)vanadium(III), V(salen)$^+$, complex in pyridine.[280] The product of the reaction corresponds to the vanadium(IV) complex VO(salen), four moles of reductant being consumed per mole of oxygen present. The observed rate law

$$-\frac{d[V(salen)^+]}{dt} = \frac{k_\alpha[V(salen)^+][O_2]}{1 + K[O_2]}$$

[278] C. De Marco, S. Dupre, C. Crifo, G. Rotilio, and D. Cavallini, *Arch. Biochem. Biophys.*, 1971, **144**, 496.
[279] E. B. Panagio, D. C. Weatherburn, and D. W. Margerum, *Chem. Comm.*, 1971, 1427.
[280] J. H. Swineheart, *Chem. Comm.*, 1971, 1443.

may be interpreted using the mechanism

$$V(salen)^+ + O_2 \underset{}{\overset{K}{\rightleftharpoons}} V(salen)O_2^+$$

$$V(salen)O_2^+ \xrightarrow{k} \text{products}$$

where $k_\alpha = kK$. Water has little effect on the reaction rate, and copper(II) ions show only a marginal catalytic action. In the reactions of the corresponding manganese(II) complexes,[281] three types of complexes have been identified in organic solvents. On reaction in an oxygen-saturated solution in DMSO, the oxidation

$$Mn^{II}(salen) + O_2 \rightleftharpoons \{Mn^{III}(salen)_2\}_2O_2$$

occurred the complex produced being formulated as the μ-peroxo-species. In pyridine or DMF, however, an insoluble complex $[Mn^{IV}(salen)O]_n$ was characterized, whereas in methanol the 3-methoxy-salen complex yielded the species $O{=}Mn^{IV}$(3-MeO-salen),$\frac{3}{2}$MeOH, which has a magnetic moment of 3.68 BM, characteristic of a high-spin state of manganese(IV). The reaction of tris(di-isopropylaminato)chromium(III) with oxygen has been shown to take place rapidly,[282] with formation of an oxygen adduct, although there is some evidence for chromium(IV) species being produced, depending on the oxygen concentration. The electrochemical preparation of the dinuclear rhodium complex ion $[(H_2O)(en)_2Rh{-}Rh(en)_2(H_2O)]^{4+}$ from *trans*-$[Rh(en)_2Cl_2]^+$ has been described.[283] On reaction with halide ions, replacement of the terminal water molecules is observed, with no evidence for dissociation of the ethylenediamine ligands. In the presence of oxygen, rapid (complete within several minutes) irreversible oxidation of the dihalide complexes occurs, the rates of oxidation following the order

iodo > bromo > chloro

the reaction of the diaquo-complex under the same conditions being fast, although in this case there would appear to be complicating side reactions. The rates of halogen interchange in *trans*-$[Rh(py)_4X_2]^+$, where X = Cl or Br, are found to be markedly inhibited by oxygen,[284] no corresponding effects being observed with the ethylenediamine analogues. The complex $Rh(OAc)PPh_3$ is formed on reaction of the dirhodium cation, $(Rh_2)^{4+}$, in methanol with triphenylphosphine in excess lithium acetate.[285] Further reaction with carbon monoxide yields the square-planar complex *trans*-$[Rh(OAc)(CO)(PPh_3)_2]$, which reacts with oxygen to give the rhodium(III) complex:

$$\textit{trans}\text{-}[Rh^{I}(OAc)(CO)(PPh_3)_2] \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} Rh^{III}(OAc)(CO)(O_2)(PPh_3)_2$$

[281] T. Yarino, T. Matsushita, I. Masuda, and K. Shinra, *Chem. Comm.*, 1970, 1317.
[282] J. C. W. Chieng, W. Kruse, D. C. Bradley, and C. W. Newing, *Chem. Comm.*, 1970, 1177.
[283] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1971, 736.
[284] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1971, 1841.
[285] R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3225.

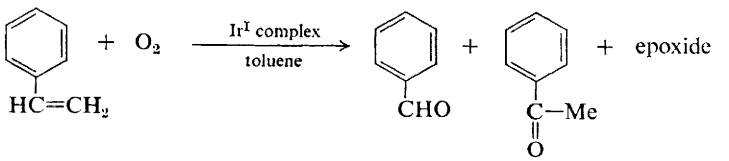
although the corresponding Rh^{I}–trifluoroacetato-complex is more reactive towards oxygen. Cationic complexes of rhodium(I), $Rh\{P(OR)_3\}_4^+$ (R = Me or Et) react in methanol in air [286] to yield stable oxygen-containing cations $Rh\{P(OR)_3\}_4O_2^+$. I.r. spectra have been used to elucidate the mechanism of oxygenated reactions catalysed by a rhodium(I) species which forms a 1 : 1 complex with molecular oxygen.[287] A solution of $[RhCl(cyclo\text{-}octene)_2]_2$ in dichloromethane containing lithium chloride rapidly interacts with oxygen at 35 °C, absorbing the oxidant to the extent of a 1 : 1 mole ratio. The reaction mechanism is consistent with hydrogen abstraction from the substrate by the co-ordinated oxygen, with oxidation of the cyclo-octene to cyclo-octenone. The data present the first evidence for hydroperoxide intermediates in such reactions of d^8 metal complexes. Redox reactions of some chromium- and molybdenum-dicarbonyl tertiary phosphine complexes have been described.[288] In acidic media, the reaction

$$cis\text{-}[Mo(CO)_2(diphos)_2] \underset{HO^-}{\overset{H^+}{\rightleftharpoons}} trans\text{-}[Mo(CO)_2(diphos)_2]^+$$

occurs in the presence of oxygen, the process being quantitative in both directions. The analogous chromium(I) cationic complex has been identified in perchlorate solutions. Reversible oxygenation of iridium(I) metal complexes has also been discussed:[289]

$$trans\text{-}[Ir(CO)Cl(R_3P)_2] \xrightarrow{O_2} [Ir(CO)Cl(O_2)(R_3P)_2]$$

(R_3P = a tertiary phosphine), with a linear free-energy relationship between the formation (and dissociation) rates of the metal–oxygen adducts and the stability constants of the dioxygenated complexes. The rate of oxygenation is, however, greatly influenced by steric effects of the group R. Complexes of this type (R = phenyl) have been used as catalysts in the oxidation of styrene,[290] the phosphine being oxidized to the corresponding phosphine oxide. The reaction may be described as

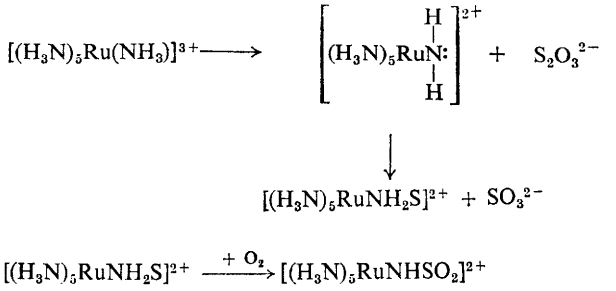


Ligand effects appear to be important, the yield of acetophenone increasing in the order $I^- < Br^- < Cl^-$, although the amounts of this product are much reduced if $SnCl_3$ or HgCl is bonded to the iridium. In the former case, a strong *trans* effect may promote formation of an iridium–styrene–oxygen intermediate. Ruthenium–oxygen complexes have also been shown to be

[286] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685.
[287] B. R. James and E. Ochiai, *Canad. J. Chem.*, 1971, **49**, 975.
[288] P. F. Crossing and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 610.
[289] L. Vaska and L. S. Chen, *Chem. Comm.*, 1971, 1080.
[290] K. Takao, Y. Fujiwara, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 1153.

catalytic in their oxidation of triphenylphosphine,[291] and dichlorotris(triphenylarsine)ruthenium(II) in benzene activates molecular oxygen [292] to yield a 1 : 1 oxygen adduct $RuCl_2(AsPh_3)_3O_2$, this being the first example of a paramagnetic d^6 metal ion. It is of interest that this species promotes the catalytic reduction (with molecular hydrogen) of maleic to succinic acid.

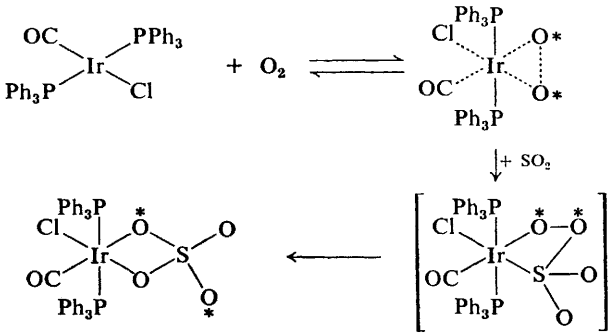
The conversion of hexa-ammineruthenium(III) to the sulphamatopenta-ammineruthenium(III) by attack on co-ordinated ammonia has been reported.[293] On passing oxygen through a solution of $Ru(NH_3)_6^{3+}$ in the presence of the sulphur-containing ions $S_2O_3^{2-}$ and SPO_3^{2-}, the complex species $Ru(NH_3)_5NHSO_3^+$ is produced. In the reaction of $Ru(NH_3)_6^{3+}$ with $S_2O_3^{2-}$ in anaerobic conditions, the product is $Ru(NH_3)_5S_2O_3^+$, whereas in glycine buffer at pH 10.2, in the presence of oxygen, yields of the sulphatamato-complex ion are in excess of 90%. The need for basic conditions is consistent with the postulate that prior dissociation of a proton from one of the ammonia molecules is required, with transfer of sulphur to the co-ordinated amide (Scheme 5), the sulphur now being oxidized by O_2. This



Scheme 5

latter process may be assisted by the metal centre. Although the thiophosphate ion gives as good yields, it is of interest to note that the reaction with SO_3^{2-} is much slower, possibly owing to the poor (SO_2) donor properties of this ion. The reaction of SO_2 and oxygen in the inner co-ordinated sphere of iridium and ruthenium complexes does result in the formation of chelated sulphate.[294, 295] The reaction mechanism may be shown to involve the formation of 1 : 1 oxygen adducts, which react with the SO_2, and using isotopic-labelling techniques the participation of a peroxysulphite intermediate is postulated, *e.g.* Scheme 6 (* indicates labelled oxygen atoms). It is of interest that treatment of the sulphur dioxide complex $Ir(CO)Cl(SO_2)(PPh_3)_2$ with oxygen leads to no detectable chemical change.

[291] B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, *Chem. Comm.*, 1970, 1272.
[292] M. M. Taqui-Khan, R. K. Andal, and P. T. Manoharan, *Chem. Comm.*, 1971, 561.
[293] J. N. Armor and H. Taube, *Inorg. Chem.*, 1971, **10**, 1570.
[294] J. Valentine, D. Valentine, and J. P. Collman, *Inorg. Chem.*, 1971, **10**, 219.
[295] R. W. Horn, E. Weiseberger, and J. P. Collman, *Inorg. Chem.*, 1970, **9**, 2367.



Scheme 6

The kinetics of the auto-oxidation of hydroxylamine in basic solutions in the presence of H_4edta have been reported.[296] The reaction rate increases with increasing hydroxide-ion concentration, gradually levelling off at high $[HO^-]$ values, the rate law

$$-\,d[NH_2OH]/dt = k[NH_2O^-][O_2]$$

confirming the suggested mechanism involving a deprotonated hydroxylamine species in the rate-determining step of the oxidation:

$$NH_2OH + HO^- \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} NH_2O^- + H_2O$$

$$NH_2O^- + O_2 \xrightarrow{\text{slow}} \text{products}$$

Electron transfer is considered to take place to the oxygen molecule to give the O_2^- radical with subsequent hydrogen-atom abstraction from the hydroxylamine yielding HO_2^- and HNO. The mechanism of auto-oxidation of triethylborane in the presence of iodine has been described.[297] Induction periods observed are dependent on the iodine : oxygen concentration ratios, and a chain-reaction mechanism is proposed involving both ethyl and ethylperoxy-radicals.

4 Reactions of Hydrogen Peroxide

The oxidation of alcohols in iron(II)–hydrogen peroxide systems has been re-examined, and the effects of copper(II) ions described.[298] A new kinetic analysis has been developed, and the nature of the interactions of the radicals produced on reaction of the peroxide with the metal ion indicates that, in the reaction with isopropyl alcohol, β-hydroxyalkyl radicals are not oxidized by iron(III) but dimerize, whereas in the presence of copper(II) they are oxidized to glycols. It is suggested that oxidation of radicals by iron(III) involves an electron-transfer process, which may in some cases be reversible,

[296] M. N. Hughes, H. G. Hicklin, and K. Shrimanker, *J. Chem. Soc.* (*A*), 1971, 3485.
[297] J. Grotewold, J. Hernandez, and E. A. Lissi, *J. Chem. Soc.* (*B*), 1971, 182.
[298] C. Walling and S. Kato, *J. Amer. Chem. Soc.*, 1971, **93**, 4375.

whereas with copper(II) either an organo-copper intermediate or ligand transfer is the preferred route. The reduction of iron(III) during catalytic decomposition of H_2O_2 has been investigated,[299] the extent of formation of Fe^{II} varying with the initial concentration of metal ion. In uranyl nitrate solutions, however,[300] the catalytic behaviour of iron(III) and copper(I) is considered, the activation energy for the process being independent of catalyst concentration. The mechanism may be represented as involving the formation of a peroxo-uranyl complex [present in high equilibrium concentration in excess uranium(VI)], which dissociates under the acidic conditions:

$$UO_4(aq) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2$$

$$H_2O_2 \xrightarrow[Cu^{II}]{Fe^{III}} H_2O + \tfrac{1}{2}O_2$$

The catalytic decomposition of cobaloximes in the hydrogen peroxide decomposition has been described.[301] For a series of complexes of the type $CoX(dmgH)_2(base)$, where $dmgH^-$ represents the dimethylglyoximinato-anion and X = Cl, CN, OH, or Me, with bases such as pyridine, imidazole, and water, the effect of changing the axial bases is considered to be small. The activity for the cyano-cobaloxime complex is markedly less than those for the other species. In the case of the chloroaquo-complex, the rate law is of the type

$$-\,d[H_2O_2]/dt = k_1[\text{cobaloxime}][H_2O_2)/[H^+]$$

As the reaction proceeds, a gradual degradation of the cobalt complex is observed. The mechanism is considered to involve the HO_2^- ion as a reacting species which may co-ordinate with the cobalt centre to form a hydroperoxo-cobaloxime. Nickel(II) complexes with 2-aminoethanol (L) also take part in reactions of this type.[302] The rate law for the reaction is complex, showing a marked dependence on H_2O_2 concentration. The data are, however, consistent with intermediate complex formation to yield the species $NiL_3^{2+}\cdot(HO_2^-)\cdot(H_2O_2)$; the most active isomer is a form in which the two ligands HO_2^- and H_2O_2 are situated in positions *trans* to each other. In the corresponding reaction involving triethanolamine complexes,[303] the reaction may involve polynuclear complexes. At low $[H_2O_2]$ a dependence on $[H_2O_2]^2$ is observed, but at higher substrate concentrations the increase in rate becomes linear in $[H_2O_2]$. Intermediates have been described in the reaction of H_2O_2 with horse-radish peroxidase.[304] Copper chelates with bidentate and quadridentate amines show catalytic activity in phosphate buffers,[305] the rates of oxygen evolution being first order with respect to the copper(II) complexes and HO_2^-. The four-co-ordinated complex with

[299] A. P. Rudenko and I. V. Tsibanova, *Zhur. fiz. Khim.*, 1971, **45**, 387.
[300] U. Rosick, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1443.
[301] Y. Hohokabe and N. Yamazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 738.
[302] L. N. Arzamasnova and A. P. Purmal, *Zhur. fiz. Khim.*, 1971, **45**, 186.
[303] L. N. Arzamasnova and A. P. Purmal, *Zhur. fiz. Khim.*, 1970, **44**, 2948.
[304] S. Bagger and R. J. P. Williams, *Acta Chem. Scand.*, 1971, **25**, 976.
[305] V. S. Sharma and J. Schubert, *Inorg. Chem.*, 1971, **10**, 251.

triethylenetetramine shows little action, the five-membered chelated rings of Cu(II)–en complexes being more active, although the formation of six-membered rings with 1,3-diaminopropane results in the greater reactivity. A possible mechanism may be written as

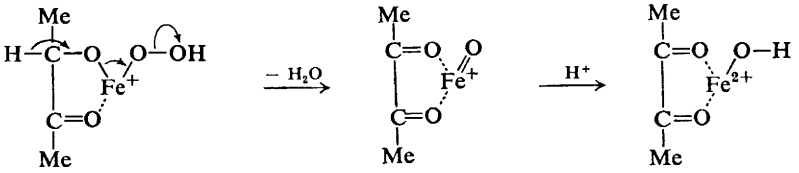
$$2H_2O_2 \rightleftharpoons 2HOO^- + 2H^+$$
$$Cu^{II}L^{2+} + HOO^- \xrightarrow{\text{slow}} L\cdot CuOOH^+$$
$$L\cdot Cu(OOH)^+ + HOO^- \longrightarrow L\cdot Cu^{II}(OH)_2 + O_2$$
$$L\cdot Cu(OH)_2 + 2H^+ \longrightarrow Cu^{II}L^{2+} + 2H_2O_2$$

with the possible involvement of the copper(I) oxidation state in the intermediate complex formed. The reduction of a copper(II) ion co-ordinated to two nitrogens appears to be kinetically faster than that of the aquo-ion, and for the reaction to proceed it is suggested that the redox potential of the copper complex must be such that electron transfer from the hydroperoxide anion to the central metal will be facilitated, and that there must be two adjacent free sites in the complex to enable interaction between the intermediate species formed and the second hydroperoxide ion, the inactivity of the triethylenetetramine complex probably resulting from this second requirement. These findings are also supported by a study involving copper(II)–bipyridyl complexes,[306] where at ratios $[\text{bipyridyl}]_0 : [Cu^{II}]_0 > 3$ no reactivity is observed. It is considered that at ratios lower than this intermediate peroxo-complexes are formed, although the peroxo-dimer $[Cu(\text{bipy})\cdot HO_2]_2^{2+}$ which has been characterized spectrophotometrically is not an active intermediate.

In the iron(III)-catalysed oxidation of acetoin by hydrogen peroxide,[277] the rate law

$$-d[H_2O_2]_0/dt = k[H_2O_2][Fe^{III}][ac]/[H^+]$$

is observed, and a mechanism may be postulated in which no iron(II) is observed as an intermediate, strongly indicating that it proceeds not by a free-radical mechanism but *via* complex formation (Scheme 7), followed by



Scheme 7

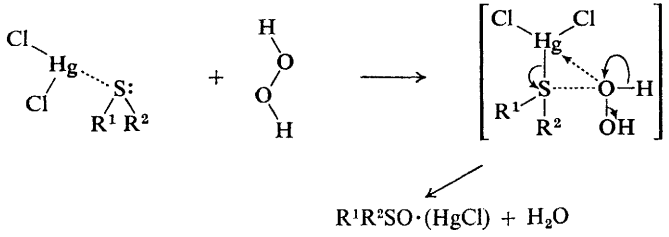
release of a water molecule and the formation of a doubly bonded Fe=O system. Reaction with two protons would then regenerate the aquo-iron(III) species and yield the observed product.

[306] T. P. Borob'eva, V. M. Berdnikov, A. P. Purmal, and Y. I. Skurlatov, *Zhur. fiz. Khim.*, 1971, **45**, 183.

A ternary vanadium(v)–edta–hydrogen peroxide complex of the type $[V(edta)(H_2O_2)]^{3-}$ has been characterized [307] in solutions of pH 1.0—3.4 with little evidence for the occurrence of an intramolecular redox reaction. The reaction with neptunium(v) has been shown to result in an equilibrium between Np^{IV} and Np^{VI}.[308] H_2O_2 slowly reduces Np^{V} to Np^{IV} in strongly acidic (6—8M HNO_3) media, but some oxidation to Np^{VI} is also considered to take place. Studies of the oxidation of tin(II) have also been reported,[309] and the rate constant for the formation of the CrO_5 species from $HCrO_4$ and H_2O_2 has been used in a calibrating reaction for high resolution fast-reaction devices.[310] The nature of the induction period in the oxidation of iodide in the presence of ruthenium(IV) has been described.[311] The oxidations of addition compounds between organic sulphides and mercury(II) chloride have been described.[312] Adducts of the form $R^1R^2S\cdot(HgCl_2)_n$ where $n = 1$ or 2 may be oxidized by H_2O_2 to give sulphoxide-containing species:

$$R^1R^2S\cdot(HgCl_2)_n + H_2O_2 \longrightarrow R^1R^2SO(HgCl_2)_m + H_2O + (n - m)HgCl_2$$

The oxidations, which are acid catalysed, are considered to involve a nucleophilic attack on the oxidizing agent by either the free sulphide or the adduct, and may be represented as ($n = 1$)



$$R^1R^2SO\cdot(HgCl) + H_2O$$

the existence of a bond between the sulphoxidic group and the metal atom *via* the incorporated oxygen being demostrated using spectroscopic techniques.

[307] A. T. Pilipenko and N. V. Loriya, *Zhur. neorg. Khim.*, 1971, **16**, 1031.
[308] N. N. Krot and L. G. Shuisakaya, *Radiokhimiya*, 1971, **13**, 79 (*Chem. Abs.*, 1971, **74**, 116 450d).
[309] J. H. Niewahner, *Diss. Abs.*, 1971, **31**, 4562 (*Chem. Abs.*, 1971, **75**, 40 891).
[310] J. I. Morrow, *Chem. Instrumentation*, 1970, **2**, 375.
[311] I. I. Alekseeva, A. P. Ryser, N. K. Ignatova, and A. I. Yakshiniskii, *Zhur. neorg. Khim.*, 1971, **16**, 1654.
[312] P. Biscarini, L. Fusina, and G. D. Nivellini, *J. Chem. Soc.* (*A*), 1971, 1128.

Part II

SUBSTITUTION AND RELATED REACTIONS

By
J. BURGESS
D. N. HAGUE

1
Non-metallic Elements

BY J. BURGESS

In this chapter substitution, dissociation, and association reactions of compounds of the non-metals will be covered. Such intramolecular processes – inversion, restricted rotation about bonds – as are of inorganic rather than primarily of organic interest will also be mentioned. Simple compounds and organometallic derivatives of the Group III and Group IV metals are also included here rather than in Chapters 2—4 since their chemistry is so closely related to the non-metallic members of these Groups. Elements are arranged in Periodic Table order.

1 Group III

Boron.—Reactions of boron trichloride with aromatic amines may proceed by formation of the Cl_3B,NH_2R adduct and then by hydrogen chloride elimination to give $Cl_2B{=}NHR$ *en route* to the ultimate product $(ClB{-}NR)_3$. The mechanism of these reactions has been probed by isolation and characterization of intermediates, and stoicheiometric and kinetic studies – the kinetics can be followed by monitoring the evolution of hydrogen chloride.[1] Photochemical reaction of triethylboron with iodine in cyclohexane takes place by a free-radical mechanism, indicated by the determined rate law.[2]

A qualitative ^{11}B n.m.r. study of the solvolysis of 1-bromopentaborane (1-BrB_5H_8) in dimethyl ether, diethyl ether, di-isopropyl ether, and 2,6-lutidine shows that isomerization of 1-BrB_5H_8 to 2-BrB_5H_8 is an important feature of the mechanism, with both isomers undergoing solvolysis.[3] μ-Dimethylborylpentaborane(9), which can be prepared from lithium octahydropentaborate (LiB_5H_8) and dimethylboron chloride, is thought to be a stable intermediate in the conversion of tetragonal-pyramidal B_5 into pentagonal-pyramidal B_6 *via* boron insertion.[4] Kinetics of thermal decomposition of perborate, including the effects of added copper(II), added polyphosphate, and temperature variation, have been studied.[5] The

[1] J. R. Blackborow, J. E. Blackmore, and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1971, 49.
[2] E. A. Lissi and E. Sanhueza, *J. Organometallic Chem.*, 1971, **26**, C59.
[3] C. B. Murphy and R. E. Enrione, *J. Inorg. Nuclear Chem.*, 1971, **33**, 584.
[4] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 1970, **92**, 4571.
[5] L. M. M. Tijskens and F. M. Schimmel, *Melliand Textilber.*, 1970, **51**, 309 (*Chem. Abs.*, 1970, **73**, 18 959m).

rate-determining step in reduction of perrhenate by tetrahydroboronate is hydrolysis of $[BH_4]^-$ to $[BH(OH)_3]^-$, which is the active reductant.[6]

The effects of structural modifications on the mechanism of substitution at tetrahedral boron have been probed by a series of kinetic investigations in which the determination of rate laws and activation parameters, of deuterium isotope effects, and of Hammett correlations, have featured. The reactions were of *N*-alkyl and of *B*-alkyl and *B*-aryl derivatives of H_3B,NH_3 with tri-n-butyl phosphine or with 2,2′-diphenylethylamine. The results can all be accommodated by the two-term rate law:

$$-\text{d[B,N adduct]}/dt = (k_1 + k_2[\text{Y}])\,[\text{B,N adduct}] \qquad (1)$$

where Y = incoming phosphine or amine. For the reaction of H_3B,NMe_3 or H_3B,NEt_3 with tri-n-butylphosphine, k_1 approximates to zero,[7] but for the majority of *B*-alkyl and *B*-aryl derivatives of H_3B,NMe_3 the k_1 and k_2 terms are of comparable importance,[8] whereas for reaction of the $(p\text{-X}\cdot C_6H_4)_2BH,NH_2Me$ series with 2,2′-diphenylethylamine, first-order kinetics, *i.e.* $k_1 \gg k_2[\text{Y}]$, are observed.[9] Activation parameters for a selection of these reactions are collected in Table 1. A much more qualitative account of substitution at tetrahedral boron concerns mono- and di-iodoborane adducts of trimethylamine reacting with polyamines.[10]

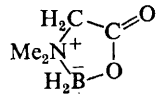
Table 1 *Activation parameters corresponding to the first-order* (k_1) *and second-order* (k_2) *terms* [*of equation* (1) *in text*] *for reaction of* N- *and* B-*substituted derivatives of* H_3B,NH_3 *with tri-n-butylphosphine* (P *in Table*) *or* 2,2′-*diphenylethylamine* (N); $\Delta H^{\ddagger}$ *values in* kcal mol^{-1} *and* $\Delta S^{\ddagger}$ *values in* cal deg^{-1} mol^{-1}

			k_1 *term*		k_2 *term*		
Adduct	*Reagent*	*Solvent*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
H_3B,NMe_3	P	*o*-$C_6H_4Cl_2$	—	—	23	− 5	7
Bu^iH_2B,NMe_3	P	*o*-$C_6H_4Cl_2$	32	+ 18	22	− 9	8
Bu^sH_2B,NMe_3	P	*o*-$C_6H_4Cl_2$	31	+ 19	26	+ 5	8
Bu^tH_2B,NMe_3	P	*o*-$C_6H_4Cl_2$	32	+ 25	19	− 17	8
$(p\text{-Cl}\cdot C_6H_4)_2HB,NH_2Me$	N	*o*-$C_6H_4Cl_2$	34	+ 29	—	—	9
$(p\text{-Cl}\cdot C_6H_4)_2HB,NH_2Me$	N	diglyme	26	+ 11	—	—	9
$(p\text{-MeO}\cdot C_6H_4)_2HB,NH_2Me$	N	diglyme	37	+ 38	—	—	9
$(C_6H_5)_2HB,NH_2Me$	N	diglyme	28	+ 11	—	—	9

[6] V. S. Khain, N. N. Antsygina, V. N. Shchuka, and L. K. Grebenshchikova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1137.
[7] W. L. Budde and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1971, **93**, 3147.
[8] D. E. Walmsley, W. L. Budde, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1971, **93**, 3150.
[9] F. J. Lalor, T. Paxson, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1971, **93**, 3156.
[10] S. A. Genchur, G. L. Smith, and H. C. Kelly, *Canad. J. Chem.*, 1971, **49**, 3165.

The mechanism of hydrolysis of the borane cation (1), derived from *NN*-dimethylglycinate, has been probed by a determination of the dependence of rates, monitored by hydrogen evolution, and synthesis of intermediates. There is an induction period, followed by a first-order reaction. Initial loss of the ester ethyl group is followed by slow loss of NMe_3 to give the cyclic intermediate (2), which has been isolated.[11] Base hydrolysis

$[Me_3N,BH_2\cdot NMe_2\cdot CH_2\cdot CO_2Et]^+$ (1)



(2)

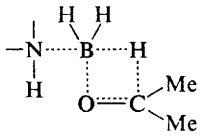
in aqueous solution of *O*-ethylboranocarbonate, $[H_3B\cdot CO_2Et]^-$, follows a first-order rate law, and thus resembles the base hydrolysis of monoethylcarbonate (S_N1 mechanism) rather than that of ethyl acetate (S_N2).[12]

A ^1H n.m.r. kinetic study of trimethylphosphine exchange at Me_3B,PMe_3 in toluene indicates a dissociative mechanism, as for Me_3N exchange at Me_3B,NMe_3. At the larger atoms aluminium, gallium, or indium, analogous Group V base-exchange reactions are more likely to have some associative character. The activation enthalpy for PMe_3 exchange at Me_3B,PMe_3 is 63 kJ mol^{-1} (15.1 kcal mol^{-1}) and the activation entropy is 36 J K^{-1} mol^{-1} (8.6 cal deg^{-1} mol^{-1}).[13] Exchange of PMe_3 at F_3B,PMe_3 is fast on the n.m.r. time scale.[14] Reactions of F_3B,NH_3 with phosphorus pentachloride, and several reactions of the product $[Cl_3P{=}N{=}PCl_3]^+[BCl_4]^-$, are described in the Group V section later in this chapter. The relative reactivity of adducts XCl_2B,NR^1R^2H, where R^1 is an aryl group, in boiling benzene has been determined qualitatively by monitoring the evolution of hydrogen chloride;[15] some related reactions are included in the general study of reactions of boron trichloride with aromatic amines mentioned earlier.[1] The rate law for reduction of ketones by the morpholine–borane adduct:

$$-\text{d[morpholine–borane]}/dt = (k_2 + k_3[H^+])\,[\text{morpholine–borane}]\,[\text{ketone}] \quad (2)$$

and activation parameters corresponding to the k_2 and k_3 terms indicate a *mechanism of two parallel* reactions; the transition state for the k_2 path is probably specifically orientated, as in (3), whereas the k_3 term arises from rate-determining attack of the adduct on the protonated carbonyl group of the ketone.[16]

[11] N. E. Miller, *J. Amer. Chem. Soc.*, 1970, **92**, 4564.
[12] B. D. Hoewe, L. J. Malone, and R. M. Manley, *Inorg. Chem.*, 1971, **10**, 930.
[13] K. J. Alford, E. O. Bishop, P. R. Carey, and J. D. Smith, *J. Chem. Soc.* (*A*), 1971, 2574.
[14] J. Grobe and U. Möller, *Z. Naturforsch.*, 1971, **26b**, 639.
[15] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1971, 1343.
[16] S. S. White and H. C. Kelly, *J. Amer. Chem. Soc.*, 1970, **92**, 4203.



(3)

Aluminium.—Recent kinetic results, from two proton n.m.r. studies,[17] on exchange reactions in the system trimethylaluminium plus trimethylgallium have been reinterpreted. Both sets of results can be accommodated by the following reaction scheme:

$$Al_2Me_6 \rightleftharpoons 2AlMe_3$$

$$AlMe_3 + GaMe_3 \rightleftharpoons Me_2Al(\mu\text{-}Me)_2GaMe_2$$

with both $AlMe_3$ and $AlGaMe_6$ present in small concentrations.[18] The determination [19] of the structure of $Me_3N,Al(BH_4)_3$ provides stereochemical information pertinent to the hydrogen-exchange processes observed in solutions of tetrahydroborates.[20]

Gallium, Indium, and Thallium.—A single relaxation time is observed in electric-field-jump relaxation studies of gallium(III) and of indium(III) perchlorate solutions. This relaxation can be assigned to one of two possible hydrolysis steps.[21] The present results complement recent *T*-jump studies [22] of dimerization of $[InOH]^{2+}$ and of $[GaOH]^{2+}$, the products of hydrolysis of indium(III) and of gallium(III) in perchlorate solution. Decomposition of alkylthallium(III) halides $RTlX_2$, in pyridine solution, to TlX plus RX occurs principally by attack of pyridine or of a halide at the alkyl group R. The key to the elucidation of this mechanism was the neo-pentyl compound, which reacts slowly and without rearrangement. These observations are not consistent with the possible alternative mechanism in which decomposition takes place by thallium—carbon bond homolysis with concerted reductive elimination of alkyl halide.[23]

2 Group IV

Carbon.—In the first volume of this Specialist Periodical Report we mentioned the novel suggestion that the two fundamental mechanisms of nucleophilic substitution, S_N1 and S_N2, might combine into one mechanism in which ion-pairing between the leaving group and the remaining organic

[17] K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 1966, **88**, 5460; E. A. Jeffery and T. Mole, *Austral. J. Chem.*, 1969, **22**, 1129.
[18] D. S. Matteson, *Inorg. Chem.*, 1971, **10**, 1555.
[19] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Inorg. Chem.*, 1968, **7**, 1575.
[20] N. A. Bailey, P. H. Bird, N. Davies, and M. G. H. Wallbridge, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3116.
[21] P. Hemmes, L. D. Rich, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, 1970, **74**, 2859.
[22] E. M. Eyring and J. D. Owen, *J. Phys. Chem.*, 1970, **74**, 1825; J. D. Owen and E. M. Eyring, *J. Inorg. Nuclear. Chem.*, 1970, **32**, 2217.
[23] M. D. Johnson, *Chem. Comm.*, 1970, 1037.

moiety formed the essential link. This hypothesis has since been subjected to close scrutiny in many laboratories.[24] Final conclusions do not seem to have been reached yet, but there are strong indications, for example from kinetic studies of reactions of halogenoacetic acids [25] and of benzyl and of diphenylmethyl chlorides,[26] that the unified S_N1–S_N2-ion-pairing hypothesis cannot be applied in general to all organic nucleophilic substitutions.

Carbon dioxide is often considered an inorganic compound, so it is relevant to mention that the kinetics of ^{18}O exchange between carbon dioxide and water have been investigated, under both homogeneous and heterogeneous conditions.[27] The rate law and appropriate rate constants have been determined for the reaction of carbon dioxide with aqueous alkali in the presence of $[As(OH)_2O]^-$ as catalyst.[28]

General.—A particularly extensive study has been made of the kinetics of reaction with iodine of compounds containing Group IV element to Group IV element bonds, $R^1_3M^1—M^2R^2_3$, where R^2 may or may not be the same as R^1, and likewise M^2 and M^1:

$$R^1_3M^1 \cdot M^2R^2_3 + I_2 \longrightarrow R^1_3M^1I + R^2_3M^2I$$

In all cases second-order kinetics, first-order in each reactant, were observed. Some of the kinetic results are reproduced in Tables 2 and 3. The range of rate constants is illustrated by the values in Table 2; reaction with bromine instead of iodine was too fast to follow. Table 3 contains all the activation parameters reported. The kinetic results have been discussed in terms of

Table 2 *Rate constants (k_2) for reaction of $R^1_3M^1—M^2R^2_3$ with iodine in chlorobenzene (from ref. 29)*

Compound	*Temperature*/°C	k_2/l mol^{-1} s^{-1}
$Me_3Si \cdot SiMe_3$	20	0.97×10^{-3}
$Et_3Si \cdot SiEt_3$	20	7.0×10^{-5}
$Pr^i_3Si \cdot SiPr^i_3$	40	$< 10^{-5}$
$Me_3Ge \cdot GeMe_3$	20	9.2×10^{-2}
$Et_3Ge \cdot GeEt_3$	20	6.35×10^{-2}
$R_3Sn \cdot SnR_3$ [a]	—	fast
$Ph_3Sn \cdot SnPh_3$	24	390
$Et_3Ge \cdot SnEt_3$	—	fast

[a] R = alkyl only.

[24] See, *inter alia*, J. M. W. Scott, *Canad. J. Chem.*, 1970, **48**, 3807; P. D. Gillespie and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 503; and refs. 25 and 26.
[25] J. L. Kurz and J. C. Harris, *J. Amer. Chem. Soc.*, 1970, **92**, 4117.
[26] B. J. Gregory, G. Kohnstam, A. Queen, and D. J. Reid, *Chem. Comm.*, 1971, 797.
[27] R. Gerster, *Internat. J. Appl. Radiation Isotopes*, 1971, **22**, 339 (*Chem. Abs.*, 1971, **75**, 53 812w).
[28] C. N. S. McLachlan, *New Zealand J. Sci.*, 1971, **14**, 634.

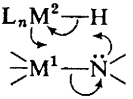
Table 3 *Activation parameters for reaction of* $R^1_3M^1—M^2R^2_3$ *with iodine (from ref. 29)*

Compound	*Solvent*	E_a/kcal mol^{-1}	$\text{Log}_{10} A$
$Me_3Si \cdot SiMe_3$	PhCl	14.2	7.5
$Et_3Si \cdot SiEt_3$	PhCl	15.1	7.2
$Me_3Ge \cdot GeMe_3$	PhCl	9.0	5.8
$Et_3Ge \cdot GeEt_3$	PhCl	9.7	6.0
$Me_3Sn \cdot SnMe_3$	acetone–I^-	14.0	7.8
$Me_3Sn \cdot SnEt_3$	acetone–I^-	13.7	7.6
$Et_3Sn \cdot SnEt_3$	acetone–I^-	12.4	6.9
$Ph_3Sn \cdot SnPh_3$	acetone–I^-	19.8	10.6
$Et_3Sn \cdot SiMe_3$	MeOH–I^-	13.9	8.5

steric and electronic effects of the alkyl groups R^1 and R^2, of the polarizability of M^1 and M^2, and of $M^1—M^2$ bond strengths. A positive salt effect on reaction rate in methanol suggests an open transition state, but a cyclic transition state seems more likely in chlorobenzene.[29] Thermodynamic and kinetic control of products when an unsymmetrical $R^1_3M^1—M^2R^2_3$ compound reacts with an unsymmetrical reagent such as iodine monochloride has been discussed in the light of known products in specific cases.[30] The mechanism of the reactions of alkylamino-compounds of the Group IV elements with transition metal hydrides,

$$R_3M^1 \cdot NMe_2 + L_nM^2H \longrightarrow R_3M^1 \cdot M^2L_n + NHMe_2$$

which is a useful synthetic method, has been discussed. There is insufficient evidence at present to state the relative timing of the bond-breaking and -making processes in



Indeed the precise mechanism probably depends on the natures of M^1 and M^2. An S_N2 mechanism is suggested for $M^1 = Sn^{IV}$, $M^2 = Pt^{II}$ and an S_N1cb mechanism for hydrides of the Group VI metals.[31]

Silicon.—Considerable efforts have been made over a period of many years to obtain evidence for the intermediacy of R_3Si^+ cations in mechanisms of nucleophilic substitution at silicon. The only report [32] claiming evidence for substitution involving transient R_3Si^+ has now been retracted,[33] since more sophisticated techniques applied to the reaction in question, which

[29] M. Gielen, J. Nasielski, and G. Vandendunghen, *Bull. Soc. chim. belges*, 1971, **80**, 165.
[30] C. F. Shaw and A. L. Allred, *Inorg. Chem.*, 1971, **10**, 1340.
[31] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1970, 2594.
[32] L. H. Sommer, F. O. Stark, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 5683.
[33] L. H. Sommer, G. D. Homer, A. W. Messing, J. L. Kutschinski, F. O. Stark, and K. W. Michael, *J. Amer. Chem. Soc.*, 1971, **93**, 2093.

was halide exchange at silicon, have failed to confirm the earlier results and interpretation. A recent study of racemization of naphthylphenylalkylchlorosilanes (alkyl = Me, Et, Pr^n, or Pr^i) and analogous germanium compounds has again failed to reveal any evidence for reaction *via* R_3Si^+ or R_3Ge^+; as usual, a transition state of increased co-ordination number is indicated.[34] Relevant to these kinetic studies is a description of the chemistry of silicon compounds in SbF_5–SO_2ClF. Whereas it is easy to generate R_3C^+ in this solvent mixture it proved impossible to generate any R_3Si^+ cations.[35] Some background evidence relating to the ease of associative substitution at silicon is provided by an o.r.d. study of cyclic α-silyl ketones, which has demonstrated co-ordination of solvent to the silicon in solutions of these compounds.[36] Solvent-induced racemization could occur through a five-co-ordinate intermediate which can undergo pseudorotation, or through a six-co-ordinate intermediate. For chlorosilanes the five-co-ordinate-plus-pseudorotation route is unattractive since it would be necessary to place the electronegative groups (chloride and solvent) in equatorial positions during the process. Thus a mechanism through a six-co-ordinate intermediate would seem preferable, and indeed there is kinetic evidence to support this route. In inert solvents, such as carbon tetrachloride or toluene, containing small and varied concentrations of racemization-promoting solvents such as dimethyl sulphoxide or dimethyl formamide, the rate law for racemization of, for instance, chloroethyl-1-naphthylphenylsilane, is first-order in silane but second-order in concentration of active solvent, which indicates a six-co-ordinate bis-solvent transition state or intermediate in the racemization mechanism.[37] An earlier study of the kinetics and mechanism of isomerization of $Me_3Si(acac)$ [38] has been extended to the series of alkyl derivatives $Me_2RSi(acac)$.[39] Here the transition state is thought to contain five-co-ordinate silicon; acac is bonded through one oxygen in the initial state, but chelates the silicon in the transition state. The activation energy for isomerization of the complex $Me_3Si(acac)$ in chlorobenzene solution is 13.8 kcal mol^{-1}.

The activation enthalpy for degradation of polysilicates varies with pH. It has a maximum value of 18.5 kcal mol^{-1} (at pH = 3.3) and a minimum value of 15.6 kcal mol^{-1} (at pH = 4.3) in the range $1.3 < pH < 5.5$. Polysilicate degradation is catalysed by nucleophiles, for example dimethylamine, thiosulphate, or hydroxide, and by hydrogen fluoride.[40] References to formation [41] and hydrolysis [42] of silico- and germano-molybdates are mentioned in slightly greater detail in the opening section on tetrahedral complexes in Part II, Chapter 2.

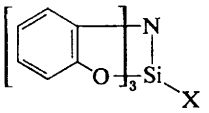
[34] F. Carre, R. J. P. Corriu, and M. Leard, *J. Organometallic Chem.*, 1970, **24**, 101.
[35] G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, 1971, **93**, 4942.
[36] R. J. P. Corriu and J. Masse, *Tetrahedron*, 1970, **26**, 5123.
[37] R. J. P. Corriu and M. Leard, *Chem. Comm.*, 1971, 1086.
[38] J. T. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.*, 1969, **91**, 5378.
[39] T. J. Pinnavaia, W. T. Collins, and J. T. Howe, *J. Amer. Chem. Soc.*, 1970, **92**, 4544.
[40] H. Stade and W. Wieker, *Z. anorg. Chem.*, 1971, **384**, 53.
[41] L. G. Hargis, *Analyt. Chem.*, 1970, **42**, 1494.
[42] M. Biquard and M. Lamache, *Bull. Soc. chim. France*, 1971, 32.

The kinetic inertness of the complexes $[Si(ox)_3]^{2-}$ and $[Ge(ox)_3]^{2-}$, in contrast to the lability of, for example, $[Ge(mal)_3]^{2-}$, has been demonstrated by the slowness of attainment of equilibrium in redistribution reactions of these complexes with $[SiF_6]^{2-}$ and $[GeF_6]^{2-}$. The complexes $[Ti(ox)_3]^{2-}$ and $[Sn(ox)_3]^{2-}$ are much more labile. $[Si(mal)F_4]^{2-}$ and several related complexes have ^{19}F n.m.r. spectra lacking in fine structure, which suggests fast exchange, thought to occur both by intermolecular malonate exchange and by intramolecular reorganization.[43]

Variable-temperature n.m.r. spectroscopic studies of exchange processes at $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ indicate activation energies of 11.3 and 11.1 kcal mol^{-1} for the silicon compound in xylene and in triethylamine respectively, and 12.1 kcal mol^{-1} for the germanium compound in toluene. From this and earlier work the order of reactivity with respect to exchange can be established:[44]

$$(Me_3Sn)_2Hg > (Me_3Ge)_2Hg > (Me_3Si)_2Hg > (MeCl_2Si)_2Hg$$

The nitrilotriphenoxysilanes (4) are five-co-ordinate at the silicon, and so may be regarded as models for transition states for S_N2 reactions of



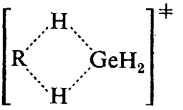
(4)

four-co-ordinate silicon compounds. The kinetics of reactions of these compounds in aqueous dioxan containing hydrochloric acid suggest that the mechanism depends on the nature of X. For X = Me, Ph, or *p*-tolyl, the rate-determining step is silicon—oxygen bond cleavage, but for X = Cl reaction proceeds *via* an $SiO_3N^+Cl^-$ ion-pair.[45]

Germanium.—Some germanium compounds and their reactions have already been alluded to in the preceding paragraphs on silicon. These include racemization of alkylaryl chlorogermanes,[34] exchange reactions of $(Me_3Ge)_2Hg$,[44] and redistribution reactions of $[Ge(ox)_3]^{2-}$ and $[GeF_6]^{2-}$.[43]

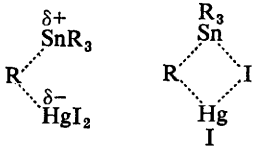
The $[GeH_3]^-$ anion reacts, in diglyme solution, with alkyl halides RX which readily undergo nucleophilic substitution to give organogermanes $RGeH_3$. But with halides RX which are reluctant to undergo nucleophilic substitution $[GeH_3]^-$ reacts, perhaps through the cyclic transition state (5), to give the alkane RH, polymeric $[GeH_2]_n$, and X^-.[46] Germanium—sulphur bonds, as in $Bu^n_3Ge{\cdot}S{\cdot}C_6H_4{\cdot}R$, where R = *p*-Me or *p*-Bu^t, are cleaved by electrophiles less readily than are tin—sulphur bonds in analogous compounds.[47]

[43] P. A. W. Dean and D. Evans, *J. Chem. Soc.* (*A*), 1970, 2569.
[44] T. F. Schaaf and J. P. Oliver, *J. Organometallic Chem.*, 1971, **32**, 307.
[45] R. E. Timms, *J. Chem. Soc.* (*A*), 1971, 1969.
[46] R. M. Dreyfus and W. L. Jolly, *Inorg. Chem.*, 1971, **10**, 2567.
[47] J. L. Wardell, R. D. Taylor, and T. J. Lillie, *J. Organometallic Chem.*, 1971, **33**, 25.



(5)

Tin.—There has been much further work on reactions of tetra-alkyltin compounds with mercury(II) salts, with particular reference to solvent effects on reactivity. Standard free energies of transfer of transition states for reactions of R_4Sn with mercury(II) chloride between methanol and methanol–water mixtures, estimated from standard free energies of transfer of the reactants and from determined reaction rates, show little variation with solvent composition. The marked decrease in rates going from methanol to methanol–water mixtures arises mainly from the large increase in initial-state free energies.[48] From estimates of electrostatic contributions to free energies of transfer of initial and transition states between various solvents for the reaction of R_4Sn with mercury(II) chloride, it can be suggested with some confidence that there is considerable separation of charge in the transition states for these reactions, which can better be explained in terms of an S_E2 (open) [transition state (6)] than an S_E2 (cyclic) [transition state (7)] mechanism.[49] An S_E2 (cyclic) mechanism is less unlikely in poor



(6) (7)

solvents such as acetonitrile or t-butyl alcohol than in good solvents such as methanol. However, an investigation of steric effects on the reaction of R_4Sn with mercury(II) chloride suggests an S_E2 (open) mechanism in the poor solvents as well as in methanol and methanol–water mixtures.[50] The particular case of the reaction of Et_4Sn with mercury(II) compounds has been investigated in some detail. In acetonitrile solvent, Et_4Sn reacts with mercury(II) chloride by an S_E2 (open) mechanism,[51] and in methanol–t-butanol mixtures Et_4Sn reacts with mercury(II) chloride or iodide again by an S_E2 (open) mechanism,[52] but with mercury(II) acetate, Et_4Sn may react by an S_E2 (cyclic) mechanism, at least in less polar methanol–t-butanol solvent mixtures.[52] Kinetic parameters for some of the above reactions are collected in Table 4.

[48] M. H. Abraham, *J. Chem. Soc.* (*A*), 1971, 1061.
[49] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1971, 1610.
[50] M. H. Abraham, F. Behbahany, and M. J. Hogarth, *J. Chem. Soc.* (*A*), 1971, 2566.
[51] M. H. Abraham and M. J. Hogarth, *J. Chem. Soc.* (*A*), 1971, 1474.
[52] M. H. Abraham and F. Behbahany, *J. Chem. Soc.* (*A*), 1971, 1469.

Table 4 *Activation parameters for reaction of tetra-alkyltin compounds with mercury*(II) *salts, at* 25 °C

Reactants	*Solvent*	$\Delta G^{\ddagger}$ kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}	*Ref.*
$Me_4Sn + HgCl_2$	MeCN	16.84	8.0	− 29.6	50
	MeOH	17.19	10.6	− 22.1	53
$Et_4Sn + HgCl_2$	MeCN	19.81	11.3	− 28.5	51
	MeOH	20.83	14.4	− 21.7	53
$Et_4Sn + HgI_2$	MeCN	19.46	10.2	− 31.0	51
	MeOH	21.00	13.0	− 26.7	51
$Bu^i_4Sn + HgCl_2$	MeCN	21.45	13.3	− 27.3	50
	MeOH	23.04	16.2	− 23.1	53

The kinetics and stereochemical course of reactions between tetra-alkyltin compounds and bromine indicate an S_E2 (open) mechanism, with a transition state (8), rather than an S_E2 (cyclic) mechanism.[54] Solvent

$$[R_3M\cdots\cdots R\cdots\cdots Br\cdots\cdots Br]^{\ddagger}$$

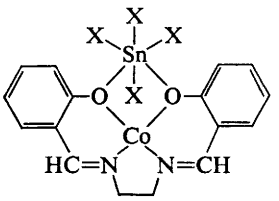
(8)

effects on rates of reaction between tetrabutyltin and iodine have been explained by formation of iodine–solvent complexes, whose presence reduces the concentration of free iodine available for reaction and hence the observed rate. Association constants for formation of these iodine–solvent complexes have been estimated from the kinetic measurements. Thus, for example, the association constant for iodine and benzene is estimated as 0.175 l mol^{-1}, that for iodine and toluene as 0.185, and that for iodine and benzonitrile at 0.75, at 20 °C, from the kinetic measurements. These values compare satisfactorily with literature values of 0.135—0.15, 0.16, and 0.80 respectively determined by other methods. One can thus have confidence in association constants determined by this kinetic method for association of iodine with solvents where non-kinetic values are unavailable – for example for association with nitrobenzene (0.41 l mol^{-1}) and 1,2-dichloroethane (0.08 l mol^{-1}).

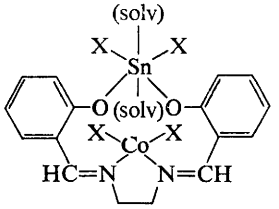
There is considerable disagreement between recent[56] and earlier[57] interpretations of kinetic measurements obtained for ethanolysis of tri-isopropyltin halides. The recent work suggests that tin—halide bond breaking is remarkably slow, even at relatively high temperatures. It is unfortunate that no product analysis is given for this recent work, for the reported rates are characteristic of tin—alkyl rather than of tin—halogen bond breaking. One cannot therefore be sure that the recently reported activation parameters, whose precision is in any case somewhat low since only three points are available to define each Arrhenius plot, do refer to tin—halide bond breaking.

[53] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 193.
[54] F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, 1971, **93**, 4048.
[55] G. Martino and J.-C. Jungers, *Bull. Soc. chim. France*, 1970, 3392.
[56] S. C. Chan and F. T. Wong, *Z. anorg. Chem.*, 1971, **384**, 89.
[57] R. H. Prince, *J. Chem. Soc.*, 1959, 1783.

A detailed n.m.r. study of six asymmetric tin compounds, *e.g.* methylphenylisobutyltin chloride, suggests a close relation between configurational inversion and halogen exchange.[58] Tin—carbon bond cleavage in bis(trimethylstannyl)diazomethane, $(Me_3Sn)_2CN_2$, proceeds by loss of nitrogen and consequent intermediacy of the carbene $(Me_3Sn)_2C$:.[59] Tin tetrahalides (SnX_4) react with the salen complex of cobalt(II) to produce [Sn(salen)X_2]. In polar solvents the solvent (solv) displaces two halide ligands from tin on to cobalt to convert the intermediate adduct (9) into (10).[60]



(9)



(10)

Rates of halide exchange with trimethyltin halides *decrease* as the temperature increases. This anomalous behaviour has been ascribed to the following pre-equilibrium association:

$$2R_3SnX \rightleftharpoons (R_3SnX)_2$$

with perhaps small amounts of trimers or higher aggregates being formed.[61]

All the tin(IV) compounds whose reactions have been discussed so far have been four-co-ordinate. One kinetic study of an octahedral six-co-ordinate complex of tin concerns solvolysis and chloride substitution at [Sn(isoquinoline)$_2Cl_4$] in nitrobenzene or nitromethane solution. Both reactions proceed by a dissociative mechanism.[62]

Lead.—Tetra-alkyl-lead and tetra-alkyltin compounds react with hydrochloric acid in methanol or methanol–benzene mixtures thus:

$$R_4M \xrightarrow{k_1} R_3MCl \xrightarrow{k_2} R_2MCl_2$$

The variations of the rate constants k_1 and k_2 with the nature of R and of M correlate satisfactorily with lead—alkyl and tin—alkyl bond strengths and with solvation energies.[63] Kinetics and products of reaction of hexaphenyldilead, and some of its substituted derivatives $(XC_6H_4)_6Pb_2$, with mercury(II) chloride or acetate in methanol–dioxan mixtures, indicate that

[58] D. V. Stynes and A. L. Allred, *J. Amer. Chem. Soc.*, 1971, **93**, 2666.
[59] M. F. Lappert, J. Lorberth, and J. S. Poland, *J. Chem. Soc.* (*A*), 1970, 2954.
[60] M. D. Hobday and T. D. Smith, *J. Chem. Soc.* (*A*), 1971, 1453.
[61] G. Redl and M. Winokur, *J. Organometallic Chem.*, 1971, **26**, C36.
[62] S. A. Sandhu and J. C. Bhatia, *Indian J. Chem.*, 1971, **9**, 70.
[63] V. Bade and F. Huber, *J. Organometallic Chem.*, 1970, **24**, 387.

initial electrophilic lead—carbon bond cleavage is followed by parallel reactions of the Pb_2Ph_5Cl or Pb_2Ph_5OAc intermediates, in which lead—carbon and lead—lead bonds are cleaved by the mercury(II) species.[64] Intermediates Ph_2PbNH and $Ph_2Pb(NH_2)_4^{2-}$ (as its potassium salt) have been isolated from the reaction of diphenyl-lead di-iodide in a solution of KNH_2 in liquid ammonia, whose final product is $K_4[Pb(NH_2)_6]$.[65]

Kinetic results for the reaction of tetramethyl-lead with perdeuterioacetic acid have been used to exemplify the method for determining the concentrations of various intermediate species in a competitive, consecutive reaction scheme.[66]

3 Group V

Nitrogen.—The effects of a range of alkali-metal chlorides on rates of ^{18}O-exchange between nitrate and water have been described.[67] The reactions, and their mechanisms, resulting from radiolysis of aqueous nitrate solutions have been probed by ^{18}O-tracer experiments, by systematic variation of concentration of nitrate, and by observing the effects of added species such as oxygen and hydrogen. The reaction sequence is complicated and very sensitive to experimental conditions.[68] Contrary to earlier reports, it seems that the decay of nitrate radicals occurs solely *via* bimolecular reaction between two radicals.[69] Mechanisms of formation of NO_2, N_2O_3, and N_2O_4 in photolysis of aqueous solutions of nitrites have been discussed; some kinetic data are reported.[70]

In the isomerization of peroxonitrous acid, HOONO, to nitric acid the main reaction path involves generation of hydroxyl radicals:[71]

$$HOONO \longrightarrow HO\cdot + NO_2$$

The formation of peroxonitrous acid in aqueous perchloric acid, whose kinetics have been determined by stopped-flow techniques, follows the rate law

$$\frac{d[HOONO]}{dt} = \frac{a[H^+]\,[H_2O_2]\,[HNO_2]}{b + c[H_2O_2]}$$

This rate law is consistent with a mechanism involving NO^+ as an intermediate.[72] The decomposition of peroxonitrous acid in weakly acidic,

[64] V. G. Kumar Das, D. A. Moyes, and P. R. Wells, *J. Organometallic Chem.*, 1971, **33**, 31.
[65] O. Schmitz-Du Mont and W. Janson, *Z. anorg. Chem.*, 1970, **375**, 98.
[66] V. Bade and F. Huber, *J. Organometallic Chem.*, 1970, **24**, 691.
[67] A. V. Kuprik, M. O. Tereshkevich, G. I. Lysenko, V. S. Yatsenko, N. Ya. Khramtsova, Ya. A. Priven, and M. I. Valenchuk, *Zhur. obshchei Khim.*, 1971, **41**, 3 (*Chem. Abs.*, 1971, **74**, 146 767e).
[68] M. Faraggi, D. Zehavi, and M. Anbar, *Trans. Faraday Soc.*, 1971, **67**, 701.
[69] R. W. Glass and T. W. Martin, *J. Amer. Chem. Soc.*, 1970, **92**, 5084.
[70] A. Treinin and E. Hayon, *J. Amer. Chem. Soc.*, 1970, **92**, 5821.
[71] L. R. Mahoney, *J. Amer. Chem. Soc.*, 1970, **92**, 5262.
[72] D. J. Benton and P. Moore, *J. Chem. Soc.* (*A*), 1970, 3179.

neutral, and alkaline solutions has been studied kinetically hitherto;[73] the kinetics of its decomposition have now been studied under more strongly acidic conditions ($HClO_4$; $0 < pH < 2$). The reaction follows first-order kinetics, but the observed first-order rate constants vary with pH: $k_{obs} = k_1 + k_2[H^+]$. Activation parameters for the two paths are $\Delta H^{\ddagger} = 19.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 7.4$ cal deg^{-1} mol^{-1} for the k_1 path, and $\Delta H^{\ddagger} = 14.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 5.3$ cal deg^{-1} mol^{-1} for the k_2 path.[72] With reference to kinetics of peroxonitrous acid decomposition, a possible ambiguity in determining rate constants for consecutive first-order reactions has been pointed out.[74] A similar possibility of ambiguity has been discussed for consecutive reactions in palladium(II)–ammine or –amine-plus-chloride systems.[75]

The stoicheiometry of the reaction between hydroxylamine and nitric oxide, in aqueous solution, is

$$2NO + 2NH_2OH \longrightarrow N_2O + N_2 + 3H_2O$$

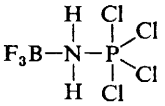
^{15}N-Tracer experiments show that for both N_2O and N_2 one nitrogen atom comes from nitric oxide and the other from hydroxylamine.[76] The reaction sequence for oxidation of hydroxylamine by oxygen in alkaline solution, $12 < pH < 13$, is firstly formation of a deprotonated form of hydroxylamine, which is oxidized to nitroxide ion and then to peroxonitrite, which in turn decomposes to nitrite if traces of heavy metal cations are present.[77]

The reaction of difluoramine, HNF_2, with hydroxide is thought to proceed by an S_N1cb mechanism, in which the formation of NF_2^- is followed by dissociation of this anion to F^- and NF, *en route* to a variety of products. Further evidence to support this hypothesis is provided by trapping experiments and by the determination of the activation volume, which is + 7 cm^3 mol^{-1}, for the reaction. Values of the second-order rate constant do not vary with hydroxide concentration over a wide range of hydroxide concentrations; from the available kinetic results the pK_a of difluoramine must be 15 or higher.[78] The reaction of azide with iodide is strongly catalysed by free thiocyanate ion, but less effectively catalysed by thiocyanate complexes of chromium(III), cobalt(III), and rhodium(III).[79]

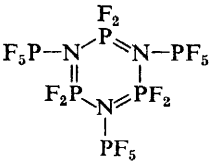
The mechanism of the reaction between F_3B,NH_3 and PCl_5, whose products include $[Cl_3P{=}N{=}PCl_3]^+[BCl_4]^-$, involves bond formation between nitrogen and phosphorus *via* elimination of hydrogen chloride to

[73] M. N. Hughes and H. G. Nicklin, *J. Chem. Soc.* (*A*), 1968, 450; W. G. Keith and R. E. Powell, *J. Chem. Soc.* (*A*), 1969, 90.
[74] N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, 1970, **66**, 2210.
[75] R. A. Reinhardt and J. S. Coe, *Inorg. Chim. Acta*, 1969, **3**, 438.
[76] J. N. Cooper, J. E. Chilton, and R. E. Powell, *Inorg. Chem.*, 1970, **9**, 2303.
[77] M. N. Hughes and H. G. Nicklin, *J. Chem. Soc.* (*A*), 1971, 164.
[78] W. J. le Noble, E. M. Schulman, and D. N. Skulnik, *J. Amer. Chem. Soc.*, 1971, **93**, 4710.
[79] L. Dozsa, D. A. Durham, and M. T. Beck, *Magyar Kém. Folyóirat*, 1970, **76**, 555 (*Chem. Abs.*, 1971, **74**, 68 192x); M. T. Beck and G. Bazsa, *Magyar Kém. Folyóirat*, 1971, **77**, 76 (*Chem. Abs.*, 1971, **74**, 116 399u).

form (11), which subsequently eliminates another molecule of hydrogen chloride, reacts with a second molecule of PCl_5, and eliminates further hydrogen chloride.[80] The mechanisms of analogous reactions of primary and secondary amine adducts of boron trifluoride have been briefly discussed.[81] The salt $[Cl_3P{=}N{=}PCl_3]^+[BCl_4]^-$ reacts with arsenic trifluoride to give $[NPF_2 \cdot PF_5]_3$ (12) and boron trifluoride. The reaction sequence



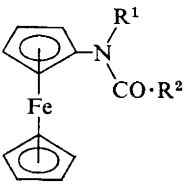
(11)



(12)

seems to involve perfluorination of the anion, fluorine transfer thence to the cation with concurrent liberation of boron trifluoride, and finally cyclotrimerization of the fluorinated P=N=P unit.[82] Interestingly, the salt $[Cl_3P{=}N{=}PCl_3]^+[BCl_4]^-$ reacts with thiocyanate not only by reaction of the thiocyanate at the phosphorus atom but also with formation of the novel $[B(NCS)_4]^-$ anion.[83] In the reaction of $[MeN \cdot PCl_3]_2$ with boron trifluoride, two of the chlorides on phosphorus are replaced by fluorides at axial positions of the trigonal bipyramids.[84] Exchange reactions of R_3N,BX_3 and of R_3P,BX_3 adducts have already been discussed in the section on boron.

Intramolecular Processes. The effects of electronegative and conjugative groups on rates of inversion at nitrogen have been calculated by *ab initio* SCF–LCAO–MO methods. The calculated value of 20.3 kcal mol^{-1} for the barrier to inversion at nitrogen in fluoramine, H_2NF, compares satisfactorily with the value of > 18 kcal mol^{-1} reported from experimental data for the barrier to inversion in difluoramine, HNF_2.[85] The effect of an adjacent ferrocenyl group on the inversion barrier at pyramidal nitrogen has been investigated for the amide (13). The results appear inconclusive

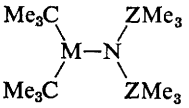


(13)

[80] H. Binder and E. Fluck, *Z. anorg. Chem.*, 1971, **381**, 21.
[81] H. Binder and E. Fluck, *Z. anorg. Chem.*, 1971, **381**, 116, 123.
[82] H. Binder, *Z. anorg. Chem.*, 1971, **383**, 130.
[83] H. Binder, *Z. anorg. Chem.*, 1971, **383**, 279.
[84] H. Binder, *Z. anorg. Chem.*, 1971, **384**, 193.
[85] J. M. Lehn and B. Munsch, *Chem. Comm.*, 1970, 1062.

as it seems impossible to decide whether the change in environment of the nitrogen arises from inversion or from restricted rotation about the nitrogen to amide-carbon bond.[86]

Estimates of barriers to restricted rotation about bonds between two inorganic atoms have been determined by n.m.r. techniques for a variety of compounds containing Group V atoms. The changes in the ^{19}F n.m.r. spectrum of the hydrazine derivative $F_2P\cdot NMe\cdot NMe\cdot PF_2$ with varying temperature suggest that there is restricted rotation both about the nitrogen—nitrogen and about the nitrogen—phosphorus bonds. For rotation about the nitrogen—nitrogen bond $\Delta G^{\ddagger}(30\,°C) = 13.0$ kcal mol^{-1} and $\Delta H^{\ddagger} = 8.4$ kcal mol^{-1}. For rotation about the nitrogen—phosphorus bonds $\Delta G^{\ddagger}(-120\,°C) = 6.4$ kcal mol^{-1} for the *cis*-isomer and 6.9 kcal mol^{-1} for the *trans*-isomer. These values are slightly lower than those for the related compounds $(CF_3)_2P\cdot NMe_2$ and $Cl_2P\cdot NMe_2$, where $\Delta G^{\ddagger}$ values are in the range 8—9 kcal mol^{-1}. The barriers to rotation about the nitrogen—nitrogen and nitrogen—phosphorus bonds in the hydrazine derivative are pretty well independent of solvent, for the solvents isopentane, n-undecane, 1,1,2,2-tetrachloroethane, and difluorodichloromethane.[87] Barriers to restricted rotation about phosphorus—nitrogen bonds in $O{=}P{-}NR_2$ and $S{=}P{-}NR_2$,[88] about arsenic—nitrogen and antimony—nitrogen bonds in compounds (14) with M = As or Sb and Z = Si or Ge,[89] and about sulphur—nitrogen bonds in dialkylsulphamoyl chlorides,[90] have been investigated.



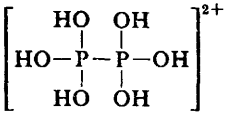
(14)

Phosphorus.—Reaction between $Cl_2P(O)\cdot NHMe$ and $POCl_3$ or $POCl_2Ph$ probably occurs by nucleophilic attack of $Cl_2P(O)\cdot NMe^-$ from the first-named (the reaction was conducted in the presence of Et_3N) at the phosphorus atom of the $POCl_3$ or $POCl_2Ph$.[91] Possible mechanisms for reactions of POF_2H have been discussed qualitatively; this compound can act as an electrophile or as a nucleophile.[92] Hydrogen–deuterium exchange at the ion $[H_3B,PH_2]^-$ takes place at the phosphorus, not at the boron. The suggested mechanism involves tautomerization of this ion into a species with

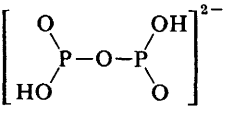
[86] R. Damrauer, *J. Organometallic Chem.*, 1971, **32**, 121.
[87] T. T. Bopp, M. V. Havlicek, and J. W. Gilje, *J. Amer. Chem. Soc.*, 1971, **93**, 3051.
[88] W. B. Jennings, *Chem. Comm.*, 1971, 867.
[89] O. J. Scherer and W. Janssen, *Chem. Ber.*, 1970, **103**, 2784.
[90] W. B. Jennings and R. Spratt, *Chem. Comm.*, 1970, 1418.
[91] R. Keat, *J. Chem. Soc.* (*A*), 1970, 2732.
[92] L. F. Centofanti and R. W. Parry, *Inorg. Chem.*, 1970, **9**, 2709.

an increased co-ordination number at the phosphorus, as has similarly been suggested for hydrogen–deuterium exchange at phosphoric acid.[93]

Several references deal with hydrolysis of a variety of oxoanions of phosphorus. The rate law for hydrolysis of hypophosphate in hydrochloric acid suggests that the main route is hydrolysis of the diprotonated species $H_6P_2O_6^{2+}$ (15). The activation energy is 19.9 kcal mol^{-1} [94] ^{32}P-Tracer techniques have been used to probe both the hydrolysis [95] and the formation [96] of polyphosphates. The latter study is specifically concerned with formation of tripolyphosphate. Catalytic effects of H^+, Na^+, and K^+ on pyrophosphate hydrolysis rates are inversely related to the radii of these ions. The activation energy for the acid-catalysed reaction is 28—30 kcal mol^{-1} over the pH range 5.6—10.4.[97] More spectacular effects of (unspecified) catalysts have been reported for hydrolysis of tripolyphosphate, whose activation energy varies between 10 and 22 kcal mol^{-1} in various parts of Lake Ontario.[98] The effects of added H^+, OH^-, and Ca^{2+} on hydrolysis rates for pyrophosphate and for tripolyphosphate have been determined by ^{31}P n.m.r. spectroscopy.[99] The effects of added alkali-metal, alkaline-earth, and transition-metal cations on the hydrolysis of pyrophosphite, $[H_2P_2O_5]^{2-}$ (16), have been explained in terms of complex



(15)



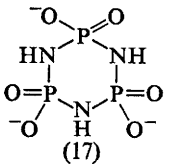
(16)

formation, with the cation attaching itself to the bridging oxygen. Copper(II) ions were the most effective catalysts observed.[100] Radical mechanisms have been postulated for photolytic reactions of peroxodiphosphates in water and in aqueous ethanol and aqueous propan-2-ol. Reaction sequences for peroxodiphosphates are compared with those for the much more intensively studied peroxodisulphates.[101]

Kinetics of hydrolysis have been reported for $[PO_2F_2]^-$ and $[PO_3F]^{2-}$, themselves products of hydrolysis of $[PF_6]^-$, in the presence of acid, aluminium(III), thorium(IV), or zirconium(IV).[102] Both kinetic results and

[93] E. Mayer, *Inorg. Chem.*, 1971, **10**, 2259.
[94] N. Yoza, I. Koga, and S. Ohashi, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1435.
[95] L. J. Anghileri and E. S. Miller, *Z. Naturforsch.*, 1971, **26b**, 543.
[96] T. Iida, N. Takai, and T. Yamabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 686.
[97] M. Watanabe, T. Takahara, and T. Yamada, *Chubu Kogyo Diagaku Kyo*, 1969, **5**, 155 (*Chem. Abs.*, 1970, **73**, 7751m).
[98] G. W. Heinke, Proceedings of the 12th Conference on Great Lakes Research, 1969, p. 766 (*Chem. Abs.*, 1971, **74**, 16 053h).
[99] M. Kawabe, O. Ohashi, and I. Yamaguchi, *Bull. Chem. Soc. Japan*, 1970, **43**, 3705.
[100] S. Ueda and Y. Sasaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 1972.
[101] R. J. Lussier, W. M. Risen, and J. O. Edwards, *J. Phys. Chem.*, 1970, **74**, 4039.
[102] H. R. Clark and M. M. Jones, *Inorg. Chem.*, 1971, **10**, 28.

product analysis have shed some light on the mechanism of hydrolysis of the trimetaphosphimate anion (17).[103]

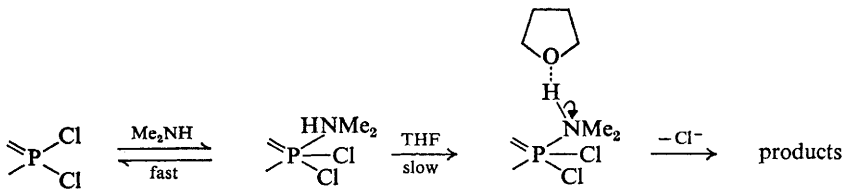


(17)

^{31}P N.m.r. and product-composition studies of the reaction of ammonium chloride with phosphorus pentachloride in 1,1,2,2-tetrachloroethane suggest that the mechanism can be broken down into two main stages, the production of $[Cl_3P{=}N{=}PCl_3]^+[PCl_6]^-$ and the subsequent reaction with further ammonium chloride and concomitant cyclization to give the cyclophosphazene product, $[PNCl_2]_3$.[104] The products and stoicheiometry of the reaction of $[PNCl_2]_3$ with diphenylmagnesium in dioxan provide clues relating to the mechanism and possible intermediates on the way to the characterized cyclic and acyclic products, of which the former are magnesium-free but the latter contain magnesium.[105] Reaction of $[PNCl_2]_3$ with liquid ammonia produces $[PN(NH_2)_2]_3,H_2O$ and $[PN(NH_2)_2]_3,HCl$.[106] The cyclophosphazenes $[PNCl_2]_3$ and $[P_3N_3Cl_5(NMe_2)]$ react with dimethylamine in tetrahydrofuran solution according to a second-order rate law. Rate constants and activation parameters (Table 5) were determined, and a mechanism (Scheme) was suggested in which the rate-determining step is

Table 5 *Activation parameters for reaction of cyclophosphazenes with dimethylamine in tetrahydrofuran (from ref.* 107)

Reactant	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
$[P_3N_3Cl_6]$	1.7	− 47
$[P_3N_3Cl_5(NMe_2)]$	5.1	− 38

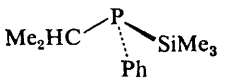


Scheme

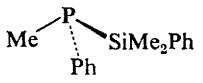
[103] W. Waněk and E. Thilo, *Coll. Czech. Chem. Comm.*, 1970, **35**, 2712.
[104] J. Emsley and P. B. Udy, *J. Chem. Soc.* (*A*), 1970, 3025; *ibid.*, 1971, 768.
[105] M. Biddlestone and R. A. Shaw, *J. Chem. Soc.* (*A*), 1971, 2715.
[106] E. Kobayashi, *Bull. Chem. Soc. Japan*, 1971, **44**, 2280.
[107] J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc.* (*A*), 1971, 2429.
[108] B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc.* (*A*), 1971, 3487.

the approach of tetrahydrofuran to the dimethylamino-group forcing the expulsion of chloride from the adjacent phosphorus.[107] Fluorination of $[P_3N_3Cl_3(NMe_2)_3]$ and of $[P_3N_3Cl_2(NMe_2)_4]$ by antimony trifluoride involves formation of a Lewis acid–base adduct in which the most basic ring nitrogen-atom acts as the donor base.[108]

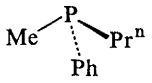
Intramolecular Processes. Whereas silylamines are planar, silylphosphines are pyramidal. Hence there is the possibility of inversion at the phosphorus, and indeed the barrier to inversion is fairly low. For the silylphosphine (18) $\Delta G^{\ddagger}(62\,^{\circ}C) = 18.9$ kcal mol^{-1}, whereas for (19) $\Delta G^{\ddagger}(70\,^{\circ}C)$ is *ca.* 19 kcal mol^{-1}. In a range of solvents of widely differing polarities, racemization of (+)-methyl-n-propylphenylphosphine (20) is a first-order process



(18)



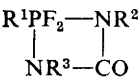
(19)



(20)

with an activation energy of 30 ± 3 kcal mol^{-1}. This very small variation with solvent suggests that there is only a small change in dipole in going from the pyramidal initial state to the planar transition state.[109]

Pseudorotation in PF_5 has been discussed from a theoretical viewpoint;[110] pseudorotation in five-co-ordinate phosphorus compounds has been reviewed;[111, 112] and the role of pseudorotation in the mechanism of nucleophilic substitution at phosphorus has been discussed.[113] The Berry mechanism for stereochemical rearrangement at five-co-ordinate phosphorus is by far the most commonly invoked, but some alternative mechanism involving internal rotation may possibly be operative in some reactions. Evidence has been presented that such an alternative mechanism, the 'turnstile rotation' path, is quite likely in certain instances.[112] For a recent illustration of pseudorotation in a five-co-ordinate phosphorus compound we may cite the study of the phosphadiazetidinones (21), which



(21)

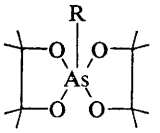
have the built-in steric restriction of having the phosphorus in a four-membered ring. For the particular case where $R^1 = R^2 = Me$ and $R^3 = Ph$, the activation energy, determined from variable-temperature ^{19}F n.m.r. spectroscopy, is 18 kcal mol^{-1}.[114]

[109] H. D. Munro and L. Horner, *Tetrahedron*, 1970, **26**, 4621.
[110] J. Brickmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 747.
[111] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266.
[112] I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Accounts Chem. Res.*, 1971, **4**, 288.
[113] K. Mislow, *Accounts Chem. Res.*, 1970, **3**, 321.
[114] R. E. Dunmur, M. Murray, R. Schmutzler, and D. Gagnaire, *Z. Naturforsch.*, 1970, **25b**, 903.

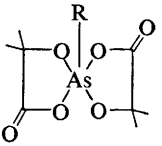
Variable-temperature ^1H n.m.r. studies of Me_2PF_3 and of Me_3PF_2 show that P—C—H coupling persists, but that F—P—C—H coupling does not persist, as the temperature increases. This indicates an intermolecular exchange of fluorine atoms, and not rearrangement by a Berry pseudorotation process. The difference in behaviour between these compounds and, for example, $Me_2N \cdot PF_4$, where the fluorines do exchange environments intramolecularly by pseudorotation, is ascribed to the impossibility of keeping the electropositive methyl groups out of the axial positions in Berry pseudorotations for the compounds Me_2PF_3 and Me_3PF_2. The activation parameters for the intermolecular fluoride exchange processes for these compounds are $\Delta H^{\ddagger} = 3.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -43$ cal deg^{-1} mol^{-1} for Me_3PF_2 and $\Delta H^{\ddagger} = 3.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -41$ cal deg^{-1} mol^{-1} for Me_2PF_3.[115]

Arsenic.—Just as fluorine exchange in Me_2PF_3 and in Me_3PF_2 is not intramolecular but intermolecular (see preceding paragraph), so also is fluorine exchange in $(PhCH_2)_3AsF_2$ intermolecular in mechanism. In methylene chloride solution this intermolecular exchange follows a first-order rate law, which indicates a dissociative mechanism.[116]

It has been suggested[117] that pseudorotation, *i.e.* intramolecular ligand rearrangement by the Berry mechanism, should be faster at arsenic(v) incorporated into a five-membered spiroarsorane ring than at phosphorus(v) in an analogous spirophosphorane. However, variable-temperature n.m.r. studies of compounds (22), with R = Me, CH_2Ph, Ph, p-$C_6H_4 \cdot OMe$, or p-$C_6H_4 \cdot NO_2$, and (23), with R = Me or Ph, show that barriers are comparable, at around 20—23 kcal mol^{-1}, for such arsenic and phosphorus compounds.[118] Pseudorotation in AsF_5 has been discussed theoretically.[110]



(22)



(23)

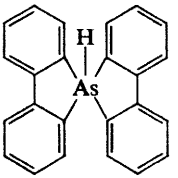
The kinetics of the equilibrium

$$Me_2AsD + Et_2AsH \rightleftharpoons Me_2AsH + Et_2AsD$$

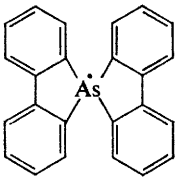
have been followed by ^1H n.m.r. spectroscopy. In perdeuteriodiethyl ether at 35 °C the second-order rate constant for the left to right reaction is 4.9×10^{-5} l mol^{-1} s^{-1}; the equilibrium constant is 1.2.[119] Possible

[115] T. A. Furtsch, D. S. Dierdorf, and A. H. Cowley, *J. Amer. Chem. Soc.*, 1970, **92**, 5759.
[116] G. G. Moreland, R. J. Beam, and C. W. Wooten, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 243.
[117] H. Goldwhite, *Chem. Comm.*, 1970, 651.
[118] J. P. Casey and K. Mislow, *Chem. Comm.*, 1970, 1410.
[119] W. R. Cullen and W. R. Leeder, *Canad. J. Chem.*, 1970, **48**, 3757.

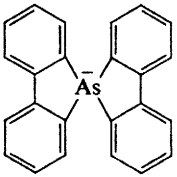
intermediates in decomposition of bis-(2,2′-biphenylylene)arsenic hydride (24) are the radical (25), the arsenic anion (26), and the arsine carbanion (27).[120]



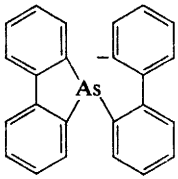
(24)



(25)



(26)



(27)

Antimony.—Rate constants for the forward and reverse reactions of the equilibrium

$$SbCl_5 + Ph_3CCl \rightleftharpoons [Ph_3C]^+[SbCl_6]^-$$

have been determined in a range of solvents by *T*-jump techniques. Equilibrium constants for the reaction were estimated both from the rate constants and spectrophotometrically. The rate constants for the left to right reaction are inversely related to the donor properties of the respective solvents.[121]

4 Group VI

Oxygen.—A kinetic study of the reaction $D_2O_3 \rightarrow D_2O + O_2$, in D_2O solution, has revealed the rate law for this process. The activation energy is 17.5 kcal mol^{-1} in 0.01M-$DClO_4$.[122]

Sulphur.—Discussion continues as to whether nucleophilic substitution at sulphur(II) is a one-stage associative process or involves an intermediate adduct of significant lifetime. There is kinetic evidence for an intermediate in reactions of *p*-nitrobenzenesulphenyl chloride with aniline[123] and with substituted anilines,[124] but no evidence for an intermediate was obtained in

[120] D. Hellwinkel, B. Knabe, and G. Kilthau, *J. Organometallic Chem.*, 1970, **24**, 165.
[121] V. Gutmann and R. Schmid, *Monatsh.*, 1971, **102**, 1217.
[122] B. H. J. Bielski, *J. Phys. Chem.*, 1970, **74**, 3213.
[123] E. Ciuffarin and F. Griselli, *J. Amer. Chem. Soc.*, 1970, **92**, 6015.
[124] E. Ciuffarin and L. Senatore, *J. Chem. Soc.* (*B*), 1970, 1680.

the *trans*-sulphenylation of γ-hydroxyalkyl-2-nitrobenzenesulphenates.[125] Nucleophilic substitution at sulphur(II) is also the primary step in the reaction sequence for base-catalysed hydrolysis of ethyl and of t-butyl 2-nitrobenzenesulphenates, Ar·S·OEt and Ar·S·OBu^t respectively.[126] The mechanism of metal cation (Hg^{2+} or Ag^+) promoted hydrolysis of thioesters *p*-R·C_6H_4·CO·SEt depends on the nature of R, ranging from bimolecular for R = NO_2 to unimolecular for R = OMe. Mercury(II)-promoted hydrolysis of thiobenzoic acid and of dibenzoyl sulphide occurs by a dissociative reaction.[127]

The painstakingly precise kinetic investigation[128] of solvolysis of sulphur(VI)—chlorine bonds alluded to in the first volume of this Specialist Periodical Report has been extended to include a series of 4-substituted benzenesulphonyl chlorides. In this case values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, of $\Delta C_p^{\ddagger}$ from $\partial\Delta H^{\ddagger}/\partial T$, and even of $\partial\Delta C_p^{\ddagger}/\partial T$, have been reported. An S_N2 mechanism with a trigonal-bipyramidal transition state is indicated.[129] The variation of rates with substituents and solvent composition (in aqueous dioxan) for another series of benzenesulphonyl chlorides also indicates an S_N2 mechanism, except in the case of 2,4,6-trimethylbenzenesulphonyl chloride, where an S_N1 mechanism seems more likely.[130] Kinetic solvent isotope effects, D_2O *vs.* H_2O, for hydrolysis of substituted benzenesulphonyl chlorides have been determined and contrasted with those for analogous organic chloride solvolyses.[131] Kinetic data have also been obtained for hydrolysis of methane- and ethane-sulphonyl chlorides in methanol, ethanol, and ethanol–benzene, –carbon tetrachloride, and –2,2,4-trimethylpentane solvent mixtures. These results have been discussed in terms of the effects of solvation of initial and transition states on reactivities.[132]

Kinetic studies have been reported of formation, decomposition, and oxygen exchange of several oxoanions of sulphur. $^{35}SO_3$ Tracer experiments show that monoperoxotetrasulphate, $S_4O_{14}^{2-}$, is formed from peroxodisulphate and sulphur trioxide by simultaneous co-ordination of the latter to the terminal oxygen of the peroxodisulphate and insertion of another sulphur trioxide molecule into a sulphur-bridging oxygen bond of the peroxodisulphate.[133] The decomposition of thiosulphate in alkaline solution at elevated temperatures, in fact 220—280 °C, is a first-order process with an activation energy of 46.8 kJ mol^{-1} (11.2 kcal mol^{-1}).[134]

[125] D. R. Hogg and P. W. Vipond, *J. Chem. Soc.* (*C*), 1970, 2142.
[126] D. R. Hogg and P. W. Vipond, *J. Chem. Soc.* (*B*), 1970, 1242.
[127] D. P. N. Satchell and I. I. Secemski, *J. Chem. Soc.* (*B*), 1970, 1306.
[128] R. E. Robertson, B. Rossall, S. E. Sugamori, and L. Treindl, *Canad. J. Chem.*, 1969, **47**, 4199.
[129] R. E. Robertson and B. Rossall, *Canad. J. Chem.*, 1971, **49**, 1441.
[130] M. L. Tonnet and A. N. Hambly, *Austral. J. Chem.*, 1971, **24**, 703.
[131] B. Rossall and R. E. Robertson, *Canad. J. Chem.*, 1971, **49**, 1451.
[132] R. Foon and A. N. Hambly, *Austral. J. Chem.*, 1971, **24**, 713.
[133] A. Blaschette and B. Bressel, *Z. anorg. Chem.*, 1970, **377**, 174.
[134] A. V. Kalyakina, A. A. Kozhakova, E. A. Buketov, and A. N. Polukarov, *Trudy khim.-met. Inst., Akad. Nauk Kaz. SSR*, 1969, **9**, 72 (*Chem. Abs.*, 1970, **73**, 18 980m).

The kinetics and mechanism of decomposition of dithionite in aqueous solution are complicated;[135] two groups of workers in this area have briefly pointed out and discussed differences between their interpretations.[136] The cations In^{3+}, Cd^{2+}, and Zn^{2+} have a significant retarding effect on the decomposition of aqueous dithionite solutions.[137] The rate law for oxygen exchange between sulphite and water suggests two reaction paths, one of which is second-order in sulphite and involves the $S_2O_5^{2-}$ ion as an intermediate. Rate constants for hydration of sulphur dioxide and for the forward and backward reactions of the following equilibrium have been evaluated:[138]

$$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$$

The exchange of ^{18}O between thiosulphate ions, sulphite ions, and water has also been described.[139]

Micellar effects on rate constants for the S_N2 hydrolysis of the adduct Et_3N,SO_3 have been studied. Both anionic, *e.g.* sodium hexadecylsulphonate, and cationic, *e.g.* dodecyltrimethylammonium bromide, surfactants have a marked accelerating effect.[140]

Intramolecular Processes. What is claimed to be the first direct and unambiguous determination of barriers to restricted rotation about sulphur—sulphur bonds relates to compounds $Ph \cdot CH_2 \cdot S \cdot S \cdot R$, in various solvents. Determined barriers to rotation about S—S are $7.0 < \Delta G^{\ddagger} < 9.4$ kcal mol^{-1}, $6.6 < \Delta H^{\ddagger} < 9.1$ kcal mol^{-1} and $-7 < \Delta S^{\ddagger} < -1$ cal deg^{-1} mol^{-1}.[141] Far-i.r. spectra of sulphur tetrafluoride suggest that the barrier to intramolecular pseudorotation for this molecule in the gas phase is 10.0 kcal mol^{-1}. This figure may be compared with the activation energy of about 4.5 kcal mol^{-1} for intermolecular fluoride exchange in the liquid phase.[142] Two references to inversion at sulphur bonded to platinum or palladium[143] are discussed in the chapter on complexes of those metals (Part II, Chapter 2).

Selenium.—Fluoride exchange at the newly prepared and characterized series of compounds R_2SeF_2 has been studied by ^1H and ^{19}F n.m.r. spectroscopy. The variation of fluoride exchange rates with the size of the alkyl group R and with the concentration of R_2SeF_2 suggests a dissociative

[135] See, *e.g.*, M. Wayman and W. J. Lem, *Canad. J. Chem.*, 1970, **48**, 776, 782; L. Burlamacchi, G. Guarini, and E. Tiezzi, *Trans. Faraday Soc.*, 1969, **65**, 496.
[136] L. Burlamacchi, G. Guarini, and E. Tiezzi, *Canad. J. Chem.*, 1971, **49**, 1139; M. Wayman and W. J. Lem, *ibid.*, p. 1140.
[137] W. J. Lem and M. Wayman, *Canad. J. Chem.*, 1970, **48**, 2778.
[138] R. H. Betts and R. H. Voss, *Canad. J. Chem.*, 1970, **48**, 2035.
[139] R. H. Betts and S. Libich, *Canad. J. Chem.*, 1971, **49**, 180.
[140] M. D. Bentley, S. E. Bowie, and R. D. Limoges, *J. Phys. Chem.*, 1971, **75**, 1763.
[141] R. R. Fraser, G. Boussard, J. K. Saunders, J. B. Lambert, and C. E. Mixan, *J. Amer. Chem. Soc.*, 1971, **93**, 3822.
[142] I. W. Levin and W. C. Harris, *J. Chem. Phys.*, 1971, **55**, 3048.
[143] H. A. O. Hill and K. A. Simpson, *J. Chem. Soc.* (*A*), 1970, 3266; R. J. Cross, G. J. Smith, and R. Wardle, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 191.

mechanism with a dialkylfluoroselenium cation intermediate:

$$R_2SeF_2 \rightleftharpoons R_2SeF^+ + F^-$$

This situation contrasts with fluoride exchange at SF_4 and at SeF_4, where an associative mechanism is more likely.[144]

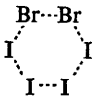
Tellurium.—Rates of halide exchange between diphenyltellurium, Ph_2Te, and diphenyltellurium halides, Ph_2TeX_2, in chloroform solution, increase in the order X = F < Cl < Br < I. The mechanism of fluoride exchange is dissociative, with rate-determining loss of fluoride from Ph_2TeF_2:

$$Ph_2TeF_2 \longrightarrow Ph_2TeF^+ + F^-$$

(*cf.* fluoride exchange at R_2SeF_2, above). The mechanism of chloride and of bromide exchange is associative with a four-centre transition state. Exchange of iodide is very fast, and presumably also associative in nature.[145]

5 Group VII

The kinetics of the reaction between iodine and bromine to form iodine monobromide in concentrated sulphuric acid (96% H_2SO_4) indicate a termolecular process, which is consistent with Woodward–Hoffmann orbital-symmetry considerations. The suggested transition state is cyclic (28).[146]



(28)

Oxygen exchange between iodate and water has been followed by ^{17}O n.m.r. of both iodate-oxygen and solvent-oxygen resonances. It is catalysed by acid. The present study, conducted over a wider range of pH than earlier investigated, indicates that the full rate law is

$$\text{rate} = (k_1[H^+] + k_2[H^+]^2)\,[IO_3]$$

with the $[H^+]^2$ term only significant at high acid concentrations.[147] In aqueous solutions containing cadmium bromate and ammonium bromide, bromine exchange between the bromate and bromide occurs through a mixed bromide–bromate complex of cadmium.[148]

Chlorite reacts with hypochlorous acid to produce chlorine dioxide. The stoicheiometry and rate law

$$d[ClO_2]/dt = k[HClO]^m[ClO_2^-]^n$$

[144] K. J. Wynne, *Inorg. Chem.*, 1971, **10**, 1868.
[145] V. D. Nefedov, E. N. Sinotova, A. N. Sarbash, E. A. Kolobov, and V. K. Kapustin, *Radiokhimiya*, 1971, **13**, 435 (*Chem. Abs.*, 1971, **75**, 122 676u).
[146] P. Schweitzer and R. M. Noyes, *J. Amer. Chem. Soc.*, 1971, **93**, 3561.
[147] R. A. Dwek, Z. Luz, S. Peller, and M. Shporer, *J. Amer. Chem. Soc.*, 1971, **93**, 77.
[148] H. J. Arnikar and A. S. Gijare, *J. Indian Chem. Soc.*, 1971, **48**, 315.

have been established, and the values of m and n determined under various conditions. The intermediacy of Cl_2O_2 is suggested.[149] Decomposition reactions of oxohalogen anions are generally redox processes overall, but substitution steps often play an important role in their mechanism. Thus the rate-determining step in thermal decomposition of perchloric acid appears to be a bimolecular reaction between two perchloric acid molecules.[150] Other investigations and reinvestigations of oxohalogen-anion decompositions include those of hypochlorite,[151] hypobromite,[152] and bromite in acid [153] and in alkaline [154] solution.

[149] M. L. Granstrom and B. M. Israel, Amer. Chem. Soc., Div. Water, Air Waste Chem., Gen. Pap. 1969, p. 137 (*Chem. Abs.*, 1970, **73**, 134 306v).
[150] M. P. Henderson, V. I. Miasek, and T. W. Swaddle, *Canad. J. Chem.*, 1971, **49**, 317.
[151] B. P. Nikol'skii, V. G. Krunchak, T. V. L'vova, V. V. Pal'chevskii, and R. I. Sosnovskii, *Doklady Akad. Nauk SSR*, 1970, **191**, 1324; B. P. Nikol'skii, V. G. Krunchak, V. V. Pal'chevskii, and R. I. Sosnovskii, *ibid.*, 1971, **197**, 140 (*Chem. Abs.*, 1970, **73**, 91 945h; 1971, **75**, 10 857x).
[152] M. W. Lister and P. E. McLeod, *Canad. J. Chem.*, 1971, **49**, 1987.
[153] A. Massagli, A. Indelli, and F. Pergola, *Inorg. Chim. Acta*, 1970, **4**, 593.
[154] C. L. Lee and M. W. Lister, *Canad. J. Chem.*, 1971, **49**, 2822.

2

Inert Metal Complexes: Co-ordination Number Four

BY J. BURGESS

1 Tetrahedral Complexes

The rate of oxygen exchange between ferrate and water in basic solution is $1.62 \times 10^{-2}\ s^{-1}$; the reported activation parameters are $E_a = 15.4$ kcal mol^{-1} and $\log A = 9.5$. In acidic solution ferrate oxidizes water too rapidly for accurate oxygen exchange rates to be obtained, but it seems probable that the exchange rate depends on the square of the hydrogen-ion concentration.[1] The rate of oxygen exchange between per-rhenate and water changes little as the concentration of water in methanol–water mixtures varies. This behaviour favours a dissociative mechanism of oxygen exchange.[2] Further kinetic results on the forward and reverse rate constants for the chromate ⇌ dichromate equilibrium have been obtained in lithium perchlorate–perchloric acid solutions.[3] The rate of formation of peroxo-complexes of tantalum from tantalate decreases with decreasing concentration of sulphuric acid, but the activation parameters increase then decrease with varying sulphuric acid concentration. The large, negative values of the activation entropy indicate an associative mechanism.[4]

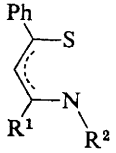
Much work continues to be carried out on the complicated heteropolytungstates and -polymolybdates. The greatest difficulty in discussion of the fairly extended rate law for formation of β-12-molybdosilicic acid, from silicate plus molybdate in perchloric acid, is the lack of knowledge of the exact nature of the molybdenum(VI) species. The increasing order of reaction with respect to molybdenum(VI) as the pH decreases obviously arises from increasing condensation of molybdate units as the acidity increases – the order in molybdenum(VI) is one at high pH, where the monomeric unit MoO_4^{2-} is the predominant species.[5] The existence of $[SiMo_{11}O_{39}]^{8-}$ and of $[GeMo_{11}O_{39}]^{8-}$ has been demonstrated, and the very small range of conditions in which they can exist determined. The mechanistic significance of this work lies in the possible intermediacy of these species in both formation and hydrolysis of germano- and silico-12-molybdates; a

[1] H. Goff and R. K. Murmann, *J. Amer. Chem. Soc.*, 1971, **93**, 6058.
[2] R. K. Murmann, *J. Amer. Chem. Soc.*, 1971, **93**, 4184.
[3] J. R. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, 1971, **10**, 634.
[4] V. P. Vasil'ev and G. A. Zaitseva, *Russ. J. Inorg. Chem.*, 1970, **15**, 518.
[5] L. G. Hargis, *Analyt. Chem.*, 1970, **42**, 1494.

few kinetic results on $[SiMo_{12}O_{40}]^{4-} \rightarrow [SiMo_{11}O_{39}]^{8-} + \frac{1}{7}[Mo_7O_{24}]^{6-}$ are given.[6] A further small contribution to the study of even more complicated systems consisting of the above type of heteropolyanions with additional metal ions is provided by a description of the inclusion of nickel(II) into the phospho- and silico-tungstates $[ZW_{11}O_{39}]^{n-}$, where Z = Si or P.[7] In contrast, the mechanism of formation of the simpler paratungstate species, previously formulated as $[HW_6O_{21}]^{5-}$ but apparently better represented as $[W_6O_{19}(OH)_3]^{5-}$, has been elucidated in some detail. The siting of the hydrogen atoms in the polytungstate intermediates is important, for this controls the water elimination which accompanies condensation.[8]

The hydrolysis of $TiCl_4$, whose ultimate products are TiO_2 and hydrochloric acid, is at least initially a first-order process.[9] Whereas exchange of fluoride, and reaction of chloride, with $[CrO_3F]^-$ are both slow processes, at least on the n.m.r. time-scale, there is rapid halide exchange between CrO_2F_2 and CrO_2Cl_2, presumably *via* the known compound CrO_2FCl. The difference in reactivity between these systems may be due at least in part to electrostatic effects.[10]

In order to balance this section on tetrahedral complexes we shall now mention some studies on transition-metal compounds which are relatively labile. In fact ligand exchange at $Zn(LL)_2$, where LL = β-aminothionato ligands (1) with R^1 = H or Me, is surprisingly slow, much slower than



(1)

inversion, which can readily be followed by n.m.r. and must be intramolecular. The analogous cadmium complexes undergo inversion and ligand exchange at comparable rates, so bond rupture may in this case be important in inversion.[11] The rate law for chloride exchange at $[CoCl_4]^{2-}$ and at $[CoCl_3py]^-$ in nitromethane, determined from ^{35}Cl n.m.r. studies, is

$$\text{rate} = (k_1[Cl^-] + k_2[py])\,[CoCl_3py^-]$$

which bears a close resemblance to the standard two-term rate law for substitution at (inert) d^8 square-planar complexes (see next section). The simplest mechanism consistent with this rate law is of parallel associative reactions involving chloride ion and pyridine respectively; associative

[6] M. Biquard and M. Lamache, *Bull. Soc. chim. France*, 1971, 32.
[7] R. Ripan, M. Puşcaşiu, D. Stănescu, and P. Boian, *Z. anorg. Chem*, 1971, **384**, 297.
[8] K.-H. Tytko and O. Glemser, *Z. Naturforsch.*, 1971, **26b**, 659.
[9] J. Shiokawa, A. Matsumoto, and H. Kawakami, *Asahi Garasu Kogyo Gijutsu Shoreika Kenkyu Hokoku*, 1970, **16**, 431 (*Chem. Abs.*, 1971, **74**, 116 426a).
[10] A. M. Akena, D. S. Brown, and D. G. Tuck, *Canad. J. Chem.*, 1971, **49**, 1505.
[11] S. S. Eaton and R. H. Holm, *Inorg. Chem.*, 1971, **10**, 1446.

reaction should be relatively easy for cobalt in the low co-ordination number of four.[12] Chloride exchange at the similar complexes $[Co(ethylenethiourea)_2Cl_2]$ and $[Co(p\text{-toluidine})_2Cl_2]$ has, perhaps not surprisingly, been found to be too fast to follow by classical ^{36}Cl-tracer techniques.[13] Equilibrium positions for phosphine loss from $[CoX_2(PR_3)_2]$ and $[CoX_3(PR_3)]^-$ have been determined in the co-ordinating solvents acetonitrile and methylene chloride. There is considerable phosphine separation in methylene chloride, and in acetonitrile $[CoX_2(PR_3)_2]$ is almost completely dissociated into CoX_2 and free phosphine. Phosphine exchange with these complexes might therefore be expected to take place by a dissociative mechanism.[14]

Redistribution reactions of the type

$$Ni(L^1L^2)_2 + Ni(L^1L^3)_2 \rightleftharpoons 2\,Ni(L^1L^3)(L^1L^2)$$

have been studied for *N*-t-butylsalicylaldiminonickel(II) or *N*-isopropyltrifluoroacetyliminonickel(II) with *N*-isopropylacetyliminonickel(II) in tetrachloroethylene. The kinetic pattern corresponds to reversible second-order processes, with activation parameters in the ranges $64 < \Delta E^{\ddagger} < 89$ kJ mol^{-1} ($15 < \Delta E^{\ddagger} < 21$ kcal mol^{-1}) and $-150 < \Delta S^{\ddagger} < -80$ JK^{-1} mol^{-1} ($-36 < \Delta S^{\ddagger} < -19$ cal deg^{-1} mol^{-1}). The rate laws and activation parameters are all consistent with associative mechanisms.[15] Ligand redistribution at $[Be(acac)_2]$ occurs by parallel dissociative and associative pathways. The relative importance of these two paths depends on the solvent. In chloroform or methylene chloride the dissociative route is of negligible importance, but in tetrahydrofuran the associative route accounts for about three-quarters of the redistribution reaction.[16]

The steric course of substitution at tetrahedral transition-metal centres can only be followed if optical isomers of asymmetric complexes $ML^1L^2L^3L^4$ can be separated. This is very difficult since tetrahedral complexes of cations tend to be labile. A recent study of the stereochemical course of reaction at complexes of the type $[Co(CO)(NO)(h^5\text{-}C_5H_5)(PPh_3)]$ or $[Fe(CO)(I)(h^5\text{-}C_5H_5)(PPh_3)]$ has been presented as an investigation of the stereochemistry of substitution at tetrahedral centres. These complexes are certainly relatively inert to substitution and thus convenient for study; it is much less certain that they can be considered typical tetrahedral complexes.[17]

2 Square-planar Complexes

Kinetics and mechanisms of substitution at d^8 centres have been the subject of a general and extensive review.[18]

[12] R. E. Gentzler, T. R. Stengle, and C. H. Langford, *Chem. Comm.*, 1970, 1257.
[13] A. M. Elatrash and M. E. Sobeir, *Z. phys. Chem.* (*Frankfurt*), 1970, **69**, 305.
[14] L. Sestili, C. Furlani, and G. Festuccia, *Inorg. Chim. Acta*, 1970, **4**, 542.
[15] J. C. Lockhart and W. J. Mossop, *Chem. Comm.*, 1971, 61.
[16] A. Barabás, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 775.
[17] H. Brunner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 249.
[18] L. Cattalini in 'Progress in Inorganic Chemistry', ed. J. O. Edwards, Wiley, New York, 1970, vol. 13, p. 263.

Platinum(II).—*General.* The rate law common to almost all substitution reactions of square-planar complexes is

$$-\mathrm{d[complex]}/\mathrm{d}t = (k_1 + k_2[\mathrm{Y}])\,[\mathrm{complex}] \qquad (1)$$

where Y is the incoming nucleophile. The k_2 term in this rate law is ascribed to an associative process in which the incoming group Y is bonded to platinum in the transition state. In several systems there is kinetic evidence that the (five-co-ordinate) species formed by Y bonding to the platinum atom of the starting complex has a significant lifetime, in other words it is an intermediate, rather than a transition state. A recently reported example of this occurs in the reaction of *trans*-[PtCl(mesityl)(PEt_3)$_2$] with pyridine in methanol.[19] The most likely conditions for detecting and isolating such a five-co-ordinate intermediate are displacement of a reluctant leaving group, such as a nitro-ligand, by an incoming group with a high affinity for platinum(II), for example iodide or thiourea. However, in the reactions of [Pt(NO_2)(dien)]$^+$ with iodide or with thiourea there is not even any kinetic evidence for a non-transient five-co-ordinate intermediate.[20] The possibility and consequences of pseudorotation in five-co-ordinate intermediates in substitutions at platinum(II) have been reviewed.[21]

Solvent Effects. The rate of catalysed isomerization of platinum(II) complexes in an inert solvent such as cyclohexane is relatively fast, but is reduced by adding a polar solvent, for example acetonitrile, nitromethane, or methanol. The isomerization rate is related to the reciprocal concentration of the added polar solvent. When a polar solvent is present the rate is reduced since the catalyst has now to displace a molecule of solvent from the platinum(II) before it can bond to the metal and effect the isomerization. A detailed study of the kinetics shows that, as might be expected, only one solvent molecule need be displaced; what is surprising is that the intermediate resulting from the loss of this one molecule of polar solvent appears to be identical with the analogous 'intermediate' for catalysed isomerization in cyclohexane. In other words, in the cyclohexane–polar solvent mixtures the platinum(II) complexes have only one molecule of solvent associated with each complex molecule (except in the presence of methanol, where solvation by two solvent molecules seems likely). Moreover it is thence implied that the catalyst molecule has to displace this one solvent molecule rather than take the more obvious route of approaching the platinum from the opposite and free-of-associated-solvent side of the complex.[22] Although this kinetic study is restricted to catalysed isomerization it obviously has great relevance to substitution at platinum(II) complexes in general.

Other reactions in which solvent effects on kinetics have been studied

[19] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Soc. Peloritana Sci. Fis. Mat. Natur.*, 1968, **14**, 341 (*Chem. Abs.*, 1971, **74**, 35 109x).
[20] P. Haake, S. C. Chan, and V. Jonas, *Inorg. Chem.*, 1970, **9**, 1925.
[21] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266.
[22] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 5243.

include those of *trans*-$[Pt(Ph)(X)(SeEt_2)_2]$ in methanol and dimethylformamide [23] and of *trans*-$[PtCl_2(py)_2]$ in aqueous (H_2O and D_2O) dimethyl sulphoxide.[24] In the latter case the importance of solvation at the leaving group in determining reactivity is stressed.

Hydrolysis and Anation. Rates of hydrolysis of $[Pt(NO_2)_4]^{2-}$ and of $[PtCl_3(NO_2)]^{2-}$ vary with acid concentration. Rates increase as the acid concentration increases, up to concentrations of 8M-H_2SO_4 or 11M-$HClO_4$, and then decrease. The initial increase of rate with increasing acid concentration is presumably due to protonation of the nitro-ligands. The difference in rates between hydrolyses in sulphuric and in perchloric acid of the same concentration is ascribed to interaction of the respective anions with the leaving nitrosonium group. Rates of hydrolysis in basic solution vary only slightly with pOH, which is the normal behaviour for platinum(II) complexes; there is no possibility of an S_N1CB mechanism for these complexes.[25] Aquation rates for the complexes $[Pt(NH_3)_2Br_2]$ and $[Pt(NH_3)_2I_2]$ have been reported. For these complexes and the chloro-analogue rates decrease in the order chloride > bromide > iodide, which order of lability parallels the platinum(II)—halide bond strengths.[26] Kinetics both of aquation [27] and of chloride anation [28] of several aquo-chloro-platinum(II) complexes, and of aquation and bromide anation of analogous aquo-bromo-platinum(II) complexes,[29] have been described; rate laws, rate constants, and activation parameters are reported.

Ligand Exchange. The rate law for chloride exchange at $[Pt(dien)Cl]^+$ is of the usual form:

$$\text{rate} = (k_1 + k_2[Cl^-])\,[Pt(dien)Cl^+]$$

At 25 °C, and an ionic strength of 0.1 mol l^{-1}, $k_1 = 8.74 \times 10^{-5}$ s^{-1} and $k_2 = 4.23 \times 10^{-4}$ l mol^{-1} s^{-1}. Activation parameters for the k_1 path are $\Delta H^{\ddagger} = 19.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -12.8$ cal deg^{-1} mol^{-1}, and for the k_2 path $\Delta H^{\ddagger} = 20.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.2$ cal deg^{-1} mol^{-1}. These new kinetic parameters,[30] unlike earlier values, which may have been in error owing to heterogeneous catalysis of the chloride exchange by silver chloride (precipitated in the radiochloride assay method used), correlate well with those for other reactions of the general pattern

$$[Pt(dien)X]^+ + Y^- \longrightarrow [Pt(dien)Y]^+ + X^-$$

[23] S. Sergi, R. Pietropaolo, and F. Faraone, *Ricerca sci.*, 1969, **39**, 592 (*Chem. Abs.*, 1970 73, 39 108y).
[24] R. N. Collins and D. A. Johnson, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1861.
[25] D. Humphreys and P. J. Staples, *J. Chem. Soc.* (*A*), 1970, 2708.
[26] Yu. A. Makashev, F. Ya. Kul'ba, R. A. Zlotnikova, and A. A. Korableva, *Russ. J. Inorg. Chem.*, 1970, **15**, 1716.
[27] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1527.
[28] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1341.
[29] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 2546, 2557.
[30] J. R. Paxson, U.S. Atomic Energy Commission, Report IS-T-403, 1970 (*Chem. Abs.*, 1971, **75**, 122 736p).

where X and Y are from the group chloride, bromide, and iodide.[31] A kinetic study of bromide exchange at the Zeise's salt analogue $[Pt(C_2H_4)Br_3]^-$ reveals that the three bromides are not equally labile; the activation energy for bromide exchange is about 14 kcal mol^{-1}.[32]

Exchange of ethylene with $[PtCl(acac)(C_2H_4)]$ has been followed by ^1H n.m.r. spectroscopy. The reaction is first-order in complex and in free ethylene, and rates are not solvent-dependent, though the reaction was only studied in poor solvents such as chloroform and benzene. The activation energy is low, only 2.7 kcal mol^{-1}, and the activation entropy is − 36 cal deg^{-1} mol^{-1}. Exchange *via* a five-co-ordinate intermediate is the suggested mechanism.[33]

Leaving Groups. In this section we mention references in which interest centres on the nature of the leaving group, and in the following section studies whose main interest lies in the nature of the entering nucleophile are reported.

Rates of displacement of thioethers from $[Pt(bipy)Cl(R^2SR^1)]^+$ by a range of incoming ligands depend strongly both on the nature of R^2SR^1 and on the nature of the incoming ligand.[34] The authors suggest that the highest maximum in the profile of energy plotted against reaction co-ordinate lies between the five-co-ordinated intermediate resulting from the incoming ligand bonding to the platinum and the products. In other words, there is an intermediate of real if transient existence in this reaction, as in the reaction of *trans*-$[Pt(mesityl)(PEt_3)_2Cl]$ with pyridine mentioned briefly earlier.[19] The kinetic behaviour of another leaving group containing a Group VI ligating atom has been investigated in the reactions of *trans*-$[Pt(Ph)X(SeEt_2)_2]$ with nucleophiles in methanol and in dimethylformamide.[23]

The kinetic behaviour of $[PtCl_3L]^-$ with bipyridyl is different when L = the unsaturated derivatives $[allyl\text{-}NH_3]^+$, $[allyl\text{-}PEt_3]^+$, $[allyl\text{-}SO_3]^-$, or $[pent\text{-}4\text{-}enyl\text{-}NH_3]^+$ from when L = ethylene. For the former four compounds the observed first-order rate constant (k_{obs}) can be expressed in terms of chloride-ion and bipyridyl concentration, thus:

$$1/k_{obs} = k_1 + k_2[Cl^-]/[bipy]$$

The suggested mechanism here is slow formation of a solvento (solv) species $[Pt(L)(solv)Cl_2]$ with subsequent slow displacement of L by bipyridyl.[35] For L = ethylene there is evidence for a labile intermediate $[Pt(C_2H_4)(bipy)Cl]^+$, but not, in acidic aqueous methanol, for a solvento-intermediate.[36]

[31] J. R. Paxson and D. S. Martin, *Inorg. Chem.*, 1971, **10**, 1551.
[32] A. A. Grinberg and M. A. Kuz'mina, *Radiokhimiya*, 1970, **12**, 496 (*Chem. Abs.*, 1971, **74**, 16 096z).
[33] C. E. Holloway and J. Fogelman, *Canad. J. Chem.*, 1970, **48**, 3802.
[34] L. Cattalini, G. Marangoni, S. Degetto, and M. Brunelli, *Inorg. Chem.*, 1971, **10**, 1545.
[35] R. Pietropaolo, P. Uguagliati, M. Graziani, and U. Belluco, *Inorg. Chim. Acta*, 1970, **4**, 637.
[36] P. Uguagliati, U. Belluco, U. Croatto, and R. Pietropaolo, *J. Amer. Chem. Soc.*, 1967, **89**, 1336.

Rates of displacement of amino-acids (L) from *trans*-$[Pt(tu)_2L_2]$ by thiourea (tu) decrease from L = an α-amino acid to L = β-, γ-, and so on.[37] Reaction of *trans*-$[Pt(PEt_3)_2(mesityl)(SnCl_3)]$ with nucleophiles, for example pyridine or its dimethyl derivatives, results in formation of *trans*-$[Pt(PEt_3)_2(mesityl)Cl]$ plus tin(II) chloride. The rate law, the lack of direct substitution products, and steric considerations all indicate that reaction proceeds by attack of the nucleophile at the tin, and thus that this is not direct substitution of $-SnCl_3$ by incoming ligand at platinum.[38]

Entering Groups. In all these examples the leaving group is chloride while the entering groups are a variety of nitrogen- and sulphur-bonding ligands. Reaction of *trans*-$[Pt(py)_2Cl_2]$ with 4,4′-disubstituted diphenyl sulphides in methanol follows the usual two-term rate law. Values of k_2 [equation (1)] correlate with Hammett σ constants for the respective substituents; the extreme case of the 4,4′-dinitrodiphenyl sulphide fits the k_2 *vs.* σ graph qualitatively in that this ligand does not attack *trans*-$[Pt(py)_2Cl_2]$, and an extrapolation of the k_2 *vs.* σ graph for other substituents does suggest an extremely small value of k_2 for the 4,4′-dinitro-compound. The kinetic results for these reactions suggest that bond-making to the incoming ligand provides the driving force.[39] A kinetic study of reactions of $[PtCl_4]^{2-}$ with a variety of amines, both aliphatic, for example hexamethylenediamine or benzylamine, and heterocyclic, for example piperidine or piperazine, provides a routine extension of earlier work on reaction of $[PtCl_4]^{2-}$, and of $[PtBr_4]^{2-}$, with simple amines.[40] The observation that the displacement of chloride from $[Pt(dien)Cl]^+$ by acetonitrile is much slower (the reader is referred in a footnote to values of k_1, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ which are 'unpublished data') than that by pyridine is used to predict that cyanopyridines are likely to co-ordinate to platinum(II) by the pyridine nitrogen rather than the cyano-nitrogen when $[Pt(dien)Cl]^+$ reacts with cyanopyridines.[41]

Activation enthalpies for reaction of unidentate amines with $[Pt(bipy)Cl_2]$ in methanol lie between 15 and 17 kcal mol^{-1}; for bidentate amines the range is 11—12 kcal mol^{-1}. The corresponding activation entropies are − 12 to − 17 cal deg^{-1} mol^{-1} for unidentate amines, − 27 to − 28 for bidentate. The explanation of these differences is that the transition state for reaction with a bidentate amine is thought to be more compact and to be more strongly bonded. Anchoring of the other end of the amine, presumably by hydrogen bonding to one of the chlorides, is suggested.[42]

[37] L. M. Volshtein and L. F. Krylova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1276.
[38] M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Soc. Peloritana Sci. Fis. Mat. Natur.*, 1968, **14**, 325 (*Chem. Abs.*, 1971, **74**, 35 123x).
[39] J. R. Gaylor and C. V. Senoff, *Canad. J. Chem.*, 1971, **49**, 2390.
[40] Yu. N. Kukushkin and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, 1970, **15**, 1269.
[41] S. C. Chan and F. T. Wong, *Austral. J. Chem.*, 1971, **24**, 1519.
[42] L. Baracco, L. Cattalini, J. S. Coe, and E. Rotondo, *J. Chem. Soc.* (*A*), 1971, *1800*.

Kinetics of intramolecular ring closure have been studied for two series of complexes, $[Pt(glycinate)_2X_2]^{2-}$ [43] and *cis*- and *trans*-$[Pt(aminoethanol)_2Cl_2]$.[44] In both cases the reaction studied is

$$[Pt(LL)_2X_2]^{n-} \longrightarrow [Pt(LL)_2]^{(n-2)-} + 2X^-$$

In the aminoethanol complexes the rates of closure of the first and second chelate rings are similar for the *cis*-complex, but for the *trans*-complex there is a large difference between the two ring-closure rates and it is possible to isolate the intermediate *trans*-[Pt(aminoethanol)(aminoethoxide)Cl].

The rate law for reaction of the bridged diplatinum(II) complex $[Pt_2Br_6]^{2-}$ with alkenes in acetone solution is

$$-\mathrm{d}[Pt_2Br_6^{2-}]/\mathrm{d}t = \{k_1 + k_2(\text{alkene})\}\,[Pt_2Br_6^{2-}] \qquad (2)$$

which is the usual form for square-planar substitution [*cf.* equation (1)]. In reactions with the unidentate alkenes styrene, hex-1-ene, cyclohexene, and allyl alcohol, symmetrical cleavage of the bridged complex occurs, but in the reaction with cyclo-octa-1,5-diene there is unsymmetrical cleavage to produce $[Pt(cod)Br_2]$ and $[PtBr_4]^{2-}$. The rate-determining step is cleavage of a bromide bridge by nucleophilic attack of solvent, corresponding to the k_1 term of rate law (2), or of alkene, k_2 term of (2), at a platinum atom; cleavage of the second bromide bridge is fast.[45] This bridged complex $[Pt_2Br_6]^{2-}$ reacts similarly, though more rapidly, with ethylenediamine to produce $[Br_3Pt\cdot en\cdot PtBr_3]^{2-}$; there is a precedent for such an ethylenediamine-bridged diplatinum(II) complex.[46] In the reaction of $[Pt_2Br_6]^{2-}$ with ethylenediamine the rates of cleavage of the first and second bromide bridges are comparable, and a singly bridged intermediate has been detected.[47]

Effects of Non-reacting Ligands. The two important effects of non-reacting ligands on the reactivity of platinum(II), as of other square-planar complexes are the *trans* effect and steric effects of bulky substituents. The latter lead to the so-called pseudo-octahedral behaviour wherein associative attack by the incoming nucleophile is prevented by the bulk of the non-reacting ligand. This results in a purely dissociative mechanism and a rate law

$$-\mathrm{d}[\text{complex}]/\mathrm{d}t = k_1[\text{complex}]$$

reminiscent of octahedral complexes of the classical cobalt(III)-amine-halide type.

[43] L. M. Volshtein and T. R. Lastushkina, *Russ. J. Inorg. Chem.*, 1970, **15**, 1267.
[44] Yu. N. Kukushkin, V. B. Ukraintsev, and A. I. Mokhov, *Russ. J. Inorg. Chem.*, 1971, **16**, 879.
[45] M. M. Muir and E. M. Cancio, *Inorg. Chim. Acta*, 1970, **4**, 565.
[46] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1959, 3089.
[47] M. M. Muir and E. M. Cancio, *Inorg. Chim. Acta*, 1970, **4**, 568.

Investigation of rates of reaction of $[PtCl_3L]^-$, where L = ethylene or DMSO, with ammonia or methylamine, has confirmed an earlier suggestion that ethylene and DMSO exert similar *trans* influences.[48] The *trans* effect is also involved in determining the different kinetic patterns for chelate-ring closure in the *cis*- and *trans*-isomers of $[Pt(aminoethanol)_2Cl_2]$.[44]

Activation parameters have been determined for the reaction of $[Pt(LL)(SCN)_2]$ with thiourea (tu) in DMF solution, to give successively $[Pt(LL)(SCN)(tu)]^+$ and $[Pt(LL)(tu)_2]^{2+}$. Here LL = ethylenediamine or one of its *N*-alkyl derivatives; the object of the investigation was to study the steric effects of the alkyl substituents on reactivity through their effects on the activation parameters.[49] Whereas there have been a large number of studies of similar reactions in which the effects of bulky substituents in non-leaving ligands on rate laws and rate constants have been assessed, determination of activation parameters for such processes is rarely attempted.[50]

Photochemistry. Photodecomposition of $[Pt(PPh_3)_2(ox)]$ produces carbon dioxide and results in reduction of the platinum(II) to platinum(0). In ethanol the platinum(0) product is the dimer $[Pt_2(PPh_3)_4]$, in the presence of an excess of triphenylphosphine the product is $[Pt(PPh_3)_4]$, and in the presence of an alkyne it is $[Pt(PPh_3)_2(alkyne)]$. In all cases the first step is photochemical generation of radical ions:[51]

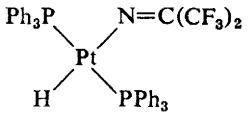
$$[(Ph_3P)_2Pt(ox)] \xrightarrow{h\nu} [(Ph_3P)_2Pt]^{+\bullet} + [C_2O_4]^{-\bullet}$$

Several examples are known of the effectiveness of organic compounds sensitizing photochemical reactions of cobalt(III) and of chromium(III) complexes, and biacetyl is known to photosensitize the aquation of $[PtCl_4]^{2-}$. Now the first example of photosensitization of substitution at platinum(II) by an inorganic species has been reported: $[Ru(bipy)_3]^{2+}$ sensitizes photoaquation of the $[PtCl_4]^{2-}$ anion.[52]

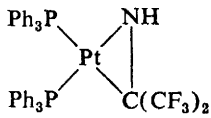
Isomerization. Kinetics of phosphine-catalysed isomerization of square-planar complexes have been interpreted in terms of formation of a five-co-ordinated intermediate of sufficient lifetime to permit internal rearrangement, analogous to pseudorotation at phosphorus centres.[53] It has now been demonstrated that catalysis of isomerization of compounds *cis*-$[PtL^2_2X_2]$ by ligands L^1 results in no exchange of L^2 and L^1. This implies that any five-co-ordinate intermediate cannot be of regular geometry since pseudorotation would make L^2 and L^1 equivalent at some stage. Hence a distorted five-co-ordinate intermediate, perhaps with a long Pt—L^1 bond,

[48] Yu. N. Kukushkin and Yu. E. Vyaz'menskii, *Russ. J. Inorg. Chem.*, 1970, **15**, 1713.
[49] R. J. Mureinik and W. Robb, *Inorg. Chim. Acta*, 1971, **5**, 333.
[50] See, *e.g.*, pp. 147—148 of vol. 1 of this Specialist Periodical Report for numerous illustrations.
[51] D. M. Blake and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5359.
[52] J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, 1971, **93**, 1800.
[53] P. Haake and R. M. Pfeiffer, *Chem. Comm.*, 1969, 1330.

is suggested; there is supporting evidence from recent *X*-ray structural determinations of five-co-ordinate d^8 compounds for such a non-regular geometry. The activation enthalpies for these catalysed isomerizations are considerably lower than for ligand-exchange reactions, so the distorted five-co-ordinate intermediate in the isomerization reactions may have a square-pyramidal structure with the long Pt—L^1 bond normal to the plane of the $[PtL_2X_2]$.[54] The application of kinetic studies on these phosphine-catalysed isomerizations to determining solvation numbers for square-planar platinum(II) complexes has already been discussed.[22] Phosphine-catalysed isomerization is also the first step in the conversion of (2) into (3).[55]



(2)



(3)

The rate of the (uncatalysed) isomerization of *cis*-$[Pt(PEt_3)_2(o\text{-tolyl})Cl]$ to its *trans*-isomer is decreased by adding chloride ion, which indicates a mechanism involving reversible loss of chloride ion followed by stereochemical reorganization in the three-co-ordinate intermediate.[56] Theoretical calculations [57] support an earlier suggestion [58] that photochemical *cis–trans* isomerization of $[Pt(gly)_2]$ takes place by a torsional-twist mechanism, whereas thermal isomerization has an intermolecular mechanism.

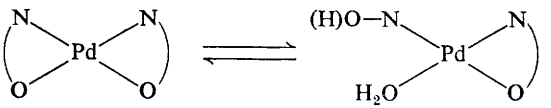
The final paragraph of a paper on the preparative and structural chemistry of amino-acid–alkene mixed complexes of platinum(II) reports some qualitative observations on racemization rates of complexes of formula [Pt(alkene)(L-prolinate)Cl]. These rates correlate with platinum—olefin bond strengths.[59] MO calculations of barriers to internal rotation in platinum–alkene and –alkyne complexes have been made.[60]

Carbonyl Insertion. The reaction of $PtClEt(CO)(AsPh_3)$ with $AsPh_3$ to produce $PtCl(COEt)(AsPh_3)_2$ is ethyl migration rather than simple substitution. Nevertheless it is a reaction worth mentioning here since the kinetic results – the rate law, activation parameters, and dependence of rate on solvent – indicate that the migration takes place without any assistance either from the solvent or from the incoming ligand.[61] This is surprising, both in the context of substitution reactions of square-planar

[54] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 4996.
[55] B. Cetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215.
[56] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc.* (*A*), 1971, 1877.
[57] F. S. Richardson, D. D. Shillady, and A. Waldrop, *Inorg. Chim. Acta*, 1971, **5**, 279.
[58] V. Balzani, V. Carassiti, F. Scandola, and L. Moggi, *Inorg. Chem.*, 1965, **4**, 1243.
[59] K. Konya, J. Fujita, and K. Nakamoto, *Inorg. Chem.*, 1971, **10**, 1699.
[60] K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1970, **92**, 5110.
[61] R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 854.

complexes and in the context of carbonyl insertion (alkyl migration) reactions of other organometallic compounds.

Palladium(II).—Rate constants for aquation of *trans*-$[Pd(NH_3)_2Cl_2]$, *trans*-$[Pd(NH_3)_2(OH_2)Cl]^+$, and *trans*-$[Pd(NH_3)_2(OH_2)(NO_2)]^+$ in methanol–, acetone–, dioxan–, and dimethylformamide–water mixtures correlate linearly, though with only three points to define each line, with the function $(D - 1)/(2D + 1)$ of the dielectric constants (D) of the respective solvent mixtures for each pair of solvents. The slopes of these linear plots are very different for each organic co-solvent. An associative mechanism is assumed to operate since in all cases the activation entropies are large and negative.[62] Aquation of $[Pd(NO_2)_4]^{2-}$ is subject to acid catalysis but not, as would be expected, to base catalysis.[25] The mechanism of aquation of the *cis*- and *trans*-isomers of $[Pd(gly)_2]$ involves a fast pre-equilibrium:



followed by rate-determining fission of the palladium—nitrogen bond to the unidentate glycine ligand.[63] Reactions of amines with $[Pd(Ph{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}Ph)X_2]$ in dimethoxyethane follow a second-order rate law. Logarithms of second-order rate constants correlate linearly with pK_a values of the respective incoming amines for each ligand X, which is Cl, Br, I, SCN, or N_3. In contrast with the $[Pd(gly)_2]$ aquation mentioned above, here the rate-determining step is opening of the palladium–dithioether chelate ring.[64] Kinetics of reactions of $[PdCl_4]^{2-}$ with ammonia have been investigated. The replacement of the first chloride to give $[Pd(NH_3)Cl_3]^-$ follows the usual two-term rate law [equation (1)].[65] The reaction of $[PdCl_4]^{2-}$ with allyl alcohol has as its first stage the rapidly established pre-equilibrium:

$$[PdCl_4]^{2-} + OH_2 \rightleftharpoons [Pd(OH_2)Cl_3]^- + Cl^-$$

This is followed by a fast reaction with the allyl alcohol. The rate-determining step is a subsequent $\pi \rightarrow \sigma$ allyl process with concomitant hydroxide transfer in an allyl-hydroxo-intermediate.[66] Reactivity trends in solution and in the solid state have been compared for the conversion of $[Pd(en)(enH)X]^{2+}$ in the presence of X^- to $[Pd(en)X_2]$.[67]

[62] V. D. Panasyuk and T. I. Denisova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1422.
[63] J. S. Coe and J. R. Lyons, *J. Chem. Soc.* (*A*), 1971, 829.
[64] L. Cattalini, G. Marangoni, J. S. Coe, M. Vidali, and M. Martelli, *J. Chem. Soc.* (*A*), 1971, 593.
[65] R. A. Reinhardt and W. W. Monk, *Inorg. Chem.*, 1970, **9**, 2026.
[66] R. Pietropaolo, P. Uguagliati, T. Boschi, B. Crociani, and U. Belluco, *J. Catalysis*, 1970, **18**, 338.
[67] D. A. Johnson and W. H. Delphin, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 717.

Rates of isomerization of *trans*-[Pd(gly)$_2$] to the *cis*-isomer have been reported.[63] The effect of ligands *trans* to the sulphur on rates of inversion at sulphur in thioethers complexed to palladium(II) and platinum(II) is that inversion rates increase as the metal—sulphur bond strength decreases. Interaction between electron lone-pairs on sulphur and orbitals on the palladium or platinum has here, as in earlier examples,[68] a large effect on inversion rates.[69] The interconversion of *syn*- and *anti*-isomers of *cis*-dithioether complexes of palladium(II) may take place by inversion at sulphur. Unfortunately one cannot be sure that these reactions are intramolecular since with palladium complexes, in contrast to platinum complexes, there is no metal–proton coupling whose persistence or otherwise could be observed in the n.m.r. spectra of the complexes.[70] Both inversion and proton exchange at nitrogen in palladium(II) complexes of aliphatic amines occur through a common deprotonated intermediate. An estimated absolute rate constant for inversion at nitrogen bonded to palladium(II) is between 1 and 8 $\times$ 10^6 s^{-1}.[71]

Gold(III).—Kinetics of reaction of $[AuCl_4]^-$ with pyridine, and of the reverse reaction, $[Au(py)Cl_3]$ plus chloride, in methanol follow the usual two-term rate law [equation (1) on p. 130].[72] A similar kinetic pattern is shown by the forward reactions of the following equilibria, studied in aqueous solution:

$$trans\text{-}[Au(CN)_2Br_2]^- + Cl^- \rightleftharpoons trans\text{-}[Au(CN)_2ClBr]^- + Br^-$$

$$trans\text{-}[Au(CN)ClBr]^- + Cl^- \rightleftharpoons trans\text{-}[Au(CN)_2Cl_2]^- + Br^-$$

Equilibrium constants for these reactions are reported.[73] The reaction of thiomorpholin-3-one (T) with $[AuCl_4]^-$ or $[AuBr_4]^-$ eventually results in reduction of the gold to gold(I), but the initial steps are substitutions:

$$[AuX_4]^- + OH_2 \rightleftharpoons [AuX_3(OH)]^- + H^+ + X^-$$

$$[AuX_3(OH)]^- + T \longrightarrow [AuX_3T] + OH^-$$

$$[AuX_3T] + OH_2 \longrightarrow [AuX_2(OH)T] + H^+ + X^-$$

with reduction occurring at the next step in which $[AuX_2(OH)T]$ reacts with a second molecule of T, giving ultimately $[Au^IXT]$.[74] This reaction scheme is very similar to those reported earlier for reactions of platinum(IV) and palladium(IV) complexes with thiomorpholin-3-one.[75] The activation

[68] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1967, **89**, 4611, 4617.
[69] R. J. Cross, G. J. Smith, and R. Wardle, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 191.
[70] H. A. O. Hill and K. A. Simpson, *J. Chem. Soc.* (*A*), 1970, 3266.
[71] T. P. Pitner and R. B. Martin, *J. Amer. Chem. Soc.*, 1971, **93**, 4400.
[72] B. I. Peshchevitskii, G. I. Shamovskaya, and G. D. Mal'chikov, *Russ. J. Inorg. Chem.*, 1971, **16**, 181.
[73] W. R. Mason, *Inorg. Chem.*, 1970, **9**, 2688.
[74] D. de Filippo, F. Devillanova, and C. Preti, *Inorg. Chim. Acta*, 1971, **5**, 103.
[75] D. de Filippo and C. Preti, *Gazzetta*, 1968, **98**, 64; D. de Filippo and C. Preti, *Inorg. Chim. Acta*, 1969, **3**, 287.

enthalpy for hydrolysis of $[AuCl_4]^-$ here is about 60% of that for hydrolysis of $[PdCl_6]^{2-}$, whereas the reduction steps have similar activation energies for the gold and palladium systems. The azide complex $[Au(N_3)_4]^-$, like $[Pb(N_3)_6]^{2-}$, decomposes in solution in THF or methylene chloride in daylight to give gold(I) [lead(II)] products. The first step is azide to metal charge-transfer, followed by separation of the $[N_3]^0$ radical.[76]

Several examples of ligand exchange at gold(III) in square-planar organometallic derivatives will be found in the appropriate section of Part IV, Chapter 1.

Cobalt(III).—In acetone solution the bis(maleonitriledithiolato)cobalt(III) anion exists as a dimer $[Co(mnt)_2]_2^{2-}$, but kinetics of reaction of this species with triphenyl-phosphine, -arsine, pyridine, or 1,10-phenanthroline show that the reaction sequence involves a rapidly established equilibrium between dimer and monomer, with reaction of the square-planar $[Co(mnt)_2]^-$ monomer with the Group V base as the rate-determining step. This step is a second-order process; the second-order rate constants for reaction with PPh_3, $AsPh_3$, and py correlate with the equilibrium constants for adduct formation between these bases and $[Co(mnt)_2]^-$. The reaction with phen is slightly more complicated owing to the bidentate nature of this ligand. The kinetics correspond to a two-stage process in which formation of a square-pyramidal adduct of $[Co(mnt)_2]^-$ and unidentate phen is followed by concurrent chelate ring formation and the necessary stereochemical reorganization around the cobalt to permit this *cis*-chelation.[77] The mechanisms of ligand-exchange processes of square-planar dithiolen complexes of copper, gold, nickel, palladium, and platinum, as well as of cobalt, have been discussed.[78]

[76] W. Beck and K. Schorpp, *Angew. Chem. Internat. Edn.*, 1970, **9**, 735.
[77] Hon Gee Tsiang and C. H. Langford, *Canad. J. Chem.*, 1970, **48**, 2776.
[78] A. L. Balch, *Inorg. Chem.*, 1971, **10**, 388.

3

Inert Metal Complexes: Co-ordination Numbers Five and Higher

BY J. BURGESS

1 Introduction

This chapter deals with substitution reactions, including aquation, base hydrolysis, formation, and ligand exchange and replacement, and isomerization of inert metal complexes in which the metal has a co-ordination number of five or more. In fact the great majority of the references reported are concerned with octahedral complexes; references to complexes of other co-ordination numbers have been collected together at the end of this chapter (Section 10).

2 Aquation: Cobalt(III) Complexes

Unidentate Leaving Groups.—The complexes *trans*-$[Co(en)_2(N_3)X]^+$, where X = Cl or Br, aquate in acidic solution with complete retention of configuration. The bromide complex aquates slightly more rapidly than the chloride; the activation parameters are equal within experimental uncertainty (Table 1).[1] For the complexes *cis*-$[Co(en)_2(py)X]^{2+}$ aquation is again slightly faster for X = Br than for X = Cl, and this time the difference in rates is reflected in a lower activation enthalpy for the bromo-complex. This activation enthalpy trend parallels the cobalt–halide bond strengths and is thus consistent with a dissociative mechanism for aquation.[2] The kinetics of aquation of *cis*-$[Co(en)_2Br_2]^+$ have been reinvestigated in order to obtain more precise activation parameters. Whereas *cis*-$[Co(en)_2Cl_2]^+$ and *cis*-$[Co(en)_2ClBr]^+$ aquate to 100% *cis*-aquo-products, the *cis*-$[Co(en)_2Br_2]^+$ cation aquates to a mixture of *cis*- and *trans*-products.[3] *cis*-$[Co(en)_2(N_3)Cl]^+$ exhibits similarly unusual behaviour in undergoing 15% steric change on aquation.[1]

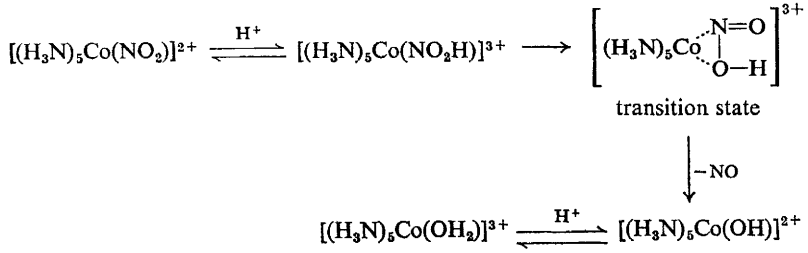
Both *cis*- and *trans*-$[Co(en)_2(NH_3)(PO_4H_3)]^{3+}$ aquate by cobalt–oxygen bond fission,[4] but $[Co(NH_3)_5(AsO_4)]$ has been shown by ^{18}O tracer experiments to aquate by arsenic–oxygen bond fission.[5] $[Co(NH_3)_5(NO_2)]^+$, and

[1] V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1785.
[2] C. Várhelyi and I. Zsakó, *Rev. Roumaine Chim.*, 1971, **16**, 1185.
[3] C. G. Barraclough, R. W. Boschen, W. W. Fee, W. G. Jackson, and P. T. McTigue, *Inorg. Chem.*, 1971, **10**, 1994.
[4] S. F. Lincoln and A. L. Purnell, *Inorg. Chem.*, 1971, **10**, 1254.
[5] T. A. Beech and S. F. Lincoln, *Chem. Comm.*, 1970, 1568.

Table 1 *First-order rate constants and activation parameters for aquation of cobalt(III)–amine–ligand complexes*

Complex	k/s^{-1} (*temp*/°C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Conditions*	*Ref.*
trans-$[Co(en)_2(N_3)Cl]^+$	8.5×10^{-4} (25)	20.7 ± 0.3	− 6 ± 2	$[H^+] = 0.01M$	1
trans-$[Co(en)_2(N_3)Br]^+$	2.6×10^{-4} (25)	20.0 ± 0.5	− 6 ± 2	$[H^+] = 0.01M$	1
cis-$[Co(en)_2(py)Br]^{2+}$	0.43×10^{-4} (50)	23.8 ± 0.4	− 5.1 ± 1.2	$[H^+] = 0.001M$; $\mu = 0.1$ mol l^{-1}	2
cis-$[Co(en)_2Br_2]^+$	9.3×10^{-4} (25)	21.3 ± 0.3	− 1.0 ± 1.0	0.1M-HNO_3 or 0.01M-$HClO_4$	3
cis-$[Co(en)_2(NH_3)(PO_4H_3)]^{3+}$	1.7×10^{-4} (70)	27.1 ± 0.8	− 2.8 ± 2.4	3.7M-$HClO_4$	4
trans-$[Co(en)_2(NH_3)(PO_4H_3)]^{3+}$	1.65×10^{-4} (70)	27.0 ± 0.3	− 2.6 ± 0.8	3.7M-$HClO_4$	4
$[Co(NH_3)_5(AsO_4H)]^+$	2.8×10^{-6} (22)	—	—	2.58 < pH < 4.96;	5
$[Co(NH_3)_5(AsO_4H_2)]^{2+}$	4.2×10^{-4} (22)	—	—	$\mu = 1.0$ mol l^{-1} ($NaClO_4$)	5
$[Co(NH_3)_5(proline)]^{3+}$	0.28×10^{-6} (55)	—	—		7
$[Co(NH_3)_5(anthranilic\ acid)]^{3+}$	0.05×10^{-6} (55)	—	—	$\mu = 1.0$ mol l^{-1};	7
$[Co(NH_3)_5(benzoic\ acid)]^{3+}$	1.0×10^{-6} (55)	—	—	all k values for the non-acid-catalysed path	7
$[Co(NH_3)_5(CH_2ClCO_2H)]$	0.37×10^{-6} (55)	—	—		7

its rhodium and iridum analogues, are hydrolysed in strong acid by a mechanism which involves loss of NO^+:



and does not involve participation of incoming water in the transition state. It has not proved possible to determine whether there is participation of incoming water in the transition states for aquation of the linkage isomers $[M(NH_3)_5(ONO)]^{2+}$, where M = Co, Rh, or Ir. However, the activation enthalpies for aquation of these three complexes are all equal within experimental uncertainty, which suggests the aquation involves nitrogen–oxygen rather than metal–oxygen bond breaking.[6] Rate constants for aquation of a series of aliphatic and aromatic amino-acid complexes $[Co(NH_3)_5(LH)]^{3+}$ have been reported. In a few cases rate constants for the reverse anation are known and hence equilibrium constants (K_{eqm}) for the displacement of amino-acid ligand by water can be calculated. Logarithms of aquation rates correlate with logarithms of K_{eqm}; the slope of the best straight line is 0.6. The difference between this slope and the slope of 1.0 for earlier free energy plots may be due to greater solvent assistance in aquation of the amino-acid complexes or to the effect of the charged NH_3^+ group on outer-sphere complex formation.[7]

On heating in perchloric acid solution, the complex $[Co(NH_3)(OH_2)_5]^{3+}$ disproportionates. With the $[Co(OH_2)_6]^{3+}$ produced being reduced by water, the overall reaction is

$$8\,[Co(NH_3)(OH_2)_5]^{3+} + 2\,H_2O = 4\,[Co(NH_3)_2(OH_2)_4]^{3+} + 4\,[Co(OH_2)_6]^{2+} + 4H^+ + O_2$$

The few preliminary kinetic results suggest that this is a second-order reaction.[8]

Recent examples of investigations of kinetics of aquation of dioximato-complexes $[Co(LLH)_2X_2)]^-$ include those of anions with LLH_2 = $dmgH_2$ and X = NO_2,[9] NCS,[10] or NCSe,[11] and with LLH_2 = 1,2-cyclopentadione

[6] B. E. Crossland and P. J. Staples, *J. Chem. Soc.* (*A*), 1971, 2853.
[7] T. Murakami, K. Ogino, H. Kobayashi, H. Yamazaki, and K. Saito, *Bull. Chem. Soc. Japan*, 1971, **44**, 120.
[8] J. D. White, J. C. Sullivan, and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 4733.
[9] C. Várhelyi, I. Zsakó, and Z. Finta, *Studia Univ. Babes-Bolyai, Ser. Chim.*, 1970, **15**, 27 (*Chem. Abs.*, 1971, **75**, 53 831b).
[10] Z. Finta, C. Várhelyi, and I. Zsakó, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3013.
[11] C. Várhelyi, I. Zsakó, and Z. Finta, *Monatsh.*, 1970, **101**, 1013.

dioxime and X = NCSe.[12] Rate constants and activation parameters are compared with earlier results for analogous halide complexes in Table 2.

Table 2 *First-order rate constants and activation parameters for aquation of cobalt(III)–dioxime–halide and –pseudohalide complexes; rate constants at* 50 °C *in aqueous solution*

	10^5 k/s^{-1}	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
$[Co(dmgH)_2Cl_2]^-$	716	24.1	+ 6	10
$[Co(dmgH)_2Br_2]^-$	362	24.4	+ 6	10
$[Co(dmgH)_2I_2]^-$	32.2	25.9	+ 5	10
$[Co(dmgH)_2(NCS)_2]^-$	0.08	32.2	+ 13	10
$[Co(dmgH)_2(NCSe)_2]^-$	0.044	33.0	+ 15	11

The activation energy for aquation of $[Co(LLH)_2(NCSe)_2]^-$ with LLH_2 = 1,2-cyclopentadione dioxime is 31.9 kcal mol^{-1}, which is slightly lower than that for the analogous dimethylglyoxime complex, whose activation energy is 33.0 kcal mol^{-1}.

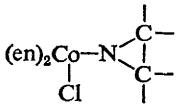
Multidentate Leaving Groups.—The hydrolysis of $[Co(ox)_3]^{3-}$ and of $[Co(ox)_2(OH_2)_2]^-$, which ultimately produces cobalt(II) and carbon dioxide, involves the formation of an intermediate containing a unidentate oxalate ligand previous to the rate-determining step.[13] Free radical intermediates are thought unlikely in the decomposition of these oxalato-complexes, but malonate ion-radicals are thought to be intermediates both in the thermal and photochemical hydrolysis of the $[Co(mal)_3]^{3-}$ anion.[14] Kinetics are reported for a third example of these aquation–redox processes, $[Co(acac)_3]$ in acidic solution.[15]

The aquation of complexes of ethylenediamine and its derivatives is often thought to proceed through intermediates containing unidentate ethylenediamine. To support such hypotheses, several chromium(III) complexes containing unidentate ethylenediamine have been isolated, and their aquation kinetics studied. The preparation of the first cobalt(III) complex containing unidentate ethylenediamine has now been reported.[16] There is kinetic evidence for the formation of an intermediate $[Co(tren)(OH_2)(CO_3H)]^{2+}$, containing unidentate $-CO_3H^-$, in the aquation of $[Co(tren)(CO_3)]^+$ in strongly acidic solutions.[17]

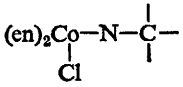
Effects of Non-leaving Ligands.—The usual way of assessing the effect of a unidentate non-leaving ligand L on reactivity of cobalt(III)–amine–halide complexes is to investigate aquation kinetics of compounds $[Co(en)_2LCl]^{n+}$. Recently described examples include complexes of *cis*-geometry,

[12] C. Várhelyi, I. Zsakó, and Z. Finta, *Studia Univ. Babes-Bolyai, Ser. Chim.*, 1970, **15**, 81 (*Chem. Abs.*, 1970, **73**, 102 473f).
[13] Lee Hin-Fat and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1970, 2836, 2842.
[14] R. van Eldik and J. A. van den Berg, *J. S. African Chem. Inst.*, 1969, **22**, 175 (*Chem. Abs.*, 1970, **72**, 125 452s).
[15] D. Banerjea and S. D. Chaudhuri, *J. Inorg. Nuclear Chem.*, 1971, **33**, 515.
[16] M. D. Alexander and C. A. Spillert, *Inorg. Chem.*, 1970, **9**, 2344.
[17] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 1971, **93**, 91.

where L = glycinenitrile or glycinamide,[18] aminoethanol,[19] and aziridine or 2-methylaziridine.[20] The difference in aquation rate constants between these aziridine complexes and analogous complexes containing isopropylamine, which is the primary amine of comparable size, is attributed to differences in the solvation shell immediately adjacent to the complex. The two carbon atoms bonded to the nitrogen in the aziridines (1) take up more space than the one carbon atom bonded to the nitrogen in primary amines (2), thus



(1)



(2)

reducing the amount of solvating water in the proximity of the leaving chloride.[20] The product of aquation of *cis*-$[Co(en)_2(NH_2CH_2CH_2OH)Cl]^{2+}$ in acidic solution (pH < 4; base hydrolysis is significant at higher pH) is not $[Co(en)_2(NH_2CH_2CH_2OH)(OH_2)]^{3+}$ as previously postulated,[21] but $[Co(en)_2(NH_2CH_2CH_2OH)]^{3+}$; the reaction involves intramolecular chelation as well as chloride ion loss. The activation energy for this reaction is *ca.* 2 kcal mol^{-1} less than the activation enthalpies for aquation of $[Co(en)_2LCl]^{2+}$, where L = an exclusively unidentate amine.[19]

A comparison of rate constants and activation entropies for aquation of $[Co(tren)Br_2]^+$ and $[Co(tren)(OH_2)Br]^{2+}$ suggests that the mechanism is closer to pure S_N1 for the aquo-bromo- than for the dibromo-complex.[22] For many years it was thought that the presence of π-acceptor ligands, typically nitro, facilitated substitution *via* an associative mechanism. Aquation kinetics for the π-acceptor ligand containing complexes *trans*-$[Co(cyclam)(NO_2)Cl]^+$ and *trans*-$[Co(cyclam)(CN)Cl]^+$ have been interpreted in terms of a dissociative mechanism, despite the negative activation entropies for reaction of both complexes.[23] First-order rate constants and activation parameters for aquation of cobalt(III) complexes which involve non-leaving ligand effects are collected in Table 3.

The series of aquation rate constants 180 × 10^{-6} s^{-1} (25 °C) for $[Co(NH_2Bu^i)_5Cl]^{2+}$, 37 × 10^{-6} s^{-1} for $[Co(NH_2Me)_5Cl]^{2+}$, and 1.7 × 10^{-6} s^{-1} for $[Co(NH_3)_5Cl]^{2+}$ suggests, despite unfortunate differences in acidities and ionic strengths, a dissociative mechanism with maximum relief of steric strain in going from the initial state to the transition state for the complex containing the most sterically demanding ligand. However, the authors prefer to interpret the rate trend in terms of some associative

[18] S. C. Chan and F. K. Chan, *Austral. J. Chem.*, 1970, **23**, 1175.
[19] V. V. Udovenko, L. G. Reiter, and E. P. Shkurman, *Russ. J. Inorg. Chem.*, 1970, **15**, 1619.
[20] S. C. Chan and C. W. Tsang, *Austral. J. Chem.*, 1971, **24**, 1521.
[21] S. C. Chan and F. Leh, *J. Chem. Soc.* (*A*), 1967, 1730.
[22] W. V. Miller and S. K. Madan, *Inorg. Chem.*, 1970, **9**, 2362.
[23] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225.

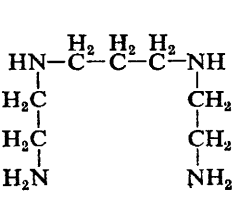
Table 3 *First-order rate constants and activation parameters for aquation of cobalt(III) complexes in which non-leaving ligand effects are of primary interest*

Complex	k/s^{-1} 40 °C	k/s^{-1} 70 °C	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	Conditions	Ref.
trans-$[Co(en)_2(glycinenitrile)Cl]^{2+}$	2.24×10^{-5}		24.1	− 3	pH 7	18
cis-$[Co(en)_2(glycinenitrile)Cl]^{2+}$		4.81×10^{-5}	30.0	+ 9		
cis-$[Co(en)_2(glycinamide)Cl]^{2+}$		2.22×10^{-5}	20.7	− 15		
cis-$[Co(en)_2(NH_2CH_2CH_2OH)Cl]^{2+}$		3.1×10^{-4}	21.7	− 12	0.1M-HNO_3	19
cis-$[Co(en)_2(2\text{-Me-aziridine})Cl]^{2+}$		2.45×10^{-5}	26.8	—	μ = 0.1 mol l^{-1} ($NaNO_3$)	20
cis-$[Co(tren)Br_2]^{+}$	9.54×10^{-2}		15.1	− 15	0.1M-$HClO_4$	24
$[Co(tren)(OH_2)Br]^{2+}$	3×10^{-5} [a]	9×10^{-4} [b]	24.4	− 2	M-$HClO_4$	22
trans-$[Co(cyclam)(NO_2)Cl]^{+}$	2.4×10^{-4} [a]		20.6	− 9	0.01M-HNO_3	23
trans-$[Co(cyclam)(CN)Cl]^{+}$		1.1×10^{-4} [a]	23.5	− 9		
$[Co(NH_3)_5Cl]^{2+}$	1.1×10^{-5}		22.9	− 6	0.01M-HNO_3	26
$[Co(NH_2Me)_5Cl]^{2+}$	2.2×10^{-4}		22.6	− 1		
$[Co(NH_2Et)_5Cl]^{2+}$	9.8×10^{-4}		21.3	− 2		
$[Co(NH_2Pr^n)_5Cl]^{2+}$	1.1×10^{-3}		20.9	− 4		
$[Co(NH_2Bu^n)_5Cl]^{2+}$	1.2×10^{-3}		20.8	− 4		
$[Co(NH_2Bu^i)_5Cl]^{2+}$	1.5×10^{-3}		16.1	− 18		

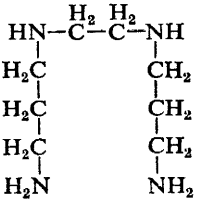
[a] Interpolated; [b] extrapolated from published data.

character to the mechanism.[25] Kinetic parameters for aquation of the series $[Co(NH_2R)_5Cl]^{2+}$ have also been interpreted in terms of an associative mechanism for all R except R = Bu^i; certainly the values for this isobutyl complex are remarkably different from those of the other amine complexes.[26] Unfortunately the precision of the activation parameters may not be too high, for they have been determined only from rate constants at 30 and 40 °C.

There have been several comparisons of reactivity between complexes of various quadridentate ligands, between complexes of various bidentate ligands, and between complexes of quadridentate ligands and their bis-bidentate and tetrakis-unidentate analogues. Rate constants for the non-acid-catalysed path for aquation of $[Co(LLLL)(CO_3)]^+$ vary little with the geometry of the quadridentate ligand, for LLLL = tren or the α- or β-forms of trien; interestingly, the rates of the acid-catalysed aquation path are very sensitive to the nature of LLLL.[17] The particular geometry of the ligands 2,3,2-tet (3) and 3,2,3-tet (4) imposes steric constraints which lead to a

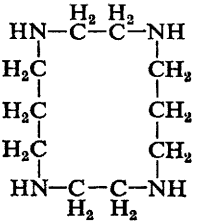


(3)



(4)

marked stereospecificity in the conversion of *trans*-$[Co(tet)(aa)_2]^+$, containing two unidentate amino-acid anions (aaH = glycine, valine, or sarcosine), to *cis*-$[Co(tet)(aa)]^{2+}$, which contains one bidentate amino-acid anion.[27] Aquation of $[Co(LLLL)Cl_2]^+$, where LLLL = racemic or *meso*-5,7,7,12,14,14-hexamethylcyclam, is faster than that of the complex with LLLL = cyclam (5); this is consistent with a dissociative mechanism.[28]



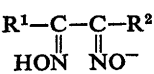
(5)

[24] S. K. Madan and J. Peone, *Inorg. Chem.*, 1967, **6**, 463.
[25] D. A. Buckingham, B. M. Foxman, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 1790.
[26] R. Mitzner, P. Blankenburg, and N. Depkat, *Z. phys. Chem.* (*Leipzig*), 1970, **245**, 260.
[27] G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 1971, **10**, 2170.
[28] W. K. Chau and C. K. Poon, *J. Chem. Soc.* (*A*), 1971, 3087.

The difference in ligand bulk is again the main factor determining the different reactivities of $[Co(LL)_2Cl_2]^+$, $[Co(LL)_2(OH_2)Cl]^{2+}$, and $[Co(LL)_2(NH_3)Cl]^{2+}$, where LL = cyclohexanediamine or ethylenediamine.[29] The difference between rate constants for aquation of *cis*-$[Co(bipy)_2Cl_2]^+$ and *cis*-$[Co(en)_2Cl_2]^+$ must be controlled by electronic rather than by steric effects of the non-leaving ligands, for it is the bulkier bipy ligand whose complex aquates the more slowly. Aquation of *cis*-$[Co(bipy)_2Cl_2]^+$ must be stereospecific since the products, like the starting complex, are only known in the *cis*-geometry, for steric reasons.[30]

Differences in reactivity between quadri-, bi-, and uni-dentate ligand complexes have been described and discussed for several series of complexes. Reactivities of $[Co(LLLL)(CO_3)]^+$, where LLLL = tren or trien, have been compared with those of analogous ethylenediamine-bisammonia complexes.[17] $[Co(tren)X_2]^+$ aquates more rapidly than $[Co(en)_2X_2]^+$ for X = F,[31] similar to that reported for X = Cl or Br. The activation enthalpy for aquation of $[Co(tren)(OH_2)Br]^{2+}$, which is 24.4 kcal mol^{-1}, is equal within experimental uncertainty to that for aquation of $[Co(NH_3)_5Br]^{2+}$, 24 kcal mol^{-1}; here one has OH_2 replaced by NH_3 as well as tren replaced by $(NH_3)_4$.[22] Rate constants for aquation of *trans*-$[Co(NH_3)_4(NO_2)X]^+$, where X = Cl or Br, are greater than for the analogous $(en)_2$ or cyclam (5) complexes.[32] While in all the foregoing examples variation of the nature of the non-leaving ligands has a greater or smaller effect on the *kinetics* of aquation, in the following system such ligand variation leads to a difference in the *products* of aquation. Whereas the vast majority of cobalt(III)–amine–chloride complexes aquate thermally with loss of chloride, the complex *trans*-$[Co(cyclam)(NH_3)Cl]^{2+}$ aquates with replacement of the ammonia ligand by water.[33] General discussion of the effects—steric, geometric, electronic, and nephelauxetic—of non-leaving ligands on reactivity of cobalt(III)–amine–halide complexes can be found in three references.[34]

One other type of complex wherein the effects of non-leaving ligands have been studied is that of the dioximato (6)–cobalt(III) series $[Co(LLH)_2(SO_3H)Cl]^-$ (Table 4). The complex with LLH_2 = methylglyoxime (mgH_2)



(6)

[29] S. C. Chan and F. K. Chan, *Austral. J. Chem.*, 1970, **23**, 1477.
[30] D. M. Palade, T. N. Volokh, G. V. Chudaeva, L. Z. Khavina, and E. A. Chebysheva, *Russ. J. Inorg. Chem.*, 1970, **15**, 1399.
[31] King-Wen Kuo and S. K. Madan, *Inorg. Chem.*, 1971, **10**, 229.
[32] C. K. Poon and H. W. Tong, *J. Chem. Soc.* (*A*), 1971, 2151.
[33] K. S. Mok and C. K. Poon, *Chem. Comm.*, 1971, 1358.
[34] K. B. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1970, **15**, 471; C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, **4**, 123; *J. Amer. Chem. Soc.*, 1970, **92**, 4467.

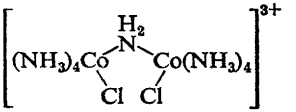
Table 4 *Kinetic parameters for aquation of bisdioxime complexes* $[Co(LLH)_2(SO_3H)(Cl)]^-$, *as their ammonium salts at* 30 °C; *solvent compositions % by weight*

LL[a]	$10^5\ k/s^{-1}$	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
Water				
dmg	7.8	13.0	− 34	36
mg	10.5	13.3	− 33	35
niox	12.0	14.4	− 30	36
40% Dioxan				
mg	6.2	13.5	− 34	35
α-fd	3.6	—	—	36
chdd	6.8	—	—	36
60% Ethanol				
dmg	3.8	—	—	36
mg	5.2	14.0[b]	− 32	35
α-fd	4.1	14.9	− 30	36
chdd	7.6	—	—	36
bd	4.1	16.2[c]	− 25	37

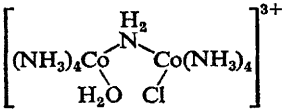
[a] Ligand abbreviations defined in text; [b] 62.0% ethanol; [c] 61.9% ethanol.

aquates slightly more rapidly than the parent complex of this series with LLH_2 = dimethylglyoxime ($dmgH_2$). This observation, and the observed large negative activation entropies, are consistent with an associative aquation mechanism.[35] Reactivities of these complexes have also been compared with those of the anions $[Co(LLH)_2(SO_3H)Cl]^-$ with LLH_2 = α-furil dioxime (α-fdH_2),[36] 1,2-cyclohexanedione dioxime ($chddH_2$),[36] or benzil dioxime (bdH_2).[37] Comparison of the reactivities of $[Co(LLH)_2(NCSe)_2]^-$ with LLH_2 = dimethylglyoxime or 1,2-cyclopentadione dioxime has already been mentioned.[11, 12]

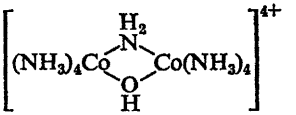
Bridged Dicobalt Complexes.—Rate constants for the forward and reverse reactions of aquation and chloride anation for the equilibrium between (7) and (8) have been determined.[38] The amido-bridged chloro-aquo-complex (8) can aquate further to give the amido-hydroxo-bridged species (9), which



(7)



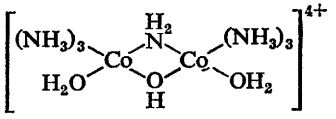
(8)



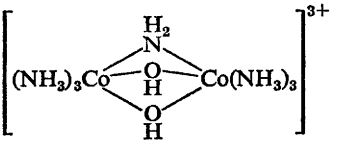
(9)

[35] G. P. Syrtsova and Nguen Zui Lyong, *Russ. J. Inorg. Chem.*, 1970, **15**, 1414.
[36] Nguen Zui Lyong and G. P. Syrtsova, *Russ. J. Inorg. Chem.*, 1971, **16**, 376.
[37] G. P. Syrtsova and Nguen Zui Lyong, *Russ. J. Inorg. Chem.*, 1971, **16**, 213.

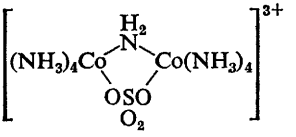
in the presence of chloride ion can undergo the reverse reaction to regenerate (8). Rate laws, rate constants, activation parameters, and the equilibrium constant have been reported for these reactions.[38] The hydroxo-amido-bridged complex (9) aquates, in perchlorate medium, by loss of one ammonia from one cobalt atom and then of one ammonia from the other, rather than by bridge cleavage. Indeed the product (10) undergoes further bridge formation to give (11). Rate constants for the equilibrium between (10) and (11) have been determined, and the relative rates of fission of variously bridged dicobalt complexes discussed.[39] In perchloric acid solution containing sulphate, the hydroxo-amido-bridged complex (9) is in equilibrium with the sulphato-amido-bridged species (12). The amido-bridged species (13) is assumed to be an intermediate in this system.[40]



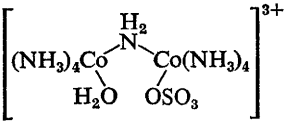
(10)



(11)

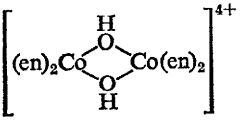


(12)



(13)

Two studies have been made of the hydroxo-bridge cleavage of the di-μ-hydroxobis[bis{ethylenediamine}cobalt(III)] complex (14).[41,42] Certain differences in the interpretation of the results are apparent. In perchloric acid, aquation and bridge cleavage take place; the same seems to happen in nitric acid, but in hydrochloric or sulphuric acids, whose anions are potential ligands, there is some anation as well as aquation and bridge

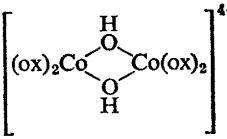


(14)

[38] S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1266.
[39] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1426.
[40] M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 3214.
[41] M. M. deMaine and J. B. Hunt, *Inorg. Chem.*, 1971, **10**, 2106.
[42] A. A. El-Awady and Z. Z. Hugus, *Inorg. Chem.*, 1971, **10**, 1415.

cleavage.[41] It is claimed that the kinetic results, at least for reactions in perchloric and hydrochloric acids, suggest monohydroxo-bridged intermediates.

Acid aquation of the bisoxalato-di-μ-hydroxo-complex (15) involves bridge fission to give dioxalatodiaquocobaltate(III) previous to electron transfer, *en route* to the final cobalt(II) product.[43] Another reaction involving substitution and redox is that of (16) with nitrous acid. The active



(15)

$[(H_3N)_5Co{-}O{-}Co(NH_3)_5]^{5+}$

(16)

reactant is probably NO_2^+ rather than N_2O_3 or NO^+. The NO_2^+ is presumably ion-paired with the highly charged bridged cation. Added chloride or bromide ion affects reaction rates, possibly through formation of chloride or bromide ion pairs of (16).[44]

Kinetic studies of photochemical reactions of bridged dicobalt complexes are discussed in the appropriate section later. Thermal deaquation of solid *cis*-$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3,3H_2O$,[45] though not of *cis*-$[Co(NH_3)_4(OH_2)(SO_4)]^+$ salts,[46] leads to the formation of the sulphate-bridged species *cis*,*cis*-$[(SO_4)(NH_3)_4Co(\mu\text{-}SO_4)Co(NH_3)_4(SO_4)]$, which aquates rapidly in aqueous solution to produce *cis*-$[Co(NH_3)_4(OH_2)(SO_4)]^+$.

Solvent Variation.—Logarithms of rate constants for aquation of *cis*-$[Co(en)_2Cl_2]^+$ correlate linearly with Grunwald–Winstein solvent Y values for the methanol–, ethanol–, acetone–, dioxan–, formic acid–, and acetic acid–water solvent mixtures containing between 0 and 40% by volume non-aqueous component. This result is consistent with a dissociative aquation mechanism. The slope (m) of these logarithms of rate constants against solvent Y values plot is 0.35, which is much less than the m value of 1.00 for the reference organic substrate t-butyl chloride. However, this difference may be ascribed to the considerably smaller solvation requirements of the inorganic leaving moiety $[Co(en)_2Cl]^{2+}$ compared with the organic analogue Me_3C^+.[47] Aquation of $[Co(NH_3)_5Cl]^{2+}$ and of *trans*-$[Co(en)_2Cl_2]^+$ in a similar range of aqueous–organic solvent mixtures has led to m values of + 0.25 and + 0.35, respectively. Indeed, from previously published series of rate constants in various aqueous–organic solvents it is possible to estimate m values for a wide range of cobalt(III)–amine–chloride complexes; these m values lie between 0.23 and 0.36, suggesting that for all

[43] Lee Hin-Fat and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1971, 2589.
[44] M. Green and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 3209.
[45] E. P. Hertzenberg and J. C. Bailar, *Inorg. Chem.*, 1971, **10**, 2371.
[46] E. P. Hertzenberg and J. C. Bailar, *Inorg Chem.*, 1971, **10**, 2377.
[47] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2703

these dissociative aquations there is a similar pattern of dependence of rate constant on solvent composition which can be characterized by an *m* value of around 0.3.

As in organic chemistry where *m* values for bromides are rather lower than for chlorides, for example $m = 0.92$ for t-butyl bromide compared with $m = 1.00$ for t-butyl chloride, *m* values for cobalt(III)–amine–bromide complexes are, at around 0.2, rather lower than for the analogous chlorides.[48] Whereas in this work the effect of solvent structure on reaction rates has been used to gain further insight into reaction mechanisms, the opposite approach has also been used, in a study of aquation of *trans*-$[Co(en)_2Cl_2]^+$ in alcohol–water mixtures, in which variation of rate with solvent composition has been used as a probe of solvent structure variation.[49] Rates of aquation of both *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ have been determined in aqueous acetonitrile ($0 <$ mole fraction MeCN < 0.104). For both complexes aquation rates decrease only slightly as the proportion of acetonitrile increases, with the *cis*-complex slightly more sensitive to solvent variation. The kinetic effects observed here are smaller than those observed in t-butyl alcohol–water solvent mixtures.[50]

Other complexes for whose aquation in mixed aqueous solvents kinetic parameters have been obtained include $[Co(RNH_2)_5Cl]^{2+}$ in aqueous dioxan,[26] and of *cis*-$[Co(NH_2CH_2CH_2OH)(en)_2Cl]^{2+}$ (ref. 19) and several dioximato-complexes $[Co(LLH)_2(SO_3H)Cl]^-$ (refs. 35—37) in several aqueous organic mixed solvents. Activation parameters are collected together in Table 5. As an extension of the dioximato-complex aquation work, one might add that the kinetics of thermal decomposition of some of these complexes have been studied in the solid state.[51]

Solvolysis of *trans*-$[Co(en)_2L_2]^+$, where L = 2-, 3-, or 4-methyl benzoate or 2,3-, 2,4-, 3,4-, or 3,5-dimethyl benzoate, has been studied in acetic acid. Rate constants do not correlate with electronic properties of the ligands, but there is a rough trend with steric factors, particularly in that compounds containing an *o*-methyl substituent in the benzoate ligands react relatively rapidly.[52]

The role of solvation in determining the reactivities of complexes of cobalt(III) and of chromium(III) has been discussed. The main point here is the surprisingly small effects of solvent variation on aquation rates for both series of complexes.[53]

pH Variation.—Variation of aquation rates of cobalt(III) complexes with acid concentration can usually be attributed to equilibrium protonation of

[48] J. Burgess and M. G. Price, *J. Chem. Soc.* (*A*), 1971, 3108.
[49] E. M. Strel'tsova, G. A. Krestov, and N. K. Markova, *Russ. J. Phys. Chem.*, 1970, **44**, 763.
[50] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2351.
[51] I. Zsakó, *Studia Univ. Babes-Bolyai, Ser. Chim.*, 1970, **15**, 113 (*Chem. Abs.*, 1971, **75**, 10 815g).
[52] A. W. Chester, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3398.
[53] C. H. Langford, *Canad. J. Chem.*, 1971, **49**, 1497.

Table 5 *Activation parameters for aquation of cobalt(III) complexes in mixed aqueous solvents (compositions quoted are by weight)*

Compound[a]	*Solvent*	E_a/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref*
cis-$[Co(en)_2(NH_2CH_2CH_2OH)Cl]^{2+}$	Water	22.3	− 12	19
	30% Dioxan	21.1	− 16	
	30% Ethanol	21.4	− 15	
$[Co(mgH)_2(SO_3H)Cl]^-$	Water	13.3	− 33	35
	21.0% Methanol	13.7	− 32	
	42.1% Methanol	13.2	− 33	
	64.5% Methanol	13.6	− 33	
	62.0% Ethanol	14.0	− 32	
	20.0% Dioxan	13.3	− 33	
	40.0% Dioxan	13.5	− 34	
	60.0% Dioxan	13.8	− 33	
$[Co(\alpha\text{-}fdH)_2(SO_3H)Cl]^-$	60.0% Ethanol	14.9	− 30	36
$[Co(bdH)_2(SO_3H)Cl]^-$	64.5% Methanol	14.8	− 29	37
	75.3% Methanol	14.7	− 30	
	84.2% Methanol	14.3	− 30	
	61.9% Ethanol	16.2	− 25	
	72.4% Ethanol	15.7	− 27	
	81.0% Ethanol	15.3	− 29	
	64.2% Isopropanol	15.1	− 29	
	75.0% Isopropanol	14.7	− 31	
	84.0% Isopropanol	16.7	− 25	
	60.0% Dioxan	15.6	− 28	
	70.0% Dioxan	14.5	− 32	
	80.0% Dioxan	14.8	− 32	
$[Co(bdH)_2(SO_3H)Br]^-$	64.5% Methanol	14.8	− 30	
	75.3% Methanol	14.7	− 31	
	84.2% Methanol	13.7	− 33	
	61.9% Ethanol	14.5	− 30	
	72.4% Ethanol	14.1	− 33	
	81.0% Ethanol	13.8	− 34	
	64.2% Isopropanol	13.9	− 33	
	75.0% Isopropanol	13.8	− 33	
	84.0% Isopropanol	13.9	− 33	
	60.0% Dioxan	13.7	− 33	
	70.0% Dioxan	14.3	− 32	
	80.0% Dioxan	14.9	− 30	

[a] Ligand abbreviations: mgH_2 = methylglyoxime, α-fdH_2 = furil dioxime, bdH_2 = benzil dioxime.

ligands, generally leaving ligands, on the metal. Recent examples include aquation of $[Co(NH_3)_5(ONO)]^{2+}$,[6] $[Co(tren)(OH_2)(CO_3)]^+$,[17] $[Co(NH_3)_5(AsO_4)]$,[5] $[Co(ox)_2(OH_2)_2]^-$,[54] and $[Co(tren)F_2]^+$;[31] sometimes it is possible to estimate the pK_a of the co-ordinated ligand from such kinetic results. An example of a similarly caused variation of aquation rate with pH is provided for a bridged dicobalt(III) complex by the cation (14), where protonation is said to occur at the hydroxo-bridges.[42] Complementary to these

[54] I. G. Murgulescu and G. Mincu, *Rev. Roumaine Chim.*, 1971, **16**, 1023.

examples is the pH variation of aquation rates for *cis*-$[Co(tren)(OH_2)Cl]^{2+}$, for here the rate variation arises from the equilibrium between water and hydroxo-ligand forms of the complex.[55]

There is disagreement about the correct interpretation of kinetics of aquation of the (probably *trans*-) $[Co(NH_3)_2(NO_2)_4]^-$ anion. Malik and McAuley [56] assumed that only one nitro-ligand was replaced by water, and interpreted their kinetic results in terms of parallel aquation of unprotonated, monoprotonated, and diprotonated forms of the complex. Zsako, Varhelyi, and Pop [57] have measured both rates of disappearance of the complex and rates of appearance of nitrite ion. They conclude that two nitro-groups are replaced by water, that aquation of the monoprotonated complex is the predominant pathway, and that the observed activation entropy suggests an S_N2ca mechanism of aquation. Interestingly, $[Co(NH_3)_2(OH_2)(NO_2)_3]^0$, the compound corresponding to loss of one nitro ligand, is the product when the ammonium salt of $[Co(NH_3)_2(NO_2)_4]^-$ is passed down an acidic ion-exchange column.[58]

Aquation of amino-acid (LH) complexes of formula $[Co(NH_3)_5(LH)]^{3+}$ follows the rate law

$$-d[Co(NH_3)_5(LH)^{3+}]/dt = \{k + k'[H^+]\}[Co(NH_3)_5(LH)^{3+}]$$

in perchloric acid of concentration 0.05 to 0.5M. This form of rate law is not consistent with equilibrium ligand protonation followed by parallel aquation of unprotonated and protonated complexes, the mechanism applying to the previous examples in this section. Indeed, this pre-equilibrium protonation is not possible here, for the amino-acid ligands are protonated throughout the pH range covered.[7]

Metal Ion Catalysis.—*Mercury*(II). The most commonly encountered catalyst for aquation of cobalt(III) complexes is mercury(II). In aquation of a series of complexes *cis*-$[Co(en)_2LCl]^{2+}$, where L = an alkylpyridine, the mechanism proposed is a rapidly established pre-equilibrium

$$cis\text{-}[Co(en)_2LCl]^{2+} + Hg^{2+} \rightleftharpoons cis\text{-}[Co(en)_2L(ClHg)]^{4+} \quad (1)$$

followed by rate-determining dissociative replacement of ClHg by water. Alkyl substituents in the pyridine ligands are said to affect aquation rates by hindering the approach of the mercury(II) to the chloride ligand.[59] A fairly stable Co—Cl—Hg bonded intermediate is also indicated by the kinetics of mercury(II)-catalysed aquation of *cis*-dichloro-(1,8-diamino-3,6-dithiaoctane)cobalt(III).[60] Whereas spontaneous aquation of *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$, where R = H, Me, Et, Pr^n, or Pr^i, goes more slowly in D_2O

[55] W. V. Miller and S. K. Madan, *Inorg. Chem.*, 1971, **10**, 1250.
[56] M. N. Malik and A. McAuley, *J. Chem. Soc.* (*A*), 1969, 917.
[57] I. Zsakó, C. Várhelyi, and R. Pop, *Russ. J. Inorg. Chem.*, 1971, **16**, 852.
[58] B. Belsot and P. Devrainne, *Compt. rend.*, 1971, **272**, *C*, 1548.
[59] S. C. Chan and S. F. Chan, *Austral. J. Chem.*, 1971, **24**, 2071.
[60] J. H. Worrell and C. R. Fortune, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3571.

than in H_2O, the opposite trend is observed for the mercury(II)-catalysed aquation of these complexes. This is attributed to solvent effects on the pre-equilibrium [*cf.* equation (1) above] between the complex and the mercury(II).[61] Spontaneous aquation of $[Co(NH_3)_5Cl]^{2+}$ decreases in rate as the proportion of organic component in ethanol–water solvent mixtures increases, but the rate of mercury(II)-catalysed aquation increases as the mole fraction of ethanol increases.[48] The observation of 15% steric change during spontaneous aquation of *cis*-$[Co(en)_2(N_3)Cl]^+$ is said to be the first reported example of stereochemical change in aquation of a *cis*-$[Co(en)_2LX]^+$ complex; mercury(II)-catalysed aquation also proceeds with 15% change of stereochemistry.[62]

Mercury(II) is also an effective catalyst for pseudohalide leaving groups, for example thiocyanate. In this connection, recently determined equilibrium data for complex formation between cobalt(III)-thiocyanate complexes and mercury(II) are of relevance.[63]

Alkylcobaloximes and alkylcobalamins are dealkylated by mercury(II) compounds. Activation parameters are consistent with an S_E2 or an S_Ei mechanism; relative reactivities of Hg^{2+} and $HgCl^+$, and effects of substituents on α- and β-carbon atoms of the leaving alkyl group, favour the S_E2 mechanism.[64] When the mercury(II) compound is the acetate, the active dealkylating agent appears to be $HgOAc^+$.[65] Methylcobaloximes react with mercury(II) compounds to produce $HgMe^+$; from methylcobalamins it is also possible to generate $HgMe_2$.[66] Mercury(II) cyanide reacts with the $[Co(CN)_5H]^{3-}$ anion. The observed kinetics suggest the following reaction sequence:

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

$$[Co(CN)_5]^{4-} \xrightarrow{HgCN^+} [(NCHg)Co(CN)_5]^{3-}$$

$$[(NCHg)Co(CN)_5]^{3-} \longrightarrow [(NC)_5Co{-}Hg{-}Co(CN)_5]^{6-}$$

with parallel attack of $Hg(CN)_2$ directly at the $[Co(CN)_5H]^{3-}$ anion.[67]

[61] S. C. Chan and S. F. Chan, *Austral. J. Chem.*, 1971, **24**, 895.
[62] V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1785.
[63] L. C. Falk and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 215.
[64] A. Adin and J. H. Espenson, *Chem. Comm.*, 1971, 653.
[65] G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Letters* 1971, 275.
[66] J.-Y. Kim, N. Imura, T. Ukita, and T. Kwan, *Bull. Chem. Soc. Japan*, 1971, **44**, 300.
[67] Hong Sup Lim and F. C. Anson, *Inorg. Chem.*, 1971, **10**, 103.

Other Ions. Thallium(III) catalyses aquation of $[Co(NH_3)_5Cl]^{2+}$, and of *cis*- and of *trans*-$[Co(en)_2Cl_2]^+$. In all cases there is a first-order dependence of rate on thallium(III) concentration. In mercury(II)-catalysed aquation of *cis*-$[Co(en)_2Cl_2]^+$ there is evidence for a stable Co—Cl—Hg bonded adduct; there is no evidence for a stable intermediate in the thallium(III)-catalysed aquation. Thallium(III) is in general a less effective aquation catalyst than mercury(II). As the stability constants for formation of the monochloro-complexes of these two cations are about the same, the difference between their catalytic effects may be attributed to their difference in charge—these reactions are of cationic complexes with cations. $TlCl^{2+}$ is somewhat less effective than Tl^{3+} as a catalyst for aquation; this time the difference in rates can be attributed to the lower chloride ion affinity of $TlCl^{2+}$.[68] In a general discussion of catalysis of cobalt(III)-chloride and chromium(III)-chloride aquation, and of hydrolysis of fluoro-anions such as $[BF_4]^-$ and $[PF_6]^-$, by metal cations such as mercury(II), thallium(III), aluminium(III), thorium(IV), *etc.*, it is shown that the rates of these reactions can be correlated fairly well with the relative 'hardness' and 'softness' of the various reactants.[69] Indeed, such a discussion can be further generalized to include metal ion catalysis of organic reactions. Solvolysis of t-butyl halides (Bu^tX) in the presence of metal ion catalysts (M^{n+}) follows the rate law

$$-\,d[Bu^tX]/dt = (k_1 + k_2[M^{n+}])[Bu^tX]$$

The rate constants k_2 can be correlated with stability constants of complexes $[MX]^{(n-1)+}$, except where M^{n+} is substitution inert (*e.g.* Cr^{3+}), and discussed in terms of the hard and soft acids and bases picture.[70]

Redox catalysis of substitution is well established for chromium(II) catalysis of substitution at chromium(III), and for platinum(II) catalysis of substitution at platinum(IV); it has also recently been demonstrated for rhodium(I) catalysis of substitution in a particular series of rhodium(III) complexes (see later, Section 4). Redox catalysis of substitution at cobalt(III) is less common, cobalt(II) being generally ineffective, but chromium(II) is an effective catalyst for aquation of $[Co(NH_3)_5(NCO)]^{2+}$.[71]

Some anions have been found to exert a small catalytic effect on aquation. Phthalate and phosphate, but not borate, increase the rate of chloride release from *trans*-$[Co(en)_2(NO_2)Cl]^+$ somewhat; the mechanism of this catalytic effect is not discussed.[72]

Photochemistry.—The most recent reinvestigation of photochemical decomposition of $[Co(NH_3)_5Cl]^{2+}$, using techniques of flash photolysis, chemical scavenging, and product analysis, leads to the conclusion that the reactive intermediate is probably a metastable charge-transfer excited state rather

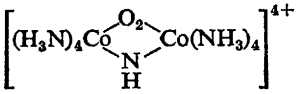
[68] S. W. Foong, B. Kipling, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 118.
[69] M. M. Jones and H. R. Clark, *J. Inorg. Nuclear Chem.*, 1971, **33**, 413.
[70] E. S. Rudakov and I. V. Kozhevnikov, *Tetrahedron Letters*, 1971, 1333.
[71] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 198.
[72] S. C. Chan and C. W. Fung, *J. Inorg. Nuclear Chem.*, 1971, **33**, 569.

than the radical-pair normally proposed.[73] An earlier study [74] of photoaquation of $[Co(NH_3)_5(O_2CCH_3)]^{2+}$ seems to have been misinterpreted, since a secondary thermal reduction step was not considered by the authors.[75] The products of photoaquation of this complex depend greatly on wavelengths of irradiation, for at 254 nm photodecomposition occurs entirely by acetate-to-cobalt charge transfer, but at 366 nm, where absorption is due almost entirely to $d \rightarrow d$ transitions with only a small contribution from the edge of the charge-transfer band, ammonia loss with formation of $[Co(NH_3)_4(OH_2)(O_2CCH_3)]^{2+}$ occurs.[76] The photochemical reaction [77] of $[Co(en)_3]^{3+}$ with $edtaH_2^{2-}$ is direct anation, and not photoaquation followed by anation, for photoaquation of $[Co(en)_3]^{3+}$ is much slower than this reaction with $edtaH_2^{2-}$. Reaction occurs within an ion-pair $\{[Co(en)_3]^{3+}, edtaH_2^{2-}\}$ whose association constant has been determined.[78]

Peroxo-complexes are not normally light sensitive, but superoxo-complexes are usually very photosensitive. The primary photochemical step in photodecomposition of the superoxo-bridged dicobalt(III) complexes (17) and (18) in aqueous perchloric acid is charge-transfer from the superoxo-group to a cobalt atom. The eventual products from (17) include $[Co(NH_3)_5(OH_2)]^{3+}$, $Co^{2+}(aq)$, and oxygen.[79] The quantum yield for photoaquation is markedly decreased by replacing the ammine ligands by chelating organic amines, for example in going from (17) to (19), or from (18) to (20).[80]

$[(H_3N)_5Co{-}O_2{-}Co(NH_3)_5]^{5+}$

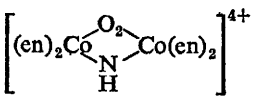
(17)



(18)

$[(tetren)Co{-}O_2{-}Co(tetren)]^{5+}$

(19)



(20)

In the most recent study of photoaquation of $[Co(CN)_6]^{3-}$, the reaction has been conducted in the presence of scavenging iodide or azide ions in an attempt to ascertain whether the mechanism is D [S_N1(lim)] or I_d. Some $[Co(CN)_5I]^{3-}$ and $[Co(CN)_5(N_3)]^{3-}$ are found amongst the products, but

[73] G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1970, **92**, 6801.
[74] E. R. Kantrowitz, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1970, **92**, 1776.
[75] R. D. Lindholm and T. K. Hall, *J. Amer. Chem. Soc.*, 1971, **93**, 3525.
[76] E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *J. Phys. Chem.*, 1971, **75**, 1914.
[77] B. Nordén, *Acta Chem. Scand.*, 1971, **25**, 2776.
[78] B. Nordén, *Acta Chem. Scand.*, 1971, **25**, 2516.
[79] J. S. Valentine and D. Valentine, *J. Amer. Chem. Soc.*, 1971, **93**, 1111.
[80] J. S. Valentine and D. Valentine, *Inorg. Chem.*, 1971, **10**, 393.

they only appear after an induction period, presumably therefore formed from $[Co(CN)_5(OH_2)]^{2-}$ and not directly from an intermediate $[Co(CN)_5]^{2-}$. Thus an I_d rather than a D mechanism seems the more likely.[81]

Naphthalene is known to be an efficient sensitizer for photoaquation of $[Co(NH_3)_6]^{3+}$;[82] biphenyl and biacetyl have now also been shown to sensitize effectively. The mechanism is of redox decomposition of a triplet charge-transfer state of the complex.[83] Radiolysis of $[Co(NH_3)_6]^{3+}$ results in decomposition by cobalt(III) reduction to cobalt(II) by hydrogen atoms.[84]

3 Aquation: Chromium(III) Complexes

Unidentate Leaving Groups.—The question of the detailed mechanism of aquation of chromium(III) complexes, particularly of the $[Cr(OH_2)_5X]^{2+}$ type, has attracted considerable interest and research effort in the past two or three years. Originally it was suggested [85] that the aquation of this type of complex took place by a purely dissociative [S_N1(lim) or D] mechanism, with a $[Cr(OH_2)_5]^{3+}$ transition state or transient intermediate. Later kinetic studies [86] showed that other mechanisms were consistent with kinetic and product data. In particular for iodo-complexes a strong *trans* labilizing influence of the iodide on the opposite water ligand was consistent with the experimental results; the mechanism:

$$[Cr(OH_2)_5I]^{2+} + Cl^- \rightleftharpoons \{[Cr(OH_2)_5I]^{2+}, Cl^-\}$$

$$\downarrow \text{slow}$$

$$trans\text{-}[Cr(OH_2)_4ClI]^+$$

$$\downarrow \text{fast}$$

$$[Cr(OH_2)_5Cl]^{2+}$$

explaining the detection of some $[Cr(OH_2)_5Cl]^{2+}$ alongside $[Cr(OH_2)_6]^{3+}$ after aquation of $[Cr(OH_2)_5I]^{2+}$ in aqueous solutions containing chloride. To try to distinguish between these two routes, several attempts to find conclusive evidence for the intermediacy of $[Cr(OH_2)_5]^{3+}$ have been made, particularly in catalysed aquation reactions. Examples of these include aquation of $[Cr(OH_2)_5X]^{2+}$ in the presence of thallium(III), mercury(II), or silver(I),[87] and aquation of $[Cr(OH_2)_5N_3]^{2+}$ in the presence of nitrous

[81] M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 5254.
[82] M. A. Scandola, F. Scandola, and V. Carassiti, *Mol. Photochem.*, 1969, **1**, 403.
[83] M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, 1970, **92**, 7278.
[84] I. G. Murgulescu and I. Mihalcea, *Rev. Roumaine Chim.*, 1970, **15**, 3.
[85] M. Ardon, *Inorg. Chem.*, 1965, **4**, 372.
[86] P. Moore, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1966, **5**, 223.
[87] S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, 1970, **92**, 1215.

acid.[87, 88] Both approaches have yielded some evidence favouring the intermediacy of $[Cr(OH_2)_5]^{3+}$. The most recent study of the chromium(III)–azide–nitrous acid reaction, conducted in the presence of added chloride, bromide, thiocyanate, or bisulphate to scavenge any $[Cr(OH_2)_5]^{3+}$ formed, shows that although this species may be formed, it must be very reactive and of low discriminating ability.[89]

The complexes $[Cr(OH_2)_5X]^{2+}$ lack a stereochemical label for determining the steric course of reaction. From this point of view the complexes $[Cr(NH_3)_4(OH_2)X]^{2+}$ are preferable. Aquation of *trans*-$[Cr(NH_3)_4(OH_2)I]^{2+}$ in the presence of chloride or bromide results in the formation of some *trans*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$ or *trans*-$[Cr(NH_3)_4(OH_2)Br]^{2+}$ as well as the direct aquation product *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$. These observations may readily be interpreted in terms of the *trans* labilizing power of the iodide ligand and the consequent reactions set out above.[90] But they are also consistent with a transient five-co-ordinate intermediate $[Cr(NH_3)_4(OH_2)]^{3+}$, although the 100% retention of configuration observed for the chloro- and bromo-products implies some restrictions on the geometry of such a five-co-ordinate intermediate; a square-pyramidal structure would be the simplest model consistent with the observed stereochemical retention. Further results consistent with strong *trans* labilization by an iodide ligand are reported for aquation of *trans*-$[Cr(NH_3)_4IC1]^{+}$. Activation parameters for several direct and chromium(II)-catalysed aquations of this type of tetra-ammine-chromium(III) complex are listed in Table 6.[91]

Table 6 *Activation parameters for aquation [simple and chromium(II) catalysed] of some tetra-ammine–chromium(III) complexes*[91]

	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
Uncatalysed:		
cis-$[Cr(NH_3)_4(OH_2)I]^{2+}$	19.7	− 6
trans-$[Cr(NH_3)_4(OH_2)I]^{2+}$	21.4	− 5
cis-$[Cr(NH_3)_4(OH)I]^{+}$	17.0	+ 2
trans-$[Cr(NH_3)_4(OH)I]^{+}$	18.7	+ 6
trans-$[Cr(NH_3)_4ClI]^{+}$	18.0	+ 9
Chromium(II)-catalysed:		
cis-$[Cr(NH_3)_4(OH_2)I]^{2+}$	8.7	− 24
trans-$[Cr(NH_3)_4(OH_2)I]^{2+}$	7.1	− 24

The relative merits of the aquation mechanism theories have been tested by kinetic and product characterization studies of aquation of $[Cr(OH_2)_5X]^{2+}$, where X = Br, I, NO_3, or NCS, in the presence of chloride. The results suggest a similarity of aquation mechanism for the four complexes, but are not wholly consistent either with an S_N1(lim) or *D* mechanism, or with *trans* labilization as the major reaction-determining factor. The most satisfactory explanation is that there is some degree of associative character;

[88] R. C. Thompson and E. J. Kaufmann, *J. Amer. Chem. Soc.*, 1970, **92**, 1540.
[89] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1970, 2819.
[90] R. Buchacek, D. W. Hoppenjans, and G. Gordon, *Inorg. Chem.*, 1971, **10**, 422.
[91] D. W. Hoppenjans, G. Gordon, and J. B. Hunt, *Inorg. Chem.*, 1971, **10**, 754.

an I_a mechanism is suggested. In contrast, an I_d mechanism seems more likely for aquation of the conjugate base species, $[Cr(OH_2)_4(OH)X]^+$, derived from the above complexes.[92]

Determination of activation volumes, although none too common on account of apparatus requirements, is a useful approach to assignment of mechanism. Recent results for substitution at chromium(III) are collected in Table 7. The mechanism of aquation of $[Cr(NCS)_6]^{3-}$ is probably one of

Table 7 *Activation volumes* ($\Delta V^{\ddagger}$) *and* $\partial\Delta V^{\ddagger}/\partial P$ *for substitution at chromium*(III)

Complex	*Reaction*	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	$(\partial\Delta V^{\ddagger}/\partial P)$/cm^3 katm^{-1}	*Ref.*
$[Cr(NCS)_6]^{3-}$	Aquation	+ 16	+ 15	93
$[Cr(NH_3)_2(NCS)_4]^-$	Aquation	− 2.4	0	93
$[Cr(OH_2)_6]^{3+}$	Exchange	− 9.3	Small	94
$[Cr(OH_2)_5(NO_3)]^{2+}$	Aquation	− 12.7	—	92

dissociative interchange (I_d), with the positive activation volume representing the increased size of the transition state arising from Cr—NCS bond stretching. For aquation of $[Cr(NH_3)_2(NCS)_4]^-$ an associative mechanism is suggested, with a water molecule hydrogen bonded to the leaving thiocyanate in the transition state.[93] The negative activation volume for water exchange at $[Cr(OH_2)_6]^{3+}$ also suggests an associative process. The activation entropy value of approximately zero favours an associative interchange (I_a) over a simple associative (A) mechanism.[94]

Plots of logarithms of rate constants against pressure are often markedly curved, *i.e.* activation volumes are not independent of pressure. In organic solvolyses large values of $\partial\Delta V^{\ddagger}/\partial P$ have been observed for unimolecular reactions, small values for bimolecular. While the magnitudes of $\partial\Delta V^{\ddagger}/\partial P$ for substitutions at carbon and at chromium(III) are unlikely to be directly comparable, the $\partial\Delta V^{\ddagger}/\partial P$ values in Table 7 are correspondingly small for substitutions suggested to be associative in character and larger for the probably dissociative aquation of the $[Cr(NCS)_6]^{3-}$ anion.

Thus the present situation regarding mechanisms of substitution in this type of chromium(III) complex is not entirely clear. It seems, from evidence such as activation volumes and linear free-energy plots of free-energies of activation against free energies of overall reaction, that there is considerable associative character to substitution in chromium(III)–aquo–halide complexes. However, when a ligand with a strong *trans* labilizing effect, such as iodide[86] or methyl,[95] is present, then the substitution mechanism is more dissociative in character.

Halides. Kinetics and mechanisms of aquation of chromium(III)–amine– or –ammine–halide complexes are discussed in an extensive review of the

[92] L. R. Carey, W. E. Jones, and T. W. Swaddle, *Inorg. Chem.*, 1971, **10**, 1566.
[93] D. L. Gay and R. Nalepa, *Canad. J. Chem.*, 1971, **49**, 1644.
[94] D. R. Stranks and T. W. Swaddle, *J. Amer. Chem. Soc.*, 1971, **93**, 2783.
[95] W. Schmidt, J. H. Swinehart, and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 1117; M. Ardon, K. Woolmington, and A. Pernich, *Inorg. Chem.*, 1971, **10**, 2812.

chemistry of these complexes.[96] Kinetic parameters for aquation of further complexes of this type are collected in Table 8. Aquation of *cis*- and of

Table 8 *Kinetic parameters for aquation of chromium*(III)*-chloride complexes* (*loss of first chloride in each case*)

Complex	*Conditions*	k_{25}/s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
cis-$[Cr(cyclam)Cl_2]^+$	0.01M-HNO_3	2.5×10^{-5}	22.4	− 5	97
trans-$[Cr(cyclam)Cl_2]^+$	0.01M-HNO_3	2×10^{-8}	27	− 2	97
trans-$[Cr(NH_3)_2(OH_2)_2Cl_2]^+$	0.6M-$HClO_4$	5.4×10^{-5}	—	—	99
cis-$[Cr(bipy)_2Cl_2]^+$	0.1—0.5M-HCl	5.4×10^{-5} (70 °C)	22.8	− 12	98

trans-$[Cr(cyclam)Cl_2]^+$ proceeds with complete retention of configuration,[97] as does aquation of *cis*-$[Cr(bipy)_2Cl_2]^+$, which is as expected from steric constraints imposed by the bipyridyl ligands. Aquation of *cis*-$[Cr(bipy)_2(OH_2)Cl]^{2+}$ seems to involve both chromium(III)–chloride and chromium(III)–nitrogen bond breaking.[98]

Oxoanions. The main mechanistic question for oxoanions as leaving groups is whether their displacement involves chromium–oxygen bond breaking or oxygen–central atom of the oxoanion bond breaking. It is well established[100] that acid-catalysed aquation of nitrito-chromium(III) complexes takes place by oxygen–nitrogen rather than oxygen–chromium bond fission. It has now been shown that the non-acid-catalysed aquation path for *cis*- and for *trans*-$[Cr(en)_2L(ONO)]^{n+}$ proceeds by oxygen–chromium bond fission.[101] These en complexes are preferable to the analogous ammines used in earlier kinetic studies, since ammonia is easily lost from chromium(III), but en is much less labile. Aquation of monosulphitochromium(III) is a rapid process, which suggests that its mechanism is oxygen–sulphur bond breaking.[102] The activation volume, -12.7 cm^3 mol^{-1}, for aquation of $[Cr(OH_2)_5(NO_3)]^{2+}$ in 1.1M-$HClO_4$ suggests chromium–oxygen rather than oxygen–nitrogen bond fission here.[103] The rate constant for aquation of

[96] C. S. Garner and D. A. House, in 'Transition Metal Chemistry', ed. R. L. Carlin, Marcel Dekker, New York, 1970, vol. 6.
[97] E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1781.
[98] S. Y. J. Ng and C. S. Garner, *Inorg. Chim. Acta*, 1971, **5**, 365.
[99] M. C. Couldwell, D. A. Pickering, and D. A. House, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3455.
[100] T. C. Matts and P. Moore, *Chem. Comm.*, 1969, 29; *J. Chem. Soc.* (*A*), 1969, 219, 1977.
[101] W. W. Fee, J. N. MacB. Harrowfield, and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 290.
[102] D. W. Carlyle and E. L. King, *Inorg. Chem.*, 1970, **9**, 2333.
[103] L. R. Carey, W. E. Jones, and T. W. Swaddle, *Inorg. Chem.*, 1971, **10**, 1566.

$[Cr(O_3SCF_3)]^{2+}$ is 7.6×10^{-4} s^{-1} at 25 °C, which is intermediate between those for aquation of the analogous perchlorate and nitrate complexes.[104]

Cyanides. The complete aquation of $[Cr(CN)_6]^{3-}$ to $[Cr(OH_2)_6]^{3+}$ involves six steps. Rates and activation parameters for the last two stages, *viz.* aquation of the dicyanotetra-aquo- and of the monocyanopenta-aquo-cations, were reported three or four years ago.[105] Since then the rate law, rate constants, and some of the activation parameters for aquation of 1,2,3-$[Cr(OH_2)_3(CN)_3]^0$ have been determined.[106] It has also been shown that the product of a previous study[107] of aquation of $[Cr(CN)_6]^{3-}$ was not $[Cr(CN)_4(OH_2)_2]^-$ but $[Cr(CN)_5(OH_2)]^{2-}$.[108] This does not affect the reported kinetics, for the earlier report assumed that the rate-determining step was $[Cr(CN)_6]^{3-}$ aquation to $[Cr(CN)_5(OH_2)]^{2-}$, with subsequent rapid formation of $[Cr(CN)_4(OH_2)_2]^-$.

Other Ligands. The rate law for aquation of $[Cr(OH_2)_5py]^{3+}$ is

$$-\mathrm{d}[\{Cr(OH_2)_5py\}^{3+}]/dt = \{k_0 + k_{-1}[H^+]^{-1}\}[\{Cr(OH_2)_5py\}^{3+}]$$

in which the $k_{-1}[H^+]^{-1}$ term corresponds to aquation of the conjugate base species $[Cr(OH_2)_4(OH)py]^{2+}$. Rate constants and activation parameters are reported for both aquation paths.[109] Kinetic parameters have also been obtained for aquation of a mixture of *cis*- and *trans*-$[Cr(OH_2)_4(NCS)(SCN)]^+$. This mixture of complexes,* prepared by reduction of $[Fe(NCS)]^{2+}$ by chromium(II) in the presence of thiocyanate, aquates with loss of sulphur-bonded thiocyanate first.[110]

Multidentate Leaving Groups.—Following the isolation of chromium(III) complexes containing unidentate ethylenediamine and uni- and bi-dentate diethylenetriamine, complexes containing triethylenetetramine acting as a uni-, bi-, or ter-dentate ligand have now been prepared.[111] The first part of a complete kinetic investigation of stepwise aquation of chromium(III)–triethylenetetramine complexes reports kinetic parameters, both rate constants and activation parameters, for several steps in the aquation of both the 1,2,3- and the 1,2,6-isomers of the complexes $[Cr(trienH)(OH_2)_3]^{4+}$ containing terdentate trien. These kinetic results are compared with those for aquation of analogous complexes of ethylenediamine and of diethylenetriamine.[112] Rate constants and activation parameters have been determined

[104] A. Scott and H. Taube, *Inorg. Chem.*, 1971, **10**, 62.
[105] J. P. Birk and J. H. Espenson, *Inorg. Chem.*, 1968, **7**, 991; D. K. Wakefield and W. B. Schaap, *ibid.*, 1969, **8**, 512, 811.
[106] D. K. Wakefield and W. B. Schaap, *Inorg. Chem.*, 1971, **10**, 306.
[107] R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, 1967, **6**, 1338.
[108] L. Jeftić and S. Feldberg, *J. Amer. Chem. Soc.*, 1970, **92**, 5272.
[109] A. Bakač and M. Orhanović, *Inorg. Chem.*, 1971, **10**, 2443.
[110] L. D. Brown and D. E. Pennington, *Inorg. Chem.*, 1971, **10**, 2117.
[111] R. L. Wilder, D. A. Kamp, and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 1393.
[112] D. A. Kamp, R. L. Wilder, S. C. Tang, and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 1396.

* The S-bonded thiocyanate is too labile to permit separation of the *cis*- and *trans*-isomers.

for each stage in the stepwise unwrapping of the quinquedentate ligand tetren from chromium in $[Cr(tetren)(OH_2)]^{3+}$. The relative rates of chromium–nitrogen bond dissociation are 550 : 2100 : 24 : 1 : 0.17, in 4M-$HClO_4$. The activation enthalpy increases steadily, from 20.7 kcal mol^{-1} to 27.7 kcal mol^{-1}; the irregularity in the sequence of rates arises from the irregular trend of activation entropy values.[113]

The product of aquation of *trans*-$[Cr(en)_2F_2]^+$ is $[Cr(en)(enH)(OH_2)F_2]^{2+}$, which only slowly undergoes subsequent reaction to give *cis*-$[Cr(en)_2(OH_2)F]^{2+}$ and $[Cr(en)(OH_2)_2F_2]^+$. The activation parameters for the first aquation step for *trans*-$[Cr(en)_2F_2]^+$ are $\Delta H^{\ddagger} = 24.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0.3$ cal deg^{-1} mol^{-1}.[114] The ring opening $\rightleftharpoons$ closing equilibrium

$$[Cr(OH_2)_4(SCH_2CO_2)]^+ + H^+ + OH_2 \rightleftharpoons [Cr(OH_2)_5(O_2CCH_2SH)]^{2+}$$

provides another example of a kinetic study of one step in stepwise aquation of a complex of a multidentate ligand with chromium(III).[115]

Kinetic parameters have been reported for the equilibrium

$$2\,cis\text{-}[Cr(ox)_2(OH_2)_2]^- \rightleftharpoons [Cr(ox)_3]^{3-} + [Cr(ox)(OH_2)_4]^+$$

A dimeric oxalate-bridged intermediate is suggested.[116]

Effects of Non-leaving Ligands.—An appraisal of the relation between aquation constants for the two series of complexes $[Cr(OH_2)_5X]^{n+}$ and $[Cr(NH_3)_5X]^{n+}$ suggests that the effect of the non-leaving water and ammonia ligands on the lability of the leaving groups X can be attributed to the respective σ-donor abilities of these non-leaving ligands.[117] The rate of aquation of *trans*-$[M(pn)_2Cl_2]^+$ is slightly greater than that of *trans*-$[M(en)_2Cl_2]^+$ for M = chromium(III) and for M = cobalt(III).[118] The rate of aquation of *cis*-$[M(bipy)_2Cl_2]^+$ is much less than aquation rates of analogous en and trien complexes, again for M = chromium(III) and for M = cobalt(III).[98] Sulphite ligands (O-bonded) on chromium(III) have a strong labilizing effect on chloride ligands attached to the same cation.[102]

Solvolysis in Mixed Solvents.—The n.m.r. method for probing the solvation shell of complexes in mixed solvents, developed with particular reference to aquation of $[Cr(NCS)_6]^{3-}$ in aqueous acetonitrile,[119] has proved useful in investigating details of the mechanism of solvolysis[120] of $[Cr(ox)_3]^{3-}$, this time in aqueous dimethyl sulphoxide. There is preferential solvation by the

[113] S. J. Ranney and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 2437.
[114] S. C. Pyke and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2445.
[115] R. H. Lane and L. E. Bennett, *Chem. Comm.*, 1971, 491.
[116] K. L. Stevenson, M. S. Matson, and R. D. Patrick, *J. Inorg. Nuclear Chem.*, 1971, **33**, 147.
[117] C. H. Langford, *Canad. J. Chem.*, 1971, **49**, 1497.
[118] R. R. Barona and J. A. McLean, *Inorg. Chem.*, 1971, **10**, 286.
[119] S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, 1969, **91**, 2236; L. S. Frankel, *J. Phys. Chem.*, 1969, **73**, 3897; 1970, **74**, 1645; L. S. Frankel, C. H. Langford, and T. R. Stengle, *ibid.*, p. 1376.
[120] S. T. Spees and A. W. Adamson, *Inorg. Chem.*, 1962, **1**, 531.

dimethyl sulphoxide in this case, but it is the amount of water in the solvation shell of the complex which controls reactivity, for the solvation mechanism involves solvating water hydrogen bonding to the leaving oxalate group and thus assisting its departure.[121] In ethanol–water mixtures, $[Cr(p\text{-anisidine})_2(NCS)_4]^-$ solvates by parallel loss of thiocyanate and of *p*-anisidine. The rate of the former reaction is insensitive to solvent composition (24—97% ethanol); the rate of the latter reaction increases as the proportion of ethanol in the mixed solvents increases. A dissociative mechanism is suggested for replacement of the thiocyanate, but an associative mechanism with ethanol rather than water replacing the outgoing ligand for replacement of the *p*-anisidine.[122] A similar reactivity pattern for solvolysis of $[CrL_2(NCS)_4]^-$, where L = *p*-ethylaniline,[123] *p*-toluidine,[124] or *p*-phenetidine,[124] has been similarly interpreted in terms of dissociative replacement of thiocyanate by water, but associative replacement of L by ethanol. In the case of, for example, the *p*-ethylaniline complex, the activation entropy for thiocyanate replacement is positive, that for *p*-ethylaniline replacement is negative, which observations are consistent with the above assignments of mechanism.

pH Variation.—Acid catalysis of aquation of $[Cr(LL)_3]^{3-}$ and of $[Cr(OH_2)_2(LL)_2]^-$, where LL = oxalate or malonate, has been described earlier.[125] The variation of rates and of activation parameters with acid ($HClO_4$) concentration for aquation of $[Cr(OH_2)_4](LL)^+$, again where LL = oxalate or malonate, has now been described to complete this series of kinetic studies. The dependence of rates on acid concentration, particularly on the acidity function H_0, is interpreted in terms of a change in mechanism as pH varies. At relatively low acid concentrations, about 1—2 M, the mechanism is claimed to be predominantly dissociative, but associative at acid concentrations above 3M.[126] The rate law for aquation of 1,2,3-$[Cr(OH_2)_3(CN)_3]$ in acidic aqueous solutions suggests that the reactive species are the protonated forms $[Cr(OH_2)(CN)_2(CNH)]^+$ and $[Cr(OH_2)_2(CN)(CNH)_2]^{2+}$.[106] Conversely a term in $[H^+]^{-1}$ in the rate law for aquation of $[Cr(OH_2)_5py]^{3+}$ indicates concurrent aquation of this and the $[Cr(OH_2)_4(OH)py]^{2+}$ cation.[109] Both azide protonation and ligand-water deprotonation are important in determining the overall rate of aquation of $[Cr(OH_2)_5(N_3)]^{2+}$:

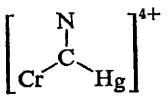
$$-\,d[Cr(OH_2)_5(N_3)^{2+}]/dt = \{k_1[H^+] + k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}\}[Cr(OH_2)_5(N_3)^{2+}]$$

[121] V. S. Sastri and C. H. Langford, *J. Phys. Chem.*, 1970, **74**, 3945.
[122] I. Zsakó, I. Gănescu, C. Várhelyi, and A. Popescu, *Z. anorg. Chem.*, 1971, **380**, 216.
[123] I. Zaskó, I. Gănescu, C. Várhelyi, and A. Popescu, *Rev. Chim. minérale*, 1970, **7**, 927 (*Chem. Abs.*, 1971, **74**, 91 731f).
[124] I. Zsakó, *Studia Univ. Babes-Bolyai, Ser. Chim.*, 1970, **15**, 93 (*Chem. Abs.*, 1970, **73**, 102 471d).
[125] D. Banerjea and M. S. Mohan, *J. Inorg. Nuclear Chem.*, 1964, **26**, 613; 1965, **27**, 1643; D. Banerjea and C. Chatterjee, *ibid.*, 1967, **29**, 2387; 1968, **30**, 3354.
[126] D. Banerjea and S. D. Chaudhuri, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2985.

This rate law has been known for some time;[127] recent investigations[128] of this reaction have been concerned with determining the effects of added salts on each of the four rate constants. The observed salt effects have been interpreted in terms of modified forms of the Debye–Hückel theory, especially that due to Mayer.[129] In the rate law for ring opening of $[Cr(OH_2)_4(SCH_2CO_2)]^+$, there is a term first-order in hydrogen ion concentration, which can be assigned to protonation of the ligand sulphur atom.[115]

Catalysis.—An investigation[130] of the catalysis of aquation of *cis*- and *trans*-$[Cr(OH_2)_4Cl_2]^+$ by Hg^{2+} has been followed by an investigation of catalysis of these reactions by species HgX^+, where X = Cl, Br, I, or CN; rate laws and activation parameters are reported for these four catalysts. Whereas there is evidence for a doubly bridged intermediate in the Hg^{2+}-catalysed aquation of *cis*-$[Cr(OH_2)_4Cl_2]^+$, there is no evidence for such an intermediate in the $HgCl^+$-catalysed aquation of this complex. This difference in behaviour reflects the much lower stability of $HgCl_3^-$ units than of $HgCl_2$.[131] The relative effectiveness of metal ions M^{n+}, for example Ag^+, Hg^{2+}, or Tl^{3+}, in promoting aquation of chromium(III)–chloride complexes can be correlated with the hardness or softness of these catalysts.[69]

Mercury(II) is also an effective catalyst for aquation of pseudohalide complexes, for example of $[Cr(OH_2)_5(N_3)]^{2+}$ (ref. 132) and of $[Cr(OH_2)_5(NCS)]^{2+}$ (ref. 133). In the latter case the dinuclear $[Cr{-}NCS{-}Hg]^{4+}$ intermediate is particularly stable, with hard–hard interaction at the nitrogen end and soft–soft interaction at the sulphur end of the bridging thiocyanate. The rate of aquation of this $[Cr{-}NCS{-}Hg]^{4+}$ species is independent of hydrogen ion concentration. The mechanism of aquation is thought to be dissociative; the activation parameters are $\Delta H^{\ddagger} = 20.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.5$ cal deg^{-1} mol^{-1}. The rate law for the mercury(II)-catalysed aquation of $[Cr(OH_2)_5(CN)]^{2+}$ is complicated as there is a major reaction path through formation of $[Cr{-}CN{-}Hg]^{4+}$, which rearranges intramolecularly to $[Cr{-}NC{-}Hg]^{4+}$, and a minor path in which the $CrCN^{2+}$ isomerizes to $CrNC^{2+}$, which then reacts with mercury(II) to give $[Cr{-}NC{-}Hg]^{4+}$ again. The $[Cr{-}CN{-}Hg]^{4+}$ intermediate of the major pathway may have a structure (21), reminiscent of bridged carbonyls, rather



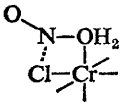
(21)

[127] T. W. Swaddle and E. L. King, *Inorg. Chem.*, 1964, **3**, 234.
[128] A. Indelli and R. de Santis, *J. Chem. Phys.*, 1971, **55**, 4811.
[129] J. E. Mayer, *J. Chem. Phys.*, 1950, **18**, 1426.
[130] J. P. Birk, *Inorg. Chem.*, 1970, **9**, 735.
[131] J. P. Birk, *Inorg. Chem.*, 1971, **10**, 66.
[132] V. Mahalec and M. Orhanović, *Inorg. Chim. Acta*, 1971, **5**, 457.
[133] J. N. Armor and A. Haim, *J. Amer. Chem. Soc.*, 1971, **93**, 867.

than $[Cr—C—N—Hg]^{4+}$; structure (21) could more readily rearrange to the $[Cr—NC—Hg]^{4+}$ product.[134] Methods for estimating stabilities of this type of ligand-bridged dinuclear intermediate from stabilities of mononuclear analogues have been discussed.[135]

Redox catalysis of substitution occurs in the aquation of $[Cr(CN)_6]^{3-}$ in the presence of chromium(II); an outer-sphere mechanism is proposed.[136]

The catalysis of aquation of $[Cr(OH_2)_5X]^{2+}$, where X = Cl or Br, of *cis*- and of *trans*-$[Cr(OH_2)_4Cl_2]^+$, and of *cis*- but not of *trans*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$ by nitrous acid *via* an *O*-nitrosation mechanism has now been fully described[137] subsequent to the original preliminary communications.[100]



(22)

The contrast between the behaviour of the *cis*- and *trans*-isomers of $[Cr(NH_3)_4(OH_2)Cl]^{2+}$ indicates an anchimeric interaction between the nitrosated water ligand and the leaving chloride [see (22)].

Photochemistry.—There has been much discussion of Adamson's empirical rules as a result of recent observations on a variety of chromium(III)–amine– or –ammine–halide complexes. In some cases there is an acceptable explanation of failure of a compound to conform to these rules. Thus, for example, the photochemical inertness of *trans*-$[Cr(cyclam)Cl_2]^+$ is surprising in view of the normal behaviour of *trans*-$[Cr(en)_2Cl_2]^+$, but the particular stereochemical requirements of the cyclic cyclam ligand may explain this deviation from the rules.[138] The observations that irradiation of the isomers of $[Cr(en)_2Cl_2]^+$ at $d \rightarrow d$ frequencies results in parallel chloride loss and formation of a unidentate monoprotonated en complex from the *cis*-complex, and chloride loss accompanied by 70% isomerization for the *trans*-complex are qualitatively, but not quantitatively, consistent with Adamson's rules.[139] Another discussion[140] of the stereochemical course of aquation of $[Cr(en)_2Cl_2]^+$ disagrees with some parts of an earlier discussion[141] on photoaquation of $[Cr(NH_3)_5Cl]^{2+}$ and similar complexes. Thus the status of Adamson's rules remains uncertain, and it may be that an

[134] J. H. Espenson and W. R. Bushey, *Inorg. Chem.*, 1971, **10**, 2457.
[135] R. D. Cannon, *Nature*, 1970, **228**, 644.
[136] L. Jeftić and S. W. Feldberg, *J. Phys. Chem.*, 1971, **75**, 2381.
[137] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1971, 1632.
[138] C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc.*, 1971, **93**, 5581.
[139] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Canad. J. Chem.*, 1971, **49**, 1524.
[140] A. D. Kirk, *J. Amer. Chem. Soc.*, 1971, **93**, 283.
[141] M. M. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, 1971, **10**, 207.

alternative approach based on considerations of relative chromium–ligand σ-bond strengths, and illustrated by photoaquation of *trans*-$[Cr(en)_2F_2]^+$,[142] may lead to a more widely applicable generalization of photochemical behaviour of this class of chromium(III) complexes.

Previous studies of photoaquation of $[Cr(en)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$ are linked by a study of photoaquation of the mixed complexes $[Cr(en)_2ox]^+$ and $[Cr(en)(ox)_2]^-$. Both of these ions photoaquate to intermediates containing unidentate monoprotonated en. These intermediates aquate further thermally, with loss of the ethylenediamine.[143] The rate of photoracemization of $[Cr(ox)_3]^{3-}$ in water–dimethyl sulphoxide decreases as the proportion of dimethyl sulphoxide increases, since solvating water plays a vital part in the racemization mechanism.[121]

Naphthalene is an efficient sensitizer for the photoaquation of chromium(III) complexes. Both $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_3)_5Cl]^{2+}$ lose ammonia, to produce $[Cr(NH_3)_5(OH_2)]^{3+}$ and *cis*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$, respectively. Energy is transferred to the chromium(III) complex from the lowest triplet state of the naphthalene.[144] Bimolecular quenching constants of naphthalene by several chromium complexes, including $[Cr(NH_3)_5Cl]^{2+}$, have been determined by flash spectroscopy.[145]

4 Aquation: Other Complexes

d^1: **Molybdenum**(V).—The first step in the complicated hydrolysis of molybdenum pentachloride is, in a dilute solution of water in carbon tetrachloride, the production of $MoOCl_3$. The isolation of this intermediate is facilitated by its insolubility in carbon tetrachloride.[146]

d^2: **Molybdenum**(IV).—Further studies of photoaquation of the eight-co-ordinate complex $[Mo(CN)_8]^{4-}$ have shown that naphthalene, phenanthrene, anthraquinone, and benzophenone are effective photosensitizers, but that biacetyl is not. The rates of photoaquation and of thermal aquation are little affected by the medium, which suggests some similarity between the excited state for the former and the transition state for the latter.[147] The final products of aquation of $[Mo(CN)_8]^{4-}$ appear to remain uncharacterized, although this and other recent work confirms that the primary step in photoaquation is cyanide loss, which is reversible.[148]

d^2: **Tungsten**(IV).—The eight-co-ordinate complexes $W(LL)_4$, where LL = oxine or one of its substituted derivatives, are very inert to substitution, even to hydroxide ion attack in alcoholic potassium hydroxide

[142] S. C. Pyke and R. G. Linck, *J. Amer. Chem. Soc.*, 1971, **93**, 5281.
[143] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Canad. J. Chem.*, 1971, **49**, 375.
[144] E. Zinato, P. Tulli, and P. Riccieri, *J. Phys. Chem.*, 1971, **75**, 3504.
[145] H. F. Wasgestian and G. S. Hammond, *Theor. Chim. Acta*, 1971, **20**, 186.
[146] I. A. Glukhov, S. S. Eliseev, and M. S. Pulatov, *Russ. J. Inorg. Chem.*, 1970, **15**, 730.
[147] R. D. Wilson, V. S. Sastri, and C. H. Langford, *Canad. J. Chem.*, 1971, **49**, 679.
[148] V. Balzani, M. M. Manfrin, and L. Moggi, *Inorg. Chem.*, 1969, **8**, 47.

solution. This behaviour parallels that of the eight-co-ordinate cyano-complexes, the only other examples of inert eight-co-ordinate species known previously.[149]

d^4: Manganese(III).—The decomposition of $[Mn(mal)_2(OH_2)_2]^-$ in aqueous solution is acid catalysed. Under both thermal and photochemical conditions free radicals derived from the malonate ligands are important intermediates.[150] The transient formation of the oxalate radical $C_2O_4^{\cdot-}$ in the decomposition of $[Mn(ox)_2(OH_2)_2]^-$ has been demonstrated by trapping experiments. The fate of the oxalate radicals, both here and in similar decomposition reactions of oxalates of other metals, remains unclear.[151] Radiolysis of oxalates of manganese(III) and of other metal(III) cations in aqueous solution proceeds by parallel attack of hydrogen atoms and of solvated electrons, both of which produce oxalato–metal(II) complexes initially.[152]

d^5: Iron(III).—The rate law for aquation of the monosulphite complex of iron(III) is

$$-\,d[FeSO_3^+]/dt = (k_1 + k_2[H^+] + k_3[HSO_3^-])[FeSO_3^+]$$

indicating three parallel aquation pathways. Rate constants and activation parameters for each path have been determined. Discussion of the mechanism is hampered by uncertainty as to whether the ligand is sulphur- or oxygen-bonded to the iron, though the former seems considerably more likely.[153] The activation enthalpy for uncatalysed iron–ligand bond breaking (k_1 term of above rate law) is low: 8.4 kcal mol^{-1}.

Kinetics of the uncatalysed and thallium(III)-catalysed aquation of $[FeCl]^{2+}$ have been reported earlier;* kinetics of mercury(II)-catalysed aquation of this complex have now been investigated. In fact, in the presence of mercury(II) the catalysed and uncatalysed paths operate in parallel. Presumably the mercury(II)-catalysed path goes through a chloride-bridged transition state; there is no evidence for a stable Fe—Cl—Hg bridged intermediate.[154]

Three papers [155] describing the kinetics of decomposition of the hydroxo-iron(III) dimer $[FeOH]_2^{4+}$ have been followed by a fourth,[156] in which the

[149] W. D. Bonds and R. D. Archer, *Inorg. Chem.*, 1971, **10**, 2057.
[150] R. van Eldik and J. A. van den Berg, *J. S. African Chem. Inst.*, 1970, **23**, 85.
[151] T. Onescu, *Rev. Roumaine Chim.*, 1970, **15**, 209.
[152] I. G. Murgulescu and J. Paun, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 624.
[153] D. W. Carlyle, *Inorg. Chem.*, 1971, **10**, 761.
[154] D. Gibson and D. W. Carlyle, *Inorg. Chem.*, 1971, **10**, 2078.
[155] H. Wendt, *Z. Elektrochem.*, 1962, **66**, 235; T. J. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Amer. Chem. Soc.*, 1965, **87**, 926; B. Lutz and H. Wendt, *Ber. Bunsengesellschaft phys. Chem.*, 1970, **74**, 372.
[156] B. A. Sommer and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 2517.

* Unfortunately the thallium(III)-catalysed aquation kinetics have only been reported qualitatively (J. J. Conocchioli, G. H. Nancollas, and N. Sutin, *Proc. Chem. Soc.*, 1964, 113; N. Sutin, *Ann. Rev. Phys. Chem.*, 1966, **17**, 119). It is not therefore possible to compare the relative effectiveness of thallium(III) and mercury(II) as catalysts here with their effectiveness in aquation of cobalt(III)–chloride complexes (*cf.*, *e.g.*, ref. 68 of this chapter).

main features are the wide range of acid concentration used (0.05—3.5M-$HClO_4$) and the determination of activation parameters corresponding to the k_1 and k_2 terms of the rate law

$$-\,d[Fe_2(OH)_2^{4+}]/dt = \{k_1 + k_2[H^+]\}[Fe_2(OH)_2^{4+}]$$

A fifth paper on this reaction seeks to clear up discrepancies between two sets of activation parameters reported for the k_1 and k_2 terms of this rate law.[157] This paper also briefly discusses reactivities of oxo- and hydroxo-bridged transition-metal complexes. Reactivities of these compounds can be compared with those for similar actinide species through kinetic results for decomposition of, for example, the $[UO_2OH]_2^{2+}$ dimer,[158] and the peroxo-bridged plutonium species $[Pu—O_2—PuOH]^{5+}$.[159] The rate of decomposition of this last complex is proportional to hydrogen ion concentration—there is just one acid-catalysed path here, in contrast to the parallel pH-dependent and pH-independent paths for the $[Fe(OH)]_2^{4+}$ dimer.

d^5: Ruthenium(III).—Kinetics of the three steps for loss of the three chlorides from $[Ru(NO)(OH_2)_2Cl_3]$ have been determined in aqueous solution over the range $3.6 < pH < 11.4$. The rates are a function of pH since there can be protonation of, and proton loss from, the aquo-ligands. The unknown variation of pK values for the co-ordinated water molecules as the number of chloride ions displaced varies makes discussion of the kinetic results difficult.[160] The complexes $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_5Cl]^{2+}$ are fairly unreactive towards photoaquation, no matter whether the irradiating frequency corresponds to $d \rightarrow d$ or to charge-transfer absorption bands. There is a little photoaquation, with loss of ammonia; no photoreduction could be detected.[161]

d^5: Iridium(IV).—Irradiation of $[IrCl_6]^{2-}$ at charge-transfer or $d \rightarrow d$ frequencies results in substitution and redox processes. At the 254 nm charge-transfer band, $[IrCl_5(OH_2)]^-$ and $[IrCl_5(OH_2)]^{2-}$ are the products. At $d \rightarrow d$ frequencies, only $[IrCl_5(OH_2)]^-$ is formed, except in the presence of added chloride when $[IrCl_6]^{3-}$ is produced.[162]

d^6: Iron(II).—A comparison of photochemical aquation of $[Fe(CN)_6]^{4-}$ under conditions of intermittent (laser pulses) or of continuous illumination suggests that the formation of $[Fe(CN)_5(OH_2)]^{3-}$ from photoexcited states of $[Fe(CN)_6]^{4-}$ is complete within 1 ns.[163]

Kinetics of aquation of $[Fe(phen)_3]^{2+}$ and related complexes have been thoroughly studied in aqueous solution, rather less in mixed aqueous

[157] H. N. Po and N. Sutin, *Inorg. Chem.*, 1971, **10**, 428.
[158] V. Frei and H. Wendt, *Ber. Bunsengesellschaft phys. Chem.*, 1970, **74**, 593.
[159] A. S. Ghosh Mazumdar, P. R. Natarajan, and S. Vaidyanathan, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3363.
[160] A. F. Leroy and J. C. Morris, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3437.
[161] W. L. Wells and J. F. Endicott, *J. Phys. Chem.*, 1971, **75**, 3075.
[162] L. Moggi, G. Varani, M. F. Manfrin, and V. Balzani, *Inorg. Chim. Acta*, 1970, **4**, 335.
[163] M. Shiron and G. Stein, *J. Chem. Phys.*, 1971, **55**, 3379.

solvents. The dissociation of $[Fe(4,7\text{-diPh-phen})_3]^{2+}$ in the presence of varying concentrations of sulphuric acid in 50% aqueous methanol has been described.[164] Aquation kinetics for $[Fe(LL)_3]^{2+}$, where LL = phen, 3-SO_3^--phen, 5-NH_3^+-phen, 5-NO_2-phen, 5-SO_3^--phen, or 4,7-diMe-phen, have been investigated in the presence of a variety of acids in aqueous acetonitrile, $0 <$ mole fraction acetonitrile < 0.18. Rates are strongly dependent both on the solvent composition and on the nature of the added acid, though whether the kinetic effects of the latter are a consequence of ion-pairing or of effects of the added ions on the structure of the solvent mixture has not been established.[50]

Reactions of $[Fe(phen)_3]^{2+}$ and its derivatives with a variety of reagents very often follow the two-term rate law

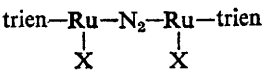
$$-\,d[Fe(phen)_3^{2+}]/dt = \{k_1 + k_2[Y]\}[Fe(phen)_3^{2+}]$$

The k_1 term corresponds to rate-determining dissociation of the complex followed by fast reaction of dissociation products with the reagent Y, *e.g.* rapid protonation of free phen or rapid reaction of free Fe^{2+} with cyanide after rate-determining iron–nitrogen bond breaking. The k_2 term represents direct reaction of the complex with Y. Recent examples of this kinetic pattern include reaction with peroxodisulphate in aqueous acetonitrile [50] (the reaction in aqueous solution has been known for some time to obey the above two-term rate law), reaction with hypochlorous acid or hypochlorites,[165] and reaction with cyanide (*cf.* Section 7 of this chapter). Many years ago a similar rate law was found to apply to reaction of $[Fe(phen)_3]^{2+}$ and related compounds with hydroxide ion.[166] The nature of the products was not established at that time, nor was it clear why the very similar nickel(II) complexes reacted at a rate independent of hydroxide ion concentration. It was hazarded that the difference in kinetic characteristics between the iron(II) and nickel(II) complexes might be due to the ease of oxidation to iron(III) and the difficulty of oxidation of nickel(II).[166] This suggestion has now been confirmed, for it has been shown that the presence of (dissolved) oxygen is essential for the reaction of $[Fe(phen)_3]^{2+}$ or of $[Fe(bipy)_3]^{2+}$ with hydroxide ion to take place.[167]

d^6: Ruthenium(II).—Kinetic parameters for the aquation of $[Ru(NH_3)_5(N_2)]^{2+}$ are $k_{25} = 2.1 \times 10^{-6}\ s^{-1}$, $\Delta H^{\ddagger} = 27.7$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 8$ cal deg^{-1} mol^{-1}.[168] Irradiation of $[Ru(NH_3)_5py]^{2+}$ at a metal–ligand charge transfer frequency leads to loss of ammonia or pyridine, the products being $[Ru(NH_3)_5(OH_2)]^{2+}$ and *cis*- and *trans*-$[Ru(NH_3)_4(OH_2)py]^{2+}$. The quantum yield is a function of the pH, which is surprising for a complex which lacks easily-protonated ligands. The authors suggest that this pH-dependence

[164] P. Legittimo, F. Pantani, and G. Ciantelli, *Gazzetta*, 1970, **100**, 931.
[165] M. G. Ondrus and G. Gordon, *Inorg. Chem.*, 1971, **10**, 474.
[166] D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728.
[167] G. Nord and T. Pizzino, *Chem. Comm.*, 1970, 1633.
[168] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 6170.

might arise either from protonation of pyridine in a loosely associated species $[(NH_3)_5Ru\cdots py]^{2+}$ or from protonation of a photoexcited state.[169] A preliminary report of a kinetic study of aquation of the bridged complex (23) states that the halide ligands (X^-) are lost previous to ruthenium–



(23)

dinitrogen–ruthenium bridge fission, and that this bridge fission is faster at high pH.[170]

***d*⁶: Rhodium(III) and Iridium(III).**—Rates and activation parameters have been determined for aquation of the linkage isomers $[M(NH_3)_5(NO_2)]^{2+}$ and $[M(NH_3)_5(ONO)]^{2+}$, where M = Rh, Ir, or Co, in acidic solution. The nitro-complexes aquate in strong acid by loss of NO^+; the nitrito-complexes aquate by oxygen–nitrogen rather than by oxygen–metal bond fission.[6] Comparisons of aquation, anation, and water exchange rates for $[Ir(NH_3)_5X]^{2+}$ and $[Ir(NH_3)_5(OH_2)]^{3+}$ provide evidence for some associative character in the mechanism of substitution at iridium(III).[171] Irradiation of solutions of $[Rh(NH_3)_5I]^{2+}$ at charge-transfer frequencies leads predominantly to the formation of *trans*-$[Rh(NH_3)_4(OH_2)I]^{2+}$, which suggests an excited state with a long and weak $Rh—NH_3$ bond *trans* to the iodide, and a transition state of square-pyramidal geometry.[172] Mercury(II)-catalysed aquation of $[Rh(NH_3)_5Cl]^{2+}$ in aqueous solution and in ethanol–water mixtures has been studied. The variations of rate constant with solvent composition for this rhodium(III) complex and for its cobalt(III) analogue $[Co(NH_3)_5Cl]^{2+}$ are very similar, which is consistent with a common mechanism, S_N1(lim) at the rhodium or cobalt centre though S_E2 at the chloride, and similar solvation requirements for the $[M(NH_3)_5]^{3+}$ moieties.[48]

The preliminary account of rhodium(I) catalysis of substitution in *trans*-$[Rh(py)_4X_2]^+$ has been followed by a full report.[173] Rate constants for aquation of $[IrBr_6]^{3-}$ in M-$HClO_4$ have been determined electrochemically and indicate an activation energy of 23.2 kcal mol^{-1} for replacement of the first bromide ligand by water.[174]

***d*⁶: Platinum(IV).**—Aquation rates for $[Pt(NH_3)_2Br_4]$ and $[Pt(NH_3)_2I_4]$ have been determined and compared with the rate of aquation of $[Pt(NH_3)_2Cl_4]$.

[169] P. C. Ford, D. A. Chaisson, and D. H. Stuermer, *Chem. Comm.*, 1971, 530.
[170] R. O. Harris and B. A. Wright, *Canad. J. Chem.*, 1970, **48**, 1815.
[171] E. Borghi, F. Monacelli, and T. Prosperi, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 667; E. Borghi and F. Monacelli, *Inorg. Chim. Acta*, 1971, **5**, 211.
[172] T. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, 1970, **92**, 5733; *Chem. Comm.*, 1971, 1061.
[173] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1971, 1840; R. D. Gillard, *Rec. Chem. Progr.*, 1971, **32**, 17.
[174] V. I. Kravtsov, N. V. Titova, and G. P. Tsayun, *Elektrokhimiya*, 1970, **6**, 573 (*Chem. Abs.*, 1970, **73**, 29 388a).

Aquation rates increase in the order chloride < bromide < iodide, which is the opposite order of reactivity to that observed for the platinum(II) complexes $[Pt(NH_3)_2X_2]$. The order of reactivity of the platinum(IV) complexes reflects a connection between lability and reducing power of the halide ligand.[175] A polarographic study [176] of the reaction of $[PtCl_5(OH_2)]^-$ with nioxime indicates rate-determining loss of water followed by reduction to platinum(II); the product is $[Pt(nioxH)_2Cl_2]$. The activation parameters are $\Delta H^{\ddagger} = 19.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19.2$ cal mol^{-1} deg^{-1}. Irradiation of aqueous solutions of $[Pt(NH_3)_4(NH_2)(NO_2)]^{2+}$ results in photoisomerization to the nitrito-complex and redox reactions, as well as photoaquation with replacement of the nitro-ligand. Quantum yields are reported, but no kinetic results.[177]

5 Base Hydrolysis

Cobalt(III) Complexes.—Three investigations provide further experimental support for the S_N1cb mechanism, rather than S_N2 or S_N2ip, for base hydrolysis of cobalt(III)–amine–halide complexes. Second-order rate constants (k_2) for base hydrolysis of $[Co(RNH_2)_5Cl]^{2+}$ increase enormously as the size of the alkyl group R increases: for R = H, $k_2 = 0.25$; for R = Me, $k_2 = 3.4 \times 10^3$; for R = Pr^n, $k_2 = 1.1 \times 10^4$; and for R = Bu^i, $k_2 = 1.5 \times 10^5$ l mol^{-1} s^{-1} at 25 °C. This rate trend is consistent with a large decrease in steric strain in going from the initial to the transition state in a dissociative, *i.e.* S_N1cb, mechanism.[25] The thermochemical demonstration of the S_N1cb mechanism, based on the constancy of the enthalpy change from transition state to products for base hydrolysis of the series of halide complexes $[Co(NH_3)_5X]^{2+}$, has now been reported fully.[178] Spectrophotometric evidence for the formation of the conjugate base $[Co(NH_3)_5(NH_2)]^{2+}$ rather than of the ion-pair $\{[Co(NH_3)_6]^{3+}, OH^-\}$ in strongly alkaline solutions of salts of $[Co(NH_3)_6]^{3+}$ provides further support for the S_N1cb mechanism.[179] A review of the kinetics of base hydrolysis of this type of cobalt(III) complex concludes that S_N1cb is indeed the mechanism normally operative.[180]

The base hydrolysis of $[Co(en)_2mal]^+$ takes place in two kinetically distinguishable steps, with an intermediate complex $[Co(en)_2(mal)(OH)]^0$ containing unidentate malonate.[181] This behaviour parallels that recently reported for $[Co(en)_2(CO_3)]^+$. A kinetic and stereochemical study of base hydrolysis of $[Co(en)_2ox]^+$ produces results which are consistent with an

[175] Yu. A. Makashev, F. Ya. Kul'ba, R. A. Zlotnikova, and A. A. Korableva, *Russ. J. Inorg. Chem.*, 1970, **15**, 1716.
[176] C. G. Macarovici, F. Mánok, and C. Várhelyi, *Rev. Roumaine Chim.*, 1970, **15**, 895.
[177] N. Sabbatini, L. Moggi, and G. Varani, *Inorg. Chim. Acta*, 1971, **5**, 469.
[178] D. A. House and H. K. J. Powell, *Inorg. Chem.*, 1971, **10**, 1583.
[179] L. Heck, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 657.
[180] M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377.
[181] V. Carunchio, F. Giannetta, and G. G. Strazza, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3025.

S_N1cb mechanism at low hydroxide ion concentration, but hints at the possibility of direct S_N2 attack at high hydroxide ion concentrations.[182]

There has been the usual generous supply of second-order rate constants for base hydrolysis of cobalt(III) complexes, including *trans*-$[Co(NH_3)_4(NO_2)Cl]^+$ and its bromide analogue,[32] *cis*-$[Co(en)_2(NH_2Bu^n)Cl]^{2+}$,[183] *cis*-$[Co(en)_2(NH_2CH_2CH_2Br)Br]^{2+}$,[184] *trans*-$[Co(en)_2(glycinenitrile)Cl]^{2+}$ and its glycinamide analogue,[18] *cis*-$[Co(en)_2(aziridine)Cl]^{2+}$ and its 2-methylaziridine analogue,[20] and $[Co(cyclohexanediamine)_2LCl)^{n+}$, where L = *trans*-$NH_3$, *cis*-OH, or *cis*- or *trans*-Cl.[29] The second-order rate constant for base hydrolysis of the bridged dicobalt complex $[(en)_2Co(\mu\text{-}OH)_2Co(en)_2]^{4+}$ has also been determined.[42] The use of a pH-stat method rather than of spectrophotometry for the determination of base hydrolysis rates has been described. The pH-stat method gave results consistent with an earlier spectrophotometric study for $[Co(NH_3)_5(NO_3)]^{2+}$. A combination of present pH-stat and earlier spectrophotometric results for $[Co(NH_3)_5I]^{2+}$ permits the estimation of the activation enthalpy for base hydrolysis of this iodide complex as 27.8 ($\pm$0.3) kcal mol^{-1}.[185]

Other Complexes.—*Titanium.* The mechanism of base hydrolysis of $[TiF_6]^{2-}$ is thought to be S_N1cb in character. The activation energy is 19.8 kcal mol^{-1} and the activation entropy -9.4 cal deg^{-1} mol^{-1}, at relatively low hydroxide ion concentration. At high concentrations of hydroxide ion a complicated kinetic pattern is observed.[186]

Chromium. The rate law for the base hydrolysis of *cis*- or of *trans*-$[Cr(cyclam)Cl_2]^+$ is

$$-\,d[Cr(cyclam)Cl_2^+]/dt = \{k_1 + k_2[OH^-]\}[Cr(cyclam)Cl_2^+]$$

The k_1 term is very small, though it is significant for the *cis*-complex; it corresponds to the rate constant for aquation in acidic solution. Rates of hydroxide ion attack here are much less than for analogous cobalt(III) complexes.[97] An I_a mechanism is thought to operate for base hydrolysis of $[Cr(NH_3)_5X]^{2+}$, with X = Cl, Br, or I. Kinetic results for the complex $[Cr(NH_3)_5F]^{2+}$ now show that the point for this complex lies on the same linear free energy plot of logarithms of second-order rate constants against pK values of the acids HX as the points for $[Cr(NH_3)_5X]^{2-}$ with X = Cl, Br, or I. Thus base hydrolysis of all four halide complexes would seem to have a common mechanism.[187]

[182] M. E. Farago and C. F. V. Mason, *J. Chem. Soc.* (*A*), 1970, 3100.
[183] R. W. Hay and D. J. Barnes, *J. Chem. Soc.* (*A*), 1970, 3337.
[184] D. A. Buckingham, C. E. Davis, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1970, **92**, 6159.
[185] A. L. Cunningham, D. A. House, and H. K. J. Powell, *J. Inorg. Nuclear Chem.*, 1971, **33**, 572.
[186] I. G. Ryss and V. G. Korovina, *Kinetika i Kataliz*, 1970, **11**, 603 (*Chem. Abs.*, 1970, **73**, 48 912h).
[187] T. P. Jones and J. K. Phillips, *J. Chem. Soc.* (*A*), 1971, 1881.

Iron.—The reaction of $[Fe(phen)_3]^{2+}$ with hydroxide ion in aqueous solution, whose kinetics but not whose final products were established some fifteen years ago, only proceeds if there is oxygen present in the reaction mixture. It thus seems that oxidation of iron(II) to iron(III) is essential to enable this reaction to take place.[167]

Ruthenium.—There is spectrophotometric evidence for the intermediacy of the conjugate base $[Ru(NH_3)_5(NH_2)]^{2+}$ in base hydrolysis of $[Ru(NH_3)_6]^{3+}$. The conjugate base here is, in contrast to cobalt(III) analogues, relatively stable, and it has proved possible to obtain values for its formation constant and of its enthalpy and entropy of formation.[188] Some kinetic results have been reported for hydrolysis of $[RuCl_3(NO)(OH_2)_2]$ in basic solution.[160]

Rhodium.—The mechanism of base hydrolysis of $[Rh(NH_3)_5(NCS)]^{2+}$ is stated to be S_N2ip, with solvent participation in transition-state formation.[189]

General.—Whereas there is some unanimity of opinion in favour of the S_N1cb mechanism for base hydrolysis of cobalt(III)–ammine– or –amine–halide complexes, there is much less information and more and varied speculation on mechanisms of base hydrolysis at other transition metal centres.[180]

6 Formation

Kinetics and mechanisms of formation of complexes of labile metal cations are discussed elsewhere (Part II, Chapter 4). Here formation reactions at inert transition metal centres are discussed, with cations arranged in order of increasing number of *d* electrons.

d^2: Vanadium(III).—There has recently been some discussion[190] about the possible associative character to substitution at this cation, whose d^2 electronic configuration leaves one t_{2g} orbital vacant for easy approach by nucleophiles. Rates of formation of thiocyanate, 2,2′-bipyridyl, and sulphosalicylate complexes from $[V(DMSO)_6]^{2+}$ show some ligand dependence, but the authors appear reluctant to take this as firm evidence for some associative character to the mechanisms of these substitutions.[191]

d^3: Chromium(III).—A list of activation parameters for complex formation with $[Cr(OH_2)_6]^{3+}$ has been compiled;[192] this supplements an earlier tabulation of rate constants for these much-studied reactions.[193] Activation parameters for complex formation with $[Cr(OH_2)_6]^{3+}$ and with $[Cr(OH_2)_5(OH)]^{2+}$ have been compared; activation enthalpies are markedly lower for

[188] D. Waysbort and G. Navon, *Chem. Comm.*, 1971, 1410.
[189] C. Chatterjee, P. Chaudhuri, and D. Banerjea, *Indian J. Chem.*, 1970, **8**, 1123 (*Chem. Abs.*, 1971, **74**, 103 572v).
[190] See, *e.g.*, J. H. Espenson and J. R. Pladziewicz, *Inorg. Chem.*, 1970, **9**, 1380.
[191] C. H. Langford and Fine Man Chung, *Canad. J. Chem.*, 1970, **48**, 2969.
[192] D. Thusius, *Inorg. Chem.*, 1971, **10**, 1106.
[193] J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 1554.

the latter hydroxo-complex.[192] Kinetics of formation of bromide complexes from $[Cr(OH_2)_6]^{3+}$ in hydrobromic acid and in hydrobromic–perchloric acid mixtures of concentration up to 9M were determined in an attempt to gain further insight into outer-sphere ion association [both ion pairs and triplets $\{Cr^{3+}, (Br^-)_2\}$] and kinetics of formation of inner-sphere complexes, and their inter-relation. The rate of bromide incorporation into $[Cr(OH_2)_6]^{3+}$ increases greatly with increasing concentration of bromide ion, but unfortunately there are too many unresolved uncertainties for the results to be analysed into precise ion association constants and rate constants.[194] The reaction of sulphite with $[Cr(OH_2)_6]^{3+}$ appears to involve sulphur–oxygen bond formation, rather than displacement of a whole water molecule from the metal by the incoming sulphite.[102] There is some discussion of kinetics of anation in a general review of the chromium(III)–amine–halide series of complexes.[96]

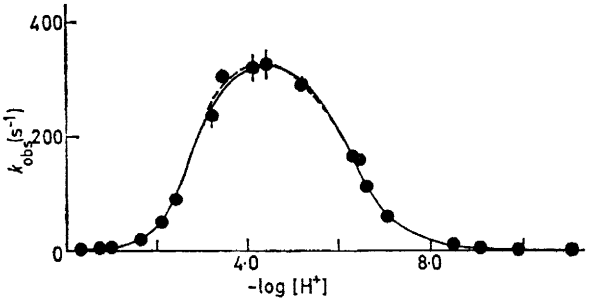
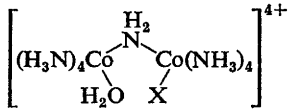


Figure *The variation of* k_{obs} *(average values) with* $-\log[H^+]$ *for the quadridentate to quinquedentate conversion at* 25 °C, $\mu = 1.0$ mol l^{-1} ($NaClO_4$), *for the chromium(III)–edta aquo-complex. The solid and broken lines refer to two different possible curve fitting solutions*
[Reproduced from *J. Chem. Soc.* (*A*), 1971, 1494]

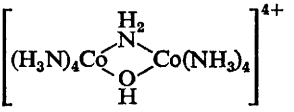
Formation reactions of chromium(III)–carboxylate complexes often do not follow the normal kinetic pattern, as has been illustrated by the study of the reaction of $[Cr(NH_3)_5(OH_2)]^{3+}$ with amino-acids. Here reaction takes place exclusively by a carbon dioxide-catalysed pathway in which ammonia is displaced to give an intermediate carbonato-chelate.[195] The rate-determining step in the formation of chromium(III)–edta complexes is a ligand interchange process. The dependence of rates on pH can be explained in terms of the relative reactivities of variously protonated forms of edta and of the $[Cr(OH_2)_6]^{3+}$ and $[Cr(OH_2)_5(OH)]^{2+}$ cations.[196] The chelation step in the conversion of the quadridentate chromium(III)–edta complex to the quinquedentate form in aqueous solution has been studied over the pH range 0—12. From the rate–pH profile (see Figure) it is apparent that

[194] L. O. Spreer and E. L. King, *Inorg. Chem.*, 1971, **10**, 916.
[195] J. E. Earley, D. J. Surd, L. Crone, and D. Quane, *Chem. Comm.*, 1970, 1401.
[196] J. Geher and M. T. Beck, *Magyar Kém. Folyoirat*, 1970, **76**, 150 (*Chem. Abs.*, 1970, **72**, 125 467a).

unco-ordinated $-CO_2H$ does not readily displace an OH_2 ligand, nor $-CO_2^-$ displace $-OH$. But $-CO_2^-$ does very readily replace OH_2, with a rate constant of 330 s^{-1} at 25 °C. The magnitude of this rate constant for substitution at a chromium(III) centre is remarkable, and is consistent with a high degree of associative character. This can be ascribed to the forced proximity of the unco-ordinated $-CO_2^-$ group and the absence of electrostatic repulsion.[197] A similar situation has been reported for intramolecular bridge formation reactions in dicobalt-complexes, for example for the reaction of (24) to (25), where X = Cl or Br.[198]



(24)



(25)

The rate law for ring closure in $[Cr(OH_2)_5(O_2CCH_2SH)]^{2+}$ to give $[Cr(OH_2)_4(O_2CCH_2S)]^+$, with chromium–sulphur bond formation, shows an inverse dependence on hydrogen ion concentration, ascribable to the loss of a proton accompanying this ring closure.[115]

Whereas the great majority of aquo–chromium(III) complexes are inert to formation reactions, the tetra-(*p*-sulphonatophenyl)porphine complex is remarkably labile—stopped-flow techniques are required to monitor replacement of the co-ordinated waters of this complex by, for instance, chloride, cyanide, or pyridine. Analogous cobalt(III) complexes are also substitution labile. This has been attributed to the possibility of a redox mechanism for substitution. In view of the difficulty of reducing chromium(III) to chromium(II) such a mechanism seems unlikely here, so that the porphine ligand may be promoting reactivity to substitution by electronic effects.[199]

***d*^{5}: Iron(III).**—Formation reactions of the aquated iron(III) cation, whether reacting as $[Fe(OH_2)_6]^{3+}$ or $[Fe(OH)(OH_2)_5]^{2+}$, tend to be fast, and are therefore discussed in Part II, Chapter 4. Establishment of the following equilibrium, in which the left to right reaction is formation with respect to the first complex, is however, slow:

$$[Fe(CN)_5(OH_2)]^{2-} + [Fe(CN)_6]^{3-} \rightleftharpoons [Fe_2(CN)_{11}]^{5-} + H_2O$$

Rate constants over a range of pH values have been determined for reaction in both directions. The complex $[Fe(CN)_5(OH_2)]^{2-}$ reacts, but its deprotonated derivative $[Fe(CN)_5(OH)]^{3-}$ does not; equilibrium constants have been determined from the rate constants.[200]

[197] R. N. F. Thorneley, A. G. Sykes, and P. Gans, *J. Chem. Soc.* (*A*), 1971, 1494.
[198] M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 937.
[199] E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.*, 1971, **93**, 3784.
[200] J. Duplessis-Legros and G. Emschwiller, *Compt. rend.*, 1971, **273**, *C*, 452.

d^5: Ruthenium(III).—Anation of *cis*-$[Ru(en)_2(OH_2)_2]^{3+}$, *cis*-$[Ru(en)_2(OH_2)Cl]^{2+}$, and *cis*-$[Ru(en)_2(OH_2)Br]^{2+}$ by chloride or bromide, and of $[Ru(NH_3)_5(OH_2)]^{3+}$ by chloride, bromide, or iodide, follows a second-order rate law and proceeds with complete retention of configuration; the 3+ complexes react more rapidly than the 2+ complexes. As kinetics of aquation of the products of these reactions have been studied previously, it is possible from the earlier and the present results to estimate equilibrium constants from the rate data; these 'kinetic' equilibrium constants compare satisfactorily with respective values determined spectrophotometrically. Activation parameters are reported for anation of the ethylenediamine complexes. It has not proved possible to determine the mechanisms of these reactions, but associative and interchange processes are discussed.[201]

Halide substitution at $[Ru(OH_2)_6]^{3+}$ is catalysed by $[Ru(OH_2)_6]^{2+}$. This behaviour is similar to redox catalysis of substitution at, for example, chromium(III) by chromium(II) or at platinum(IV) by platinum(II). In this ruthenium(III)–ruthenium(II) system it appears that the rate-determining step is in fact substitution at the $[Ru(OH_2)_6]^{2+}$ cation, for which the activation enthalpy is about 20 kcal mol^{-1}.[202]

d^6: Cobalt(III).—Anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by sulphate or chloride proceeds by a dissociative interchange mechanism, in which the reactive species are ion-pairs and ion-triplets.[203] The activation enthalpy for anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by glycine is 29 kcal mol^{-1}; again a dissociative mechanism is operative.[7] An earlier study of oxalate anation of $[Co(en)_2(OH_2)_2]^{3+}$ in acidic solution is complemented by a study of oxalate anation of $[Co(en)_2(OH_2)(OH)]^{2+}$ in basic solution.[204] Several examples of anation reactions of bridged dicobalt complexes have been mentioned in the section on aquation of these complexes.[205]

It has been known for a few years that anation of *trans*-$[Co(dmgH)_2(Me)(OH_2)]$ is fast, since the methyl group has a powerful *trans* labilizing influence on the co-ordinated water. Recently activation parameters have been determined for replacement of this water by pyridine and by thiocyanate. Activation enthalpies are low by cobalt(III) standards: 20.5 kcal mol^{-1} for reaction with pyridine and 17.5 kcal mol^{-1} for thiocyanate. However, these values are comparable with those for anation of the analogous, but much less reactive, complex *trans*-$[Co(dmgH)_2(NO_2)(OH_2)]$; in fact it is the difference in activation entropies which determines the different reaction rates for these methyl and nitro-complexes.[206] The

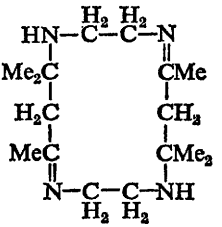
[201] J. A. Broomhead and L. A. P. Kane-Maguire, *Inorg. Chem.*, 1971, **10**, 85.
[202] T. W. Kallen and J. E. Earley, *Inorg. Chem.*, 1971, **10**, 1149.
[203] M. G. Burnett, *J. Chem. Soc.* (*A*), 1970, 2480, 2486, 2490.
[204] S. C. Chan and G. M. Harris, *Inorg. Chem.*, 1971, **10**, 1317.
[205] See, *e.g.*, S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1266; R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1426; M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1971, 3214.
[206] T. Sakurai, J. P. Fox, and L. L. Ingraham, *Inorg. Chem.*, 1971, **10**, 1105.

rate law for anation of the complex *trans*-[Co(α-amino-oximate)$_2$(NO_2)-(OH_2)] by nitrite, thiocyanate, or azide (Y^-) is

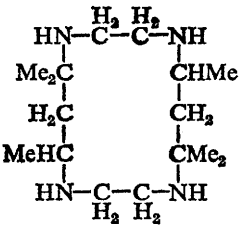
$$-\,d[complex]/dt = k[complex][Y^-]$$

which is of the same form as that for anation of $[Co(CN)_5(OH_2)]^{2-}$. Rates of water exchange at the α-amino-oximate complexes are faster than rates of anation, which suggests that in the anation process there may be competition between water and the anion for the vacant site at the cobalt in the activated intermediate.[207]

Some kinetic results are available on dimerization of *trans*-[Co(*trans*-14-diene)(OH_2)(OH)]$^{2+}$ [*trans*-14-diene is formula (26)]; *trans*-[Co(tet-a)-(OH_2)(OH)]$^{2+}$ [tet-a is formula (27)] dimerizes extremely slowly.[208]



(26)



(27)

***d*^{6}: Iron(II).**—The only slow formation reactions of iron(II) complexes are those in which a low-spin complex is formed from the high-spin aquated (solvated) cation. It is well established from kinetic studies that in the formation of $[Fe(LL)_3]^{2+}$, where LL = bipy, phen, or one of their analogues or derivatives, there is no evidence for appreciable concentrations of the (high-spin) intermediates $[Fe(LL)_2(OH_2)_2]^{2+}$ and $[Fe(LL)(OH_2)_4]^{2+}$. Mössbauer studies of the reaction between Fe^{2+}(aq) and 2,2′-bipyridyl now lend further support to the kinetic evidence for the absence of significant amounts of the mono- and bis-2,2′-bipyridyl intermediates during the formation of the $[Fe(bipy)_3]^{2+}$ cation.[209]

***d*^{6}: Ruthenium(II).**—The rates of dinitrogen uptake by the complexes $[Ru(NH_3)_5(OH_2)]^{2+}$, *cis*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$, *cis*-$[Ru(en)_2(OH_2)_2]^{2+}$, and *cis*-$[Ru(trien)(OH_2)_2]^{2+}$ are all very similar.[210] The kinetics of the reaction of the first-named complex with dinitrogen have been further studied in order to determine the activation parameters for this reaction, which are $\Delta H^{\ddagger} = 18.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2$ cal deg^{-1} mol^{-1}. The rate of reaction of the product $[Ru(NH_3)_5(N_2)]^{2+}$ with $[Ru(NH_3)_5(OH_2)]^{2+}$, to

[207] S. M. Abdulnour and R. K. Murmann, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3617.
[208] M. P. Liteplo and J. F. Endicott, *Inorg. Chem.*, 1971, **10**, 1420.
[209] A. Vertes, I. Dezsi, and M. Suba, *Acta Chim. Acad. Sci. Hung.*, 1970, **64**, 347 (*Chem. Abs.*, 1970, **73**, 81 059h).
[210] L. A. P. Kane-Maguire, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3964.

produce the nitrogen-bridged diruthenium cation $[\{Ru(NH_3)_5\}_2(N_2)]^{4+}$, is strongly acid-dependent.[168]

In the course of establishing the kinetics of ruthenium(II)-catalysed anation of ruthenium(III) it was found that the activation enthalpies of substitution of chloride, bromide, or iodide at $[Ru(OH_2)_6]^{2+}$ were all equal, within experimental uncertainty, at 19.8 ± 0.4 kcal mol^{-1}. This strongly suggests a dissociative mechanism for these substitutions.[202] The redox reaction between ruthenium(II) and perchlorate ion also appears to involve rate-determining substitution at the $[Ru(OH_2)_6]^{2+}$ cation.[211]

d^6: Platinum(IV).—The kinetics of reaction of *trans*-$[Pt(CN)_4Br(OH_2)]^-$ with chloride and with bromide have been examined in connection with an investigation of the oxidation of platinum(II) complexes by bromine.[212]

7 Ligand Exchange and Replacement

Solvent Exchange.—There have, as usual, been relatively few reports on kinetics of solvent exchange at inert metal centres, and most of these concern solvent exchange at mixed ligand complexes. However, there has been one important kinetic study of solvent exchange with a transition metal solvate: of water at $[Cr(OH_2)_6]^{3+}$, for which determination of the variation of rate with pressure has given a value for the activation volume for the reaction.[94] The activation volume here is − 9.3 cm^3 mol^{-1}, which may be compared with a value of + 1.2 cm^3 mol^{-1} for the probably dissociative water exchange at $[Co(NH_3)_5(OH_2)]^{3+}$. The closeness to linearity of the log k against pressure plot is said to support an associative interchange (I_a) rather than a simple associative (A, or S_N2) mechanism. Likewise the activation entropy, + 0.3 cal mol^{-1} deg^{-1}, estimated from the present kinetic results and those of Hunt and Plane,[213] is more consistent with an I_a than with an A mechanism. Either way this work lends further support to the idea of greater associative character in substitution at chromium(III) than at cobalt(III). An ^{18}O tracer study of water exchange at $[Ir(NH_3)_5(OH_2)]^{3+}$ indicates an activation enthalpy of 28.2 kcal mol^{-1} and an activation entropy of + 3 cal deg^{-1} mol^{-1}. A comparison of these kinetic results with rates of aquation and anation of similar rhodium(III) and cobalt(III) as well as iridium(III) complexes suggests that the mechanism of water exchange is at least partially associative in character at iridium(III) and rhodium(III).[171] The remaining study of water exchange is at the platinum(IV) complex $[PtMe_3bipy(OH_2)]^+$, where the activation energy is 19.2 kcal mol^{-1}. The discussion is in terms of a dissociative mechanism, though the possibility of some associative character is recognized.[214] It is possible to estimate the rate of water exchange with $[Ru(OH_2)_6]^{2+}$ as about 10^{-1} s^{-1}

[211] T. W. Kallen and J. E. Earley, *Inorg. Chem.*, 1971, **10**, 1152.
[212] W. R. Mason, *Inorg. Chem.*, 1971, **10**, 1914.
[213] J. P. Hunt and R. A. Plane, *J. Amer. Chem. Soc.*, 1954, **76**, 5960.
[214] D. E. Clegg, J. R. Hall, and N. S. Ham, *Austral. J. Chem.*, 1970, **23**, 1981.

at 25 °C, from the kinetic results of an investigation of rhuthenium(II)-catalysed substitution at ruthenium(III).[202]

Ligand Exchange: Unidentate.—Chloride exchange at d^3 rhenium(IV) in $[ReCl_6]^{2-}$ is very slow in acidic solution, but is very fast at d^2 rhenium(V) in $[ReOCl_5]^-$.[215] Chloride exchange with the cluster cation $[Nb_6Cl_{12}]^{2+}$ is also extremely slow, and in fact the only reaction in aqueous solution is slow formation of hydrated Nb_2O_5.[216] Rates of chloride exchange at iridium(III)– and rhodium(III)–amine–chloride complexes[217] show an initial rapid increase followed by an asymptotic approach to a limiting value as the chloride concentration increases. This behaviour is typical of systems in which there is ion pairing, though it is somewhat surprising to find significant ion pairing between chloride ions and these large, singly charged, cations in aqueous solution. It has proved difficult to estimate ion-pairing constants from the variation of observed rate constants with chloride concentration since it is difficult to estimate the reactivity of the free cation at zero chloride concentration. However, the approximate ion association constants are 25 for *trans*-$[Rh(en)_2Cl_2]^+$, 30 for *trans*-$[Ir(en)_2Cl_2]^+$, 60 for *cis*-$[Rh(trien)Cl_2]^+$, and again 60 for *cis*-$[Ir(en)_2Cl_2]^+$; these values show the expected relation between *cis*- and *trans*-complexes. Steric effects in the non-leaving ligand have been investigated by comparing chloride exchange rates at $[Co(LLLL)Cl_2]^+$, where LLLL = cyclam or its hexamethyl derivative. The observed faster reaction for the hexamethylcyclam complex is consistent with a dissociative mechanism for chloride exchange.

The rate law for fluoride exchange at $[TaF_6]^-$ in hydrogen fluoride is[218]

$$\text{rate} = \{k_1 + k_2[F^-]\}[TaF_6^-]$$

This two-term form, normal for square-planar complexes, is extremely unusual for substitution at an octahedral complex. The tantalum(V) appears to be present in the reaction system solely as $[TaF_6]^-$, but of course $[TaF_7]^{2-}$ is a stable anion so that parallel associative and dissociative paths for fluoride exchange represent a reasonable mechanism. Rate constants and activation parameters are listed in Table 9. The activation entropy for the k_2 term is entirely consistent with associative fluoride exchange *via* a

Table 9 *Kinetic parameters for fluoride exchange at* $[TaF_6]^-$ *in hydrogen fluoride*

	k_1 *path*	k_2 *path*
k (25 °C)	4.9×10^2 s^{-1}	2.9×10^4 l mol^{-1} s^{-1}
$\Delta H^{\ddagger}$/kcal mol^{-1}	1.8 ± 0.3	2.4 ± 0.5
$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	− 40 ± 4	− 31 ± 4

[215] J. D. Woods, J. Gruca, and C. M. Pietrzak, *Proc. Iowa Acad. Sci.* (*1969*), 1970, **76**, 119.
[216] J. E. Land, H. H. Musgrove, and J. E. Teggins, *J. Less-Common Metals*, 1971, **23**, 307.
[217] K. R. Bowker, E. R. Gardner, and J. Burgess, *Trans. Faraday Soc.*, 1970, **66**, 2065; 1971, **67**, 3076.
[218] N. A. Matwiyoff, L. B. Asprey, and W. E. Wageman, *Inorg. Chem.*, 1970, **9**, 2014.

TaF_7^{2-} transition state, but it is surprising that the activation entropy for the k_1 term is also negative and large. This suggests that this k_1 term cannot arise from a simple dissociative mechanism; the authors suggest an HF-assisted mechanism. The activation enthalpies for both paths are remarkably low. Fluoride exchange at $[ScF_6]^{3-}$ has also been studied by ^{19}F n.m.r.; an activation enthalpy of about 8 kcal mol^{-1} has been determined, but the mechanism of the process has not been precisely defined.[219]

Examples of kinetic studies of exchange of polyatomic ligands include those of phosphate exchange at uranyl nitrate–phosphate complexes,[220] and of nitrile (RCN) exchange at niobium(v) and tantalum(v) complexes MCl_5,NCR.[221] The activation energies for tributyl phosphate, dibutyl cresyl phosphate, and dicresyl butyl phosphate at their respective uranyl nitrate–phosphate complexes are all close to 9 kcal mol^{-1}. Activation enthalpies for RCN exchange at MCl_5,NCR are collected in Table 10; change in solvent produces a more dramatic change in activation enthalpy than does change in metal or ligand.

Table 10 *Activation enthalpies for nitrile* (RCN) *exchange at* MCl_5,NCR

M	RCN	*Solvent*	$\Delta H^{\ddagger}$/kcal mol^{-1}
Nb	Acetonitrile	MeCN	10.5 ± 1.1
	Acetonitrile	CH_2Cl_2	17.8 ± 2.3
	Pivalonitrile	CH_2Cl_2	18.4 ± 2.4
Ta	Acetonitrile	MeCN	12.4 ± 1.6

Ligand Replacement: Unidentate by Unidentate.—Replacement of the hydroxo-ligand in [Co(salen)(OH)py] by malononitrile is thought to take place by nucleophilic substitution of the carbanion from malononitrile at the cobalt atom.[222] Rate constants have been determined for the four-stage process by which the rhodium(II) acetate dimer is converted by reaction with trifluoroacetic acid into the rhodium(II) trifluoroacetate dimer.[223] Rates have also been determined for the reaction of nitrato–zirconium(IV) species with bis-(2-ethylhexyl) hydrogen phosphate.[224]

Ligand substitution at platinum(IV) generally involves a redox substitution mechanism, as in the recent example of halide substitution reactions of *trans*-$[Pt(en)_2Cl_2]^{2+}$ and of *trans*-$[Pt(en)(LL)X_2]^{2+}$, where LL = *NNN'N'*-tetramethylethylenediamine.[225] Conversely, reduction of $PtCl_4$ by phosphine in the presence of iodide ion involves preliminary substitution

[219] E. H. Pfadenhauer and D. C. McCain, *J. Phys. Chem.*, 1970, **74**, 3291.
[220] Y. Egozy and S. Weiss, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1451.
[221] A. Merbach, J. C. Brenzli, and F. Gnagi, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 285.
[222] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 591.
[223] J. L. Bear, J. Kitchens, and M. R. Willcott, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3479.
[224] G. A. Yagodin and V. V. Tarasov, *Radiokhimiya*, 1970, **12**, 666 (*Chem. Abs.*, 1971, **74**, 57 686k).
[225] A. J. Poë and D. H. Vaughan, *J. Amer. Chem. Soc.*, 1970, **92**, 7537.

processes at the platinum(IV).[226] Ring closure of platinum(IV) complexes containing unidentate glycine or alanine ligands might also be classed as a ligand replacement reaction.[227]

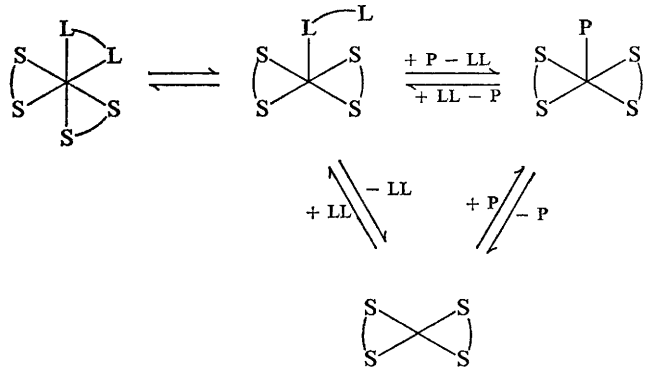
The photochemical reaction of nitroprusside, $[Fe(CN)_5(NO)]^{2-}$, with thiourea or with diethylthiourea in methanol follows a second-order rate law, first-order in each reactant. The activation parameters are reported in Table 11.[228] As in the reaction of nitroprusside with sulphide, one does not

Table 11 *Activation parameters*[228] *for reaction of thiourea or of its diethyl derivative with nitroprusside,* $[Fe(CN)_5(NO)]^{2-}$

	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
Thiourea	30.7	+ 39
Diethylthiourea	33.0	+ 44

know the nature of the product. This may have sulphur bonded to nitrosyl-nitrogen or to the iron, in the latter case probably with displacement of a cyanide ligand.

Ligand Replacement: Multidentate by Unidentate.—The kinetic study of the reaction of $[Co(mnt)_2(LL)]^{n-}$ with tri-n-butylphosphine, in which the



Scheme 1

displaced ligand LL is en, bipy, phen, or mnt^{2-}, is complementary to that of the reaction of the five-co-ordinated complexes $[Co(mnt)_2(PPh_3)]^-$ with bidentate ligands.[229] The mechanisms suggested for these reactions are shown in Scheme 1, where P represents PBu^n_3 or PPh_3 and S—S represents the mnt ligands.

The kinetics of reaction of nickel(II) aminocarboxylates with cyanide, and of the reverse reaction, can all be accommodated by the following reaction

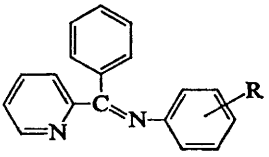
[226] D. V. Sokol'skii, Ya. A. Dorfman, and V. S. Emel'yanova, *Doklady Akad. Nauk S.S.S.R.*, 1971, **198**, 1110 (*Chem. Abs.*, 1971, **75**, 80 764p).
[227] Yu. N. Kukushkin and G. P. Gur'yanova, *Russ. J. Inorg. Chem.*, 1971, **10**, 455.
[228] D. X. West and D. J. Hassemer, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2717.
[229] D. A. Sweigart and D. G. DeWit, *Inorg. Chem.*, 1970, **9**, 1582; D. G. DeWit, M. J. Hynes, and D. A. Sweigart, *ibid.*, 1971, **10**, 196.

scheme (wherein charges are omitted for clarity; the charge on NiL varies with the nature of L):

$$\begin{aligned}
NiL + CN &\rightleftharpoons NiL(CN) && \text{fast}\\
NiL(CN) + CN &\rightleftharpoons NiL(CN)_2 && \text{fast}\\
NiL(CN)_2 + CN &\rightleftharpoons NiL(CN)_3 && \text{rate-determining}\\
NiL(CN)_3 + CN &\rightleftharpoons Ni(CN)_4 + L && \text{fast}
\end{aligned}$$

This scheme, which applies to a variety of monoaminocarboxylate ligands L, including *inter alia*, edta, edda, nta, or ida, is different from the reaction scheme for reaction of $[Ni(OH_2)_6]^{2+}$ or of $[Ni(trien)]^{2+}$ with cyanide, where four cyanides per nickel are required in the transition state for the rate-determining step.[230]

The cations $[Fe(LL)_3]^{2+}$, where LL = phen or substituted phen,[231] or a Schiff base of type (28),[232] react with cyanide to form initially compounds



(28)

$[Fe(LL)_2(CN)_2]$; further reaction to $[Fe(LL)(CN)_4]^{2-}$ and to $[Fe(CN)_6]^{4-}$ is very slow. The formation of the Schiff base complexes $[Fe(LL)_2(CN)_2]$ follows a simple second-order rate law, but for the analogous phen compounds the rate law is

$$-\,d[Fe(phen)_3^{2+}]/dt = \{k_1 + k_2[CN^-]\}[Fe(phen)_3^{2+}]$$

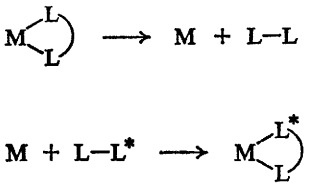
The k_1 term is assigned to rate-determining dissociation of the iron(II) complex; the k_2 term is assigned to bimolecular nucleophilic attack of the cyanide at the iron. For both the phenanthroline and the Schiff base complexes the rate of reaction with cyanide increases greatly as the mole fraction of alcohol increases in methanol– or ethanol–water mixed solvents.

Ligand Replacement: Unidentate by Multidentate.—1,2-Cyclohexanedione dioxime replaces the two chlorides of *trans*-$[Co(en)_2Cl_2]^+$, in aqueous solution, by a complicated mechanism whose essential features are an S_N2 reaction of the incoming ligand with the complex and a later intramolecular S_N2 reaction in which chelate ring formation is synchronous with chloride expulsion. The evidence in favour of the bimolecularity of the first step is the activation entropy of -11 cal deg^{-1} mol^{-1}; the evidence in favour of the latter S_N2 step is that its rate is 100 times faster than normal

[230] L. C. Coombs, D. W. Margerum, and P. C. Nigam, *Inorg. Chem.*, 1970, **9**, 2081.
[231] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.
[232] J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc.* (*A*), 1971, 44.

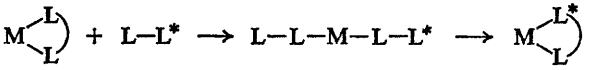
cobalt(III)–chloride bond fission.[233] The formation of $[Rh(edta)Cl]^{2-}$ from $[RhCl_6^{3-}]$ plus edta in sodium chloride–hydrochloric acid solution involves the intermediacy of outer-sphere units $[RhCl_6]^{3-}\cdots H_2edta^{2-}$ and $[RhCl_6]^{3-}\cdots H_3edta^{-}$. The former is said to react by a dissociative, the latter by a displacement, mechanism.[234]

Ligand Replacement: Multidentate by Multidentate.—There are three or four mechanisms for this type of reaction. In the first mechanism, the outgoing ligand (L—L)† is completely dissociated from the metal cation (M) before association between M and the incoming ligand (L—L*) starts:



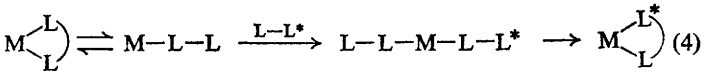
(2)

Alternatively, association of the metal cation with the incoming ligand may begin before dissociation of the outgoing ligand is complete. In this mechanism there will thus be an intermediate in which both ligands are bonded to the one cation:



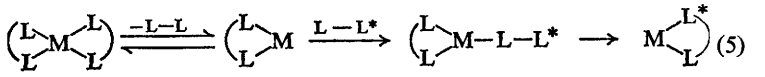
(3)

A variation on this mechanism is the case of pre-equilibrium partial dissociation of the starting complex:



(4)

The last scheme is a modification of this which can apply when two multi- *e.g.* ter-, dentate ligands are replaced by one multi-, *e.g.* quinque- or sexi-, dentate ligand:



(5)

Kinetic studies of ligand replacement are summarized in Table 12. Where it is possible to classify the mechanism according to the above equations

[233] I. Zsakó, C. Várhelyi, and F. Kormos, *Rev. Roumaine Chim.*, 1971, **16**, 1045.
[234] D. Banerjea and B. Chattopadhyay, *Indian J. Chem.*, 1970, **8**, 993 (*Chem. Abs.*, 1971, **74**, 80 289s).

† In this section the symbol L—L is used to represent any multidentate ligand.

Table 12 *Mechanisms of ligand replacement in chelates*

Complex[a]	*Incoming ligand*[a]	*Mechanism*[b]	*Ref.*
Chromium(III)–acac	edta	*D, DA*	235
–big	edta	*D, DA*	235
Cobalt(II)–dimedta	en		236
–edta	cal	*D*	237
–hedta	cal	*D*	237
Nickel(II)–dien	cydta	*DA*	238
–dien	dtpa	*DA*	238
–edda	par	*DA*	239
–edma	dtpa	*DA*	238
–edta	cal	*D*	237
–en	cydta	*DA*	238
–hedta	cal	*D*	237
–heida	cydta	*QDA*	240
–heida	edta	*QDA*	240
–nta	dtpa[c]	*QDA*	240
–nta	par	*DA*	239
Copper(II)–egta	par[d]	*DA*	241
Lead(II)–edta	cydta	*DA*	242
–pdta	cydta	*DA*	243
Mercury(II)–par	cydta	*QDA*	244

[a] For abbreviations see list at start of this volume; [b] abbreviations as defined in text; [c] in the presence of en (see text); [d] in the presence of M^{2+} cations (see text).

(2)—(5) without too gross a simplification, this has been done. In Table 12 the dissociative mechanism of equation (2) is symbolized by *D*, the dissociative–associative mechanism of equation (3) by *DA*, and the pre-equilibrium dissociation followed by association mechanism of equations (4) and (5) by *QDA*. It is often very difficult to distinguish between *DA* and *QDA* mechanisms.

In many of these multidentate ligand replacement reactions the rate law contains terms in various powers of the hydrogen ion concentration, which arise from the possible ways of protonating the ligands both free and in complexed form. Dissociation of the starting complex can also be catalysed by the presence of added cations, as in the reaction of the copper(II)–egta complex with par in the presence of alkaline-earth cations.[241] The effect of added anions on rates of these multidentate ligand replacements has also been studied, specifically for the reaction of the mercury(II)–par complex with cydta.[244] Some useful background kinetic information is provided by a

[235] D. Banerjea and P. Chaudhuri, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2697.
[236] R. M. Countryman and H. M. N. H. Irving, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1819.
[237] M. Kodama, *Nippon Kagaku Zasshi*, 1970, **91**, 134 (*Chem. Abs.*, 1970, **73**, 18 953e).
[238] M. Kodama, Y. Fujii, and T. Ueda, *Bull. Chem. Soc. Japan*, 1970, **43**, 2085.
[239] S. Funahashi and M. Tanaka, *Inorg. Chem.*, 1970, **9**, 2092.
[240] M. Kodama, S. Karasawa, and T. Watanabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 1815.
[241] S. Funahashi, S. Yamada, and M. Tanaka, *Inorg. Chem.*, 1971, **10**, 257.
[242] P. E. Reinbold and K. H. Pearson, *Inorg. Chem.*, 1970, **9**, 2325.
[243] J. D. Carr and D. R. Baker, *Inorg. Chem.*, 1971, **10**, 2249.
[244] S. Funahashi, M. Tabata, and M. Tanaka, *Bull. Chem. Soc. Japan*, 1971, **44**, 1586.

polarographic study of the dissociation of the aminocarboxylate complexes of nickel(II) with edma and hedta. The $Ni(edma)_2$ complex is a model for the first part of the *QDA* mechanism of equation (5), for the bis-complex is in rapid equilibrium with mono-complex plus free ligand; it is dissociation of the mono-complex which is rate-determining in dissociation.[245] Kinetic results for dissociation of the iminodiacetate complex of nickel(II) have also been reported.[246]

Further kinetic results relevant to the ligand replacement reactions discussed in this section are those for dissociation of lanthanide(III)–cydta complexes. Nearly all the tervalent rare-earth cations were included in this investigation, along with the closely related complexes of scandium(III) and yttrium(III). Dissociation rates vary with pH, but are unaffected by the addition of copper(II) ions. Thus there is no direct transfer of cydta from Ln^{3+} to Cu^{2+} in the manner of equation (7) (next section). The rate constants for the acid-dependent dissociation path show a large variation with the nature of the lanthanide cation; they vary from 129 l mol^{-1} s^{-1} (at 25 °C, μ = 0.1 mol l^{-1}) for lanthanum(III) to 0.017 l mol^{-1} s^{-1} for lutecium(III); the trend of rate constants is one of regular decrease as the ionic radius decreases. The rate constant of 0.019 l mol^{-1} s^{-1} for dissociation of the scandium(III) complex is, however, much higher than would be expected from the ionic radius of Sc^{3+}. Activation parameters for dissociation of these cydta complexes are reported for the La^{III}, Gd^{III}, Dy^{III} Tm^{III}, Lu^{III}, and Y^{III} compounds.[247]

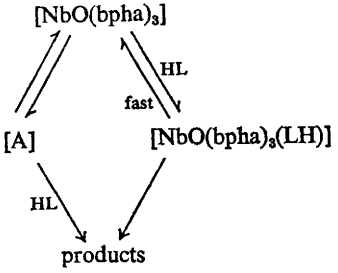
Stereochemical aspects of these multidentate ligand replacements have been described and discussed for the reaction of $[Co(dimedta)]^-$ with ethylenediamine,[236] of $[Pb(edta)]^{2-}$ with D-(−)-cydta^{4-},[242] of the D- and L-pdta complexes of lead(II) with D-, L-, and DL-forms of cydta,[243] and of $[Co(glycine)_2(CO_3)]^-$ with *S*-(+)-glutamic acid.[248] An *X*-ray crystal structure of L-(+)-glutamatobisethylenediaminecobalt(III) perchlorate has yielded results which help to shed some light on the mechanism of reactions of $[Co(en)_2(CO_3)]^+$ with amino-acids.[249]

The replacement of en by edta in the reaction of the latter with $[Co(en)_3]^{3+}$ under photochemical conditions is a direct anation process and does not proceed through an aquo-intermediate.[77, 250]

The replacement of bpha (benzoylphenylhydroxylamine) in the seven-co-ordinated niobium(v) complex $[NbO(bpha)_3]$ by tropolone or oxine, in chloroform or dichloroethane solution, follows first-order kinetics. For reaction with some substituted oxines, rates decrease on increasing the concentration of the oxine. Rates are enhanced by the presence of water, acids, alcohols, or n-butylamine, but decrease in the presence of pyrrole or

[245] M. Kodama and N. Oyama, *Bull. Chem. Soc. Japan*, 1971, **44**, 2849.
[246] M. Kodama, H. Nunokawa, and N. Oyama, *Bull. Chem. Soc. Japan*, 1971, **44**, 2387.
[247] G. A. Knyssen and D. A. Margerum, *Inorg. Chem.*, 1970, **9**, 1814.
[248] F. Jursík and B. Hájek, *Coll. Czech. Chem. Comm.*, 1971, **36**, 3362.
[249] R. D. Gillard, N. C. Payne, and G. B. Robertson, *J. Chem. Soc.* (*A*), 1970, 2579.
[250] B. Nordén, *Acta Chem. Scand.*, 1970, **24**, 1703.

pyridine. All these facts can be accommodated by the mechanism of Scheme 2, where [A] is probably $[NbO(bpha)_3]$ containing one unidentate bpha ligand, and where L is added oxine, pyrrole, or other base.[251] An example of substitution at six-co-ordinated niobium(v), RCN exchange at $[NbCl_5(NCR)]$, has been mentioned earlier in this section.[221]



Scheme 2

Ligand Exchange: Multidentate.—Kinetic studies of exchange of amino-carboxylate ligands at metal cations are listed in Table 13. Further studies of carbonate exchange at *cis*- and at *trans*-$[Co(en)(NH_3)_2(CO_3)]^+$ in basic solution confirm earlier postulations of parallel reaction by bimolecular

Table 13 *Mechanisms of ligand exchange for complexes of multidentate ligands*

Cation	*Ligand*	*Mechanism*[a]	*Ref.*
Calcium(II)	edta		252
Zinc(II)	edta	*D*	253
	heedta	*D*	253
Cadmium(II)	egta		253
Lead(II)	nta	*D*, *DA*	254
Europium(III)	4,4′-di-Bu^n-bipy	*D*	255

[a] Abbreviations defined in the text, near Table 12.

associative interchange and by dissociative interchange with water followed by associative interchange of this aquo-intermediate with incoming carbonate.[256]

Zirconium tetrakistetrahydroborate, $Zr(BH_4)_4$, is effectively a twelve-co-ordinate complex of zirconium(IV), for there are twelve hydrogens, three

[251] R. C. Johnson and A. Syamal, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2547.
[252] A. Bryson and I. S. Fletcher, *Austral. J. Chem.*, 1970, **23**, 1095.
[253] G. H. Reed and R. J. Kula, *Inorg. Chem.*, 1971, **10**, 2050.
[254] D. L. Rabenstein, *J. Amer. Chem. Soc.*, 1971, **93**, 2869.
[255] F. A. Hart, J. E. Newbery, and D. Shaw, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3585.
[256] R. J. Dobbins and G. M. Harris, *J. Amer. Chem. Soc.*, 1970, **92**, 5104.

from each BH_4^- ligand, equidistant from the metal.[257] The mechanism of BH_4^- exchange with $LiBH_4$ in ethereal solution has been discussed; the intermediate $Li[Zr(BH_4)_5]$ is proposed. This contrasts with exchange reactions involving $Zr(BH_4)_4$ in the gas phase, where dissociative mechanisms seem more likely.[258]

The complex $[Eu(NO_3)_3(LL)_2]$, with LL = 4,4′-di-n-butyl-2,2′-bipyridyl, appears to contain ten-co-ordinate europium(III).[259] The rate of exchange of the substituted bipyridyl with the complex is, in chloroform solution, independent of the concentration of added bipyridyl, indicating a dissociative mechanism. The activation parameters for the exchange are $\Delta H^{\ddagger} = 5.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -40$ cal deg^{-1} mol^{-1}. This surprisingly negative value for the activation entropy is explained by solvation effects.[255]

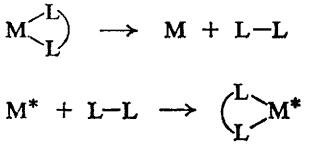
8 Metal Exchange and Displacement

The majority of kinetic studies of cation exchange processes concern aminocarboxylate complexes of lanthanide cations. Rates of cation exchange with edta and cydta complexes of cerium(III), neodymium(III), gadolinium(III), terbium(III), and lutecium(III) are independent of the concentration of added Ln^{3+}, which indicates a dissociative mechanism. Rates decrease greatly, by a factor of 10^4, in going from cerium to lutecium; exchange with cydta complexes is about 50 times slower than with the respective edta complexes.[260] Kinetics of terbium(III) exchange with its edta, hedta, and cydta complexes have been reported,[261] while a general discussion of the effects of the number of *f* electrons on exchange rates is based on another determination of the rate of exchange of terbium(III) with its edta complex.[262] Exchange of europium(III) with its edta complex is dissociative in mechanism, with $\Delta H^{\ddagger} = 11.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7$ cal deg^{-1} mol^{-1} for the dissociation step.[263]

Rate laws for the exchange of Y^{3+} with yttrium(III) complexes of the aminocarboxylate ligands edta, cydta, and dtpa have terms in hydrogen ion concentration and in yttrium(III) concentration. The terms in which hydrogen ion concentration, or its square, appears relate to dissociation of mono- and di-protonated forms of the complex. Terms in yttrium(III) concentration relate to bimolecular attack by the incoming Y^{3+}. Yttrium(III) exchange with its hedta complex has a rate law in which the yttrium(III) ion concentration does not appear, so the mechanism here must be purely dissociative.[264]

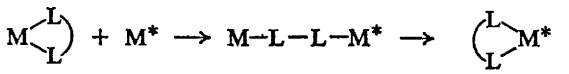
[257] P. H. Bird and M. R. Churchill, *Chem. Comm.*, 1967, 403.
[258] N. Davies, D. Saunders, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1970, 2915.
[259] F. A. Hart and J. E. Newbery, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1725.
[260] E. Brücher and P. Szarvas, *Inorg. Chim. Acta*, 1970, **4**, 632.
[261] P. Szarvas and E. Brücher, *Monatsh.*, 1970, **101**, 1321.
[262] K. Neelakantan and R. E. Jervis, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 131.
[263] W. D'Olieslager, G. R. Choppin, and K. R. Williams, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3605.
[264] P. Glentworth and D. A. Newton, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1701.

Mechanisms of metal displacement can be either dissociative:



(6)

or associative:



(7)

in character. The mechanisms of recently reported metal cation displacement reactions are indicated in Table 14; equations (6) are represented by *D*, equations (7) by *DA*.

Table 14 *Mechanisms of cation displacement in multidentate ligand complexes*

Complex	*Replacing cation*	*Mechanism*[a]	*Ref.*
Cadmium(II)–ttha	M^{II} [b]	*DA*	265
–cydta	Copper(II)	*D*	266
Copper(II)–edta	Nickel(II)[c]	*DA*	267
–hedta	Nickel(II)[c]	*DA*	267
Lanthanum(III)–cydta	M^{III} [d]	*D*	268
Lanthanide(III)–cydta	Copper(II)	*D*	269
Praseodymium(III)–xyl	Iron(III)	*D*, *DA*[e]	270
Europium(III)–edta	Amercium(III)	*D*	263

[a] Symbols defined in text; [b] M^{II} = cobalt(II), nickel(II), copper(II), or zinc(II); [c] the reactions were carried out in ammoniacal solution, so both hexa-aquonickel(II) and mixed aquoammononickel(II) species are reactants; [d] M^{III} = cerium(III), europium(III), or americium(III); [e] relative importance of *D* and *DA* pathways is a function of pH.

9 Isomerization

General.—Possible routes for intramolecular rearrangements of four-, five-, and six-co-ordinated structures have been reviewed.[271] The isomerization pathways are represented by Schlegel diagrams; these representations are correlated, where relevant, with specific mechanisms such as those discussed by Muetterties,[272] and the Berry pseudorotation process for five-co-ordinate species.

[265] L. Neubauer and M. Kopanica, *Coll. Czech. Chem. Comm.*, 1971, **36**, 1121.
[266] M. Kimura, *Bull. Chem. Soc. Japan*, 1970, **43**, 1594.
[267] R. R. Das, T. R. Bhat, and J. Shankar, *J. Indian Chem. Soc.*, 1970, **8**, 997 (*Chem. Abs.*, 1971, **74**, 80 257e).
[268] W. D'Olieslager and G. R. Choppin, *J. Inorg. Nuclear Chem.*, 1971, **33**, 127.
[269] E. Brücher and P. Szarvas, *Acta Chim. Acad. Sci. Hung.*, 1971, **67**, 449 (*Chem. Abs.*, 1971, **74**, 130 912n).
[270] L. I. Budarin, T. A. Rumyantseva, and K. B. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1970, **15**, 911.
[271] M. Gielen and N. Vanlautem, *Bull. Soc. chim. belges*, 1970, **79**, 679.
[272] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266.

Chromium(III) Complexes.—The isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ to the *cis*-complex obeys a first-order rate law. The activation parameters, calculated from rate constants determined over the temperature range 40—70 °C in 1.0M-$NaClO_4$, pH = 3, are $\Delta H^{\ddagger} = 30.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 17.6$ cal deg^{-1} mol^{-1}. Isomerization rates are *ca.* 100 times smaller for this malonate complex than for the oxalate analogue $[Cr(ox)_2(OH_2)_2]^-$. This difference in kinetic behaviour might be connected with the sizes and consequent stabilities of the chelate rings, which are five-membered for the oxalate complex, but six-membered for the malonate.[273] Two further reports of kinetic results for *cis* ⇌ *trans* isomerization of $[Cr(ox)_2(OH_2)_2]^-$ have appeared.[274, 275] Rate constants and activation parameters have been determined in D_2O as well as in H_2O. The isomerization mechanism suggested involves a trigonal-bipyramidal intermediate containing unidentate oxalate ligand. The determined activation entropies, for both *cis* → *trans* and *trans* → *cis*, in D_2O and in H_2O, are all negative (between − 36 and − 54 J K^{-1} mol^{-1}, *i.e.* between − 9 and − 13 cal deg^{-1} mol^{-1}). This seems a trifle surprising for a mechanism in which there is an increase of freedom, at least for one oxalate ligand, in forming the transition state. Perhaps the separation of one charged end of the oxalate ligand from the metal results in a decrease in entropy of the solvent in its vicinity. Alternatively, the loss in entropy may arise from association of cations with the free end of the unidentate oxalate.[275] The variation of the rate of isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ with solvent composition in alcohol–, dioxan–, or acetone–water mixtures is consistent with a five-co-ordinate transition state or intermediate containing unidentate oxalate rather than with a fully intramolecular twist mechanism.[276] The role of solvation in determining racemization rates of $[Cr(ox)_3]^{3-}$ has been investigated in DMSO–water mixed solvents, using n.m.r. techniques to monitor the composition of the solvation shell.[121]

Rates and activation parameters have been determined for the racemization of the cationic complexes $[Cr(ox)(bipy)_2]^+$, $[Cr(ox)(phen)_2]^+$, and $[Cr(ox)(en)_2]^+$, in aqueous solution. The mechanism is intramolecular, but both twist and partial dissociation mechanisms may operate in parallel.[277]

Rates and activation parameters have also been determined for the linkage isomerization

$$[Cr(NCS)(SCN)(OH_2)_4]^+ \longrightarrow [Cr(NCS)_2(OH_2)_4]^+$$

In this case, as in the case of isomerization of $[Cr(SCN)(OH_2)_5]^{2+}$, there is a close similarity between the kinetic parameters for isomerization and for aquation. This suggests a common activated complex as intermediate,

[273] K. R. Ashley and K. Lane, *Inorg. Chem.*, 1970, **9**, 1795.
[274] J. E. Brady and D. Thompson, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 663.
[275] M. W. Rophael and M. A. Malati, *J. Chem. Soc.* (*A*), 1971, 1903.
[276] H. Kelm, H. Steiger, and G. M. Harris, *Chem. Ber.*, 1971, **104**, 2743.
[277] J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, 1971, **10**, 955.

probably a 'tight' ion pair in which the thiocyanate can either return to the chromium, resulting in isomerization, or be displaced by water, resulting in aquation.[110]

Cobalt(III) Complexes.—Two kinetic studies of *cis–trans* isomerization of cobalt(III) complexes of simple ligands have been described, for the complexes *cis*-$[Co(en)_2(glycinenitrile)Cl]^{2+}$ [18] and $[Co(en)_2(OH_2)(N_3)]^{2+}$.[1] Possible mechanisms of isomerization and racemization for complexes containing flexible quadridentate ligands have been discussed in general terms,[278] for amino-acid complexes $[Co(trien)(LL)]^{2+}$,[279] and for the specific case of the complex [Co(trien)(*N*-methyl-*S*-alaninato)]$^{2+}$.[280] The rearrangement of the $\alpha\beta$-*R*- to the $\alpha\beta$-*S*-form of $[Co(tetren)(NCS)]^{2+}$ follows the rate law

$$\text{rate} = \{k_1 + k_2[NCS^-]\}[Co(tetren)(NCS)^{2+}]$$

Values of k_1 and k_2 have been determined over a range of temperatures; the activation parameters are $E_a = 30.9$ kcal mol^{-1} and log $A = 15.0$ for the k_1 path, and $E_a = 34.5$ kcal mol^{-1} and log $A = 16.7$ for the k_2 path.[281] The first example of inversion without isomerization at octahedral cobalt(III) has been reported, for the $[Co(CO_3)(L\text{-valinato})_2]^-$ anion.[282]

An intercomparison of rates and activation parameters for ^{18}O-exchange, aquation, oxalate exchange, and racemization of $[Co(ox)_3]^{3-}$ rules out both complete and partial (one end) dissociation mechanisms for racemization. This must therefore occur by an intramolecular twist mechanism.[283]

Complexes of acac and Related Ligands.—Mechanisms of isomerization of β-diketone complexes have been the subject of a review.[284] Two studies of isomerization and racemization rates of diketone complexes establish orders of relative reactivity for complexes of various cations. For complexes $M(tfac)_3$, rates of isomerization are in the following order:[285]

$$Fe^{3+} \approx In^{3+} > Mn^{3+} > Ga^{3+} > Al^{3+} > V^{3+} > Co^{3+} > Ru^{3+} > Rh^{3+}$$

For complexes $M(acac)_3$, racemization rates in chlorobenzene solution decrease in the order:[286]

$$Co^{3+} > Cr^{3+} > Ru^{3+} \approx Rh^{3+}$$

Kinetic parameters for isomerization or racemization of particular complexes of transition-metal cations of general formula $M(diketone)_3$ are listed in Table 15. For unsymmetrical β-diketone ligands, rates of isomeriza-

[278] G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 1970, **9**, 2373.
[279] M. H. Ghandehari, T. N. Anderson, D. R. Boone, and H. Eyring, *J. Amer. Chem. Soc.*, 1970, **92**, 6466.
[280] D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 2663.
[281] A. A. El-Awady and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3627.
[282] R. D. Gillard and M. G. Price, *J. Chem. Soc.* (*A*), 1971, 2271.
[283] J. A. Broomhead, I. Lauder, and P. Nimmo, *J. Chem. Soc.* (*A*), 1971, 645.
[284] J. J. Fortman, *Co-ordination Chem. Rev.*, 1971, **6**, 331.
[285] J. G. Gordon, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, 1971, **5**, 381.
[286] R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, 1970, **92**, 7056.

Table 15 *Rate constants and activation parameters for isomerization and racemization of transition-metal complexes* M(diketone)$_3$

Compound[a]	*Solvent*	*Reaction*	$10^5\ k/s^{-1}$ (*temp*/°C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	*Ref.*
Cr(acac)$_3$	Chlorobenzene	Racemization	8.06 (98)	34.3	+ 7	286
Co(acac)$_3$	Chlorobenzene	Racemization	0.17 (98)	34.2	+ 14	286
cis-Co(bzac)$_3$	Chlorobenzene	Inversion	22.5 (96)	32.3	+ 12	287
	Chlorobenzene	Isomerization	17.3 (96)	32.1	+ 11	287
	Benzene	Isomerization	13.0 (96)	—	—	287
	Chloroform	Isomerization	21.5 (96)	—	—	287
	Acetone	Isomerization	26.4 (96)	—	—	287
	Acetonitrile	Isomerization	18.9 (96)	—	—	287
trans-Co(bzac)$_3$	Chlorobenzene	Inversion	19.6 (96)	31.7	+ 10	287
	Chlorobenzene	Isomerization	6.8 (96)	32.1	+ 9	287
cis-Co(mhd)$_3$	Chlorobenzene	Racemization	10 (90)	29.9	+ 2	288
	Chlorobenzene	Isomerization	5.8 (90)	32.9	+ 9	288
trans-Co(mhd)$_3$	Chlorobenzene	Racemization	15 (90)	31.6	+ 7	288
	Chlorobenzene	Isomerization	2.8 (90)	32.6	+ 6	288
cis-Ru(tfac)$_3$	Tetrachloroethane	Isomerization	1.24 (141)	32.1	− 8	285
trans-Ru(tfac)$_3$	Ttrachloroethane	Isomerization	0.19 (141)	27.3	− 23	285

[a] For ligand abbreviations see list at front of this volume.

tion, racemization, and ligand exchange can be compared in order to gain some idea of mechanisms. For the examples mentioned here, rates of ligand exchange are very much less than rates of isomerization and of racemization. This indicates an intramolecular mechanism for each of the latter reactions. The close similarity of the kinetic parameters for isomerization and for racemization suggests a common, or at least very similar, rate-determining step and transition state for the two processes for any one complex. Whether this intramolecular mechanism involves twisting of the ligands with no metal–oxygen bond breaking, or involves an intermediate or intermediates containing one unidentate β-diketone ligand, is difficult to establish unequivocally, but the available evidence favours the latter type of mechanism. Whereas isomerization and racemization of these β-diketone complexes of transition metals are slow processes, the same reactions of substituted tropolone complexes of cobalt(III) are very much faster, taking place on the n.m.r. time-scale at around room temperature.[289]

Isomerization and racemization of β-diketone complexes of aluminium and of gallium are still the subject of kinetic investigations; recently reported results are collected in Table 16. As for these reactions of transition-metal

Table 16 *Activation parameters for isomerization or racemization of β-diketone complexes of aluminium and of gallium*

Compound[a]	*Solvent*	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal deg^{-1} mol^{-1}	*Ref.*
Al(pmhd)$_3$	C_6H_5Cl	27.6[b]	+ 13[b]	290
Ga(pmhd)$_3$	C_6H_5Cl	20.1[b]	+ 3[b]	290
Al(bzbz)$_3$	C_6H_5Cl	14.7	—	291
Al(acac)(hfac)$_2$	C_6H_6	19.0	+ 3	292
	CH_2Cl_2	21.3	+ 11	292
	$C_6H_5NO_2$	19.5	+ 6	292
Al(acac)$_2$(hfac)	CH_2Cl_2	18.4	+ 10	292
Al(acac)$_2$(bzbz)	*o*-$C_6H_4Cl_2$	22.0	+ 1	292
Ga(acac)$_2$(hfac)	CH_2Cl_2	15.3	+ 4	292, 293
Ga(acac)$_2$(bzbz)	C_6H_6	20.2	+ 2	292, 293

[a] For ligand abbreviations see list at front of this volume; [b] activation parameters for rearrangement *via* the twist pathway.

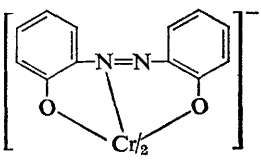
complexes, the mechanisms are certainly intramolecular, probably usually involving five-co-ordinate intermediates containing one unidentate β-diketone ligand.[290–292]

Kinetic results for rearrangement of several complexes of the type [M(diketone)$_2$L$_2$] have been reported. A qualitative study of a series of compounds [Co(acac)$_2$(NO$_2$)(amine)] has demonstrated an order of

[287] A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, 1970, **92**, 7061.
[288] J. G. Gordon and R. H. Holm, *J. Amer. Chem. Soc.*, 1970, **92**, 5319.
[289] S. S. Eaton and R. H. Holm, *J. Amer. Chem. Soc.*, 1971, **93**, 4913.
[290] J. R. Hutchison, J. G. Gordon, and R. H. Holm, *Inorg. Chem.*, 1971, **10**, 1004.
[291] B. Jurado and C. S. Springer, *Chem. Comm.*, 1971, 85.
[292] D. A. Case and T. J. Pinnavaia, *Inorg. Chem.*, 1971, **10**, 482.
[293] T. J. Pinnavaia, J. M. Sebeson, and D. A. Case, *Inorg. Chem.*, 1969, **8**, 644.

reactivities $PhNH_2$ > $MeNH_2$ > Me_2NH > piperidine for the amine ligand.[294] The rearrangement apparent from variable-temperature n.m.r. studies of $[Mo(acac)_2O_2]$ has been assigned as inversion of the *cis*-isomer, for which the activation enthalpies are 16.4 kcal mol^{-1} in benzene and 12.4 kcal mol^{-1} in chloroform.[295] Rates of intramolecular rearrangement of $[Ti(acac)_2(phenoxy)_2]$ correlate with pK_a values of the parent phenols.[296] Rearrangement of the hitherto uncharacterized compound $[Ti(acac)_2I_2]$ is fast on the n.m.r. scale, and may, from e.s.r. evidence, involve the intermediacy of the titanium(III) species $[Ti(acac)_2I]$.[297]

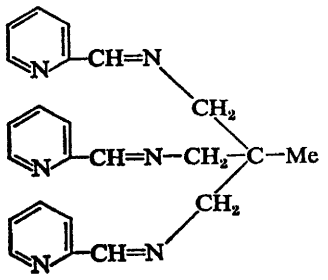
Complexes of en and Related Ligands.—Though there have been a few reports of the determination of barriers to chelate ring inversion in complexes $M(en)_3^{3+}$ by n.m.r. methods in recent years,[298] it now seems likely that such processes have too low barriers and too fast rates for investigation by n.m.r.[299] Thus the estimated barrier to inversion is only about 5 kcal mol^{-1} for a complex with metal–nitrogen bonds of length 2.0 Å, rising to about 7 kcal mol^{-1} for metal–nitrogen bonds of length 2.3 Å.[300] It seems likely that the temperature-dependent features of the n.m.r. spectra of these complexes should be assigned not to ring inversion but to relaxation processes.[301] Nevertheless, a recent paper on complexes $[Co(tn)_2X_2]^+$ claims n.m.r. evidence for slow conformational change of the trimethylenediamine (tn) ligands.[302] The rate of racemization of the 2,3-diaminobutane complex $[Ni(meso\text{-}bn)_3]^{2+}$ is estimated from variable-temperature n.m.r. spectroscopic studies to be 2.3 × 10^3 s^{-1} at 50 °C, which rate is only slightly less than that reported for the similar complex $[Ni(en)_3]^{2+}$ (5.5 × 10^3 s^{-1}). Racemization is thought to take place by a trigonal twist mechanism.[303] The possibility of slow interconversion of conformers of chromium complexes of *o,o'*-dihydroxyazo-compounds, *e.g.* (29), which may be slow as a high barrier to inversion at nitrogen is expected, has been discussed.[304]



(29)

[294] L. J. Boucher and N. G. Paez, *Inorg. Chem.*, 1971, **10**, 1680.
[295] B. M. Craven, K. C. Ramey, and W. B. Wise, *Inorg. Chem.*, 1971, **10**, 2626.
[296] J. F. Harrod and K. Taylor, *Chem. Comm.*, 1971, 696.
[297] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1970, **9**, 2048.
[298] See, *e.g.*, 'Inorganic Reaction Mechanisms', ed. J. Burgess, (Specialist Periodical Reports), The Chemical Society, London, 1971, vol. 1, p. 197.
[299] J. K. Beattie, *Inorg. Chem.*, 1971, **10**, 426; *Accounts Chem. Res.*, 1971, **4**, 253; J. L. Sudmeier and G. L. Blackmer, *Inorg. Chem.*, 1971, **10**, 2010.
[300] J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, 1971, **10**, 317.
[301] R. Bramley and R. N. Johnson, *Chem. Comm.*, 1971, 1309.
[302] I. R. Jonasson, S. F. Lincoln, and D. R. Stranks, *Austral. J. Chem.*, 1970, **23**, 2267.
[303] R. F. Evilia, D. C. Young, and C. N. Reilley, *Inorg. Chem.*, 1971, **10**, 433.
[304] G. Schetty, *Helv. Chim. Acta*, 1970, **53**, 1437.

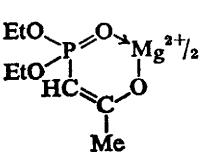
Miscellaneous.—Racemization of the iron(II) complex of the sexidentate ligand (30) has an activation enthalpy of 18.4 kcal mol^{-1} and an activation entropy of +1 cal deg^{-1} mol^{-1}. The geometry of the ligand permits racemization *via* a trigonal twist, but precludes racemization *via* a rhombic



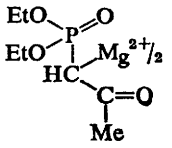
(30)

twist. However, racemization *via* breaking one iron–nitrogen bond to give a five-co-ordinate intermediate, *cf.* the M(diketone)$_3$ reactions mentioned earlier, is equally plausible.[305] The complex $[Fe(S_2CNMePh)_2\{S_2C_2(CF_3)_2\}]$, in which the iron is bonded to six sulphur atoms of the ligands, undergoes $\Lambda \rightleftharpoons \Delta$ rearrangement by a trigonal or Bailer twist mechanism, in other words the interconversion of the two forms of the octahedral complex takes place through a trigonal prismatic transition state.[306]

The only photoreaction which the 4-styrylpyridine (4-stilbazole) complexes [Ru(bipy)(*cis*-4-stilbazole)]$^{2+}$ and [Ru(bipy)(*trans*-4-stilbazole)]$^{2+}$ undergo is that of *cis* $\rightleftharpoons$ *trans* isomerization of the stilbazole ligands; there is no significant photodissociation.[307] The anion $[Pt(NH_3)_4(NH_2)(NO_2)]^{2-}$ photoisomerizes to $[Pt(NH_3)_4(NH_2)(ONO)]^{2-}$. The quantum yield has been determined for this process, but no kinetic results are available.[177]



(31)



(32)

The kinetics of isomerization ('cationotropic conversion') of magnesium diethylphosphonoacetone, (31) to (32), have been monitored by i.r. spectroscopy.[308]

[305] F. L. Urbach and S. O. Wandiga, *Chem. Comm.*, 1970, 1572.
[306] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, 1971, **93**, 360.
[307] P. P. Zarnegar and D. G. Whitten, *J. Amer. Chem. Soc.*, 1971, **93**, 3776.
[308] M. Kirilov, M. Arnaudov, G. Petrov, and L. Shishkova, *Chem. Ber.*, 1970, **103**, 3190.

10 Co-ordination Numbers other than Six

The great majority of the complexes whose reactions have been mentioned in this chapter have been of co-ordination number six and of octahedral stereochemistry. For the benefit of readers who are interested in the role of co-ordination number in determining reactivity or mechanism we have collected together in Table 17 some references to kinetic or mechanistic studies on complexes of co-ordination number five, seven, or above.

Table 17

Co-ordination number	*Compound*	*Reaction*	*Ref.*
5	$[Co(2,6\text{-lut-}N\text{-oxide})_5]^{2+}$	ligand exchange	309
7	$NbO(bpha)_3$	bpha replaced by, *e.g.*, oxine	221
8	$[Mo(CN)_8]^{4-}$	photoaquation	147, 148
	$W(oxine)_4$	substitution	149
10	$Eu(NO_3)_3(4,4'\text{-diBu}^n\text{-bipy})_2$	4,4-′diBu^n-bipy exchange	255
12	$Zr(BH_4)_4$	BH_4^- exchange	258

[309] P. M. Enriquez, S. S. Zumdahl, and L. Forshey, *Chem. Comm.*, 1970, 1527.

4
Labile Metal Complexes

BY D. N. HAGUE

1 Introduction

The framework around which most of the mechanistic discussions involving labile metal ions are built was discussed in the corresponding chapter in Volume 1 of this series (Section III, Chapter 1) and will therefore not be repeated here.* Consequently, it has been found convenient to alter the order in which the material will be presented, and in this report the chapter has been divided into three main parts. In the first section we shall consider work involving simple (*i.e.* unsubstituted) metal ions in which specific mechanistic aspects of complex formation have been discussed. A large part of this work involves non-aqueous and mixed solvents, and relevant studies on solvent exchange will also be included; specific effects which depend on the nature of the incoming ligand (*e.g.* rate-limiting chelate ring-closure) are not included. In the second section the influence of bound ligands on the reactivity of a metal ion is discussed. In several cases it appears that similar effects (*e.g.* a change in co-ordination number) may be induced by partial replacement of the inner solvation sphere and by a change of solvent, and it is likely that more and more mechanistic investigations will involve parallel studies of this type. Finally, since most (though not all) mechanistic investigations involving labile metal ions centre around kinetics, the last section consists of a summary of the kinetic studies which have been carried out with unsubstituted metal ions in the period under review. Specific effects of the incoming ligand are discussed in this section.

Recent reviews have included a discussion by Wilkins [1] of his extensive work on the mechanisms of ligand replacement in octahedral nickel(II) complexes. Hunt [2] has reviewed the water-exchange studies in labile

[1] R. G. Wilkins, *Accounts Chem. Res.*, 1970, **3**, 408.
[2] J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

* For the majority of metals, the rate constant k_f for the formation of the complex is given by

$$k_f = K_{os}\, k_{ex}$$

where K_{os} is the equilibrium constant for the formation of the outer-sphere complex and k_{ex} (k_{wl} was used in Volume 1) is the rate constant for solvent exchange at the metal ion.

aquo- and substituted aquo-transition-metal ions which have used ^{17}O n.m.r., and Kustin and Swinehart [3] have considered some aspects of complex formation involving labile metals.

2 Complex Formation Involving Unsubstituted Metal Ions

In Water.—There has been renewed interest recently in ultrasonic relaxation in aqueous salt solutions with the appearance of several papers [4] on bivalent and tervalent sulphates. Jackopin and Yeager [5] have presented some new data on manganese(II) sulphate and have critically re-examined the question of the number of relaxation peaks observed with this species.

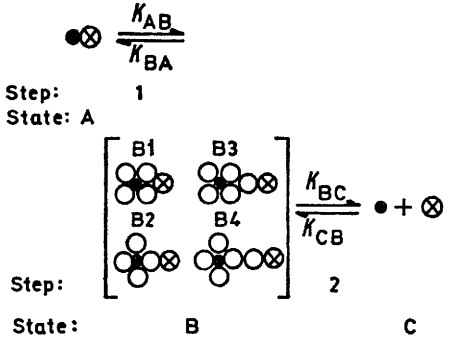


Figure 1 *Mechanism of formation of* $MnSO_4$ *(see text)*

They conclude that two chemical relaxation processes are sufficient to explain the absorption data within the range of experimental error, and that the postulation of a third relaxation is apparently not necessary and is not justified experimentally. The two relaxation processes are thought to be represented by the mechanism shown in Figure 1, in which the solid circles represent the Mn^{2+} cation, the open circles the oxygen of the water molecules, and the crossed circles one of the four oxygen atoms of SO_4^{2-} (H atoms and most of the O atoms of the hydration water molecules have been omitted). The collection of states represented by B (other, less definable states of the 'outer-sphere' type are not shown) are thought to be in rapid equilibrium, the energy barriers for interconversion being comparable in height to those for rotation of the hydrated ions, and not much higher than those for diffusion. The authors therefore prefer the three-state model represented by Figure 1 for the treatment of relaxational data to the four-state model of Eigen and Tamm,[6] which treats the two

[3] K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107.
[4] *E.g.* P. Hemmes, F. Fittipaldi, and S. Petrucci, *Acustica*, 1969, **21**, 228; P. Hemmes and S. Petrucci, *J. Phys. Chem.*, 1970, **74**, 467; K. Fritsch, C. J. Montrose, J. L. Hunter, and J. F. Dill, *J. Chem. Phys.*, 1970, **52**, 2242.
[5] L. G. Jackopin and E. Yeager, *J. Phys. Chem.*, 1970, **74**, 3766.
[6] M. Eigen and K. Tamm, *Z. Elektrochem.*, 1962, **66**, 93, 107.

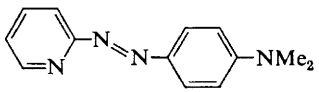
encounter complexes, one with one water molecule (B1, B2) and the other with two water molecules (B3, B4) interposed between the cation and anion, as separate states.

The formation of $BeSO_4$ has been studied[7] in aqueous solution at temperatures in the range 8—35 °C. The kinetic measurements were made with a microwave temperature-jump apparatus, incorporating conductance detection in which the accuracy was enhanced by the use of repetitive jumps on a flowing sample. It was shown that the two-step mechanism (*cf.* Figure 1) must be supplemented by a third step, which probably involves the formation of complex aggregates such as $(BeSO_4)_2$.

Two preliminary accounts have appeared which report new approaches to the problem of the mechanism of complex formation in water. The reaction between Nd^{III} and SO_4^{2-} was investigated[8] by ultrasonics in H_2O and D_2O and it was concluded from the fact that the reaction was 2.3 times slower in D_2O than in H_2O (whereas the dissociation step was accelerated) that solvent exchange at the metal ion cannot be the controlling step in lanthanoid complexation reactions. A high-pressure cell with spectrophotometric detection was used[9] in conjunction with a laser temperature-jump apparatus to measure the volumes of activation of the reaction of Co^{2+} and Ni^{2+} with the bidentate ligand pyridine-2-azo-*p*-dimethylaniline (1), and of Ni^{2+} with NH_3. In all cases the value of $\Delta V^{\neq}$ was *ca.* 8 $cm^3\ mol^{-1}$, a value which corresponds to a considerable fraction of the molar volume of water:

		$\Delta V^{\neq}$ ($cm^3\ mol^{-1}$)
$Ni^{2+} + NH_3$	(30.0 °C)	7.1 ± 1.0
Ni^{2+} + (1)	(49.0 °C)	8.2 ± 0.2
Co^{2+} + (1)	(25.3 °C)	9.1 ± 0.5

The values for the small unidentate ligand NH_3 and the bulky bidentate ligand (1) are remarkably similar, and they are consistent with a dissociative mechanism accompanied by only slight effects of solvent structure. They



(1)

compare with values of *ca.* 10 $cm^3\ mol^{-1}$ for the unimolecular decomposition of diazonium and t-alkylsulphonium salts which also involve the dissociation of cations in water.

[7] P. Brumm and H. Rüppel, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 102.
[8] H. B. Silber, *Chem. Comm.*, 1971, 731.
[9] E. F. Caldin, M. W. Grant, and B. B. Hasinoff, *Chem. Comm.*, 1971, 1351.

In Non-aqueous and Mixed Solvents.—The reaction between Ni^{II} and NH_3 has been studied by MacKellar and Rorabacher [10] in a range of methanol–water mixtures, and the results have been analysed in terms of the dissociative model used for aqueous systems. As the authors point out, the weaker co-ordinating ability of alcoholic oxygen as a donor atom compared with aqueous oxygen led initially to the suggestion that, for octahedrally solvated metal ions such as nickel(II), a dissociative mechanism, in which $Ni(H_2O)_5^{2+}$ and $Ni(MeOH)_5^{2+}$ are formed, should always be more rapid for methanol than for water. However, evidence from n.m.r. studies indicates that exactly the opposite obtains for solvent exchange when the pure solvents are involved, *i.e.* $k_{ex}(H_2O) > k_{ex}(MeOH)$. This apparent contradiction to the predictions of the dissociative mechanism is resolved, and a general theory is proposed to account for the behaviour of the solvent-exchange rate constants for all labile, solvated metal–ion species in methanol–water mixtures.

The formation rate constant for the nickel monoammine complex in methanol–water mixtures (at 25 °C and ionic strength 0.10M) varies as follows:

MeOH (wt %)	0	25	50	65	80	90	95	99
$k_f(10^8\ l\ mol^{-1}\ s^{-1})$	4.46	6.69	(5.98)	10.4	12.7	11.6	4.01	1.33

Since this can be expressed as a product between the outer-sphere equilibrium constant (K_{os}) and the rate constant for solvent exchange between inner and outer co-ordination spheres (k_{ex}), the variation in k_f must be reflected in variations in K_{os} or k_{ex} (or both). The K_{os} term is shown not to be a dominant factor in the observed rate phenomena and, for species containing only one or two methanol molecules in the inner co-ordination sphere, the value of K_{os} is assumed to be identical with that calculated from diffusion equations for $Ni(H_2O)_6^{2+}$. This implies that the observed formation rate constant is altered according to the composition of the inner sphere of the nickel ion. (It is interesting to note that Luz and Meiboom have reported [11] that the rate of methanol exchange at Ni^{2+} is increased by the addition of water, although they were unable to determine the composition of the inner solvation-sphere accompanying this acceleration.)

In order to interpret quantitatively the variation in k_{ex} with solvent composition, the relative concentrations of the individual solvated Ni^{2+} species at the various compositions are evidently required. Water is a strongly preferred ligand to methanol and it was found [12] that, for reasonably low nickel-ion concentrations, only the nickel species containing zero, one, and two methanol molecules need be considered in methanol–water

[10] W. J. MacKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, 1971, **93**, 4379.
[11] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 1964, **40**, 1066.
[12] F. R. Shu and D. B. Rorabacher, quoted in ref. 10.

mixtures up to 95% methanol or greater. Moreover, a striking correlation is obtained (Figure 2) between the nickel-monoammine-complex formation rate constant and the concentration of $Ni(H_2O)_5(MeOH)^{2+}$ as the solvent composition is changed, indicating that this species has an enhanced lability compared with the other nickel species present. In fact, it is estimated that the rate constant for nickel—methanol bond rupture in this species is (7—8) $\times$ 10^5 s^{-1}, which is approximately 800 times larger than the rate constant established for the same bond rupture in $Ni(MeOH)_6^{2+}$ and 20 times larger than the rate constant for nickel—water bond rupture in $Ni(H_2O)_6^{2+}$. MacKellar and Rorabacher rationalize the apparent contradiction between the bond-rupture data and the solvent-exchange

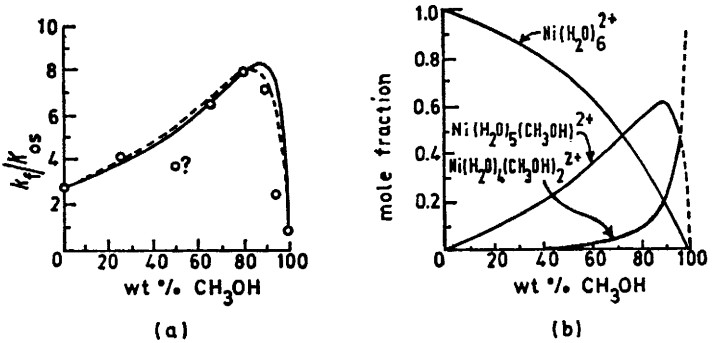


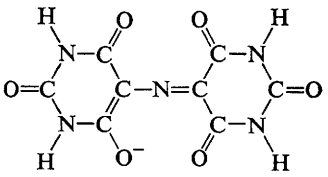
Figure 2 (a) *Variation in formation rate constant with bulk solvent composition for the reaction of* NiS_6^{2+} *with* NH_3 *in methanol–water mixtures* (b) *Mole fractional distribution of solvated nickel species in methanol–water mixtures* (Reproduced by permission from *J. Amer. Chem. Soc.*, 1971, **93**, 4379)

data in the pure solvents by proposing that a pure solvent of a strongly co-ordinating nature (*e.g.* H_2O) results in a more stable five-co-ordinated ground state (and therefore a higher exchange rate) than does a pure solvent of weaker co-ordinating power (*e.g.* MeOH). They extend the argument to cover the situation in liquid ammonia (a stronger co-ordinating ligand than either water or methanol) and note that the rate constant for solvent exchange is larger than for the other two solvents, whereas the bond-rupture rate constant is less. The reason for the larger monoammine-formation rate constant with $Ni(H_2O)_5(MeOH)^{2+}$ than with $Ni(H_2O)_6^{2+}$ is that a nickel—methanol bond is being broken in the former complex and a nickel—water bond in the latter. [The reason for the subsequent decrease in rate constant on going from $Ni(H_2O)_5(MeOH)^{2+}$ to $Ni(H_2O)_4(MeOH)_2^{2+}$ is more subtle.] The discussion is extended to cobalt(II).

The ultrasonic absorption exhibited by methanolic solutions of the *m*-benzenedisulphonates of Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} has

been attributed[13] to the outer-sphere association between the solvated cation and the anion, the activation energy for the process being similar to that for viscous flow.

The rates of complex formation of Ni^{2+} with SCN^- and the murexide anion (2) in DMSO have been reported[14] and compared with the rate of the corresponding reaction with bipy. All three complex-formation rates



(2)

are significantly less than those predicted from the solvent-exchange rate on the basis of the 'outer-sphere' mechanism (*cf.* Figure 1). It is suggested that the discrepancy can be explained by postulating the formation of $Ni(DMSO)_5^{2+}$ as a kinetically detectable intermediate:

$$Ni(DMSO)_6^{2+} \rightleftharpoons Ni(DMSO)_5^{2+} + DMSO \qquad (1)$$
$$\downarrow +L$$
$$Ni(DMSO)_5L$$

If this is the correct interpretation of the low rate constants it should be possible to increase the overall rate of complex formation by diluting the DMSO with an unreactive solvent of similar dielectric constant [thereby displacing the first step in equation (1) to the right]. When nitromethane was used as a diluent the rate was enhanced by a factor of more than ten at the lowest DMSO concentrations used (2M). Such an observation would be difficult to explain on the basis of the normal mechanism. The authors suggest that the reason for the presence of a kinetically detectable intermediate in this case might be steric.

A different approach to the mechanism of complex formation in non-aqueous solvents has been developed by Bennetto and Caldin.[15] They point out that, even for reactions in aqueous solution, equation (2)

$$k_f = K_{os}\, k_{ex} \qquad (2)$$

is obeyed much less accurately than is often supposed, and quote as an example the variation in k_f of a factor of *ca.* 20 for the reaction of nickel(II) with uncharged ligands (excluding aliphatic diamines and related species for which the internal conjugate-base mechanism has been proposed).

[13] A. Fanelli and S. Petrucci, *J. Phys. Chem.*, 1971, **75**, 2649.
[14] C. H. Langford and H. G. Tsiang, *Inorg. Chem.*, 1970, **9**, 2346.
[15] H. P. Bennetto and E. F. Caldin, *J. Chem. Soc.* (*A*), 1971, 2190, 2198, 2207; H. P. Bennetto, *J. Chem. Soc.* (*A*), 1971, 2211; *cf.* H. P. Bennetto and E. F. Caldin, *Chem. Comm.*, 1969, 599.

These variations in k_f are sometimes rationalized by adjusting the value of K_{os}, which is unfortunately not independently measurable for uncharged ligands. Results in methanol–water mixtures had suggested [16] that the part played by the solvent is important, and the authors set out to investigate the general applicability of the outer-sphere-complex model by measuring the kinetics of formation of the first complex of bipy with Ni^{2+} in several solvents for which data on the kinetics of solvent exchange are available. They also studied the reactions of Ni^{2+} with terpy and of Co^{2+} with bipy and terpy to see whether the trends observed in the Ni^{2+}–bipy reaction are general, and extended their observations on the latter system to water–methanol and methanol–acetonitrile mixed solvents.

Bennetto and Caldin point out that the mechanisms of ligand substitution and solvent exchange are similar, whether the formal stoicheiometry derives from a dissociative [equation (3)] or an interchange [equation (4)] model, and they treat the solvent-exchange data

$$MS_6 \xrightarrow{k_{ms}} MS_5 \begin{cases} \xrightarrow{L} MS_5L \\ \xrightarrow{S} MS_6 \end{cases} \qquad (3)$$

$$MS_6 + L \text{ (or S)} \xrightarrow[(\text{or } k_S)]{k_L} S + MS_5L \text{ (or } MS_6) \qquad (4)$$

in terms of a second-order rate constant k_{ex}^{II} (sometimes called the 'total exchange rate') rather than the more common first-order constant k_{ex}. The ratio R of (overall) rates for ligand substitution and solvent exchange ($\equiv k_f/k_{ex}^{II}$) then measures the ratio of rate constants for the reaction of L and S molecules, either with MS_5^{2+} or with MS_6^{2+}. They also introduce a (related) quantity n, which is defined as the chance that a ligand molecule will enter the primary solvation shell of the cation at a particular site when a solvent molecule leaves it. This quantity is therefore the fraction of departing solvent molecules which are replaced by ligand rather than by solvent and is given by $n = k_f/K_{os}k_{ex}$. If the outer-sphere mechanism, and hence equation (2), is correct, n should have the value unity in all solvents. Alternatively, if the value of K_{os} has not been chosen correctly, n will vary from solvent to solvent, but this variation would not be expected to be very large, since large fluctuations in K_{os} are not predicted for a neutral ligand. Values of n for the reaction of Ni^{2+} or Co^{2+} with bipy or terpy at 25 °C are shown in Table 1 (the value of K_{os} has been taken as 0.1 l mol^{-1} in all cases) and it is seen that the variation covers four orders

[16] H. P. Bennetto, R. Bulmer, and E. F. Caldin, in 'Hydrogen-bonded Solvent Systems', ed. A. K. Covington and P. Jones, Taylor and Francis Ltd., London, 1968, p. 335.

Table 1 *Values of n in various solvents*;[a] $n = 10\ k_f/k_{ex}$

Reaction	*Solvent*	*n*
Ni^{2+} + bipy	MeCN	17
	MeOH	0.8
	DMF	0.70
	H_2O	0.54
	D_2O	0.36
	DMSO	0.09
	Etgly	0.08
	DMMP	0.09
Ni^{2+} + terpy	H_2O	0.16
	DMSO	0.035
Co^{2+} + bipy	MeOH	1.1
	H_2O	0.9
	DMSO	0.21
Co^{2+} + terpy	MeOH	0.59
	H_2O	0.32
	DMSO	0.0026

[a] Data are from ref. 15 and refer to 25 °C; DMF = dimethylformamide; Etgly = ethylene glycol; DMMP = dimethyl methylphosphonate.

of magnitude—far more than can be attributed to changes in K_{os} with dielectric constant, for example. However, several very interesting correlations emerge involving n or R (which are related in the present case through $R = 0.1nk_{ex}/k_{ex}^{II}$) which suggest that the nature of the solvent, a parameter not usually considered in inorganic mechanistic studies, plays a central role in determining the rate and activation parameters for substitution at metal ions.

One such correlation is between $\log n$ and the enthalpy of evaporation of the solvent; another is between $\log n$ and the fluidity of the solvent (defined as the ratio density : viscosity), and a third is between the difference in the activation enthalpies for complex formation and exchange ($\Delta H_f^{\ddagger} - \Delta H_{ex}^{\ddagger}$) and the heat of evaporation of the solvent, ΔH_{evap}, as shown in Figure 3. (It is noteworthy that neither k_f, k_{ex} nor $\Delta H_f^{\ddagger}$, $\Delta H_{ex}^{\ddagger}$

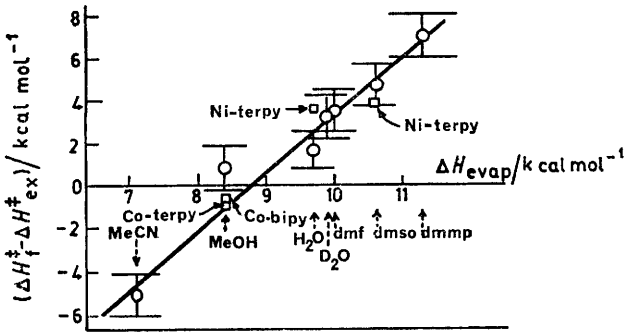


Figure 3 *Enthalpies of activation for ligand substitution relative to solvent exchange as a function of heat of vaporization of solvent*

separately show such correlations.) The latter is illustrated further in Figure 4, where values of log R are plotted against reciprocal temperature, with the temperature axes shifted so that the normal boiling points of the solvents are at the origin. This shows that k_f and k_{ex}^{II} converge to within a factor of 2 or 3 when $1/T'$ is zero; *i.e.* although the rates of exchange

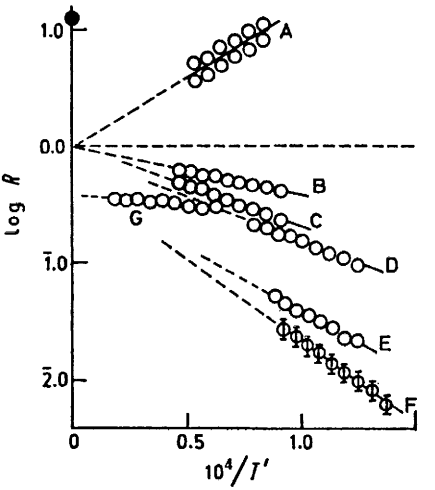


Figure 4 *Comparison of rates of substitution of* 2,2′-*bipyridyl at* Ni^{2+} *with solvent-exchange rates. Plot of* log R (*see text*) *against* T'^{-1} ($= T^{-1} - T_b^{-1}$, *where* T_b *is the normal boiling point*). A, MeCN; B, H_2O; C, D_2O; D, DMF; E, DMSO; F, DMMP; G, MeOH

and substitution differ at 25 °C by a factor of up to 100, they tend to equality at the boiling point of the solvent. This is not altogether surprising; the viscosities of the various solvents approach a fairly uniform value at their normal boiling points and, since viscosity reflects some features of solvent structure, it appears that the effects of these features tend to equalize at the boiling points. Thus the rates of ligand substitution and solvent exchange, whose differences are related to solvent structure, should tend to become equal.

The authors then develop a model for an ionic solution based on that of Frank and Wen,[17] but in this case not restricted to the solvent water. Briefly, they consider a dynamic picture of the solvated ion which takes into account the structural differences between the three regions of solvent, which they call A, B, and C (Figure 5). Region A is the inner solvation shell of the metal ion, where the solvent molecules are held by the cation. Immediately outside this first layer is region B, where two powerful directive influences are in competition: a solvent molecule may have largely

[17] H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

escaped the force field of its neighbours, yet may be unable to find its way into the saturated first shell. This region, which is in many ways comparable to a gas, may have no clearly defined boundaries, but is expected to extend not far beyond the first solvation shell, to a distance related to ΔH_{evap}. Molecules may only have a short stay in region B, where they will be in a state of high energy and high entropy relative to the bulk solvent. Region C comprises the bulk solvent.

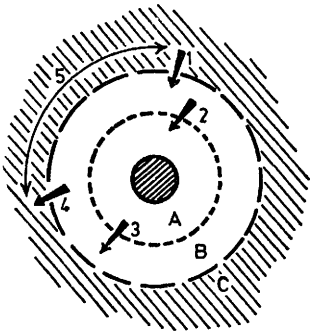
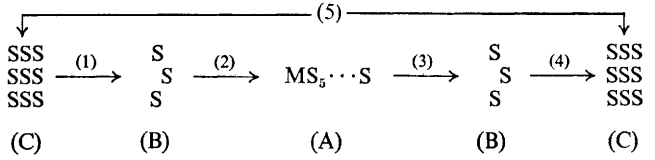


Figure 5 *Structural model for a solvated ion*

The process of solvent exchange is considered as follows. First, a solvent molecule must escape from C to B (process 1 in Figure 5); this will require an energy comparable to ΔH_{evap} for the liquid. Secondly, a molecule in region B can enter region A if an empty site is available there (process 2). Thirdly, a first-layer solvated molecule has to overcome its 'bonding' interactions with the ion and enter region B (process 3). Fourthly, a molecule which has left region A (or another in region B) must then enter a hole in the solvent C (process 4); this is comparable to a condensation process. The value of $\Delta G^{\ddagger}$ for a complete exchange will include contributions from processes 1—4 in varying degrees, but the authors suggest that it is not sufficient to describe the reaction simply as an 'interchange' because other factors are involved. Processes 1 and 4 must be mutually dependent through movements of molecules in C (the latter being termed process 5). Thus the complete reaction is a concerted movement of the molecules, represented by the scheme



This model has the advantage that the enthalpy terms in the solvent-exchange and complex-formation reactions can be identified with enthalpy terms for specific molecular processes; it also explains the importance of

ΔH_{evap}. It can be extended to include metal ions in which ligand-field effects are important in varying degrees, on the assumption that the corrections associated with the latter are purely enthalpic. It is argued that the dissociative step requires an enthalpy which is much the same from one solvent to another and that the success of the outer-sphere model in describing complex formation in water (*i.e.* the fact that R is often *ca.* unity in water) is associated with the particular property of water molecules to undergo co-operative molecular motions. The repulsive and attractive intermolecular forces are both so strong in water that, in the rare event that a molecule escapes from the structure, there is a high probability that it will rapidly return to an equivalent position in the structure. Thus in substitution reactions little net structural work is performed on the medium, and the rate-determining process is dominated by the loss of a water molecule from the first solvation shell (step 3). The model is to some extent speculative, but it is open to experimental check and is likely to stimulate further investigations of metal-complex formation and ligand-exchange in non-aqueous and mixed solvents.

3 The Effect of Bound Ligands

The effect of substitution on the water-exchange kinetics of manganese(II) has been studied [18] by ^{17}O n.m.r. The effective first-order rate constants for exchange at $Mn(H_2O)_6^{2+}$, $Mn(phen)(H_2O)_4^{2+}$, and $Mn(phen)_2(H_2O)_2^{2+}$ are calculated to be 5.9×10^6, 1.3×10^7, and 3.1×10^7 s^{-1}, respectively, at 0 °C, and the activation enthalpies for all three species are in the range (9 ± 2) kcal mol^{-1}. It thus appears that 1,10-phenanthroline, at least, has comparatively little effect on the lability of a water molecule bound to Mn^{2+}.

^{17}O water-exchange data have also been reported for $Co(H_2O)_6^{2+}$ and four substituted octahedral Co^{II} species (Table 2). In all cases the remaining water molecules are labilized. In the case of the ammines the approximate additivity of the labilizing effects at 25 °C can be rationalized [19]

Table 2 *Kinetics for water-exchange at* Co^{II} *species*

Complex	*Ref.*	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})
$Co(H_2O)_6^{2+}$	21	$(2.45 \pm 0.10) \times 10^6$	10.9 ± 0.4
$Co(H_2O)_6^{2+}$	19	$(2.24 \pm 0.05) \times 10^6$	10.3 ± 0.2
$Co(NH_3)(H_2O)_5^{2+}$	19	$(1.55 \pm 0.2) \times 10^7$	12.6 ± 0.6
$Co(NH_3)_2(H_2O)_4^{2+}$	19	$(6.5 \pm 1) \times 10^7$	9.4 ± 1.5
$Co(NCS)(H_2O)_5^{+}$	21	$(9.46 \pm 0.95) \times 10^6$	10.1 ± 1.1
$Co(malonate)(H_2O)_4$	19	2.2×10^7	12.9 ± 0.8
$Co(NCS)_2(H_2O)_2$	21	$2—4 \times 10^8$	10.4 — 13.4
$Co(NCS)_3(H_2O)^{-}$	21	$> 5 \times 10^8$	—

(Data from ref. 19 refer to 25 °C and from ref. 21 to 27 °C.)

[18] M. Grant, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1971, **10**, 71.
[19] P. E. Hoggard, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1971, **10**, 959.

(as with N-substituted Ni^{2+}) by a model in which electron donation by the ligand reduces the effective charge on the metal ion. Such a rationalization does not hold for the activation enthalpies and the authors suggest that the mechanisms for exchange at Ni^{2+} and Co^{2+} are different—the latter possibly involving a four-co-ordinate intermediate.[20]

Zeltmann and Morgan[21] have done a parallel study in which the co-ordination number of cobalt(II) and the exchange rates of the ligands were measured for both H_2O (by ^{17}O) and NCS^- (by ^{14}N) in mixtures containing various metal : ligand ratios. They were able to show that the major species present are $Co(H_2O)_6^{2+}$, $Co(NCS)(H_2O)_5^+$, $Co(NCS)_2(H_2O)_2$, $Co(NCS)_3(H_2O)^-$, and $Co(NCS)_4^{2-}$, *i.e.* that the change in co-ordination number of the metal from six to four occurs at the neutral point in going from cationic to anionic species. They also found (Table 2) that the water-exchange rate is considerably higher for the tetrahedral than for the octahedral species and that NCS^- is more labile in $Co(NCS)_4^{2-}$ (second-order $k > 1.0 \times 10^7$ l mol^{-1} s^{-1} at 27 °C) than in $Co(NCS)_3(H_2O)^-$ or $Co(NCS)_2(H_2O)_2$ ($k = 4.7 \times 10^6$ and 3.0×10^6 l mol^{-1} s^{-1}, respectively). Further magnetochemical evidence for a similar change in co-ordination number of cobalt(II) in the presence of large concentrations of chloride ions has also been presented.[22] At Cl^- concentrations below 7M it seems that the Co^{II} is predominantly in an octahedral ligand field whereas with Cl^- concentrations above 12M the equilibrium has been shifted completely towards tetrahedral Co^{II}.

It is probable that one factor contributing to the frequent interchangeability between zinc and cobalt(II) in enzymatic reactions is this ability of the two ions to change their co-ordination number comparatively easily. A preliminary report has appeared[23] of a similarity in the effects of given bound ligands L^1 on the reactions of both Zn^{2+} and Co^{2+} with pyridine-2-azo-*p*-dimethylaniline (1)

$$L^1Co\ [\text{or } Zn] + (1) \underset{k_d}{\overset{k_f}{\rightleftharpoons}} L^1Co(1)\ [L^1Zn(1)] \qquad (5)$$

A more detailed study has been made (for Co^{2+}) where L^1 is iminodiacetate (ida^{2-}), nitrilotriacetate (nta^{3-}), and polytriphosphate (tp^{5-}). It was found[24] (Table 3) that the rate constants and activation parameters for the trinegative anion $[Co(tp)]^{3-}$ were almost identical with those for the aquocation Co^{2+}, and the authors conclude that, as with nickel(II), charge as such on the bound ligand has little effect on the reactivity of the metal ion with a neutral ligand. Nonetheless, there is a significant variation in formation rate constant on passing from Co^{2+} and $[Co(tp)]^{3-}$ to [Co(ida)] and $[Co(nta)]^-$, and this is largely reflected in a variation in activation enthalpy, the

[20] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1965, **4**, 1061.
[21] A. H. Zeltmann and L. O. Morgan, *Inorg. Chem.*, 1970, **9**, 2522.
[22] J. Mardrossian and J. F. Skinner, *Inorg. Chem.*, 1971, **10**, 411.
[23] M. A. Cobb and D. N. Hague, *Chem. Comm.*, 1971, 20.
[24] M. A. Cobb and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 3069.

Table 3 *Kinetics of the reaction of* Co^{II} *species with pyridine-2-azo-*p*-dimethylaniline*[a]

	$Co(H_2O)_6^{2+}$	$[Co(ida)(H_2O)_3]$	$[Co(nta)(H_2O)_2]^-$	$[Co(tp)(H_2O)_3]^{3-}$
k_f (1 mol^{-1} s^{-1})	7.6×10^4	6.5×10^5	3.7×10^6	8.0×10^4
$\Delta H_f^{\ddagger}$ (kcal mol^{-1})	10.3	9.6	5.9	10.5
$\Delta S_f^{\ddagger}$ (cal mol^{-1} K^{-1})	− 2	0	− 8	− 1
k_b(s^{-1})	36	160	5100	74
$\Delta H_b^{\ddagger}$ (kcal mol^{-1})	15.0	13.6	10.7	15.9
$\Delta S_b^{\ddagger}$ (cal mol^{-1} K^{-1})	− 1	− 3	− 5	+ 3

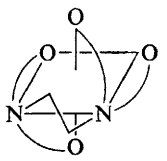
[a] Data refer to 25 °C; see ref. 24.

activation entropy remaining essentially constant at the value expected for a reaction involving a neutral species. There are similar variations in k_d and $\Delta H_d^{\ddagger}$, with the result that the overall free energy, enthalpy, and entropy changes are essentially constant for the four systems. This is interpreted in terms of an increased 'loosening' of the remaining parts of the inner co-ordination sphere of the metal on passing from Co^{2+} and $[Co(tp)]^{3-}$ to [Co(ida)] to $[Co(nta)]^-$, and it is expected that the water-exchange rate constants will mirror the substitution rate constants along the series. One feature of this work which is relevant to the discussion of the reasons for the frequent replacement of Zn^{2+} by Co^{2+} in enzymic systems is the high value of k_f (and low value of $\Delta H_f^{\ddagger}$) for the $[Co(nta)]^-$ systems, which is more typical of complex formation at Zn^{2+} than at Co^{2+}. It is evidently not necessary to place the Co^{2+} ion in a particularly unusual environment in order to alter significantly the ease with which it will react with a ligand.

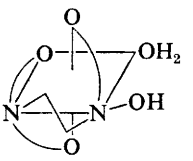
One difficult, but crucial, question to try to answer in any investigation of the effect of a bound ligand on the reactivity of a metal ion is: what is the structure adopted by the complex in solution—in the case of a multidentate ligand, how many groups are bound to the metal ion and what are their relative positions in the inner co-ordination sphere? The Ni^{II}–edta complex has been used in several studies of this type, but there is still some disagreement about its configuration in solution. ^{13}C and ^{17}O n.m.r. data have been presented [25] which suggest that this complex exists predominantly in the six-co-ordinate form (3) in the pH range 10—4, but that below pH 4 there is an equilibrium between this form and (4), in which one of the carboxylate groups has become protonated and has left the inner sphere of the metal ion. Although the ^{13}C data are not inconsistent with structure (5), the ^{17}O relaxation rates in the pH range 6—9 rule out a strong first-co-ordination-sphere interaction between the nickel ion and H_2O. Other workers report [26] a similar investigation with ^{17}O n.m.r. Their interpretation confirms the existence of (4) at pH 2 but they suggest that at pH 6—7 a temperature-dependent equilibrium exists

[25] N. A. Matwiyoff, C. E. Strouse, and L. O. Morgan, *J. Amer. Chem. Soc.*, 1970, **92**, 5222.

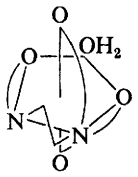
[26] M. W. Grant, H. W. Dodgen, and J. P. Hunt, *Chem. Comm.*, 1970, 1446.



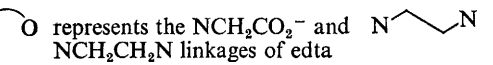
(3)



(4)

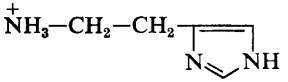


(5)



between two forms (both probably six-co-ordinate), one containing sexidentate edta and the other containing quinquedentate edta and a water molecule. N.m.r. and i.r. spectroscopy have also been used [27] to study the co-ordination of edta and other aminopolycarboxylates to Pb, Zn, Cd, and Hg.

The rate constants for the formation and dissociation of the mixed complex $[Cu(bipy)(glycinate)]^+$ have been measured,[28] and it was shown that, within experimental error, the rate-constant for attack by the glycine zwitterion is zero. For the reaction of $Cu(bipy)^{2+}$ with the glycinate ion (gly), the forward rate constant is 1.6×10^9 l mol^{-1} s^{-1} at 25 °C. This compares with values of 4×10^9 l mol^{-1} s^{-1} for Cu^{2+} + gly and 4×10^8 l mol^{-1} s^{-1} for $Cu(gly)^+$ + gly and it is suggested that the differences can be accounted for in terms of statistical factors, charge effects, and an enhancement term associated with the presence of bipy in the inner co-ordination sphere of the copper ion. A preliminary report [29] shows that the rate of complex formation between the histaminium ion (6) and Cu^{II}



(6)

(which probably involves deprotonation as the rate-determining step) is greater when serinate is co-ordinated to the metal ($k_f = 3.1 \times 10^6$ l mol^{-1} s^{-1} at 37 °C) than when either co-ordinated water ($k_f = 7.9 \times 10^4$ l mol^{-1} s^{-1}) or histamine ($k_f = 2.1 \times 10^4$ l mol^{-1} s^{-1}) is present.

We conclude this section by referring to recent work on metals, in which co-ordination-number changes have for some time been regarded as important, namely zinc and the lanthanide ions.

The presence of bound ligands on zinc has [30] comparatively little effect on the rate of complex formation with pyridine-2-azo-*p*-dimethylaniline (1).

[27] G. H. Reed and R. J. Kula, *Inorg. Chem.*, 1971, **10**, 2050.
[28] R. F. Pasternack and H. Sigel, *J. Amer. Chem. Soc.*, 1970, **92**, 6146.
[29] V. S. Sharma and D. L. Leussing, *Chem. Comm.*, 1970, 1278.
[30] G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 786.

The aquo-zinc ion is thought to be octahedral and there is good evidence that the metal in the ammines $Zn(dien)^{2+}$ and $Zn(trien)^{2+}$ has a co-ordination number of less than six, yet the formation rate constants at 25 °C for these ions are 6.8×10^6, 2.3×10^6, and 1.1×10^6 l mol^{-1} s^{-1}, respectively. Other formation rate constants quoted [30] are for the neutral species Zn(iminodiacetate), Zn(ethylenediamine-*NN'*-diacetate), and Zn(cysteinate) and the anion $[Zn(tp)]^{3-}$; the values are 1.5×10^7, 9.1×10^5, 5.4×10^6, and 1.4×10^6 l mol^{-1} s^{-1}, respectively. The exact geometries of these compounds are not known, though it is probable that at least one of the aminopolycarboxylate complexes contains five-co-ordinate Zn^{2+}, this being intermediate between the tetrahedral configuration preferred with nitrogen ligands and the octahedral configuration preferred with oxygen ligands. The fact that the geometry at Zn^{2+} is flexible and depends on the nature of the bound groups implies that the free energies of the tetrahedral, five-co-ordinate, and octahedral forms are comparable. Since the entropies of the various forms would not be comparable, this implies a large degree of compensation between ΔS and ΔH for the interconversion process. The observation that the reaction of (1) with octahedral $Zn(H_2O)_6^{2+}$ occurs at a rate which is comparable to the rates for four- and five-co-ordinate Zn shows that the process which is represented formally as an increase in co-ordination number is rapid. It thus appears that the zinc ion is behaving largely as a symmetrical sphere of positive charge, and such covalent contributions as might be involved in the binding of L^1 to Zn^{2+} [*cf.* reaction (5)] are not drastically affecting the rates of substitution. In this respect, zinc resembles magnesium and manganese(II), but contrasts with nickel(II).

The chemical properties of the tervalent ions of the lanthanides are determined largely through the interplay between charge and ionic radius, and the lack of influence of the 4*f* electrons on complex formation makes this an ideal series for a systematic investigation of the dependence of the various properties of the complexes on the size of the central ion. This is particularly true in view of the relatively large variation in ionic radius along the series. The co-ordination number of Ln^{3+} is usually larger than six and the frequent occurrence of a break in a particular property (*e.g.* the heat of complex formation) halfway along the series has usually been interpreted in terms of a change in co-ordination number of the aquo-ion from nine to eight at or around Eu^{3+}. (Alternatively, it is assumed, as in a recent report [31] of an n.m.r. investigation of various salts of La^{3+}, that an equilibrium such as

$$La(H_2O)_9^{3+} \rightleftharpoons La(H_2O)_8^{3+} + H_2O$$

exists for all tervalent lanthanide ions.) Geier and Karlen [32] have recently analysed the problem in detail and conclude that the change in co-ordination

[31] K. Nakamura and K. Kawamura, *Bull. Chem. Soc. Japan*, 1971, **44**, 330.
[32] G. Geier and U. Karlen, *Helv. Chim. Acta*, 1971, **54**, 135.

number occurs not in the aquo-ions but in the complexes, *i.e.* the presence of a chelating ligand in the inner co-ordination sphere induces a co-ordination-number change with some ions but not with others.

The 1 : 1 complexes between the lanthanides and edta form stable associates with the anions of 8-hydroxyquinoline-5-sulphonic acid (oxs), iminodiacetic acid (ida), and nitrilotriacetic acid (nta) since the characteristic co-ordination number of the Ln^{III} ions is generally greater than six. In Figure 6 the free-energy changes associated with the formation of these

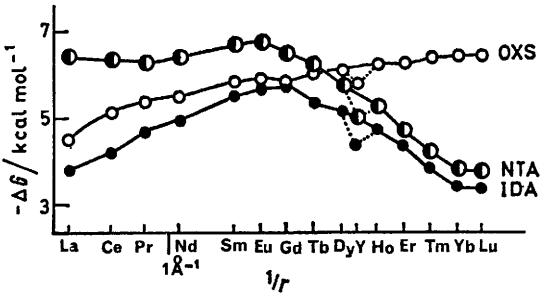


Figure 6 *Free energy of ternary-complex formation at* Ln(edta)$^-$ *as a function of reciprocal ionic radius*
(Reproduced by permission from *Helv. Chim. Acta*, 1971, **54**, 135)

ternary complexes from Ln(edta)$^-$ and L^{n-} are plotted as a function of the reciprocal ionic radius of Ln^{3+}. With the bidentate oxs the value of $-\Delta G$ increases regularly from La to Lu, whereas with the potentially ter- and quadri-dentate ligands ida and nta this increase is found only with the larger lanthanides. The free-energy changes for the formation of the Ln(edta)$^-$ complexes are shown in Figure 7, together with the corresponding entropy changes. The latter plot shows the characteristic break in the middle of the Ln-series (as does the plot of ΔH). From an analysis of a number of plots of this type, the authors are able to show that the break occurs because of a change in the co-ordination number of the metal from nine to eight in the Ln(edta)$^-$ complexes in the region Sm—Tb. In all cases the edta ion occupies six co-ordination positions and the oxs two, so that for the metals Sm—Tb the reduction in co-ordination number corresponds to the appearance of the following equilibrium:

$$[Ln(edta)(oxs)(H_2O)]^{3-} \rightleftharpoons [Ln(edta)(oxs)]^{3-} + H_2O$$

Similar equilibria hold for the ida and nta complexes. In agreement with this picture, the authors found [33] that the absorption band at 395 nm in dilute aqueous solutions of Eu(edta)$^-$ is strongly temperature-dependent. Apart from similar, but much weaker effects with Sm(edta)$^-$ and

[33] G. Geier, U. Karlen, and A. von Zelewsky, *Helv. Chim. Acta*, 1969, **52**, 1967.

Gd(edta)$^-$, solutions of neither the other edta complexes nor any of the aquo ions show significant changes in their absorption spectra in the temperature range 25—80 °C.

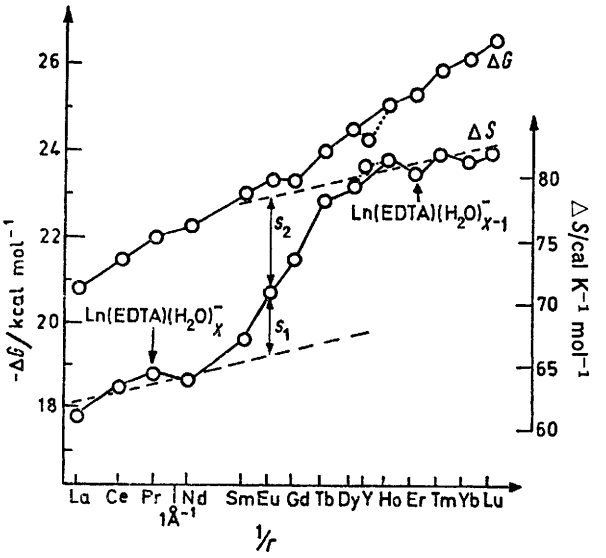


Figure 7 *Free energy and entropy of formation of* Ln(edta)$^-$ *as a function of reciprocal ionic radius*
(Reproduced by permission from *Helv. Chim. Acta*, 1971, **54**, 135)

4 Kinetics of Complex Formation Involving Unsubstituted Metal Ions

Main-group Ions, M^{2+}.—The studies on the formation of $BeSO_4$ in water with the repetitive temperature-jump technique[7] have already been mentioned. The ultrasonic relaxation method has been used[34] to measure the kinetics of lead acetate formation in aqueous solution. Formation (from Pb^{2+} and $MeCOO^-$) and dissociation rate constants of, respectively, 7.5×10^9 l mol^{-1} s^{-1} and 5.7×10^7 s^{-1} lead to an equilibrium constant which is in good agreement with the literature value. No special care was taken to keep the ionic strength constant, since it was found to have little effect on τ in the range 0.1—0.3 M. N.m.r. studies[35] on the Pb^{II}–nta system have yielded 4.4×10^6 and $< 1.5 \times 10^{11}$ l mol^{-1} s^{-1}, respectively, for the rate-constants at 25 °C for the formation of the complex [Pb(nta)$^-$] from the protonated species $Hnta^{2-}$ and the deprotonated form nta^{3-}. The comparatively low value in the former case suggests that the rate-determining step involves the deprotonation of $Hnta^{2-}$ rather than

[34] T. Yasunaga and S. Harada, *Bull. Chem. Soc. Japan*, 1971, **44**, 848.
[35] D. L. Rabenstein, *J. Amer. Chem. Soc.*, 1971, **93**, 2869.

the substitution of a water molecule at the metal ion. Similar results have been obtained [36] with Cd^{2+} (2.1×10^5 and $< 2.5 \times 10^9$ l mol^{-1} s^{-1}) and Zn^{2+} (5.1×10^5 and $< 1.0 \times 10^{10}$ l mol^{-1} s^{-1}).

Transition Metals M^{2+} (except Ni^{2+}).—Complex formation between the high-spin d^5 ion Mn^{2+} and SO_4^{2-} has been reinvestigated by the ultrasonic technique (see above [5]).

The n.m.r. line-broadening technique has been used [37] to follow the kinetics of solvent exchange in the $Fe(MeCN)_6^{2+}$–MeCN system; the first-order rate constant at 25 °C is 5.5×10^5 s^{-1}, the activation enthalpy 9.7 ± 0.7 kcal mol^{-1}, and the activation entropy *ca.* zero. Comparison is made between these results and similar data with the ions Mn^{2+}, Co^{2+}, and Ni^{2+} and the solvents NH_3, H_2O, and MeOH, and it is noted that there is a striking trend in the scalar coupling constants A/h along the series ($Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+}$) which reflects the trend in $\Delta H^{\ddagger}$. Since A/h is a measure of the delocalization of paramagnetic spin density into the vicinity of the ligand nucleus, it is tempting to speculate [37] that this indicates a correlation between metal–ligand-bonding character and $\Delta H^{\ddagger}$.

The reaction of Co^{II} with bipy and terpy has been studied in various solvents, as mentioned above.[15] The effect of the substitution of methyl groups in the 4 and 4′ positions of bipy is to double [38] the formation rate at 25 °C. The effect of substitution on ligand exchange in the system

$$[Co(AA)_2] + 2L \rightleftharpoons [Co(AA)_2L_2] \qquad (6)$$

where (AA) is a β-diketone has also been determined.[39] It is found that the rate of exchange when L is 4-picoline-1-oxide is greater than that for 4-picoline. This is probably due to a combination of factors including the lower basicity and the greater steric interaction of the oxide with the chelate ring. The reaction of Co^{2+} with monothenoyltrifluoroacetone has also been investigated [40] [*cf.* the nickel(II) system discussed below]. A preliminary report [41] has appeared of the use of ^{35}Cl n.m.r. to investigate the ligand-exchange kinetics in nitromethane of the species $CoCl_3(py)^-$ and $CoCl_4^{2-}$. The rate of exchange of 2,6-lutidine-1-oxide with $Co(2,6\text{-lutidine-1-oxide})_5^{2+}$ in CD_3NO_2–$(CD_3)_2CO$ (1 : 1 v/v) was found [42] to be independent of the free-ligand concentration, suggesting that the exchange mechanism at the trigonal-bipyramidal complex is dissociatively controlled. It appears [43] that both associative and dissociative mechanisms are important in the ligand-exchange process of a number of tetrahedral

[36] D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, 1969, **91**, 2492.
[37] R. J. West and S. F. Lincoln, *Austral. J. Chem.*, 1971, **24**, 1169.
[38] C. D. Hubbard, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 139.
[39] R. W. Kluiber, F. Thaller, R. A. Low, and W. de W. Horrocks, *Inorg. Chem.*, 1970, **9**, 2592.
[40] M. R. Jaffe, D. P. Fay, M. Cefola, and N. Sutin, *J. Amer. Chem. Soc.*, 1971, **93**, 2878.
[41] R. E. Gentzler, T. R. Stengle, and C. H. Langford, *Chem. Comm.*, 1970, 1257.
[42] P. M. Enriquez, S. S. Zumdahl, and L. Forshey, *Chem. Comm.*, 1970, 1527.
[43] D. R. Eaton and K. Zaw, *Canad. J. Chem.*, 1971, **49**, 3315.

Co^{II} complexes of thiourea, *N*-methylthiourea, and *NN'*-dimethylthiourea in [$^2H_6$]acetone.

Activation parameters have been reported[44] for the formation of complexes with Cu^{II}. The reactions were studied in the pH range 1—2.5 where both the unprotonated (L) and protonated (LH^+) forms of the attacking ligand are kinetically important. The activation energy for phen (5.1 ± 1.0 kcal mol^{-1}) is similar to those for the protonated species $bipyH^+$ (4.3 ± 1.2) and $terpyH^+$ (4.7 ± 0.9) although the rate-constant (6.4×10^7 l mol^{-1} s^{-1}) is rather higher (2.6×10^5 and 8.0×10^5 l mol^{-1} s^{-1}, respectively). The kinetics of the reaction of Cu^{2+} with monothenoyltrifluoroacetone have been measured.[40]

Nickel(II).—In view of the convenient exchange rate of Ni^{2+} and its resistance to oxidation or reduction, it is not surprising that there has been more work reported with this species than any other labile metal ion during the 18 months under review. Wilkins [1] has summarized the state of knowledge at the end of 1970 and major parts of other reviews [2,3] are devoted to this ion. Results of a polarographic study of the reaction of $Ni(H_2O)_6^{2+}$ with pyridine have appeared[45] and the discrepancies between previous results obtained with this technique and those obtained with the stopped-flow method have been explained. Other studies on Ni^{II} which have already been mentioned involve NH_3 in methanol–water mixtures,[10] SCN^- in DMSO,[14] bipy and terpy in various solvents,[15] 4,4'-dimethylbipy in water,[38] and solvent-exchange in 4-picoline-1-oxide.[39] The n.m.r. technique has been used[46] over the temperature range + 50 to − 60 °C to study the exchange reaction of 3-picoline-1-oxide with hexakis(3-picoline-1-oxide)nickel(II) in a solvent mixture comprising 50% [$^2H_3$]nitromethane and 50% [$^2H_6$]acetone by volume. The concentration of free ligand was varied over a wide range and the exchange rate found to be independent of concentration; this observation was taken to indicate a dissociative mechanism. The activation enthalpy for the exchange reaction is 12.5 ± 0.2 kcal mol^{-1}.

If the incoming ligand is bi- or multi-dentate there is always the possibility that the first metal—ligand bond will break again before the second and subsequent metal—ligand bonds can be formed; in this case the ring-closure step becomes rate limiting and the overall rate-constant k_f is less than that found for a comparable unidentate ligand. Hoffmann and Nickel have reported[47] the rate constants for the reaction of Ni^{2+} with 2- and 3-hydroxyglutarate and suggest that in both cases ring closure is rate limiting. Solutions of both nickel hydroxyglutarates give two relaxations when subjected to a pressure jump whereas nickel glutarate gives only a single effect. A complete analysis of the rate constants for

[44] T. S. Roche and R. G. Wilkins, *Chem. Comm.*, 1970, 1681.
[45] R. S. Bulmer, E. F. Caldin, and A. W. Walton, *Trans. Faraday Soc.*, 1971, **67**, 3343.
[46] M. L. Yount and S. S. Zumdahl, *Inorg. Chem.*, 1971, **10**, 1212.
[47] H. Hoffmann and U. Nickel, *Z. Naturforsch.*, 1971, **26b**, 299.

the individual steps suggests that the first metal—ligand bond to form with the hydroxyglutarate involves the carboxylate group and that the hydroxy-group is involved in the slower ring-closure step. The results show that the enhanced stability constant for the 2-hydroxyglutarate compared with the 3-hydroxy-species arises because the rate constant for the opening of the five-membered ring is a factor of three lower than that for the six-membered ring. Evidently the difference in rates for ring closure[48] is not the only factor to be considered when discussing the mechanisms of reactions involving five- and six-membered-ring systems.

The reaction of the β-diketone thenoyltrifluoroacetone with Ni^{2+} (and with Co^{2+}, Cu^{2+}, and Fe^{3+}) has been studied by Sutin and co-workers.[40] The active form of the ligand is the enol tautomer (7, HE)

$$M^{n+} + HE \underset{k_{-HE}}{\overset{k_{HE}}{\rightleftharpoons}} ME^{(n-1)+} + H^+ \qquad (7)$$

and the formation rate constant k_{HE} was found to be acid-dependent in all cases: $k_{HE} = a + b/[H^+]$. This form of the rate law is consistent with a mechanism of the following type (illustrated for Ni^{2+}):

$$\begin{array}{ccc} Ni^{2+} + HE & \underset{H^+}{\overset{K_{HE}}{\rightleftharpoons}} & Ni^{2+} + E^- \\ \Big\downarrow\uparrow{\scriptstyle k_1}\ {\scriptstyle k_{-1}} & & \Big\downarrow\uparrow{\scriptstyle k_4}\ {\scriptstyle k_{-4}} \\ \dot{N}i\dot{E}H^{2+} & \underset{H^+}{\overset{K_{NiEH}}{\rightleftharpoons}} & \dot{N}i\dot{E}^+ \\ \Big\downarrow\uparrow{\scriptstyle k_2}\ {\scriptstyle k_{-2}} & & \Big\downarrow\uparrow{\scriptstyle k_3}\ {\scriptstyle k_{-3}} \\ NiE^+ + H^+ & & NiE^+ \end{array}$$

where $\dot{N}i\dot{E}H^{2+}$ and $\dot{N}i\dot{E}^+$ are intermediates in which only one end of the diketone is attached to the metal centre. If the protonation steps are assumed to be rapid compared with those involving the formation and dissociation of metal—ligand bonds, application of the steady-state hypothesis to the intermediates $\dot{N}i\dot{E}H^{2+}$ and $\dot{N}i\dot{E}^+$ gives

$$k_{HE} = \frac{k_1 + K_{HE}k_4/[H^+]}{1 + \dfrac{k_{-1} + K_{NiEH}k_{-4}/[H^+]}{k_2 + K_{NiEH}k_3/[H^+]}}$$

Two limiting cases are considered, mechanism A, in which the formation of the intermediates is rate-determining and the subsequent ring closure is rapid, (giving $k_{HE} = k_1 + K_{HE}k_4/[H^+]$) and mechanism B, in which the ring closure is rate-limiting (giving $k_{HE} = K_1k_2 + K_{HE}K_4k_3/[H^+]$). If mechanism A obtains for the nickel(II) reaction, the values of k_1 and

[48] *cf.* K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, 1966, **88**, 4610.

k_4 at 25 °C calculated from the experimental data are 2.3 and 1.0×10^4 l mol^{-1} s^{-1}, respectively. Although this value of k_4 is not unreasonable for the reaction of Ni^{2+} with a singly charged anion, the value of k_1 is about three orders of magnitude smaller than the characteristic rate constant for the reaction of Ni^{2+} with uncharged ligands (*ca.* 4×10^3 l mol^{-1} s^{-1}). The low value of k_1 implied by mechanism A can be rationalized in terms of steric interference and/or the necessity to break the intramolecular hydrogen bond in (7). If, on the other hand, mechanism B obtains for the nickel(II) reaction, the value of k_1 is 'normal' (4×10^3 l mol^{-1} s^{-1}) but the implication is that the two monosubstituted intermediates possess very different kinetic properties. In particular, $k_1/k_{-1} \ll k_4/k_{-4}$ and $k_2/k_{-1} \ll 1$, *i.e.* ring closure is rate-limiting for the intermediate $Ni\overset{*}{E}H^{2+}$ but not for $Ni\overset{*}{E}^{+}$. The authors discuss the various factors which would tend to decrease the value of k_2. It might briefly be noted here that if k_2 were low because a six-membered ring is being formed,[48] k_3 would likewise be expected to be reduced—which it is not.

The implications of the 'low' rate-constant for the reaction of Ni^{2+} with the murexide anion (2) have also been discussed[49] in terms of the rates of the formation and dissociation of the individual metal—ligand bonds. The kinetics are reported in water, 25% DMSO–H_2O, 50% DMSO–H_2O, and 50% ethanol–H_2O.

Metals of Valency Three and Higher.—Work on the mechanism of ligand substitution in weak complexes has been extended to $AlSO_4^+$ and $GaSO_4^+$,[50] and to $Al[Co(CN)_6]$.[51] The activation energies for the forward and reverse reactions

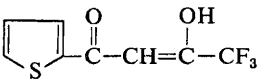
$$\text{outer-sphere complex} \rightleftharpoons \text{inner-sphere complex}$$

for $AlSO_4^+$ are 21.5 and 18 kcal mol^{-1}, respectively, and for $GaSO_4^+$ 12.5 and 9.4 kcal mol^{-1}. These are in the order of magnitude postulated by the concerted mechanism,[52] and the difference between the values for the two metals can be rationalized in terms of the different sizes of the cations.

The synthesis of hexakis(dimethyl sulphoxide)vanadium(III) perchlorate and the kinetics of its reaction with SCN^-, bipy, and sulphosalicylic acid have been reported.[53] The complex-formation rates show some dependence on the nature of the ligand but a definite mechanistic assignment cannot yet be made.

The reaction of monothenoyltrifluoroacetone (7) with iron(III) has been studied[40] but the situation is even more obscure than in the nickel(II), cobalt(II), and copper(II) systems because there are so few criteria for

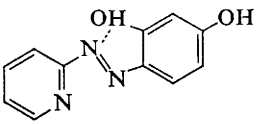
[49] C. T. Lin and J. L. Bear, *J. Phys. Chem.*, 1971, **75**, 3705.
[50] C. Kalidas, W. Knoche, and D. Papadopoulos, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 106.
[51] C. Kuehn and W. Knoche, *Trans. Faraday Soc.*, 1971, **67**, 2101.
[52] H. Strehlow and W. Knoche, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 427; M. Matušek and H. Strehlow, *ibid.*, p. 982.
[53] C. H. Langford and F. M. Chung, *Canad. J. Chem.*, 1970, **48**, 2969.



(7)

deciding whether a particular rate constant for substitution on Fe^{III} is 'normal'. Cavasino [54] has extended his work on complex formation at Fe^{III} to some bidentate ligands which form six-membered chelate rings, *viz.* malonic, methylmalonic, n-butylmalonic, and cyclobutane-1,1-dicarboxylic acids. The kinetic data obtained at various acidities have been interpreted in terms of the reactions of the $FeOH^{2+}$ ion with the undissociated acid ligands and the corresponding monoanions, and the estimated rate constants for both reactions are consistent with a mechanism in which the rate-determining step is the loss of the first water molecule from the inner co-ordination sphere of the metal ion. A similar conclusion has been drawn concerning the reaction of iron(III) with sulphosalicylic acid, salicylic acid,[55, 56] 8-hydroxyquinoline,[56] and salicylaldehyde,[56] though, as with many reactions of this metal, it is not possible to distinguish between the kinetically equivalent alternatives involving $Fe(H_2O)_6^{3+} + X^-$ and $Fe(H_2O)_5OH^{2+} + HX$. The reaction between iron(III) and the sulphate ion is also pH-dependent.[57]

In the reaction of La^{III} with 4-(2′-pyridylazo)-resorcinol (8) the rate-determining step is the rupture of the internal hydrogen bond.[58] A comparison of the rates of complex formation between Nd^{III} and SO_4^{2-} in H_2O and D_2O suggests [8] that solvent-loss at the metal ion is not the



(8)

controlling step in this reaction either. Two reports have appeared recently on the kinetics of complex formation involving cerium(IV), both of which refer to a significant pH-dependence. The rates of formation and dissociation of alcohol complexes depend [59] on the nature of the alcohol, and complex formation between Ce^{IV} and diethylenetriaminepenta-acetic acid is followed [60] by reduction of the metal to Ce^{III}.

[54] F. P. Cavasino and E. Di Dio, *J. Chem. Soc.* (*A*), 1971, 3176.
[55] G. Saini and E. Mentasti, *Inorg. Chim. Acta*, 1970, **4**, 210, 585.
[56] P. G. T. Fogg and R. J. Hall, *J. Chem. Soc.* (*A*), 1971, 1365.
[57] F. L. Baker and W. MacF. Smith, *Canad. J. Chem.*, 1970, **48**, 3100.
[58] T. Onodera and M. Fujimoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 2003.
[59] G. Boivin and M. Zador, *Canad. J. Chem.*, 1970, **48**, 3053.
[60] S. B. Hanna and R. K. Hessley, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 83.

Diebler and Timms [61] have studied the formation of the molybdate and tungstate complexes of 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulphonic acid by the temperature-jump method and the kinetic data are discussed in terms of a detailed reaction mechanism. The main reaction pathways for the complex formation in the pH range 7.5—9.8 involve the reaction of the protonated metal ions, $MO_3(OH)^-$, with the neutral oxine molecule and with the oxine anion (or the sulphonated derivatives, respectively) although part of the complex formation probably occurs by the reaction of MO_4^{2-} with oxine or 8-hydroxyquinoline-5-sulphonic acid [the rate constants for the latter processes being several orders of magnitude smaller than those for the reactions of the $MO_3(OH)^-$ species]. The reactivity of tungstate is generally up to about ten times that of molybdate and this is probably associated with the slightly larger size of W^{VI} compared with Mo^{VI}.

[61] H. Diebler and R. E. Timms, *J. Chem. Soc.* (*A*), 1971, 273; *cf.* P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, 1968, **64**, 977.

5
Reactions of Co-ordinated Ligands

BY J. BURGESS

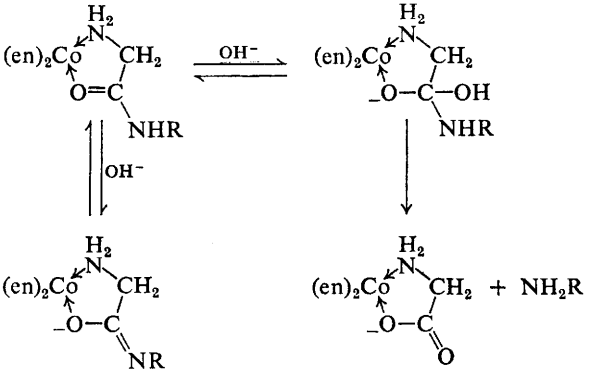
Aquation of Oxoanion Complexes.—The aquation of oxoanion complexes of transition-metal cations is sometimes a reaction of the co-ordinated ligand, in that for a complex $ML_m(XO_n)$ aquation can in principle proceed by either M—O or X—O bond breaking. It is the latter situation which may be described as a reaction of the co-ordinated ligand. The activation parameters for aquation of the complexes $[M(NH_3)_5(ONO)]^{2+}$ are nearly the same for M = Co, Rh, and Ir, which suggests that nitrogen–oxygen bond fission is taking place in each case.[1] Nitrogen–oxygen bond fission is also involved in the acid-catalysed path for aquation of nitrito-complexes of chromium(III).[2] Sulphur–oxygen bond fission occurs in the aquation of sulphito-complexes, again of chromium(III).[3] A final example is provided by arsenic–oxygen bond breaking in the aquation of $[Co(NH_3)_5(AsO_4)]$.[4]

Solvolysis of Organic Ligands.—The catalysis of hydrolysis of organic esters by metal ions or complexes has been much studied for many years. Recent examples of kinetic studies include hydrolysis of oxalate esters catalysed by a variety of M^{2+} ions,[5] and of the bis[-L-(+)-histidine methyl ester] complexes of copper(II) and of nickel(II).[6] The relative catalytic effects of several copper(II) complexes, including Cu(imda), $Cu(nta)^-$, and $Cu(dien)^{2+}$, on the hydrolysis of methyl glycinate have been determined. Rate constants for base hydrolysis of this ester correlate with stability constants for mixed complexes of this ester with the above-named copper(II) complexes.[7]

The hydrolysis of glycinamide complexes of cobalt(III), *viz.* *cis*-$[Co(en)_2Br(glyNR^1R^2)]^{2+}$ to give $[Co(en)_2(gly)]^{2+}$, has been studied in alkaline solution by kinetic, stereochemical, and ^{18}O-labelling methods. The bromide ion is displaced first, and then comes cobalt-promoted hydrolysis

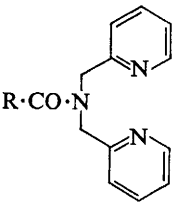
[1] B. E. Crossland and P. J. Staples, *J. Chem. Soc.* (*A*), 1971, 2853.
[2] W. W. Fee, J. N. MacB. Harrowfield, and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 290; T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1969, 219, 1977.
[3] D. W. Carlyle and E. L. King, *Inorg. Chem.*, 1970, **9**, 2333.
[4] T. A. Beech and S. F. Lincoln, *Chem. Comm.*, 1970, 1568.
[5] G. L. Johnson and R. J. Angelici, *J. Amer. Chem. Soc.*, 1971, **93**, 1106.
[6] R. W. Hay and P. J. Morris, *J. Chem. Soc.* (*A*), 1971, 1524.
[7] R. J. Angelici and J. W. Allison, *Inorg. Chem.*, 1971, **10**, 2238.

of the amide linkage.[8] The kinetics of base hydrolysis of a variety of glycinamide and glycylglycine ester complexes of cobalt(III) are consistent with attack of hydroxide ion at the carbonyl carbon of the chelated ligand; the conjugate base of the complexed amide must be unreactive. The proposed mechanism is outlined in the Scheme.[9] In this type of cation-



Scheme

promoted hydrolysis of amides, the metal ion usually co-ordinates to the amide oxygen. An unusual reaction in which this is not the case is that of copper(II) catalysis of hydrolysis or of methanolysis of the *NN*-di-(2-pyridylmethyl)amides (1), where the copper(II) cation bonds to the



(1)

three nitrogen atoms.[10] The isolation of intermediates containing α-amino-ether groups has been reported for solvolysis of polycyclic Schiff-bases co-ordinated to copper(II) or to nickel(II).[11] The first stage in the reaction of *cis*-$[Co(en)_2(NH_2 \cdot CH_2 \cdot CH_2 \cdot Br)Br]^{2+}$ with hydroxide ion in aqueous solution is base hydrolysis of the co-ordinated bromide; the second stage is the hydrolysis of the bromide of the $NH_2 \cdot CH_2 \cdot CH_2 \cdot Br$

[8] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1970, **92**, 6151.
[9] D. A. Buckingham, C. E. Davis, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1970, **92**, 5571.
[10] R. P. Houghton and R. R. Puttner, *Chem. Comm.*, 1970, 1270.
[11] V. Katović, L. T. Taylor, and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 458.

ligand. The rate law, rate constants, and mechanism of the latter stage are described.[12]

Other Ligand Substitutions.—The reactions of azide complexes of ruthenium in acid solution appear to go through nitrene intermediates, as mentioned in the first volume of this Specialist Periodical Report.[13] Recently, evidence has been presented for nitrene intermediates in reactions of the iridium(III)-azide complex $[Ir(NH_3)_5(N_3)]^{2+}$ in acid solution. The presence of $[Ir(NH_3)_5(NH_2OH)]^{3+}$ and, in the presence of chloride, $[Ir(NH_3)_5(NH_2Cl)]^{3+}$ amongst the products can most readily be explained by invoking an intermediate nitrene complex. This, from the dependence of reaction rates on acid concentration, probably exists [14] in the protonated form $[Ir(NH_3)_5(NH)]^{3+}$. Similarly, the nitrene intermediate in the analogous reactions of ruthenium(III)-azide complexes is thought to be in its protonated form. The kinetics of reactions of several ruthenium(III)-azide complexes have been investigated in acetone, in acetonitrile, and in methanol; most results are presented for *cis*-$[Ru(en)_2(N_3)_2]^+$, but results are also reported for $[Ru(edta)(N_3)]^{2-}$, *cis*-$[Ru(trien)(N_3)_2]^+$, and $[Ru(NH_3)_5(N_3)]^{2+}$, in acetone.[15]

The complex $[Ru(NH_3)_5(N_2O)]^{2+}$ is amongst the products of reaction of $[Ru(NH_3)_5(NO)]^{3+}$ with hydroxylamine, hydrazine, or ammonia. The nitrous oxide complex is thought to arise from nucleophilic attack at the co-ordinated nitrogen.[16] This type of nucleophilic attack at the ligand is an exact parallel of attack by, for instance, azide or hydrazine at the carbonyl carbon of a metal carbonyl (see Part IV, Chapter 5).

The hydrolysis of cyanato-complexes $[M(NH_3)_5(NCO)]^{2+}$, where M = Ru or Rh, in acid solution produces $[M(NH_3)_6]^{3+}$ and carbon dioxide. The rate law is, in dilute acid:

$$-\mathrm{d}[M(NH_3)_5(NCO)^{2+}]/\mathrm{d}t = k_2[M(NH_3)_5(NCO)^{2+}][H^+]$$

This simple second-order rate law is identical with that reported earlier for the hydrolysis of $[Co(NH_3)_5(NCO)]^{2+}$. At higher acid concentrations the rate law is more complicated since such intermediates as $[Rh(NH_3)_5(NH_2CO_2H)]^{3+}$, which has been isolated, exist and have relatively long half-lives. The reaction mechanism suggested is reversible protonation of the cyanate nitrogen, followed by attack of water at the cyanate carbon, followed in turn by the liberation of carbon dioxide.

[12] D. A. Buckingham, C. E. Davis, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1970, **92**, 6159.
[13] L. A. P. Kane-Maguire, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 4609.
[14] B. C. Lane, J. W. McDonald, V. G. Myers, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1971, **93**, 4934.
[15] L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1970, **92**, 5865.
[16] F. Bottomley and J. R. Crawford, *Chem. Comm.*, 1971, 201.

Kinetic parameters are listed in the Table; the extra *d*-electron on rhodium is associated with faster rates and a lower activation enthalpy in comparison with the values for the ruthenium complex.[17] In weakly acidic aqueous solution the cyanato-ligand of $[Co(dmgH)_2(NO_2)(NCO)]^-$ or of $[Co(dmgH)_2(I)(NCO)]^-$ is hydrolysed to ammonia with fission of the

Table *Kinetic parameters for the hydrolysis of cyanato-complexes* $[M(NH_3)_5(NCO)]^{2+}$ *in acid solution; data from ref.* 17

M	k_2/l mol^{-1} s^{-1} (at 25.0 °C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
Ru	0.059	12.2	− 23
Rh	0.62	10.9	− 23

cyanate carbon–nitrogen bond, but in stronger acid the cyanate is replaced by water.[18]

'Ruthenium brown', $[(NH_3)_5Ru\cdot O\cdot Ru(NH_3)_4\cdot O\cdot Ru(NH_3)_5]^{7+}$, is reduced by hydroxide ion *via* rate-determining nucleophilic attack of the hydroxide. This nucleophilic attack is suggested to take place at a bridging oxygen, to give a μ-peroxo-intermediate.[19] Hydroxide ion attacks at the carbon atom of co-ordinated CNMe in isocyanide complexes of platinum(II), *e.g.* *trans*-$[Pt(PPh_3)_2(CNMe)_2]^{2+}$, to give carboxamido-complexes.[20]

$[Ru(NH_3)_6]^{3+}$ reacts with thiosulphate or with monothiophosphate ($[PO_3S]^{3-}$) to form a sulphamato-complex $[Ru(NH_3)_5(NHSO_3)]^+$. The reaction sequence is thought to involve transfer of sulphur to the NH_2 ligand of the conjugate base, $[Ru(NH_3)_5(NH_2)]^{2+}$, of the starting complex.[21] The redox reaction between hexacyanoferrate(III) and sulphite [22] involves the intermediates $[Fe(CN)_5(CNSO_3)]^{5-}$ and $[Fe(CN)_5(CNSO_3)]^{4-}$.

Recent examples of kinetic studies of substitution in organic ligands include a qualitative investigation of the halogenation of the copper(II) complex of 8-hydroxyquinoline by the halogens themselves or by *N*-halogenosuccinimides,[23] and the establishment of the relative reactivity of the 3-position of acetylacetone co-ordinated to chromium(III) and to cobalt(III) from the relative rates of nitration and of formylation of the complexes $Cr(acac)_3$ and $Co(acac)_3$.[24]

Hydrogen Exchange.—On the n.m.r. time-scale it is proton exchange with the water ligands rather than with the (protonated) azide ligands of $[Cr(OH_2)_5(N_3H)]^{2+}$ that can be observed. The rate law is:

$$\text{rate} = \{k_1 + k_2[H^+]\}[\text{complex}]$$

[17] P. C. Ford, *Inorg. Chem.*, 1971, **10**, 2153.
[18] A. V. Ablov, N. N. Samus, and A. A. Popova, *Russ. J. Inorg. Chem.*, 1971, **16**, 215.
[19] J. E. Earley and T. Fealey, *Chem. Comm.*, 1971, 331.
[20] W. J. Knebel and P. M. Treichel, *Chem. Comm.*, 1971, 516.
[21] J. N. Armor and H. Taube, *Inorg. Chem.*, 1971, **10**, 1570.
[22] R. S. Murray and J. M. Lancaster, *J. Chem. Soc.* (*A*), 1971, 2755.
[23] H. Gershon, M. W. McNeil, and S. G. Schulman, *J. Org. Chem.*, 1971, **36**, 1616.
[24] T. Schirado, E. Gennari, R. Merello, A. Decinti, and S. Bunel, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3417.

The activation parameters for the two proton-exchange paths are: $\Delta H_1^{\ddagger} = 11.7$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = +3$ cal deg^{-1} mol^{-1} for the k_1 path, and $\Delta H_2^{\ddagger} = 3.2$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -24$ cal deg^{-1} mol^{-1} for the k_2 path.[25] Proton exchange with the cobalt(III) complexes $[Co(NH_3)_5(OH_2)]^{3+}$ and *cis*- and *trans*-$[Co(en)_2(NH_3)(OH_2)]$ has been probed by determining the dependence of ^{59}Co n.m.r. linewidths on pH. In fact, proton exchange with the aquo-ligands is fast, and it is only possible to establish lower limits to the rate constants.[26] The forward and reverse rate constants for reaction (1) have been measured using the electric-field-jump relaxation

$$[Fe(OH)]^{2+}\,aq \rightleftharpoons [Fe(OH_2)]^{+}\,aq + H^{+}\,aq \qquad (1)$$

technique. The forward rate constant has the value 6.1×10^4 s^{-1}, and the reverse has a value of 8.0×10^9 s^{-1}, at 25 °C. The latter value is of the order of that expected for diffusion control. An interesting point about proton exchange at iron(III) is that the equilibrium (2) is established too

$$Fe^{3+}\,aq \rightleftharpoons [Fe(OH)]^{2+}\,aq + H^{+}\,aq \qquad (2)$$

rapidly to be monitored, in contrast with the analogous equilibria for Al^{3+}, Cr^{3+}, Sc^{3+}, and In^{3+}, where the forward rate constants for the respective analogues of equilibrium (2) are *ca.* 10^5 s^{-1} at 25 °C. Only $[Ga(OH_2)_6]^{3+}$ appears to lose a proton at a very high rate, comparable with that for Fe^{3+} aq.[27]

The catalysis of proton exchange with ethanol by H^+ is well-established. A recent report describes metal-cation catalysis of proton exchange with ethanol. High catalytic effectiveness is associated with the presence of filled or partly filled *d*-orbitals on the cation. Activation parameters for the uncatalysed, H^+-catalysed, and Cu^{2+}-catalysed processes have been compared and discussed in terms of differences in mechanism between the catalysed and uncatalysed processes.[28] Proton exchange with the acetate portions of edta, pdta, and cydta ligands co-ordinated to nickel(II) has been studied by n.m.r. spectroscopy. Half the acetate protons exchange much more rapidly, by a factor of *ca.* 10^4, than the other half. The two types of protons are derived from 'in-plane' and 'out-of-plane' acetate groups. This great difference in rates of proton exchange suggests a large difference, estimated at 5—6 p*K* units, between their basicities.[29]

The rate of proton transfer to the nickel(II)-triglycine complex is remarkably slow when the ligand is in its twice-deprotonated form, and considerably faster for the once-deprotonated form.[30] Rates of protonation

[25] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1970, **9**, 2639.
[26] F. Yajima, A. Yamasaki, and S. Fujiwara, *Inorg. Chem.*, 1971, **10**, 2350.
[27] P. Hemmes, L. D. Rich, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, 1971, **75**, 929.
[28] A. H. Hunt and M. E. Hobbs, *J. Phys. Chem.*, 1971, **75**, 1994.
[29] L. E. Erickson, D. C. Young, F. F.-L. Ho, S. R. Watkins, J. B. Terrill, and C. N. Reilley, *Inorg. Chem.*, 1971, **10**, 441.
[30] E. J. Billo and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 6811.

have been reported for several amide and peptide complexes of nickel(II).[31] In all these cases, the fairly low rates can be attributed to the important role of nickel–ligand bond cleavage or rearrangement associated with protonation.

Other Reactions.—The compounds $[PtX(CNMe)(PR_3)_2]^+X^-$ can be demethylated by refluxing in benzene suspension; this is the reverse of the standard alkylation of metal cyanides. The mechanism suggested, on somewhat meagre evidence, is halide attack at the platinum to give a five-co-ordinate intermediate which can eliminate methyl halide.[32] Reaction of *trans*-$[Pt(mesityl)(SnCl_3)(PEt_3)_2]$ with nucleophiles, in 1,2-dichloroethane solution, proceeds by attack of the nucleophile at the tin rather than at the platinum.[33]

The autoxidation of $CoCl_2(PEt_3)_2$ to $CoCl_2(P\{OEt\}_3)_2$, which occurs in several solvents, is initially first-order in complex and first-order in molecular oxygen. Failure to detect any compounds $O{=}PR_n(OR)_{3-n}$ amongst the product contra-indicates a dissociative mechanism; a cobalt–molecular oxygen complex is the suggested intermediate.[34]

Oxygen exchange with mixed chromium(III)-oxalate complexes $[Cr(ox)(LL)_2]^+$ has been described.[35]

[31] C. F. V. Mason, P. I. Chamberlain, and R. G. Wilkins, *Inorg. Chem.*, 1971, **10**, 2345.
[32] P. M. Treichel and R. W. Hess, *Chem. Comm.*, 1970, 1626.
[33] M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti. Soc. Peloritana, Sci. fis., mat., nat.*, 1968, **14**, 325 (*Chem. Abs.*, 1971, **74**, 35 123*x*).
[34] D. D. Schmidt and J. T. Yoke, *J. Amer. Chem. Soc.*, 1971, **93**, 637.
[35] J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, 1971, **10**, 955.

Part III

REACTIONS OF BIOCHEMICAL INTEREST

By
D. N. HAGUE

1 Introduction

Mechanistic studies involving reactions of biochemical interest will be discussed under essentially the same headings as were used in the corresponding section in Volume 1 of this series (Part III, Chapter 2). As before, we shall concentrate on those reports in which the emphasis has been on the behaviour of the metal – a policy which inevitably leads to the exclusion of certain work on metal-containing systems. An excellent review by Mildvan[1] deals with the role of metals in enzyme catalysis, and the papers presented at a Bioinorganic Chemistry Symposium, held at Virginia Polytechnic Institute and State University in June 1970, have been published.[2] Malmström[3] has discussed the view, currently gaining popularity, that metalloenzymes represent 'unique' metal complexes when compared to the simpler systems generally studied by co-ordination chemists. Williams' Tilden Lecture on the biochemistry of sodium, potassium, magnesium, and calcium has appeared,[4] as have the lectures given at symposia[5] on 'Transition Elements in Biology' and 'Trace Elements in the Metabolism of Connective Tissue'. The use of paramagnetic probes for investigating enzyme mechanisms has been reviewed[6] and the oxidation state and function of copper in biological systems have been discussed.[7] Other reviews have been published during the period under consideration and these will be referred to in the appropriate sections.

2 Metal Ion Transport

The remarkable capacity of ionophores of low molecular weight, such as valinomycin, to render biological and artificial membranes selectively

[1] A. S. Mildvan in 'The Enzymes', ed. P. D. Boyer, Academic Press, New York, 1970, vol. 2, 3rd edn., p. 445.
[2] 'Bioinorganic Chemistry', A.C.S. Advances in Chemistry Series, 1971, No. 100.
[3] B. G. Malmström, *Pure Appl. Chem.*, 1970, **24**, 393.
[4] R. J. P. Williams, *Quart. Rev.*, 1970, **24**, 331.
[5] *Fed. Proc.*, 1970, **29**, 1461–1488; 1971, **30**, 983–1015.
[6] A. S. Mildvan and M. Cohn in 'Advances in Enzymology', Wiley–Interscience, New York, 1970, vol. 33, p. 1.
[7] R. Malkin and B. G. Malmström in 'Advances in Enzymology', Wiley–Interscience, New York, 1970, vol. 33, p. 177.

permeable to alkali-metal cations has stimulated further research into the properties of these species and their complexes. The complexing of various antibiotics of this type with Na^+ has been investigated [8] by ^{23}Na n.m.r. spectroscopy. Since the width of the resonance line is a function not only of the rotational correlation time of the Na^+ but also of the coupling constant between the electric field gradient at the nucleus and the quadrupole moment of the nucleus, it can be used to obtain information about the symmetry of the electromagnetic environment of the cation. The coupling constants for the 1 : 1 complexes of Na^+ with monactin, enniatin B, valinomycin, monensin, cyclohexyl ether, and nigericin are all low, indicating a very symmetric electric field around the complexed metal ion and a very small amount of covalent interaction between the cation and the ligand oxygen atoms. A good correlation between the ^{23}Na resonance positions and the logarithms of the stability constants suggests that electrostatic interaction of the oxygen atoms of the ionophore and the cation is the principal determinant of the energy of complex formation. The rates of exchange between complexed and free Na^+ in methanol are high (*cf.* the previous observations for valinomycin and nonactin with K^+ in 80 : 20 methanol : $CDCl_3$, ref. 9) and support the carrier theory of ionophore action.

The stability constants of the 1 : 1 complexes of 22 cyclic polyethers with Li^+, Na^+, K^+, Cs^+, NH_4^+, and Ag^+ have been determined [10] potentiometrically in water and methanol, using cation-selective electrodes. The methanol stability constants are three to four orders of magnitude higher than the aqueous values, presumably because water competes more strongly for the cation than methanol. Selectivity towards the different cations varies with polyether ring size, the optimum being such that the cation just fits into the hole (*i.e.* 15—18 for Na^+, 18 for K^+, and 18—21-membered rings for Cs^+). The effects of side rings fused on to the main polyether ring are comparatively small and difficult to predict, and the results are consistent with the conclusion that here, too, covalent bonding plays a very minor role (except in Ag^+ complexes of polyethers containing N or S).

Selective transport of K^+ through synthetic membranes impregnated with valinomycin in octan-2-ol in the presence of equal amounts of Li^+ or Na^+ is induced by the application of a potential difference across the membranes. By using ^{14}C-labelled valinomycin, it has been shown [11] that transport of potassium is accompanied by the movement of an equivalent amount of valinomycin within the membrane, consistent with the formation of a 1 : 1 complex between the metal and the ionophore. The exchange of ligands is

[8] D. H. Haynes, B. C. Pressman, and A. Kowalsky, *Biochemistry*, 1971, **10**, 852.
[9] D. H. Haynes, A. Kowalsky, and B. C. Pressman, *J. Biol. Chem.*, 1969, **244**, 502; B. C. Pressman, and D. H. Haynes in 'The Molecular Basis of Membrane Function', ed. D. C. Tosteson, Prentice-Hall, Englewood Cliffs, N.J., 1969, p. 221.
[10] H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, **93**, 600.
[11] H.-K. Wipf, A. Olivier, and W. Simon, *Helv. Chim. Acta*, 1970, **53**, 1605.

shown to occur during the transport process, thus providing further evidence in favour of the carrier-relay mechanism. Eyal and Rechnitz[12] have come to the same conclusion with regard to the valinomycin-based potassium-selective electrode. General accounts of the role of macrotetrolides in biological systems[13] and of their use in ion-selective electrodes[14] have appeared. The decoupling of oxidative phosphorylation in mitochondria by valinomycin and other cation-specific antibiotics has been interpreted[15] on the basis of the Mitchell chemi-osmotic hypothesis, and the roles of the proton[16] and the pyrophosphate linkage[17] in active transport have been discussed.

Considerable evidence now supports the hypothesis that the inner membrane of a rat liver mitochondrion contains a specific 'permease' or carrier for Ca^{2+}, which makes possible the inward transport of this cation from regions of low concentration in response to electrochemical gradients generated by electron transport. The carrier has a very high affinity for Ca^{2+} and it also has the ability to transport Sr^{2+} and Mn^{2+} but not Mg^{2+}. Lehninger[18] has discussed mitochondrial transport of calcium; he has also shown[19] that La^{3+} is a specific inhibitor of the Ca^{2+} carrier and is therefore a potential probe for calcium transport. The dye Ruthenium Red also inhibits calcium transport and, since this dye reacts specifically with mucopolysaccharides, it has been concluded[20] that the latter (in the form of mucoproteins or muco- or glyco-lipids) are at the active centre of the sites of mediation of mitochondrial Ca^{2+} transport. Fluorescence enhancement of 8-anilino-1-naphthalene has also been used[21] as a probe for calcium transport.

3 Metal Complex Formation

Nuclear magnetic relaxation and e.s.r. studies of enzymes containing paramagnetic probes can yield important information regarding the configuration and dynamics at the active site. The use of Mn^{II} and other paramagnetic species, such as organic nitroxide spin labels, in phosphoryl transfer enzymes has been reviewed by Cohn and Reuben.[22] (In passing, it might be noted that Mn^{2+} can even be used[23] in this way to obtain

[12] E. Eyal and G. A. Rechnitz, *Analyt. Chem.*, 1971, **43**, 1090.
[13] V. Prelog, *Pure Appl. Chem.*, 1971, **25**, 197.
[14] W. Simon, *Pure Appl. Chem.*, 1971, **25**, 811.
[15] H.-K. Wipf and W. Simon, *Helv. Chim. Acta*, 1970, **53**, 1732.
[16] J. H. Young, G. A. Blondin, G. Vanderkooi, and D. E. Green, *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **67**, 550; J. H. Young, G. A. Blondin, and D. E. Green, *ibid.*, 1971, **68**, 1364.
[17] J. H. Wang, *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **67**, 59.
[18] A. L. Lehninger, *Biochem. J.*, 1970, **119**, 129.
[19] A. L. Lehninger and E. Carafoli, *Arch. Biochem. Biophys.*, 1971, **143**, 506.
[20] C. L. Moore, *Biochem. Biophys. Res. Comm.*, 1971, **42**, 298.
[21] J. M. Vanderkooi and A. Martonosi, *Fed. Proc.*, 1970, **29**, 936; *Arch. Biochem. Biophys.*, 1971, **144**, 99.
[22] M. Cohn and J. Reuben, *Accounts Chem. Res.*, 1971, **4**, 214.
[23] D. J. Birkett, R. A. Dwek, G. K. Radda, R. E. Richards, and A. G. Salmon, *European J. Biochem.*, 1971, **20**, 494.

structural information about an enzyme such as phosphorylase b, which has no bivalent metal-ion requirement!) The broadening of the ^{39}K n.m.r. line has been used[24] to demonstrate the binding of the metal to orthophosphate, ATP, and even pyruvate kinase. It has also been shown[25] that n.m.r. line-broadening can be used to determine the Cu^{II} binding sites in nucleotides and polynucleotides. Further details have been given[26] regarding the use of thallium(I) as a probe for potassium in the activation of rabbit muscle pyruvate kinase, and several papers have expanded on the use of the lanthanides to determine calcium-binding sites. Model systems and lysozyme have been used[27] to evaluate the technique, and it has been shown[19] that La^{3+} binds to and inhibits the calcium carrier in mitochondria but is not transported by it. The suggestion[28] that the lanthanides can be used as general probes for the electrostatic binding sites in proteins has been questioned by Reuben,[29] who has found that the binding sites of bovine serum albumin for Gd^{III} are different from those for Ca^{II}. However, the author suggests that no general conclusions along these lines should be drawn yet, since albumin is a protein of rather unusual binding properties and little selectivity. Although the tervalent lanthanide ions La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, and Dy^{3+} can partially displace $^{45}Ca^{2+}$ from troponin (a protein whose reaction with Ca^{2+} is thought to be intimately involved in the mechanochemical transduction mechanism in striated muscle), the affinity of these ions for the receptor site is lower[30] than that of Ca^{2+}, despite the similarity of size.

Evidence from fluorescence, absorption, and c.d. spectra suggests[31] that the conformations of various tetracycline antibiotics in complexes with Ca^{2+} are different from those in the magnesium complexes. The optical properties of the catalytically active cobalt(II) form of liver alcohol dehydrogenase, which normally requires zinc for activity, indicate[32] an unusual binding environment for the metal (*cf.* the implications of the absorption and c.d. spectra of the cobalt proteases, which have recently been discussed[33]).

^1H n.m.r., e.s.r., and Raman techniques have been used to investigate the binding of divalent metal ions to adenosine triphosphate and related compounds, and it appears that the debate over the possible involvement of

[24] R. G. Bryant, *Biochem. Biophys. Res. Comm.*, 1970, **40**, 1162.
[25] N. A. Berger and G. L. Eichhorn, *Biochemistry*, 1971, **10**, 1847, 1857.
[26] F. J. Kayne, *Arch. Biochem. Biophys.*, 1971, **143**, 232.
[27] R. A. Dwek, R. E. Richards, K. G. Morallee, E. Nieboer, R. J. P. Williams, and A. V. Xavier, *European J. Biochem.*, 1971, **21**, 204.
[28] *cf.* E. R. Birnbaum, J. E. Gomez, and D. W. Darnall, *J. Amer. Chem. Soc.*, 1970, **92**, 5287.
[29] J. Reuben, *Biochemistry*, 1971, **10**, 2834.
[30] F. Fuchs, *Biochim. Biophys. Acta*, 1971, **245**, 221.
[31] A. H. Caswell and J. D. Hutchison, *Biochem. Biophys. Res. Comm.*, 1971, **42**, 43; 1971, **43**, 625.
[32] D. E. Drum and B. L. Vallee, *Biochem. Biophys. Res. Comm.*, 1970, **41**, 33.
[33] B. L. Vallee and S. A. Latt in 'Structure-Function Relationships of Proteolytic Enzymes', ed. P. Desnuelle, H. Neurath, and M. Ottesen, Munksgaard, Copenhagen, 1970, p. 144.

a ring-nitrogen as well as the phosphate-oxygen atoms is as healthy as ever.[34] On the basis of ^{1}H n.m.r. line-broadening measurements, it has been concluded[35] that the binding of the metal ion to ring positions in the Mn^{2+}–ATP complex is negligible. However, when solutions of Mn^{2+}–ATP are titrated[36] with acid there is a change in the Raman spectrum at the pK_a values for the dissociation of secondary phosphate and adenine, indicating that the binding of Mn^{2+} involves both the adenine and the triphosphate moieties. (A similar result was found for Zn^{2+}, but with Mg^{2+} and Ca^{2+} it appeared that the binding only involved the phosphate groups.[36])

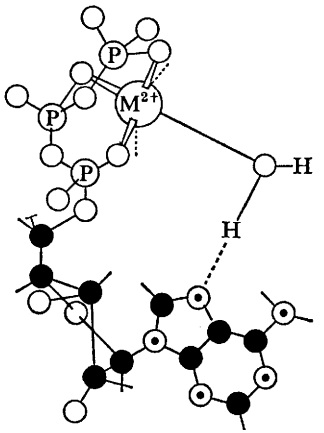


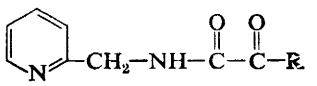
Figure 1 *A possible structure of a metal–ATP outer-sphere complex. The metal ion is octahedrally co-ordinated, and two water molecules not involved in hydrogen-bonding to the ring have been omitted*
(Reproduced by permission from *Biochemistry*, 1971, **10**, 843)

Possibly the reason for this apparent contradiction is that the Mn^{2+}–ATP complex contains a water molecule which is simultaneously co-ordinated to the metal ion and hydrogen-bonded to N-7 of the adenine ring[37] (see Figure 1; a similar structure has been proposed[37] for the ATP complexes of Co^{2+} and Ni^{2+}). Thus there is an interaction between the ring and the metal ion but it is not a direct one. Further Raman work with the calcium and magnesium complexes of ATP has indicated[38] that ATP–M–ATP interactions are more important with the larger metal than with the smaller. The relaxation spectra have been reported[39] for the reaction of nickel(II) with 9-methylpurine, adenine, and hypoxanthine. It appears that the rate

[34] R. M. Izatt, J. J. Christensen, and J. H. Rytting, *Chem. Rev.*, 1971, **71**, 439.
[35] M. J. Heller, A. J. Jones, and A. T. Tu, *Biochemistry*, 1970, **9**, 4981.
[36] L. Rimai and M. E. Heyde, *Biochem. Biophys. Res. Comm.*, 1970, **41**, 313.
[37] T. A. Glassman, C. Cooper, L. W. Harrison, and T. J. Swift, *Biochemistry*, 1971, **10**, 843.
[38] M. E. Heyde and L. Rimai, *Biochemistry*, 1971, **10**, 1121.
[39] R. L. Karpel, K. Kustin, and M. A. Wolff, *J. Phys. Chem.*, 1971, **75**, 799.

constant for the formation of the 1 : 1 complex with 9-methylpurine is normal for a neutral ligand (6.7×10^3 l mol^{-1} s^{-1} at 25 °C) while that for complexation with adenine is somewhat lower than normal (3×10^2 l mol^{-1} s^{-1}), possibly because of rate-limiting ring-closure. With hypoxanthine, a non-exponential trace indicated the existence of a multi-step process.

Three derivatives of 2-picoline (1; R = NH_2, NMe_2, or OH) form green complexes with Co^{II} which have unusual absorption spectra. A similar spectrum is observed with a sample of alkaline phosphatase in which the Zn^{2+} has been replaced by Co^{2+}, and it has been suggested [40] that the microenvironment of the metal is similar in all cases, *i.e.* that the complexes of (1) may be used as a model for the active centre of alkaline phosphatase.



(1)

N.m.r.,[41] e.s.r.,[42] and electronic [43] spectroscopy have been used to determine the structures of complexes between copper(II) and potentially terdentate amino-acids, and further stability data involving ternary complexes of Cu^{II}, Zn^{II}, Co^{II}, and Mn^{II} have been discussed [44] in terms of the possible role of such complexes in nature. The dissociative, water-loss mechanism appears to be operative in the reaction of Cu^{2+} with L-phenylalanine and L-3,4-dihydroxyphenylalanine (L-dopa), both as regards 1 : 1 and 2 : 1 complex formation.[45] A similar conclusion has been drawn [46] concerning the reaction of Cu^{II} with glycylglycine and glycylsarcosine, though in the former case an additional, slower relaxation is observed which has been ascribed to the protonation of the copper–glycylglycine complex. By way of contrast, the reaction of copper(II) with *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tet a) in the pH range 4—5.5 proceeds in two slow steps. The spectra and titration curves suggest [47] that in the first (blue) product the metal ion is bound to only two amino-groups of the ligand whereas in the final (mauve) product all four nitrogen atoms are bound. As with other cyclic aliphatic polyamines,[48] it is suggested that the

[40] P. Donatsch, A. Zuberbühler, and S. Fallab, *Experientia*, 1970, **26**, 1185.
[41] H. Sigel and D. B. McCormick, *J. Amer. Chem. Soc.*, 1971, **93**, 2041.
[42] G. Rotilio and L. Calabrese, *Arch. Biochem. Biophys.*, 1971, **143**, 218.
[43] E. W. Wilson, M. H. Kasperian, and R. B. Martin, *J. Amer. Chem. Soc.*, 1970, **92**, 5365.
[44] R. Griesser, B. Prijs, H. Sigel, W. Föry, L. D. Wright, and D. B. McCormick, *Biochemistry*, 1970, **9**, 3285.
[45] R. L. Karpel, K. Kustin, A. Kowalak, and R. F. Pasternack, *J. Amer. Chem. Soc.*, 1971, **93**, 1085.
[46] R. F. Pasternack, M. Angwin, and E. Gibbs, *J. Amer. Chem. Soc.*, 1970, **92**, 5878.
[47] Th. A. Kaden, *Helv. Chim. Acta*, 1971, **54**, 2307.
[48] *cf.* Th. A. Kaden, *Chimia* (*Switz.*), 1969, **23**, 193; *Helv. Chim. Acta*, 1970, **53**, 617; D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 2151.

low rate is associated with the less flexible nature of the ligand compared with the open-chain analogues, which precludes the facile stepwise desolvation of the metal ion.

Phosphoglucomutase requires a bivalent metal ion for enzymatic activity. The most efficient activator is Mg^{2+} though, like many other metals, manganese(II) may also be used. The results of proton relaxation rate measurements [49] with Mn^{2+} suggest that the number of water molecules directly bound to the metal in the binary complex is reduced on formation of a ternary complex involving a tightly bound substrate or inhibitor, such as glucose phosphate, xylose 1-phosphate, or glucuronic acid 1-phosphate. However, the binding of those substrates or inhibitors which form weak ternary complexes, such as the phosphates of fructose, galactose, and mannose and orthophosphate, does not involve water displacement from Mn^{2+}. This suggests that the displacement of water in the case of good substrates and inhibitors does not involve the participation of the phosphate groups of these compounds and that the metal ion in phosphoglucomutase serves primarily to orientate bound substrates at the catalytic site rather than being directly involved in bond-breaking or bond-making steps. E.s.r. spectra have been reported [50] for several ternary complexes involving manganese(II)–phosphoglucomutase. Magnetic resonance data have also been published [51] for the manganese(II)-activated enzyme β-methylaspartase. There appear to be two Mn^{2+} sites and the results are consistent with, but do not prove, a co-ordination structure in which the metal acts as a bridge between substrate and enzyme. Two tightly binding, catalytically active sites and additional weakly binding sites for Mn^{2+} on yeast apoaldolase have been detected [52] by similar methods, and it has been demonstrated that substrates form metal-bridged ternary complexes. Magnetic resonance methods have been used to study the interaction of Mn^{2+} with yeast enolase [53] and *E. coli* phosphoenolpyruvate synthetase.[54] It is interesting to note that the mean residence time of water in the hydration sphere of Mn^{II} bound to rabbit muscle pyruvate kinase is apparently shorter than that for the hexaquo ion,[55] mainly due to a lower activation enthalpy (6.6 ± 0.35 kcal mol^{-1} compared with 7.8 ± 0.3 kcal mol^{-1}). The involvement of a metal-bridged ternary complex in manganese(II)-activated pyruvate carboxylase is inferred,[56] and the nuclear relaxation times associated with the formation of an enzyme–Mn^{2+}–oxaloacetate complex have been discussed in terms of the dissociative water-loss mechanism (*cf.* Part II, Chapter 4). Magnesium, which can be replaced by Mn^{2+} and various other metals, is thought [57] not

[49] W. J. Ray and A. S. Mildvan, *Biochemistry*, 1970, **9**, 3886.
[50] G. H. Reed and W. J. Ray, *Biochemistry*, 1971, **10**, 3190.
[51] G. A. Fields and H. J. Bright, *Biochemistry*, 1970, **9**, 3801.
[52] A. S. Mildvan, R. D. Kobes, and W. J. Rutter, *Biochemistry*, 1971, **10**, 1191.
[53] J. C. W. Chien and E. W. Westhead, *Biochemistry*, 1971, **10**, 3198.
[54] K. M. Berman and M. Cohn, *J. Biol. Chem.*, 1970, **245**, 5309.
[55] J. Reuben and M. Cohn, *J. Biol. Chem.*, 1970, **245**, 6539.
[56] M. C. Scrutton and A. S. Mildvan, *Arch. Biochem. Biophys.*, 1970, **140**, 131.
[57] R. T. Lee, J. L. Denburg, and W. D. McElroy, *Arch. Biochem. Biophys.*, 1970, **141**, 38.

to act as a bridge between firefly luciferase and ATP. The role of calcium in the activation of skeletal muscle has recently been discussed.[58]

Bovine carbonic anhydrase is a comparatively well-characterized zinc-containing enzyme in which the metal is thought to play a very important role. Olander and Kaiser [59] have given a preliminary report on the use of 4-nitrothiophenol and 2,4-dinitrothiophenol as competitive inhibitors which bind specifically to the metal ion. The spectral change accompanying binding permits the direct measurement of the kinetics of this process, and at 25 °C and pH 9.3 the formation rate constants were found to be 1×10^7 and 2×10^7 l mol^{-1} s^{-1}, respectively. The kinetics have also been reported [60] for complex formation between aromatic sulphonamides and human carbonic anhydrases B and C. The stopped-flow technique, adapted for fluorescence detection, was used, and the apparent second-order rate constant for ligand binding was found to be highly dependent on pH whereas the dissociation rate constant showed no variance with pH. Interestingly, the kinetic parameters and their pH dependence are similar for the zinc and cobalt(II) forms of the enzyme. The correlation between the visible *d–d* absorption spectra of the Co^{II} enzyme and the kinetics suggests that the sulphonamide binds to the metal and that the pH dependence of the association process is governed by a proton-dependent equilibrium between different forms of the enzyme; reaction appears to occur between the neutral form of the sulphonamide and that form of the enzyme which predominates at high pH (presumably that in which a metal-bound water molecule has been deprotonated). The interaction of sulphonamides with zinc bovine carbonic anhydrase has been studied [61] by n.m.r. line-broadening, and it has been confirmed that the inhibitors bind specifically at the active site. The dramatic catalysis of CO_2 hydration and dehydration by bromine, first observed in 1940, has been found [62] to be caused by hypobromous acid. A mechanism for the carbonic anhydrase reaction has been proposed [62] in which the metal ion associated with the enzyme acts as a general acid catalyst for bicarbonate dehydration.

Alkaline phosphatase from *E. coli* is another zinc-containing enzyme in which the metal plays an important role (for a review, see ref. 63). Cottam and Ward [64] have recently used ^{35}Cl n.m.r. spectroscopy to investigate the zinc binding site and have found that the access of Cl^- to the four metal atoms in the metal-enzyme is severely restricted. They suggest that this result could be explained in two ways. In the first, the protein may provide all of the ligands necessary to completely chelate the zinc ion, thus excluding

[58] C. C. Ashley, *Endeavour*, 1971, **30**, 18.
[59] J. Olander and E. T. Kaiser, *Biochem. Biophys. Res. Comm.*, 1971, **45**, 1083.
[60] P. W. Taylor, R. W. King, and A. S. V. Burgen, *Biochemistry*, 1970, **9**, 3894.
[61] A. Lanir and G. Navon, *Biochemistry*, 1971, **10**, 1024.
[62] M. Caplow, *J. Amer. Chem. Soc.*, 1971, **93**, 230.
[63] T. W. Reid and I. B. Wilson, in 'The Enzymes', ed. P. D. Boyer, Academic Press, New York, 1971, vol. 4, 3rd edn., p. 373.
[64] G. L. Cottam and R. L. Ward, *Arch. Biochem. Biophys.*, 1970, **141**, 768.

any possible interaction of Cl^- with the bound metal. (If this situation pertains, the primary function of zinc in alkaline phosphatase is probably to hold the protein in the active conformation, rather than to form a bridged enzyme–metal–substrate complex, although the substrate could possibly displace one or more ligands from the enzyme–metal complex, to form such a bridged complex.) The second explanation is that the chloride exchange process is slow, either because the Zn—Cl bond is particularly strong or because rapid exchange is hindered by an occlusion of the complex within a protein matrix. As an interesting contrast, it has been found [65] that in the Cu^{2+}–enzyme complex (which still possesses enzymic activity, albeit severely curtailed) there are two 'tight' metal sites of type I and two 'loose' metal sites of type II. Binding of the competitive inhibitor orthophosphate ion alters both the visible and e.s.r. spectra, and direct evidence has been obtained for the participation of the copper atoms of type I in substrate binding. Further kinetic [66] and other [67] data have been published on this metal–enzyme complex, and a possible reason has been advanced [68] for the frequent discrepancy between the results from the Marseille group and other workers.

The carboxypeptidases are other zinc-containing enzymes which have received considerable attention recently.[69] A search for a covalently bound enzyme–substrate intermediate in ester hydrolyses that are catalysed by carboxypeptidase A has been unsuccessful;[70] it has, however, been possible [71] to rationalize the observation that the specific activity of this enzyme in the crystalline state is only about 0.3% of that in solution. Coupling of carboxypeptidase A crystals with diazotized arsanilic acid specifically labels tyrosine-248, which is a residue at the active site of the enzyme. The typical colour of an azophenol is yellow, whereas that of its zinc complex is red, so the fact that zinc arsanilazo-carboxypeptidase crystals are yellow suggests that the arsanilazotyrosyl group is not complexed to the metal ion. (This is consistent with the interpretation of *X*-ray data on native crystals of carboxypeptidase A, indicating that tyrosine-248 and the zinc atom are too far apart to form a bond.) However, the modified enzyme in solution is red, denoting the formation of a complex involving the zinc atom and arsanilazotyrosine-248. The most likely interpretation of the data is that the orientations of arsanilazotyrosine-248 in solution and in the crystal are different, and a similar change in orientation of the unlabelled tyrosine-248 in the native enzyme would explain the difference in

[65] C. Lazdunski, D. Chappelet, C. Petitclerc, F. Leterrier, P. Douzou, and M. Lazdunski, *European J. Biochem.*, 1970, **17**, 239.
[66] S. E. Halford, *Biochem. J.*, 1971, **125**, 319.
[67] C. N. A. Trotman and C. Greenwood, *Biochem. J.*, 1971, **124**, 25.
[68] M. Lazdunski, C. Petitclerc, D. Chappelet, and C. Lazdunski, *European J. Biochem.*, 1971, **20**, 124.
[69] For reviews see J. A. Hartsuck and W. N. Lipscomb in 'The Enzymes', ed. P. D. Boyer, Academic Press, New York, 1971, vol. 3, 3rd edn., p. 1; J. E. Folk, *ibid.*, p. 57.
[70] G. Tomalin, B. L. Kaiser, and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1970, **9** , 6046.
[71] J. T. Johansen and B. L. Vallee, *Proc. Nat. Acad. Sci. U.S.A.*, 1971, **68**, 2532.

activity between crystal and solution. If this were true, the implications regarding the drawing of mechanistic conclusions from structural data alone would evidently be serious.

The Job method has been used [72] to show that horse-liver alcohol dehydrogenase contains zinc atoms bound in two different environments, and it appears [73] that Zn^{2+} plays a functional role in the interaction of DNA with DNA polymerases from *E. coli* and sea urchins. The nature of the two metal-binding sites in transferrin has been investigated,[74] using tervalent lanthanide ions as fluorescent probes; the two sites are different and the distance between them is 43 Å or greater. The kinetics of the reaction between Fe^{III}–nta and transferrin have been measured [75] by the stopped-flow method and a reaction sequence has been proposed. The same technique, with ^{35}Cl n.m.r. detection, has been used [76] to study the extraction of the metal from the Hg^{II}–bovine serum albumin complex by various ligands.

4 Reactions involving Metals in Porphyrins and Related Ring Systems

It is probably true to say that haemoglobin has so far enjoyed pride of place among the objects of investigation in molecular biology. These studies have culminated in the complete description of its atomic structure in various functional states, but more than just a knowledge of the anatomy of this protein is required before quantitative predictions can be made about its function. Antonini and Brunori [77] have critically summarized the significant contributions in the haemoglobin field over the past few years and have given a comprehensive picture of the present state of knowledge – with the emphasis on the controversial aspects. Buse [78] has also outlined the present position, and Perutz [79] has concentrated on the stereochemistry of co-operative effects in haemoglobin. (The oxygenation of the molecule is accompanied by structural changes in the subunits, triggered by shifts of the iron atoms relative to the porphyrin rings.) Schuster and Ilgenfritz [80] have summarized their temperature-jump and electric-field-jump work on the binding of oxygen.

Although it has been known for some years that mammalian haemoglobins contain two types of chain, kinetic and equilibrium measurements

[72] D. E. Drum and B. L. Vallee, *Biochemistry*, 1970, **9**, 4078.
[73] J. P. Slater, A. S. Mildvan, and L. A. Loeb, *Biochem. Biophys. Res. Comm.*, 1971, **44**, 37.
[74] C. K. Luk, *Biochemistry*, 1971, **10**, 2838.
[75] G. W. Bates and J. Wernicke, *J. Biol. Chem.*, 1971, **246**, 3679.
[76] J. L. Sudmeier and J. J. Pesek, *Inorg. Chem.*, 1971, **10**, 860.
[77] E. Antonini and M. Brunori, *Ann. Rev. Biochem.*, 1970, **39**, 977.
[78] G. Buse, *Angew. Chem. Internat. Edn.*, 1971, **10**, 663.
[79] M. F. Perutz, *Nature*, 1970, **228**, 726.
[80] T. M. Schuster and G. Ilgenfritz in 'Symmetry and Function of Biological Systems at the Macromolecular Level', ed. A. Engström and B. Strandberg, Wiley–Interscience, New York, 1969, p. 181.

have usually been treated on the assumption that the chains are functionally equivalent. Work with isolated chains has, however, shown [81] that α- and β-chains differ in their reactivities towards O_2 and CO, and it has now been found [82] that a similar difference also exists with respect to isocyanides; the kinetics of the binding of ethyl isocyanide to human deoxyhaemoglobin can be treated satisfactorily [83] in terms of the $(\alpha\beta)$ dimer as the functional unit. The allosteric model of Monod has been used [84] to analyse the kinetics of ligand binding to mammalian haemoglobins. The effects of phosphates on the kinetics of CO binding to the haemoglobin valency hybrids $(\alpha^{III}CN\beta^{II})_2$ and $(\alpha^{II}\beta^{III}CN)_2$ have also been reported,[85] and kinetic analyses of the binding of oxygen and carbon monoxide to earthworm [86] and lamprey [87] haemoglobins have been published.

The co-ordination chemistry of metalloporphyrins has been reviewed.[88] The kinetics of incorporation of metal ions into several porphyrins [89] and of substitution reactions at the metal ion in zinc [90] and iron [91] porphyrins have been reported.

In view of the fundamental role of electron-transfer processes in biological systems, it is perhaps surprising that so few measurements of electron-exchange reactions between redox proteins have been reported to date. Antonini and co-workers [92] have investigated the reactions between horse-heart cytochrome *c* and two redox proteins from *Pseudomonas fluorescens*, azurin and cytochrome c_{551}, and have found rate constants of 1.1×10^3 and 8×10^4 l mol^{-1} s^{-1} and activation energies of 14 and 12.3 kcal mol^{-1}, respectively. Some observations on the oxidation of horse-heart ferrocytochrome *c* by mammalian cytochrome oxidase are presented [92] which suggest that it has a complicated mechanism, markedly influenced by ionic strength and cytochrome *c* concentration. Pulse radiolysis has been used [93] to follow the reaction of hydrated electrons with ferricytochrome *c*. The rate constants are pH-dependent, ranging from about 2×10^{10} l mol^{-1} s^{-1} at

[81] *cf.* R. D. Gray and Q. H. Gibson, *J. Biol. Chem.*, 1971, **246**, 5176.
[82] B. Talbot, M. Brunori, E. Antonini, and J. Wyman, *J. Mol. Biol.*, 1971, **58**, 261; J. S. Olson and Q. H. Gibson, *J. Biol. Chem.*, 1971, **246**, 5241.
[83] E. Antonini and M. Brunori, *J. Biol. Chem.*, 1970, **245**, 5412.
[84] J. J. Hopfield, R. G. Shulman, and S. Ogawa, *J. Mol. Biol.*, 1971, **61**, 425.
[85] R. Cassoly, Q. H. Gibson, S. Ogawa, and R. G. Shulman, *Biochem. Biophys. Res. Comm.*, 1971, **44**, 1015.
[86] K. J. Boelts and L. J. Parkhurst, *Biochem. Biophys. Res. Comm.*, 1971, **43**, 637.
[87] M. E. Andersen and Q. H. Gibson, *J. Biol. Chem.*, 1971, **246**, 4790.
[88] P. Hambright, *Co-ordination Chem. Rev.*, 1971, **6**, 247.
[89] D. J. Kingham and D. A. Brisbin, *Inorg. Chem.*, 1970, **9**, 2034; E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Amer. Chem. Soc.*, 1971, **93**, 3162; B. Shah, B. Shears, and P. Hambright, *Inorg. Chem.*, 1971, **10**, 1828.
[90] B. Shah and P. Hambright, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3420; B. Shears, B. Shah, and P. Hambright, *J. Amer. Chem. Soc.*, 1971, **93**, 776.
[91] H. A. Degani and D. Fiat, *J. Amer. Chem. Soc.*, 1971, **93**, 4281.
[92] C. Greenwood, A. Finazzi Agrò, P. Guerrieri, L. Avigliano, B. Mondovì, and E. Antonini, *European J. Biochem.*, 1971, **23**, 321.
[93] E. J. Land and A. J. Swallow, *Arch. Biochem. Biophys.*, 1971, **145**, 365; I. Pecht and M. Feraggi, *F.E.B.S. Letters*, 1971; **13**, 221; J. Wilting, H. Nauta, and R. Braams, *ibid.*, 1971, **16**, 147.

pH 6 to about 1×10^{10} l mol^{-1} s^{-1} at pH 13; they are similar for the reaction with ferrocytochrome *c* at pH 7. With the Fe^{III} compound at pH 7, reduction is followed within 150 ns by the appearance of the characteristic absorption bands of the Fe^{II} compound, while in alkaline solution the final ferrocytochrome *c* spectrum only appears with a half-life of about a tenth of a second at room temperature. The activation energy is 20 kcal mol^{-1} and the rapid Franck–Condon addition of an electron may be assumed to be followed by immediate transfer to the Fe atom, after which there is a relatively slow conformational change (a movement of the co-ordinating groups from positions corresponding to the equilibrium Fe^{2+}–L distances to those corresponding to the equilibrium Fe^{3+}–L distances, perhaps). An n.m.r. double-resonance study [94] of a mixture of ferricytochrome *c* and azidoferricytochrome *c* has permitted the measurement of the rate constant for the addition of N_3^- to the iron(III) atom (20 l mol^{-1} s^{-1}; dissociation rate constant = 4 s^{-1}). N.m.r. has also been used [95] to show that the ability of various modified mammalian cytochromes *c* to restore the respiration of cytochrome-*c*-depleted rat-liver mitochondria can be correlated with the presence of methionine in one of the axial positions of the haem iron in both its oxidized and reduced form.

Cytochrome *c* oxidase and the 'blue' copper-containing oxidases (ascorbic acid oxidase, laccase, and ceruloplasmin) are the only enzymes that catalyse reactions in which both atoms of molecular oxygen are reduced to water. An important mechanistic problem with these enzymes is therefore the way in which one-electron oxidation of the substrate is coupled to a four-electron transfer to oxygen. It is unlikely [96] that this reduction can occur by way of four consecutive one-electron steps because such a reaction sequence would be extremely slow (on the basis of the relatively large, positive free-energy change for the addition of the first electron to oxygen, coupled with the high standard redox potentials for the enzymes). Recent evidence [96] supports an alternative, multi-electron-transfer mechanism. Kinetic and equilibrium measurements have been reported [97] on the interaction of cyanide with reduced and oxidized cytochrome oxidase. The former involves HCN rather than CN^-, and in this respect the enzyme is similar to reduced horse-radish peroxidase but different from the Fe^{III} derivatives of respiratory haem proteins.

The kinetics of the oxidation of ferrocyanide [98] by compounds I and II from horse-radish peroxidase (HRP-I and HRP-II) and of iodide [99] by HRP-II have been reported. In the latter case the rate constant decreases linearly from 2.3×10^5 to 0.1 l mol^{-1} s^{-1} with increasing pH over the

[94] R. K. Gupta and A. G. Redfield, *Biochem. Biophys. Res. Comm.*, 1970, **41**, 273.
[95] K. Wüthrich, I. Aviram, and A. Schejter, *Biochim. Biophys. Acta*, 1971, **253**, 98.
[96] E. Antonini, M. Brunori, C. Greenwood, and B. G. Malmström, *Nature*, 1970, **228**, 936.
[97] E. Antonini, M. Brunori, C. Greenwood, B. G. Malmström, and G. C. Rotilio, *European J. Biochem.*, 1971, **23**, 396.
[98] B. B. Hasinoff and H. B. Dunford, *Biochemistry*, 1970, **9**, 4930.
[99] R. Roman, H. B. Dunford, and M. Evett, *Canad. J. Chem.*, 1971, **49**, 3059.

range 2.7—9.0 (at 25 °C and ionic strength 0.11 mol l^{-1}) and it is concluded that HRP-II exists in two forms, the protonated form (with pK_a outside the pH range studied) being at least 10^7 times more reactive towards I^- than the unprotonated form. Spectroscopic techniques have been used [100] to examine the intermediates in the reaction of peroxidase with H_2O_2, and the rate constant for the binding of CN^- to ferroperoxidase at pH 9.1 has been quoted [101] as 29 l mol^{-1} s^{-1}. The properties of cytochrome *c* peroxidase have been reviewed.[102]

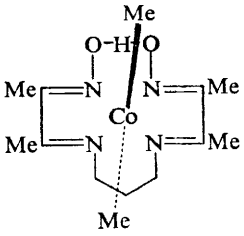
In a recent article, Stadtman [103] has pointed out the vast gaps in our knowledge of the mode of action of the vitamins B_{12}, but two recent developments point the way to a greater understanding of the structure and bonding of this interesting group of compounds. High-resolution ^1H n.m.r. spectroscopy has been used [104] to investigate the conformation of several cobalamins and cobinamides, and the co-ordination of a piperidine *N*-oxyl stable free-radical to the cobalt atoms of methyl- and 5′-deoxyadenosylcobinamide has led [105] to the preparation in good yield of spin-labelled derivatives which retain their catalytic activity. Thusius [106] has reported the rate constants for the formation and dissociation of a number of cobalamins CBM–L. The formation rate constants (for L = SCN^-, SO_3^{2-}, $S_2O_3^{2-}$, NCO^-, N_3^-, I^-, and Br^-) are rather similar (170—2300 l mol^{-1} s^{-1}) whereas the dissociation rate constants range between $< 10^{-5}$ and 590 s^{-1} at 25 °C. It will be noticed that the metal in these compounds is remarkably labile for Co^{III}, and it is found that the large rate differences between aquocobalamin and the kinetically inert model cobalamin complexes involving bis(dimethylglyoximato)cobalt(III) (the 'cobaloximes') arise largely from differences in the activation entropies (although the activation enthalpies of both series of compounds are some 10 kcal mol^{-1} lower than values normally found for replacement of water in Co^{III} complexes). The reason for these differences is not known but they evidently have serious mechanistic implications.

The order of ligands for the kinetic *trans*-effect in Co^{III} corrinoids parallels [107] that for the thermodynamic *trans*-effect, and it has been demonstrated [108] that, in the binding of corrinoids to proteins and polypeptides, the formation of hydrogen-bonds is far more important than co-ordination by the metal atom. Methyl vitamin B_{12} is capable of transferring

[100] S. Bagger and R. J. P. Williams, *Acta Chem. Scand.*, 1971, **25**, 976.
[101] C. Phelps, E. Antonini, and M. Brunori, *Biochem. J.*, 1971, **122**, 79.
[102] T. Yonetani in 'Advances in Enzymology', Wiley–Interscience, New York, 1970, vol. 33, p. 309.
[103] T. C. Stadtman, *Science*, 1971, **171**, 859.
[104] J. D. Brodie and M. Poe, *Biochemistry*, 1971, **10**, 914.
[105] P. Y. Law, D. G. Brown, E. L. Lien, B. M. Babior, and J. M. Wood, *Biochemistry*, 1971, **10**, 3428.
[106] D. Thusius, *J. Amer. Chem. Soc.*, 1971, **93**, 2629.
[107] G. C. Hayward, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1971, 196.
[108] H. A. O. Hill, J. M. Pratt, R. G. Thorp, B. Ward, and R. J. P. Williams, *Biochem. J.*, 1970, **120**, 263.

methyl groups to Hg^{II}, Tl^{III}, Pt^{II}, and Au^{I}, and it appears [109] that two different reaction paths are involved: with Hg^{II} and Tl^{III} the mechanism involves an acid–base step, while with the other metals the reaction probably involves a redox process since it requires both Pt^{II} and Pt^{IV} or Au^{I} and Au^{III}. The cycle of transmethylation for the vitamin-B_{12}-dependent methionine synthetase has also been discussed,[110] as has [111] the catalysis of alkyl halide reduction by vitamin B_{12a}. The feasibility of a mechanism of coenzyme B_{12} action in dioldehydrase involving a Co^{I} corrinoid has been further explored,[112] and a mechanism has been proposed [113] for the reaction of vitamin B_{12s} with nitrobenzene and its reduction products. The highly nucleophilic vitamin B_{12s} has been shown [114] to react even with unactivated olefins in polar acidic media, a result of significance with respect to the possible mechanism of catalytic action of corrinoid coenzymes and also of considerable use for the synthesis of new organocorrins.

Several series of model compounds for the vitamin B_{12} group have been prepared,[115] and (2) has been found [116] to behave as a methylating reagent



(2)

towards electrophilic metal atoms and protons. Exploitation of the latter result permits the preparation of several methyl-cobalt derivatives from the corresponding Co^{III} complexes by a reaction which involves the transfer of a methyl carbanion and is related to the catalytic behaviour of vitamin B_{12a} in transmethylases. A previous report on one of these models has been corrected,[117] and i.r. frequencies have been used [118] to measure the effect of axial substitution on the Co—C and Co—N bonds in cobaloximes.

[109] G. Agnes, S. Bendle, H. A. O. Hill, F. R. Williams, and R. J. P. Willlams, *Chem. Comm.*, 1971, 850.
[110] H. Rüdiger, *European J. Biochem.*, 1971, **21**, 264.
[111] H. A. O. Hill, J. M. Pratt, M. O'Riordan, F. R. Williams, and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1971, 1859.
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[113] A. E. Brearley, H. Gott, H. A. O. Hill, M. O'Riordan, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1971, 612.
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[117] G. Costa, G. Mestroni, G. Pellizer, G. Gauzher, and T. Licari, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 57.
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5 Redox Reactions involving Metals in other Biological and Model Systems

Plant ferredoxins are among the simpler iron–sulphur proteins, since their molecules contain only two Fe atoms and on reduction they take on only one electron. Their chemistry and function in photosynthesis, nitrogen fixation, and fermentative metabolism has recently been reviewed,[119] and the results of several magnetic and spectroscopic studies have appeared [120] which bear on the role of the metal in these non-haem macromolecules.

Nitrogenase, as isolated from *Azotobacter vinelandii, Clostridium pasteurianum*, and other bacteria, consists of two proteins, one containing Mo and Fe (in the ratio *ca.* 1 : 15) and the other containing only Fe. When combined, these two proteins are capable of catalysing the reduction of N_2 and a variety of other substrates (*e.g.* N_3^-, CN^-, C_2H_2, N_2O, and MeNC). Two recent preliminary reports [121] record the preparation of vanadium-containing cell-free extracts from *Azotobacter* grown in media containing V in place of Mo. These extracts possess nitrogenase activity (albeit at a reduced level compared with that from the Mo-containing bacteria) and the experiment provides the first direct evidence that Mo is directly involved in nitrogenase catalysis. Schrauzer and co-workers [122] have recently described chemical models for nitrogenase, and their reports have stimulated a discussion [123] on the significance of model studies in this case.

Further magnetic and spectroscopic evidence suggests [124] that the two iron atoms at the active site in hemerythrin are coupled, and it has been found [125] that, at neutral pH, ClO_4^- has a profound effect on the oxygen-binding properties of this protein. Preliminary evidence [126] on the reaction

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[124] T. H. Moss, C. Moleski, and J. L. York, *Biochemistry*, 1971, **10**, 840; K. Garbett, C. E. Johnson, I. M. Klotz, M. Y. Okamura, and R. J. P. Williams, *Arch. Biochem. Biophys.*, 1971, **142**, 574.

[125] H. A. de Phillips, *Arch. Biochem. Biophys.*, 1971, **144**, 122.

[126] M. Brunori, G. C. Rotilio, G. Rotilio, and E. Antonini, *F.E.B.S. Letters*, 1971, **16**, 89.

between deoxyhemerythrin and ferricyanide suggests that the oxidation of the iron atoms in a site is a highly co-operative process. Hemocyanins constitute a class of copper-containing respiratory proteins which are in many respects similar to the hemerythrins. The kinetics of the reaction between oxygen and the hemocyanin (Hc) from *Octopus vulgaris* have been studied [127] by the temperature-jump method, and the relaxation spectrum is consistent with a two-step mechanism. The shorter relaxation time reflects a bimolecular step and the longer time a coupled conformational change of the oxygen–protein complex:

$$O_2 + Hc \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} HcO_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} HcO_2^*$$

The rate constants at pH 7 in the presence of 0.2 mol l^{-1} potassium phosphate and at 24—25 °C are: $k_{12} = 1.2 \times 10^7$ l mol^{-1} s^{-1}, $k_{21} = 4 \times 10^3$ s^{-1}, $k_{23} = 1.5 \times 10^3$ s^{-1}, $k_{32} = 1.8 \times 10^3$ s^{-1}. Even in the absence of co-operative phenomena, O_2 binding by hemocyanin involves a minimum of two elementary steps, and this finding might be correlated with the presence of two metal atoms in each site. Raman spectroscopy has been used [128] to investigate the nature of the co-ordination of iron in clostridial rubredoxin, and e.s.r. and Mössbauer spectroscopy have been used to study the non-haem iron proteins cysteamine oxygenase [129] and adrenodoxin.[130]

From steady-state studies on the inhibition of xanthine oxidase by methanol at high and low xanthine concentrations, it has been possible to show [131] that Mo does not participate in the direct binding of the first substrate molecule to form the enzyme–substrate complex ES. However, inhibition by excess substrate and formation of a complex ESS are due to the disruption of the electron-transfer chain at the stage where the molybdenum atom takes part in the transfer process.

Studies on the catalatic activity of additional Cu^{II} chelates [132] confirm the previous conclusions that the complex must possess a suitable redox potential and two adjacent free sites to promote the efficient decomposition of H_2O_2. Malmström [7, 133] has discussed the asymmetric nature of oxidases which contain several copper atoms per molecule, including laccase and ceruloplasmin. The rate constant for the reaction of the hydrated electron

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[131] A. I. Kozachenko, L. S. Vartanyan, and É. M. Gonikberg, *Russ. J. Biochem.*, 1971, **36**, 21.
[132] V. S. Sharma and J. Schubert, *Inorg. Chem.*, 1971, **10**, 251.
[133] B. G. Malmström in 'Symmetry and Function of Biological Systems at the Macromolecular Level', ed. A. Engström and B. Strandberg, Wiley–Interscience, New York, 1969, p. 153.

with the oxidized form of fungal laccase at 20 °C and pH 6 is 1.5×10^8 l $mol^{-1} s^{-1}$; it indicates [134] that the Type 1 (blue) Cu^{II} is the first specific electron-accepting site in the enzyme to be reduced. The rates of electron transfer from reduced azurin and cytochrome *c* to laccase have also been measured; the electron-transfer processes are discussed [135] in terms of the three types of electron-acceptor to be found in laccase. Ceruloplasmin is a copper-containing protein, occurring in plasma, which has oxidase activity towards polyphenols, aromatic polyamines, and Fe^{II}. It contains eight copper atoms per molecule, and a recent stopped-flow study has suggested [136] that the oxidase mechanism involves a concerted electron transfer between different types of copper. A preliminary kinetic report has also appeared [137] on the reaction of azide with ceruloplasmin.

[134] I. Pecht and M. Faraggi, *Nature New Biology*, 1971, **233**, 116.
[135] B. G. Malmström, A. F. Agrò, C. Greenwood, E. Antonini, M. Brunori, and B. Mandovì, *Arch. Biochem. Biophys.*, 1971, **145**, 349.
[136] R. J. Carrico, B. G. Malmström, and T. Vänngård, *European J. Biochem.*, 1971, **22**, 127.
[137] T. Manabe, N. Manabe, K. Hiromi, and H. Hatano, *F.E.B.S. Letters*, 1971, **16**, 201.

Part IV

ORGANOMETALLIC COMPOUNDS

By
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1
Substitution

BY R. D. W. KEMMITT AND J. BURGESS

An extensive and general review of carbonyls of transition metals contains some discussion of mechanisms of their substitution reactions.[1]

1 Exchange Reactions

Exchange of labelled carbon monoxide with $Co(CO)_2(NO)(PPh_3)$ follows the rate law:

$$\text{rate} = \{k_1 + k_2[CO]\}[Co(CO)_2(NO)(PPh_3)]$$

The value of k_1 is almost the same for poor solvents such as toluene or carbon tetrachloride, but is greater and solvent-dependent for good solvents such as acetonitrile or dimethyl sulphoxide. Values of k_2 are almost constant over the whole range of solvents, but this seems to be a result of compensating changes in activation enthalpies and activation entropies for this k_2 path.[2] The ^{13}C-labelled compound *cis*-$[MnMe(CO)_4(^{13}CO)]$ has been prepared as a useful starting material for investigating the stereochemistry of reactions such as carbon monoxide exchange.[3] The exchange of ethylene with $IrCl(C_2H_4)(PPh_3)_2$ is too fast to monitor by n.m.r. techniques.[4]

Rates of trimethylphosphine exchange with the gold(I) complex $AuMe(PMe_3)$, determined from n.m.r. spectra in benzene solution, depend on the concentration of added trimethylphosphine, which suggests an associative mechanism. The activation energy for this exchange[5] is 7 kcal mol^{-1}. Trimethylphosphine exchange with the gold(III) compound $AuMe_3(PMe_3)$ is slow on the n.m.r. time-scale, but probably does take place slowly, with a half-life of several hours, since replacement of PMe_3 by PEt_3 is known to occur in about a day.[6] Exchange of pyridine with $AuMe_2Cl(py)$ or with $AuMe_2(SCN)(py)$, and of triphenylarsine with $AuMe_2(SCN)(AsPh_3)$, is fast on the n.m.r. time-scale, but exchange of the respective Group V bases with $AuMe_2Cl(PPh_3)$, $AuMe_2Cl(AsPh_3)$,

[1] E. W. Abel and F. G. A. Stone, *Quart. Rev.*, 1970, **24**, 498.
[2] G. Reichenbach, *J. Organometallic Chem.*, 1971, **31**, 103.
[3] P. W. Robinson, M. A. Cohen, and A. Wojcicki, *Inorg. Chem.*, 1971, **10**, 2080.
[4] H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *Chem. Comm.*, 1970, 1694.
[5] H. Schmidbaur, A. Shiotani, and H.-F. Klein, *Chem. Ber.*, 1971, **104**, 2831.
[6] A. Shiotani, H.-F. Klein, and H. Schmidbaur, *J. Amer. Chem. Soc.*, 1971, **93**, 1555.

$AuMe_2Cl(SbPh_3)$, or $AuMe_2(SCN)(PPh_3)$ is slow.[7] Exchange of phenyldimethylphosphine with $RhCl(CO)(PMe_2Ph)_2$ was reported to be fast on the n.m.r. time-scale,[8] but a reinterpretation of these n.m.r. observations suggests that this is not the case. Indeed, it seems that the rate constant for a bimolecular exchange process is about 2.5×10^2 l mol^{-1} s^{-1}, which is more plausible for a substitution at this type of d^8 square-planar complex.[9] The exchange of free PF_3 with planar rhodium(I)–PF_3 complexes is, however, reported to be fast by n.m.r. standards.[10]

Variable-temperature n.m.r. studies of 4-t-butylpyridine (4-Bu^t-py) exchange with Ru(CO)(isopropyltetraphenylporphine)(4-Bu^t-py) in 1,1,2,2-tetrachloroethane solution indicate an activation enthalpy of 20.6 kcal mol^{-1} and an activation entropy of 5.6 cal deg^{-1} mol^{-1}, from which the estimated rate constant[11] at 25.0 °C is 0.09 s^{-1}.

2 Substitution in Carbonyls: Carbon Monoxide Replacement

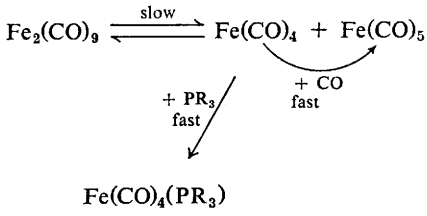
Simple Carbonyls.—*Mononuclear.* Interest here centres on the photochemical generation of reaction intermediates, often at low temperatures in inert matrices. Although such conditions are extreme, they provide much useful information, on normally very transient species, which can be applied to mechanisms of reactions of these compounds in solution at normal temperatures. Species $M(CO)_5$, where M = Cr, Mo, or W, are obtained in nearly quantitative yield in pentane–methylcyclohexane glasses at about − 180 °C, upon irradiation of $M(CO)_6$ at wavenumbers of less than 35 000 cm^{-1}. The nature of these $M(CO)_5$ compounds, and of their recombination with carbon monoxide to return to $M(CO)_6$, has been discussed.[12] Irradiation[13] of $[V(CO)_6]^-$, as its sodium diglyme salt in 2-methyltetrahydrofuran (MeTHF) glass, did not produce $[V(CO)_5]^-$ but rather $[V(CO)_5(MeTHF)]^-$. In general, irradiation of mixtures of $[V(CO)_6]^-$ in the presence of a potential ligand L is a good preparative route to $[V(CO)_5L]^-$, for direct thermal substitution at $[V(CO)_6]^-$ is generally very slow.[14]

Flash photolysis of $Cr(CO)_6$ produces two transient intermediates, which are thought to be isomeric pentacarbonyls.[15] Modes of dissociation and other subsequent reactions of $M(CO)_5$, generated photolytically from $M(CO)_6$, where M = Cr, Mo, or W, have been investigated.[16]

[7] G. C. Stocco and R. S. Tobias, *J. Amer. Chem. Soc.*, 1971, **93**, 5057.
[8] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597.
[9] J. P. Fackler, *Inorg. Chem.*, 1970, **9**, 2625.
[10] M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, 1971, **10**, 2387.
[11] S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometallic Chem.*, 1971, **32**, C52.
[12] M. J. Boylan, P. S. Braterman, and A. Fullarton, *J. Organometallic Chem.*, 1971, **31**, C29.
[13] P. S. Braterman and A. Fullarton, *J. Organometallic Chem.*, 1971, **31**, C27.
[14] A. Davison and J. E. Ellis, *J. Organometallic Chem.*, 1971, **31**, 239.
[15] J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1971, **29**, 269.
[16] M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939.

The photochemical reaction of Group VI metal hexacarbonyls with mono-enes was studied several years ago, but only recently has the reaction of one of the hexacarbonyls, $W(CO)_6$ in fact, with conjugated dienes been investigated. The $W(CO)_6$ proves to be an effective catalyst for *cis* ⇌ *trans* isomerization of such dienes; compounds of the type $W(CO)_5$(diene), which must act as intermediates in such isomerizations, have been isolated and their reactions studied.[17] Under normal conditions iron pentacarbonyl reacts with acetylene to produce a complicated mixture of products, but under irradiation in an argon matrix at − 256 °C the product is but-1-en-3-yne, complexed to the iron through the carbon–carbon triple bond only. This iron–alkyne–carbonyl compound is presumably an intermediate in the reaction under normal thermal conditions. In an argon matrix at − 256 °C, iron pentacarbonyl reacts with ethylene to give $Fe(CO)_4(C_2H_4)$.[18]

Di- and Tri-nuclear. References which deal with metal–metal bond cleavage in dinuclear carbonyls, particularly $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, will be found in the metal–metal bond cleavage section. Only references to reactions in which metal–carbonyl bond cleavage is the principal step will be mentioned here. $Fe_2(CO)_9$ reacts with phosphines by two parallel paths, one of which involves reversible breaking of the iron–bridging carbonyl bond as the first and rate-determining step,[19] as shown in Scheme 1.



Scheme 1

$Co_2(CO)_8$ decomposes in toluene to produce $Co_4(CO)_{12}$ and carbon monoxide. The reaction is reversible; the rate-determining step in the $Co_2(CO)_8$ to $Co_4(CO)_{12}$ direction is said[20] to be dimerization of $Co_2(CO)_6$ fragments. $Ru_3(CO)_{12}$ reacts with azulene to form Ru_4(azulene)$(CO)_9$, in which the azulene is bonded to one face of the tetrahedral Ru_4 cluster. The mechanism is unknown, except that Ru_3(azulene)$(CO)_7$ is though to be an intermediate.[21]

[17] M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1970, **92**, 6068.
[18] M. J. Newlands and J. F. Ogilvie, *Canad. J. Chem.*, 1971, **49**, 343.
[19] P. S. Braterman and W. J. Wallace, *J. Organometallic Chem.*, 1971, **30**, C17.
[20] F. Ungváry and L. Markó, *Inorg. Chim. Acta*, 1970, **4**, 324.
[21] M. R. Churchill, F. R. Scholer, and J. Wormald, *J. Organometallic Chem.*, 1971, **28**, C21.

The products of the photochemical reactions of $Re_2(CO)_{10}$ with $PMePh_2$ are numerous and varied, including $Re_2(CO)_9(PMePh_2)$, $Re_2(CO)_7(PMePh_2)_3$, $Re(CO)_4(PMePh_2)_2$, and the cluster compound $Re_4(CO)_{10}(PMePh_2)_6$. There is thus carbon monoxide replacement and metal–metal bond breaking included in the reaction scheme. Although these reactions appear, on the basis of most of the experimental evidence, to be simply dissociative in mechanism, a comparison of these substitutions with analogous reactions with triphenylphosphine suggests that the basicity of the phosphine has at least some effect.[22]

Mixed Ligand Carbonyls.—*General.* Solvent and structural effects on reactivities of metal carbonyl halides towards carbon monoxide replacement have been probed for manganese, iron, and ruthenium compounds. The compounds were $MnX(CO)_5$, where X = Br or I, $RuX(CO)_2(h^5\text{-}C_5H_5)$, where X = Cl or Br, and $FeX(CO)_2(h^5\text{-}C_5H_5)$, where X = Br or I. The displacing nucleophiles were triphenylphosphine or triphenyl phosphite; the solvents were n-octane, xylene, di-n-butyl ether, or nitrobenzene. Kinetic parameters for some of these reactions, with some earlier values for related systems for comparison, are listed in Table 1. The main conclusion

Table 1 *Kinetic parameters for carbon monoxide displacement from* $MnX(CO)_5$ *and from* $M(h^5\text{-}C_5H_5)X(CO)_2$, M = Fe *or* Ru; *data from ref.* 23

Compound	*Solvent*	$10^5\ k/s^{-1}$ (temp/°C)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
$MnBr(CO)_5$	xylene	49 (40)	29.3	17.9
	n-octane	99 (40)	26.4	10.1
	di-n-butyl ether	87 (40)	25.3	7.5
	chloroform	33 (40)	29.8	18.9
	nitrobenzene	10.7 (40)	30.9	22.1
$MnI(CO)_5$	xylene	1.1 (40)	29.8	14.3
$Fe(h^5\text{-}C_5H_5)Br(CO)_2$	xylene	10.8 (70)	34.6	21.5
	n-octane	27.6 (70)	31.2	14.1
	di-n-butyl ether	23.4 (70)	26.4	−0.5
	nitrobenzene	4.4 (70)	33.7	17.5
$Fe(h^5\text{-}C_5H_5)I(CO)_2$	xylene	0.44 (70)	33.2	11.6
$Ru(h^5\text{-}C_5H_5)Cl(CO)_2$	xylene	0.15 (70)	29.9	−1.0
$Ru(h^5\text{-}C_5H_5)Br(CO)_2$	xylene	0.015 (70)	31.1	−1.4

from the solvent effects on reactivities is that in all cases the transition state must be considerably less polar than the initial state.[23]

Evidence has been presented for ionic intermediates of formula $\{Mo(h^5\text{-}C_5H_5)(CO)_2[P(OR)_3]_2\}^+\{Mo(h^5\text{-}C_5H_5)(CO)_3\}^-$ in the reaction of the dimer $[Mo(h^5\text{-}C_5H_5)(CO)_3]_2$ with phosphites. The mechanism closely resembles that of the Michaelis–Arbuzov reaction of alkyl halides with

[22] J. T. Moelwyn-Hughes, A. W. B. Garner, and N. Gordon, *J. Organometallic Chem.*, 1971, **26**, 373.

[23] D. A. Brown, H. J. Lyons, and R. T. Sane, *Inorg. Chim. Acta*, 1970, **4**, 621.

tertiary phosphites.[24] Reactions of the above molybdenum dimer with phosphonites, $P(OR)_2Ph$, and with phosphinites, $P(OR)Ph_2$, also go by a Michaelis–Arbuzov mechanism,[25] as does the reaction of $FeCl(h^5\text{-}C_5H_5)(CO)_2$ with phosphites $P(OR)_3$, where R = Me, Et, or Bu^n. In this last case [26] the ionic intermediates have the general formula $\{Fe(h^5\text{-}C_5H_5)(CO)_2[P(OR)_3]\}^+Cl^-$.

The stereochemical course of displacement of carbon monoxide from compounds of the type $[Mn(h^5\text{-}C_5H_5)(CO)(NO)(PPh_3)]^+$ or $[Fe(h^5\text{-}C_5H_5)(I)(CO)(PPh_3)]$ has been studied.[27] The avowed object of this exercise was to determine the stereochemistry of substitution at tetrahedral transition-metal centres, but the normal convention for the 'denticity' of *pentahapto*-cyclopentadiene would prevent most chemists from considering these compounds to be of tetrahedral configuration.

After these reactions involving groups of complexes from various parts of the Periodic Table, the remainder of this section will deal with reactions of specific compounds, and is arranged in Periodic Table order.

Group VI. The rate law for reaction of $Mo(\pi\text{-indenyl})X(CO)_3$ with phosphorus bases (L) is:

$$-\,d[Mo(\pi\text{-indenyl})X(CO)_3]/dt = \{k_1 + k_2[L]\}[Mo(\pi\text{-indenyl})X(CO)_3]$$

This contrasts with the simpler rate law for substitution at the analogous cyclopentadienyl compound:

$$-\,d[Mo(h^5\text{-}C_5H_5)X(CO)_3]/dt = k_1[Mo(h^5\text{-}C_5H_5)X(CO)_3]$$

In both cases the k_1 path corresponds to a dissociative mechanism. The presence of an associative path (k_2 term) as well for the indenyl complex cannot be explained on steric grounds, for the bulkier indenyl group would on these grounds disfavour an associative mechanism. Rather it seems that the extra benzene ring in the indenyl ligand helps to stabilize the activated state for associative attack by the extra delocalization possible.[28] This hypothesis is neatly supported by the rate law for the analogous tetrahydroindenyl (C_9H_{11}) complex:

$$-\,d[Mo(\pi\text{-}C_9H_{11})Cl(CO)_3]/dt = k_1[Mo(\pi\text{-}C_9H_{11})Cl(CO)_3]$$

where the delocalization possibilities are the same as in the cyclopentadienyl compound. The dissociative mechanism for this tetrahydroindenyl compound is further supported by the observation that rates are independent of the nature as well as of the concentration of incoming ligand, and that the activation entropy is positive.[29]

[24] R. J. Haines and C. R. Nolte, *J. Organometallic Chem.*, 1970, **24**, 725.
[25] R. J. Haines, A. L. du Preez, and I. L. Marais, *J. Organometallic Chem.*, 1971, **28**, 97.
[26] R. J. Haines, A. L. du Preez, and I. L. Marais, *J. Organometallic Chem.*, 1970, **24**, C26; 1971, **28**, 405.
[27] H. Brunner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 249.
[28] A. J. Hart-Davis, C. White, and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 441.
[29] C. White and A. J. Mawby, *J. Chem. Soc.* (*A*), 1971, 940.

Group VII. The rate law for reaction of $Ph_3M—Mn(CO)_5$, where M = Si, Ge, or Sn, with a variety of nitrogen and phosphorus bases, both unidentate (*e.g.* phosphines) and bidentate (*e.g.* diphos, bipy), indicates parallel dissociative and associative mechanisms in all cases. This assignment of mechanisms on the basis of the rate law is supported by activation entropies determined for the respective terms.[30, 31] Exceptionally, the reaction of $Ph_3Si—Mn(CO)_5$ with trialkyl phosphites does not result in simple substitution of carbon monoxide by the phosphite, but produces *trans*-$Mn(COR)(CO)_3[P(OR)_3]_2$ by way of a Michaelis–Arbuzov reaction.[31]

It is well established that the mode of reaction of many carbonyls, particularly the Group VI compounds $M(CO)_6$, with azide involves attack of the azide at carbonyl-carbon. Group VII carbonyls also sometimes react with azide by a similar mechanism but, under the right conditions, it is possible to carry out simple replacement of carbon monoxide by azide. Azide reacts with $MnBr(CO)_5$ in aqueous ethanol to produce the dinuclear compound $(OC)_3Mn(\mu\text{-}N_3)_3Mn(CO)_3$. Replacement of bromide by azide may be the first step; at some stage replacement of carbon monoxide by azide must occur.[32] Irradiation of a tetrahydrofuran solution of $Mn(h^5\text{-}C_5H_5)(CO)_3$ and a nitrile RCN results in the replacement of one carbon monoxide molecule to give $Mn(h^5\text{-}C_5H_5)(CO)_2(NCR)$. The mechanism involves photochemical dissociation of the starting manganese compound to give $Mn(h^5\text{-}C_5H_5)(CO)_2$ as intermediate.[33]

Strong bases, for example hydroxide or methoxide, react with metal acyl carbonyls with cleavage of the metal–acyl bond. On the other hand, weak bases, for example triphenylphosphine, iodide, or cyclohexylamine, react with metal acyl carbonyls with metal–carbonyl bond cleavage, *e.g.*

$$Mn(COR)(CO)_5 + PPh_3 \longrightarrow Mn(COR)(CO)_4(PPh_3) + CO$$

Rates of such substitution reactions are independent of the nature and the concentration of the incoming ligand, and are thus dissociative. In methanol solution, substitution rates increase on adding acid, owing to protonation of the acyl ligand producing a more reactive reactant.[34] The possibility of this type of reaction proceeding by a migration mechanism, with $Mn(CO\cdot CO\cdot R)(CO)_4L$ as a transient intermediate, cannot be ruled out on kinetic grounds, but has now been shown to be untenable by the synthesis of one such compound, pyruvoylmanganesepentacarbonyl, $Mn(CO\cdot CO\cdot Me)(CO)_5$, and the demonstration that it is kinetically inert.[35] Dissociative reactions of $Mn(COR)(CO)_5$ involve a transition state, or transient intermediate, $Mn(COR)(CO)_4$. I.r. evidence has recently been

[30] G. R. Dobson and E. P. Ross, *Inorg. Chim. Acta*, 1971, **5**, 199.
[31] E. P. Ross, R. T. Jernigan, and G. R. Dobson, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3375.
[32] R. Mason, G. A. Rusholme, W. Beck, H. Englemann, K. Joos, B. Lindenberg, and H. S. Smedal, *Chem. Comm.*, 1971, 496.
[33] M. Herberhold and H. Brabetz, *Chem. Ber.*, 1970, **103**, 3896.
[34] R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 2091.
[35] C. P. Casey and C. A. Bunnell, *J. Amer. Chem. Soc.*, 1971, **93**, 4077.

obtained for the existence of the latter species (R = Me) and of $MnMe(CO)_4$, generated photolytically from $Mn(COMe)(CO)_5$ and $MnMe(CO)_5$ respectively, at − 258 °C.[36]

The kinetics of reaction of $Re(NCO)(CO)_5$ with phen, bipy, or diphos indicate rate-determining loss of carbon monoxide. Rate constants for the series $ReX(CO)_5$ are in the order NCO > Cl > Br > I.[37] The same rate trend, Cl > Br > I, is observed for reaction of $ReX(CO)_5$ with triphenylphosphine;[38] this trend is, as expected,[39] the same as that for analogous reactions of $MnX(CO)_5$. Surprisingly, an earlier study [40] of $ReX(CO)_5$ with bidentate ligands indicated the opposite rate trend, *viz.* I > Br > Cl; whether this difference is due to a difference in mechanism for bidentate entering groups or merely to large experimental uncertainties has not yet been established.

Group VIII. The compound $Fe(allyl)(CO)_2(NO)$ reacts very slowly with triphenylarsine, does not react with pyridine, but reacts at kinetically convenient rates with a range of phosphines and phosphites, in toluene, cyclohexane, or tetrahydrofuran solution. All these reactions obey a second-order rate law, indicating an associative mechanism, which is further supported by the observed negative activation entropies and small degree of dependence of rate constants on the nature of the solvent. The associative mechanism here may be contrasted with the dissociative mechanism for displacement of carbon monoxide from $Co(allyl)(CO)_3$ by phosphines; as in other comparisons between similar carbonyls and carbonyl-nitrosyls, the presence of the nitrosyl ligand seems to facilitate associative substitution.[41] Displacement of carbon monoxide by phosphorus ligands from $Ru(CO)_3(cot)$ also takes place by an associative mechanism. Here delocalization over the cyclo-octatetraene ligand facilitates bimolecular nucleophilic attack by reducing the electron density in the vicinity of the ruthenium.[42] This effect of delocalization has earlier been invoked to explain S_N2 mechanisms of reaction at similar cycloheptatrienyl and cyclopentadienyl compounds. Kinetic parameters for raction of this ruthenium compound [42] and of its iron [43] analogue $Fe(CO)_3(cot)$ with phosphines are compared in Table 2.

The products of reaction of $M(CO)_3(cod)$, M = Fe or Ru, with triphenylphosphine depend on the isomer, as shown in Scheme 2. The rate of the latter reaction is independent of the concentration of triphenylphosphine; hence the mechanism is dissociative.[44]

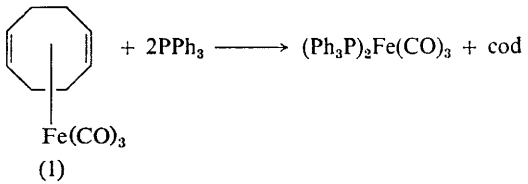
[36] A. J. Rest, *J. Organometallic Chem.*, 1970, **25**, C30.
[37] R. J. Angelici and G. C. Faber, *Inorg. Chem.*, 1971, **10**, 514.
[38] D. A. Brown and R. T. Sane, *J. Chem. Soc.* (*A*), 1971, 2088.
[39] D. A. Brown and W. J. Chambers, *J. Chem. Soc.* (*A*), 1971, 2083.
[40] F. Zingales, M. Graziani, F. Faraone, and U. Belluco, *Inorg. Chim. Acta*, 1967, **1**, 172.
[41] G. Cardaci and S. M. Murgia, *J. Organometallic Chem.*, 1970, **25**, 483.
[42] F. Faraone, F. Cusmano, and R. Pietropaolo, *J. Organometallic Chem.*, 1971, **26**, 147.
[43] F. Faraone, F. Zingales, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1968, **7**, 2362.
[44] F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4624.

Table 2 *Kinetic parameters for the replacement of carbon monoxide by phosphine from* $M(CO)_3$(cot), *with* M = Fe *or* Ru (*from refs.* 42 *and* 43)

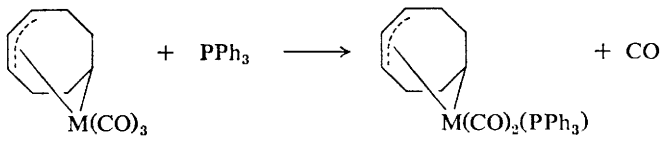
Compound	*Phosphine*	*Solvent*	$10^3\ k^a$/ $l\ mol^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal $deg^{-1}\ mol^{-1}$
$Fe(CO)_3$(cot)	Bu^n_3P	decalin	4.69	11.4	−38
	Bu^n_3P	methylcyclohexane	4.03	—	—
$Ru(CO)_3$(cot)	Bu^n_3P	methylcyclohexane	~20	14.5	−24
	diphos	methylcyclohexane	—	17.1	−18

[a] at 90 °C

The cation $[Fe(h^5\text{-}C_5H_5)(CO)_3]^+$ could react with NCO^- either by direct replacement of CO by NCO^-, or by attack of the NCO^- at carbonyl-carbon [*cf.* N_3^- or NCO^- attack at $W(CO)_6$, for instance]. Experiments with ^{14}C-labelled NCO^- indicate that at least 99% of the reaction goes by the former, direct replacement, route.[45] However, reactions of the cations $[Fe(h^5\text{-}C_5H_5)(CO)_2L]^+$, where L = CO, PPh_3, or C_2H_4, with azide do



(1)



(2)

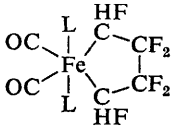
Scheme 2

proceed by attack of azide at a carbonyl-carbon, to produce $Fe(h^5\text{-}C_5H_5)$ (NCO)(CO)L as final product.[46]

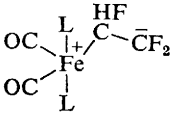
Reaction of *trans*-$[M(CO)_3L_2]$, where M = Fe or Ru and L = phosphine or phosphite, with fluoro-alkenes usually produces, under photochemical conditions, $M(CO)_2$(fluoro-alkene)L_2, though the compound with M = Fe and L = triethyl phosphite reacts with two molecules of trifluoroethylene to yield (3). These results can all be accommodated by a reaction scheme in which replacement of carbon monoxide by fluoro-alkene produces an ionic intermediate (4) which can either ring-close or

[45] L. M. Charley and R. J. Angelici, *Inorg. Chem.*, 1971, **10**, 868.
[46] M. Graziani, L. Busetto, and A. Palazzi, *J. Organometallic Chem.*, 1971, **26**, 261.

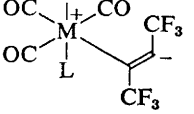
add a further molecule of fluoro-alkene.[47] Similarly, reactions of similar carbonyl compounds of iron, ruthenium, or osmium with hexafluorobut-2-yne, although they produce a variety of products depending on conditions, can also be understood if the mechanism involves an ionic intermediate of the type (5). Such a mechanism seems more attractive than a direct insertion process for alkynes with electronegative groups.[48]



(3)



(4)



(5)

The mechanism of halogenation of the dimers $[Fe(h^5\text{-}C_5H_4R)(CO)_2]_2$, where R = H or Me, involves attack of halogen at one of the iron atoms, followed by asymmetric or symmetric cleavage. Points of similarity between addition of halogens to alkenes and to these iron dimers are stressed.[49]

3 Substitution in Carbonyls: Replacement of Other Ligands

The reaction:

$$[MX(CO)_5]^- + CO \longrightarrow M[CO)_6 + X^-$$

with M = Cr, Mo, or W and X = Cl, Br, or I, is the reverse of the reactions described in the previous section. An i.r. spectroscopic study[50] of the kinetics of displacement of X^- by carbon monoxide indicates an order of reactivity consistent with the established *trans*-labilizing effects of X^-. The structure of the transition state for dissociative reactions of the type:

$$M(CO)_5L + L' \longrightarrow M(CO)_5L' + L$$

has been probed by experiments using labelled carbon monoxide. It is possible to label the equatorial carbonyl ligands in, say, $Mo(CO)_5$(piperidine). In the reaction of this compound with triphenyl-arsine, where the mechanism is predominantly dissociative, a complete scrambling of the labels is found in the products, suggesting a trigonal-bipyramidal transition state.[51]

The conversion of *trans*-$[IrX(CO)L_2]$, where L = PMe_2Ph or $AsMe_2Ph$, in the presence of an excess of L, into the five-co-ordinate species $[Ir(CO)L_4]^+X^-$ is thought to occur through the five-co-ordinate neutral

[47] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975.
[48] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981.
[49] R. J. Haines and A. L. du Preez, *J. Chem. Soc.* (*A*), 1970, 2341.
[50] J. A. Bowden and R. Colton, *Austral. J. Chem.*, 1971, **24**, 881.
[51] D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, 1971, **93**, 2807.

species $[IrX(CO)L_3]$.[52] Substitution and addition reactions of perchlorato-complexes of iridium(I) and of rhodium(I), for example *trans*-$[Rh(OClO_3)(CO)(PPh_3)_2]$, have been described and discussed;[53] the ready displacement of perchlorate from these and other complexes can provide a convenient synthetic route.[54]

In benzene solution $Fe(h^5\text{-}C_5H_5)Cl(CO)_2$ reacts with phosphites with the elimination of chloride and through a Michaelis–Arbuzov rearrangement.[26] The acetone ligand of $[Fe(h^5\text{-}C_5H_5)(CO)_2(OCMe_2)]^+$ is very labile, so it is possible to generate and isolate the compound $[Fe(h^5\text{-}C_5H_5)(CO)_2(diphos)]^+$, containing unidentate diphos. This species subsequently reacts further,[55] giving either the chelate $[Fe(h^5\text{-}C_5H_5)(CO)(diphos)]^+$ or the bridged species $[(h^5\text{-}C_5H_5)(CO)_2Fe(diphos)Fe(CO)_2(h^5\text{-}C_5H_5)]^{2+}$. In iso-octane solutions of $W(CO)_5(OCMe_2)$ and alkenes the following equilibrium is established:

$$W(CO)_5(OCMe_2) + \text{alkene} \rightleftharpoons W(CO)_5(\text{alkene}) + Me_2CO$$

which lies on the right-hand side for some alkenes; *cis*-alkenes both react faster and form more stable products than do *trans*-alkenes. The mechanisms of the forward and reverse reactions both appear to be dissociative.[56] Cyanate and cyanide react with $[Fe(h^5\text{-}C_5H_5)(CO)_2(CH_2{=}CH_2)]^+$ to displace the ethylene, but azide attacks at the carbonyl-carbon to produce ultimately the cyanate derivative $Fe(h^5\text{-}C_5H_5)(NCO)(CO)(CH_2{=}CH_2)$.[57] The two isomers (1) and (2) of $Fe(CO)_3(cod)$ react differently with triphenylphosphine; with the former compound a carbon monoxide molecule is replaced, but with the latter the triphenylphosphine displaces the cyclo-octadiene.[44]

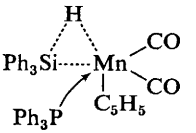
Triphenylphosphine reacts with the manganese–silicon bonded compound (6) by reductive elimination:

$$Ph_3Si\cdot Mn(H)(h^5\text{-}C_5H_5)(CO)_2 + PPh_3 \xrightarrow{\quad (6) \quad} Ph_3P\cdot Mn(h^5\text{-}C_5H_5)(CO)_2 + Ph_3SiH$$

The kinetics of the reaction in n-heptane, toluene, and tetrahydrofuran solutions were studied. $HSiPh_3$ retards the reaction, and hence the first step must be rate-determining dissociation of the silane. This process has $\Delta H^{\ddagger} = 29.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = +16.3$ cal deg^{-1} mol^{-1} in n-heptane. A crystal-structure determination shows that the hydride-hydrogen is bonded normally to the manganese, and is also close to the silicon atom, in (6). It is tempting to propose that formation of the transition state involves lengthening the manganese–hydrogen distance while decreasing

[52] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 2705.
[53] L. Vaska and J. Peone, *Suomen Kem.*, 1971, **44B**, 317.
[54] D. F. Christian and W. R. Roper, *Chem. Comm.*, 1971, 1271.
[55] M. L. Brown, T. J. Meyer, and N. Winterton, *Chem. Comm.*, 1971, 309.
[56] M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 6048.
[57] L. Busetto, A. Palazzi, R. Ros, and U. Belluco, *J. Organometallic Chem.*, 1970, **25**, 207.

the silicon–hydrogen distance, presumably with concurrent manganese–silicon bond stretching, giving the transition state (7), but one cannot



(7)

completely rule out the simpler though intuitively less appealing radical mechanism *via* direct silicon–manganese homolysis.[58]

Cleavage of chloride bridges in reactions of the dimers $[ReCl_2(CO)_2(NO)]_2$ [59] and $[RhCl(CO)_2]_2$ [60] are also examples relevant to the present section. Kinetic results for reaction of the rhenium dimer with substituted pyridines are consistent with either of two mechanisms, either pre-equilibrium cleavage of one Re—Cl—Re bridge followed by rate-determining attack of the pyridine at the vacant site on rhenium, or direct attack of the pyridine on a rhenium atom in the di-μ-chloro-dimer. The determined activation entropies, which range from -16 to -30 cal $deg^{-1}\,mol^{-1}$, are consistent with the latter S_N2 mechanism. That $[ReCl_2(CO)_2(NO)]_2$ reacts more rapidly than $[RhCl(CO)_2]_2$ is ascribed to the role of the NO ligand stabilizing the transition state from the former compound.[59] The reinvestigation [60] of the reaction of $[RhCl(CO)_2]_2$ with cyanide provides a little further kinetic information and evidence for long-lived intermediates $[RhCl(CN)(CO)_2]^-$, *trans*-$[Rh(CN)_2(CO)_2]^-$, and $[Rh(CN)_3(CO)]^{2-}$.

Compounds $FeX(NO)_2L$, where L = a phosphine or a phosphite, react with further quantities of L to produce $Fe(NO)_2L_2$ by a second-order process. The mechanism of this unusual reaction, which is both a substitution and a redox reaction, appears to be rapidly established pre-equilibration with the extra molecule of L, followed by rate-determining loss of X^- from the five-co-ordinate intermediate.[61]

4 Carbonyls: Formation

The rate laws have been determined for the formation of mono- and di-carbonyl species from the reaction of carbon monoxide with ruthenium(II) chloride solutions in dimethylacetamide. The mechanisms of these reactions are compared with those of similar reactions in hydrochloric acid, and of analogous reactions with dinitrogen rather than with carbon monoxide.[62]

[58] A. J. Hart-Davis and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1971, **93**, 4388.
[59] F. Zingales, A. Trovati, and P. Uguagliati, *Inorg. Chem.*, 1971, **10**, 510.
[60] R. A. Jewsbury and J. P. Maher, *J. Chem. Soc.* (*A*), 1971, 2847.
[61] S. Pignataro, G. Distefano, and A. Foffani, *J. Amer. Chem. Soc.*, 1970, **92**, 6425.
[62] B. C. Hui and B. R. James, *Canad. J. Chem.*, 1970, **48**, 3613.

Two studies have been reported of the reaction of polynuclear carbonyls with further carbon monoxide. The reaction sequences for such reactions of $Ir_4(CO)_9(PR_3)_3$ (R = aryl) and $Ir_4(CO)_8(PR_3)_4$ (R = alkyl) have been established by characterization of intermediates.[63] The reaction of $Os_3(CO)_8(PhC{\equiv}CPh)_2$ with carbon monoxide, to produce $Os_3(CO)_9(PhC{\equiv}CPh)_2$, is a second-order process.[64] The displacement of X^- from $[M(CO)_5X]^-$, where M = Cr, Mo, or W, by carbon monoxide should also be mentioned again here.[50]

Carbon monoxide reacts with $[Co(CN)_5]^{3-}$ according to the equation:

$$2[Co(CN)_5]^{3-} + 2CO \longrightarrow [Co(CN)_6]^{3-} + [Co(CN)_3(CO)_2]^{2-} + CN^-$$

in which the product $[Co(CN)_3(CO)_2]^{2-}$ is isoelectronic with $Fe(CO)_5$ and $[Ni(CN)_5]^{3-}$. The rate law is:

$$+ d[Co(CN)_3(CO)_2{}^{2-}]/dt = k[Co(CN)_5{}^{3-}]^2[CO][CN]^{-1}$$

and the activation parameters are $\Delta H^{\ddagger} = 14.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18$ cal deg^{-1} mol^{-1}. The suggested mechanism is pre-equilibrium formation of $[Co(CN)_4(CO)]^{2-}$, perhaps *via* the reactions:

$$[Co(CN)_5]^{3-} \underset{\text{fast}}{\overset{-CN^-}{\rightleftharpoons}} [Co(CN)_4]^{2-} \underset{\text{fast}}{\overset{+CO}{\rightleftharpoons}} [Co(CN)_4(CO)]^{2-}$$

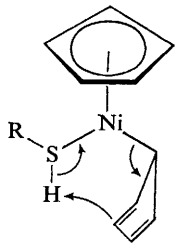
and a subsequent rate-determining reaction of the $[Co(CN)_4(CO)]^{2-}$ with another $[Co(CN)_5]^{3-}$ anion.[65]

5 Cyclopentadienyls

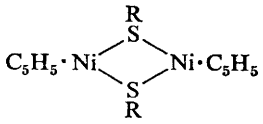
Kinetic studies of h^5-C_5H_5 as a leaving group are rare, though there have been three examples in the recent literature. In nitromethane or diethyl ether solution, $Ni(h^5\text{-}C_5H_5)_2$ reacts with Ph_3CCl with displacement of both h^5-C_5H_5 groups from the nickel; the organic product is a mixture of 2- and 3-(triphenylmethyl)cyclopentadienes. The primary step is a one-electron transfer to give the radical pair $Ni(h^5\text{-}C_5H_5)_2{}^+$, $\cdot CPh_3$; $Co(h^5\text{-}C_5H_5)_2$ also reacts with Ph_3CCl by a one-electron transfer mechanism, and here salts of $Co(h^5\text{-}C_5H_5)_2{}^+$ can of course be isolated.[66] The effect of variation of the solvent and of the nature of the thiol on the kinetics of reaction between nickelocene and thiols suggests a transition state or intermediate of the form (8), *en route* to the ultimate sulphur-bridged dinuclear product (9).[67] The h^5-C_5H_5 group is also effectively a leaving group with respect to one of the nickel atoms in the following reaction:

$$h^5\text{-}C_5H_5 \cdot Ni(CO)_2Ni \cdot h^5\text{-}C_5H_5 + 2L \longrightarrow Ni(CO)_2L_2 + Ni(h^5\text{-}C_5H_5)_2$$

[63] R. Whyman, *J. Organometallic Chem.*, 1970, **24**, C35.
[64] O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organometallic Chem.*, 1971, **30**, 381.
[65] J. Halpern and M. Pribanić, *J. Amer. Chem. Soc.*, 1971, **93**, 96.
[66] H. Werner, G. Mattmann, A. Salzer, and T. Winkler, *J. Organometallic Chem.*, 1970, **25**, 461.
[67] P. C. Ellgen and C. D. Gregory, *Inorg. Chem.*, 1971, **10**, 980.



(8)



(9)

These reactions have been studied, mainly by i.r. spectroscopy, for a variety of ligands L, *viz.* CO, $AsPh_3$, $P(OPh)_3$, and a selection of phosphines. A simple second-order rate law is followed, suggesting initial bimolecular attack of L at a nickel atom. The activation entropies, which are listed together with activation enthalpies in Table 3, for these reactions are consistent with this interpretation.[68]

Table 3 *Activation parameters for reactions of* $[Ni(h^5\text{-}C_5H_5)(CO)]_2$ *with Group V bases, in decalin solution (from ref.* 68)

Entering ligand	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
PPh_3	14.9	−16
$P(OPh)_3$	16.4	−13
$AsPh_3$	17.1	−14

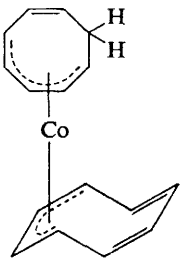
$WH_2(h^5\text{-}C_5H_5)_2$ only reacts with aromatic compounds C_6H_5R to produce $WH(C_6H_4R)(h^5\text{-}C_5H_5)_2$ in the presence of conjugated dienes. This suggests that hydrogen abstraction by the diene is an important feature of the mechanism. This, and the observation that for R ≠ H only the *p*-isomer of the product is obtained, can be accommodated by the sequence shown in Scheme 3. A free-radical mechanism seems unlikely as one would then expect *m*- and *p*-compounds.[69]

Reactions of $[MCl_2(h^5\text{-}C_5Me_5)]_2$, where M = Rh or Ir, with mono-, di-, and tri-enes, including cyclohexadiene, are slow, and are thought to involve conversion of the dimer to $M(H)(Cl)(h^5\text{-}C_5Me_5)$, which subsequently undergoes slow loss of hydrogen chloride to generate the reactive intermediate $M(h^5\text{-}C_5Me_5)(solvent)$.[70]

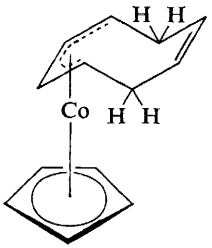
The formation of a pentamethylcyclopentadienyl derivative from hexamethyl-Dewarbenzene in the presence of $[PtCl_4]^{2-}$ and acid is thought[71] to involve $h^5\text{-}C_5Me_5$ derivatives of platinum(II) and of

[68] P. C. Ellgen, *Inorg. Chem.*, 1971, **10**, 232.
[69] M. L. H. Green and P. J. Knowles, *Chem. Comm.*, 1970, 1677; *J. Chem. Soc.* (*A*), 1971, 1508.
[70] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875; K. Moseley and P. M. Maitlis, *ibid.*, 1970, 2884.
[71] P. V. Balakrishnan and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1971, 1715.

platinum(IV). h^5-Cyclo-octatrienyl-h^4-cyclo-octatetraenecobalt (10) reacts with cyclopentadiene to produce (11). The mechanism is thought to

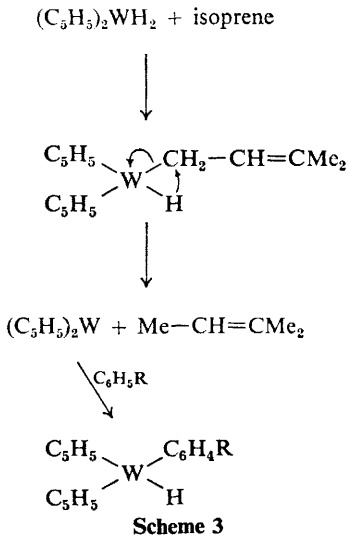


(10)



(11)

involve displacement of the cyclo-octatetraene by the cyclopentadiene, with subsequent hydrogen transfer from the cyclopentadiene to the cyclo-octatriene through a hydridic intermediate.[72]



Scheme 3

The kinetics of the displacement of the C_8-alkenyl ring by a C_7-alkene ring (cycloheptatriene) in the reaction:

$$Co(C_8H_{13})(C_8H_{12}) + C_7H_8 \longrightarrow Co(C_7H_9)(C_8H_{12}) + C_8H_{12}$$

show that the rate law, at least in n-heptane solution, is:

$$\text{rate} = k[Co(C_8H_{13})(C_8H_{12})][C_7H_8] + k'[Co(C_8H_{13})(C_8H_{12})]^{\ddagger}$$

The second term suggests the intermediacy of a dicobalt species, and indeed $[Co(C_7H_8)(C_8H_{12})]_2$ has been isolated and characterized.[73]

[72] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 285.
[73] S. Otsuka and T. Taketomi, *J. Chem. Soc.* (*A*), 1971, 579.

6 Phosphine, Phosphite, and Arsine Compounds

The kinetics of the reaction of $Ni(PF_3)_4$ and of $Pt(PF_3)_4$ with cyclohexyl isocyanide have been followed, by i.r. spectroscopy, in toluene, n-hexane, and n-heptane solution. The rate law is first-order. This, and the determined activation entropies (Table 4), indicate a dissociative mechanism

Table 4 *Activation parameters for reaction of trifluorophosphine complexes of nickel*(0) *and platinum*(0) *with cyclohexyl isocyanide* (*from ref.* 74)

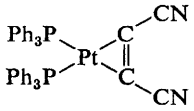
Compound	*Solvent*	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
$Ni(PF_3)_4$	n-heptane	29	+14
	toluene	28	+11
$Pt(PF_3)_4$	toluene	23	+12
	n-hexane	24	+18

here, as in analogous reactions of $Ni(CO)_4$ or of $Pt(P\{OEt\}_3)_4$. Rate comparisons between nickel, palladium, and platinum complexes of CO, PF_3, and $P(OEt)_3$ show that the reactivities of metal–PF_3 complexes approximate much more closely to those of metal–$P(OEt)_3$ complexes than to those of the metal carbonyls.[74]

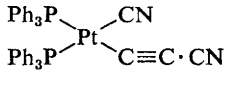
An investigation of the phosphorus ligand replacement reactions:

$$MX(CO)_2L + L' \rightleftharpoons MX(CO)_2L' + L$$

where M = Rh or Ir, and L and L′ are from the group PPh_3, $P(OPh)_3$, and $P(C_6H_{11})_3$, provides several further examples of the very much easier displacement of phosphines and of phosphites from rhodium(I) than from iridium(I).[75] One of the phosphite ligands can be displaced from the rhodium(I) cation $[Rh(P\{OR\}_3)_5]^+$ by an alkyne to give a $[Rh(P\{OR\}_3)_4(alkyne)]^+$ cation.[76] The reaction of $Pt(PPh_3)_4$, or of $Pt(PPh_3)_2(PhC{\equiv}CH)$, with dicyanoacetylene is thought to involve pre-equilibrium dissociation to $Pt(PPh_3)_2$, which then adds directly to the dicyanoacetylene to give the product (12).[77] Irradiation of (12) leads to the σ-alkyne complex (13).[78] The similar isomerization of alkene



(12)



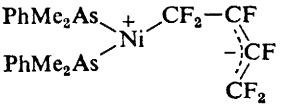
(13)

complexes to vinyl compounds is well known; this is the first example of the analogous isomerization of an alkyne complex.

[74] R. D. Johnston, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 247.
[75] W. Strohmeier, W. Rehder-Stirnweiss, and G. Reischig, *J. Organometallic Chem.*, 1971, **27**, 393.
[76] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1693.
[77] G. L. McClure and W. H. Baddley, *J. Organometallic Chem.*, 1970, **25**, 261.
[78] W. H. Baddley, C. Panattoni, G. Bandoli, D. A. Clemente, and U. Belluco, *J. Amer. Chem. Soc.*, 1971, **93**, 5590.

When Ni(LL)(Me_4-1,4-benzoquinone), where LL = a bidentate cyclic alkene such as cot, cod, nor, or *endo*-dicyclopentadiene, reacts with trimethyl phosphite, it is the alkene LL which is replaced first, *en route* to the product $Ni(P\{OMe\}_3)_4$. This first step is bimolecular, producing an intermediate containing unidentate alkene. Some kinetic parameters are reported, particularly for LL = cyclo-octa-1,5-diene.[79] The formation of the cation $[NiH(P\{OEt\}_3)_4]^+$ in perchloric acid–methanol solution appears to involve direct protonation of the nickel. Activation parameters[80] for this are $\Delta H^{\ddagger} = 13 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2 \pm 3$ cal deg^{-1} mol^{-1}.

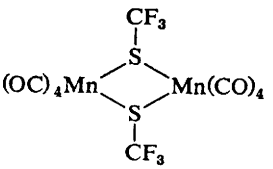
A paper on the reaction of tetra-arsine complexes of nickel(0) with hexafluorobutadiene contains the suggestion that the mechanism of these reactions may involve the intermediacy of an ionic intermediate, for example (14).[81]



(14)

7 Metal–Metal Bond Cleavage

Reactions of the Group VII carbonyls often involve metal–metal bond cleavage. Thus the reaction of $Mn_2(CO)_{10}$ with CF_3SX, where X = SCF_3, Cl, SMe, or SPh, results in cleavage of the metal–metal bond followed by formation of two sulphur bridges to produce the dimanganese compound (15).[82] E.s.r. evidence has been presented for paramagnetic species as



(15)

transient intermediates in the reaction of $Mn_2(CO)_{10}$ with triphenylphosphine, but these intermediates proved too labile to be isolated or characterized.[83] There is some evidence from polymerizations initiated by $Mn_2(CO)_{10}$ to suggest some unsymmetrical fission to produce $Mn(CO)_6$ fragments.[84] This is interesting in the light of earlier proposals[85] that

[79] A. Pidcock and G. G. Roberts, *J. Chem. Soc.* (*A*), 1970, 2922.
[80] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 4217.
[81] J. Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 453.
[82] J. Grobe and F. Kober, *J. Organometallic Chem.*, 1970, **24**, 191.
[83] J. R. Miller and D. H. Myers, *Inorg. Chim. Acta*, 1971, **5**, 215.
[84] C. H. Bamford and J. Paprotny, *Chem. Comm.*, 1971, 140.
[85] L. I. Haines and A. J. Poë, *J. Chem. Soc.* (*A*), 1969, 2826.

substitution at $Mn_2(CO)_{10}$ and at $Re_2(CO)_{10}$ proceeds by a metal-migration step to generate an intermediate $(OC)_5M(CO)M(CO)_4$. However, one should recall here that the kinetics of substitution at $Mn_2(CO)_{10}$ can be satisfactorily explained without recourse to a carbonyl-bridged intermediate or an $Mn(CO)_5$ intermediate by the following sequence of equilibria:[86]

$$Mn_2(CO)_{10} \rightleftharpoons Mn_2(CO)_9 + CO$$
$$Mn_2(CO)_9 + L \rightleftharpoons Mn_2(CO)_9L$$

The photochemical reaction of $Re_2(CO)_{10}$ with $PMePh_2$ seems to fit into this two-equilibrium scheme fairly well,[87] and so represents a recently discovered example of substitution at $M_2(CO)_{10}$ without metal–metal bond cleavage. Dinitrogen tetroxide reacts with $Re_2(CO)_{10}$ to cleave the metal–metal bond and give ultimately $Re(NO_3)(CO)_5$, by the following sequence:[88]

$$Re_2(CO)_{10} + N_2O_4 \longrightarrow Re_2(CO)_{10},N_2O_4$$
$$Re_2(CO)_{10},N_2O_4 \longrightarrow Re(NO_2)(CO)_5 + Re(ONO)(CO)_5$$
$$\left.\begin{matrix}Re(NO_2)(CO)_5\\ Re(ONO)(CO)_5\end{matrix}\right\} + N_2O_4 \longrightarrow Re(NO_3)(CO)_5 + N_2O_3$$

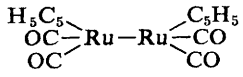
The relative reactivities of the carbonyls $M_3(CO)_{12}$, where M = Os, Ru, or Fe, towards trialkylsilicon or trialkyltin hydrides can be related to the relative strengths of the respective metal–silicon or metal–tin bonds.[89]

The compounds $M_2(PF_3)_8$, where M = Rh or Ir, react with silanes and germanes RH, where R = Ph_3Si, $(EtO)_3Si$, Cl_3Si, or Ph_3Ge, according to the equations:

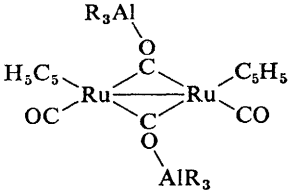
$$M_2(PF_3)_8 + RH \longrightarrow RM(PF_3)_4 + MH(PF_3)_4$$
$$MH(PF_3)_4 + RH \longrightarrow RM(PF_3)_4 + H_2$$

Kinetic results indicate that both steps are bimolecular in mechanism; the second reaction goes completely from left to right for the silanes, but goes to equilibrium for R = Ph_3Ge.[10]

Aluminium alkyls react with the ruthenium–ruthenium-bonded dimer (16) to give the di-μ-carbonyl derivative (17); the reaction can be reversed



(16)



(17)

[86] H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 113.
[87] J. T. Moelwyn-Hughes, A. W. B. Garner, and N. Gordon, *J. Organometallic Chem.*, 1971, **26**, 373.
[88] C. C. Addison, R. Davis, and N. Logan, *J. Chem. Soc.* (*A*), 1970, 3333.
[89] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3147.

by triethylamine.[90] An example of iron–iron cleavage is provided by the preparation of the products of mercury(II) insertion into the metal–metal bond of $[Fe_2(CO)_{10}]^{2-}$; mercury(II) inserts similarly into $[Cr_2(CO)_{10}]^{2-}$. These reactions are slow, even at temperatures of *ca.* 100 °C.[91]

The remaining examples concern metal–metal bonded compounds in which the two metals are different. Phosphorus bases or triethylamine react with $Cl_3Sn\cdot Co(CO)_4$, in hexane or in tetrahydrofuran, by attack of the phosphorus or nitrogen at the tin atom, followed by subsequent displacement of $[Co(CO)_4]^-$, which in turn displaces a chloride ion from the tin to yield the final product $SnCl_2[Co(CO)_4]_2$.[92] The redistribution reaction:

$$2Me_3Sn\cdot Mo(CO)_2(C_5H_5)(PPh_3) \longrightarrow Me_2Sn\cdot[Mo(CO)_2(C_5H_5)(PPh_3)]_2 + SnMe_4$$

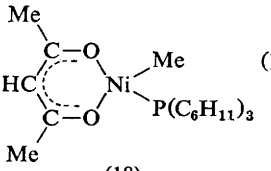
has a bimolecular mechanism, with a four-centre transition state. Distinct bond-breaking and bond-making steps seem unlikely in view of the absence of any $Me_3Sn\cdot SnMe_3$ in the products.[93]

8 Miscellaneous Reactions

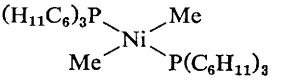
The nickel compounds $NiR_2(bipy)$ react with a variety of alkenes, including ethylene, norbornadiene, maleic anhydride, and tetracyanoethylene, to produce Ni(bipy)(alkene) or Ni(bipy)(alkene)$_2$. A kinetic study, supported by characterization of intermediates from the reactions with acrolein and with acrylonitrile, indicates that the reaction mechanism involves the intermediacy of transient complexes $NiR_2(bipy)(alkene)$, containing the alkene π-bonded to the nickel as in the products.[94] There is a correlation between the rates of these reactions and the stabilities of the respective complexes Ni(bipy)(alkene).[95] The unstable species $CoH(LL)_2$, where LL = bipy or phen, undergo substitution reactions with, for example, carbon monoxide, in which one LL ligand is replaced. One LL can also be replaced by alkyl halides; here the reaction is oxidative elimination rather than simple substitution.[96]

Ni(acac)$_2$ reacts with dinitrogen in the presence of tricyclohexylphosphine and trimethylaluminium to produce ultimately the bridged compound $[Ni(P\{C_6H_{11}\}_3)_2]_2N_2$. Intermediate methylnickel complexes (18) and (19) have been isolated.[97] Dinitrogen can be displaced from $OsX_2(N_2)L_3$ and $OsX_2(N_2)L_2L'$, where L and L′ are the phosphines PMe_2Ph, PEt_2Ph, or

[90] A. Alich, N. J. Nelson, and D. F. Shriver, *Chem. Comm.*, 1971, 254.
[91] H. Behrens, H.-D. Feilner, E. Lindner, and D. Uhlig, *Z. Naturforsch.*, 1971, **26b**, 990.
[92] K. Ogino and T. L. Brown, *Inorg. Chem.*, 1971, **10**, 517.
[93] T. A. George, *Chem. Comm.*, 1970, 1632.
[94] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3350.
[95] T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1971, **93**, 3360.
[96] G. Mestroni, A. Camus, and E. Mestroni, *J. Organometallic Chem.*, 1970, **24**, 775.
[97] P. W. Jolly, K. Jonas, C. Krüger, and Y.-H. Tsay, *J. Organometallic Chem.*, 1971, **33** 109.



(18)



(19)

$P(OEt)_2Ph$, and X = Cl or Br, by the action of phosphorus ligands. The reactions are first-order, and have positive activation entropies, between + 9 and + 17 cal deg^{-1} mol^{-1}. These observations imply a dissociative mechanism. Activation enthalpies are between 27 and 34 kcal mol^{-1}; such high values may be compared with, for instance, the activation enthalpy of 28 kcal mol^{-1} for displacement of dinitrogen from the $[Ru(NH_3)_5(N_2)]^{2+}$ cation.[98]

[98] P. K. Maples, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 765.

2

Metal–Alkyl, –Aryl, and –Allyl Bond Formation and Cleavage

BY R. D. W. KEMMITT AND J. BURGESS

1 Group V

Vanadium.—Vanadium oxochloride, $VOCl_3$, reacts with diphenylmercury to form $PhVOCl_2$ and some biphenyl. There is evidence, from deuterium labelling experiments, that the biphenyl is formed *via* an intermediate which contains two phenyl groups σ-bonded to the vanadium.[1]

2 Group VI

Chromium.—The kinetics of reactions between 2-, 3-, and 4-pyridiniomethylpenta-aquochromium(III) and mercury(II) or thallium(III) have been studied. The mechanism is bimolecular, with displacement of the $[Cr(OH_2)_5]^{3+}$ moiety by attack of the mercury(II) or thallium(III) at the saturated carbon atom bonded to the chromium. From the observed variation of rates with pH and with concentration of added chloride it is possible to determine individual rate constants for reaction with species such as $HgCl^+$, $TlCl^{2+}$, $TlOH^{2+}$, as well as Hg^{2+} and Tl^{3+} themselves.[2] A number of similar reactions are discussed in a review of electrophiles reacting with organo-transition-metal species.[3] The reaction of methoxyphenylcarbenepentacarbonylchromium(0), $Cr(CO)_5\{C(OMe)Ph\}$, with pyridine involves metal–carbon bond breaking. The mechanism of this reaction has been discussed in the light of the variation of the ratio of the products, $Cr(CO)_5(py)$ and *cis*-$[Cr(CO)_4(py)_2]$, with reaction conditions.[4] This same carbene–chromium(0) complex $Cr(CO)_5\{C(OMe)Ph\}$ reacts similarly with primary amines RNH_2 (R = Bu^n, C_6H_{11}, or CH_2Ph). The rate law for these reactions is fourth-order overall.[5]

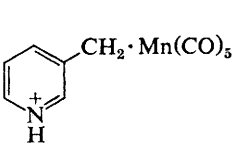
Molybdenum and Tungsten.—When $[M(CO_3(h^5\text{-}C_5H_5)]^-$, where M = Mo or W, reacts with Me_3SiCH_2I or its tin analogue, it is found to be impossible to isolate the initial molybdenum– or tungsten–carbon bonded product $Me_3SiCH_2M(CO)_3(h^5\text{-}C_5H_5)$. The neighbouring-group effect of the metal

[1] W. T. Reichle and W. L. Carrick, *J. Organometallic Chem.*, 1970, **24**, 419.
[2] D. Dodd, M. D. Johnson, and D. Vamplew, *J. Chem. Soc.* (*B*), 1971, 1841.
[3] M. D. Johnson, *Rec. Chem. Progr.*, 1970, **31**, 143.
[4] E. O. Fischer, B. Heckl, and H. Werner, *J. Organometallic Chem.*, 1971, **28**, 359.
[5] H. Werner, E. O. Fischer, B. Heckl, and C. G. Krieter, *J. Organometallic Chem.*, 1971, **28**, 367.

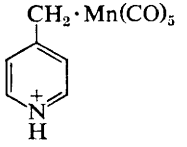
labilizes the silicon–carbon or tin–carbon bond, and the final product is $M(Me)(CO)_3(h^5\text{-}C_5H_5)$, which is thought [6] to be formed *via* the carbene $[M(CH_2)(CO)_3(h^5\text{-}C_5H_5)]^-$.

3 Group VII

Manganese and Rhenium.—The mechanism of the reaction of the 3- or 4-pyridiniomethylpentacarbonylmanganese ions (1) and (2) with mercury(II) or thallium(III) is, like that of the similar chromium(III) reactions



(1)



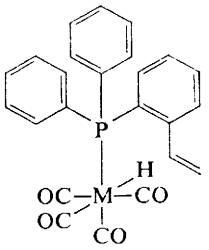
(2)

mentioned above, bimolecular – S_E2 with an open transition state. Reaction rates are a function of the concentration of added chloride; individual rate constants for reaction of the manganese compounds with Hg^{2+}, $HgCl^+$, Tl^{3+}, $TlCl^{2+}$, and higher chloride complexes have been estimated.[7]

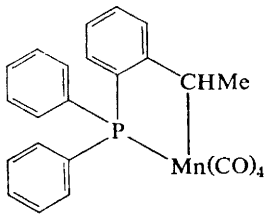
Methylmanganese pentacarbonyl reacts with hydrogen chloride, in methanol solution, to give methane and manganese pentacarbonyl chloride. This reaction is first-order in hydrogen ion concentration. Methylmanganese pentacarbonyl also reacts with mercury(II) chloride or with mercury(II) acetate. The mechanism suggested is oxidative addition to the manganese(I), generating an eight-co-ordinate, and presumably very transient, manganese(III) intermediate which gives the observed products by reductive elimination.[8]

The reaction of *o*-styryldiphenylphosphine with the hydridopentacarbonyls of manganese and of rhenium was carried out in order to prepare alkyl compounds of these metals which would serve as models for homogeneous hydrogenation, hydroformylation, and isomerization to alkenes. In fact, intermediate phosphine complexes (3), with M = Mn or Re, were isolated, which on subsequent heating under nitrogen gave, for the manganese system, the alkyl derivatives (4) and (5). These correspond to Markownikoff and anti-Markownikoff addition to the carbon–carbon double bond. In the rhenium reaction only the rhenium analogue of (5), from anti-Markownikoff addition, was found. This difference between the rhenium and manganese compounds can be explained by the differing polarities of the metal–hydrogen bonds; $ReH(CO)_5$ acts as a weaker acid than $MnH(CO)_5$.[9] The decomposition of dialkylmanganese

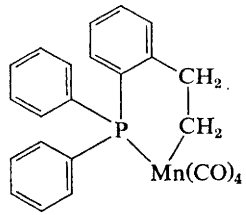
[6] M. R. Collier, B. M. Kingston, and M. F. Lappert, *Chem. Comm.*, 1970, 1498.
[7] D. Dodd, M. D. Johnson, and N. Winterton, *J. Chem. Soc.* (*A*), 1971, 910.
[8] R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 2091.
[9] M. A. Bennett and R. Watt, *Chem. Comm.*, 1971, 94.



(3)



(4)



(5)

compounds, generated from reactions of Grignard reagents with manganese(II) chloride in THF, proceeds mainly by β-elimination from a manganese alkyl species.[10]

4 Group VIII

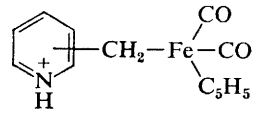
Iron.—Mercury(II) and thallium(III) perchlorates react with pyridinomethyldicarbonyl-π-cyclopentadienyliron ions (6) to cleave the iron–carbon bond, producing $[Fe(CO)_2(h^5\text{-}C_5H_5)(OH_2)]^+$ and pyridiniomethylmercury(II) or -thallium(III). As for similar reactions of pyridiniomethylchromium and -manganese compounds described in earlier paragraphs, the mechanism is S_E2(open).[11] The pyridiniomethylthallium(III) produced is itself unstable.[12]

The stereochemistry of iron–carbon bond cleavage by electrophilic attack by mercury(II) chloride or bromine, or by carbon monoxide or sulphur dioxide insertion, has been probed by n.m.r. studies of products derived from *threo*-$[Me_3C\cdot CHD\cdot CHD\cdot Fe(CO)_2(h^5\text{-}C_5H_5)]$. Predominant retention occurs in the reaction with mercury(II) chloride, predominant inversion in the reactions with sulphur dioxide or bromine. It is this last result which is of the most interest, for it affects discussions of the stereochemical course of oxidative additions (*q.v.*).[13]

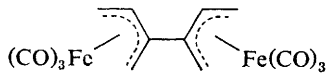
Iron carbonyls react with 2-bromobuta-1,3-diene to give a variety of products, including (7), (8), (9), and (10). The mechanism of formation of these compounds involves formation of a complex (11), into which iron carbonyl and carbon monoxide insert. The presence of (10) amongst the products suggests that a vinylacetylene derivative may be a significant intermediate.[14]

A preliminary report of an investigation of the kinetics of the reaction of the $[Fe(h^5\text{-}C_5H_5)(CO)_2]^-$ anion with allyl halides suggests that the rate-determining step is bimolecular in character.[15]

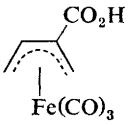
[10] M. Tamura and J. Kochi, *J. Organometallic Chem.*, 1971, **29**, 111.
[11] D. Dodd and M. D. Johnson, *J. Chem. Soc.* (*B*), 1971, 662.
[12] M. D. Johnson and D. Vamplew, *J. Chem. Soc.* (*B*), 1971, 507.
[13] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1971, **93**, 1529.
[14] R. N. Greene, C. H. DePuy, and T. E. Schroer, *J. Chem. Soc.* (*C*), 1971, 3115.
[15] J.-Y. Merour and P. Cadiot, *Compt. rend.*, 1970, **271**, *C*, 83.



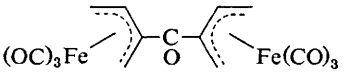
(6)



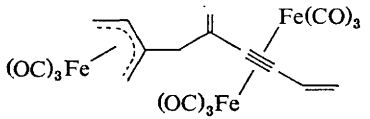
(7)



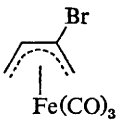
(8)



(9)

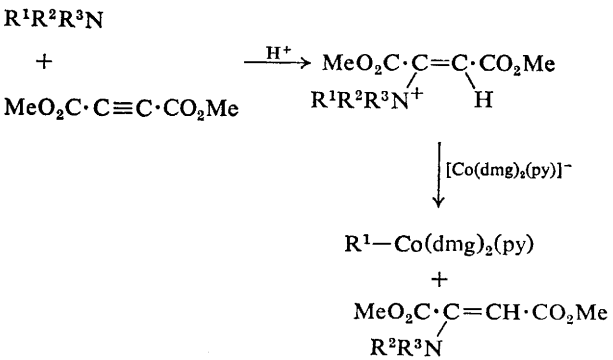


(10)



(11)

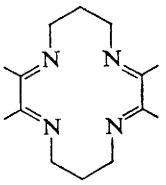
Cobalt.—The main group of compounds for which the formation and cleavage of cobalt–carbon σ-bonds have been studied is that of the cobaloximes and cobalamins. Cobalt–carbon bonds are formed in the reactions of the $[Co^{I}(dmg)_2(py)]^-$ anion with *cis*- or with *trans*-β-bromostyrene,[16] or with mixtures of tertiary amines plus the dimethyl ester of acetylenedicarboxylic acid.[17] The reaction with the bromostyrenes goes by direct substitution, with retention of configuration, and not by an elimination–addition reaction involving the intermediate production of phenylacetylene. This is consistent with analogous organic reactions, for vinyl halides react by direct substitution with soft nucleophiles but by elimination with hard nucleophiles; $[Co^{I}(dmg)_2]^-$ is a soft nucleophile.[16] The mechanism of cobalt–carbon bond formation in the reaction of $[Co^{I}(dmg)_2(py)]^-$ with the tertiary amine plus dimethylacetylenedicarboxylate is outlined in Scheme 1.[17]



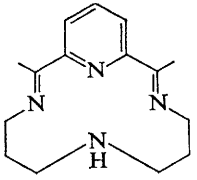
Scheme 1

[16] M. D. Johnson and B. S. Meeks, *J. Chem. Soc.* (*B*), 1971, 185.
[17] C. Bied-Charreton and A. Gaudemer, *Compt. rend.*, 1971, **272**, *C*, 1241.

The mechanism of formation of *trans*-dialkylcobalt(III) complexes from the monoalkyl compounds *trans*-[Co(R)(X)(tim)] and *trans*-[Co(R)(X)(cr)], where tim = (12) and cr = (13), is of two stages. In the first there is



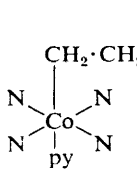
(12)



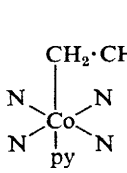
(13)

reduction, by $NaBH_4$ in methanol or sodium amalgam in acetonitrile, to the relatively stable cobalt(I) complexes $Co^{I}(R)(tim)$ or $Co^{I}(R)(cr)$. The second step is oxidative addition of alkyl halide to these cobalt(I) intermediates.[18] The formation of the malononitrile (mnH) derivatives [Co(mn)(salen)(py)] and [Co(mn)(salen)(OH_2)] from the cobalt(III) complexes [Co(OH)(salen)(py)] or [Co(OMe)(salen)] is thought to take place by nucleophilic attack of the malononitrile carbanion (mn^-) at the cobalt(III).[19]

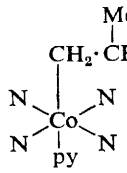
Methylcobaloximes are fairly resistant to attack by hydroxide ion, but halogeno-, dihalogeno-, and trihalogeno-methylcobaloximes are readily attacked by hydroxide. Cobalt–carbon bond cleavage gives the corresponding halogeno-methanol (carbonate from trihalogeno-compounds) and cobaloxime(I).[20] The cobaloxime compound $Co(dmg)_2(py)(CH_2CH_2OH)$, shown schematically as (14), reacts with hydrochloric acid to give ethylene and $Co(dmg)_2(py)Cl$.[21] The similar acetoxy-compounds (15) and (16) react



(14)



(15)

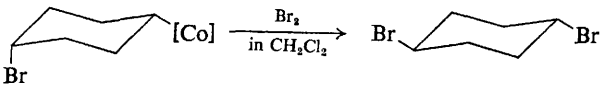


(16)

similarly, and there is evidence for intermediates containing ethylene or propylene bonded to the cobalt. For the compound (15) reacting in ethanol solution,[22] the rate constant is 4.4×10^{-6} s^{-1} at 25 °C, and the activation parameters are $\Delta H^{\ddagger} = 19.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18.2$ cal deg^{-1} mol^{-1}.

[18] K. Farmery and D. H. Busch, *Chem. Comm.*, 1970, 1091.
[19] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 591.
[20] G. N. Schrauzer, A. Ribiero, L. P. Lee, and R. K. Y. Ho, *Angew. Chem. Internat. Edn.*, 1971, **10**, 807.
[21] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1967, **89**, 143.
[22] B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, *Angew. Chem. Internat. Edn.*, 1970, **9**, 959.

Cobalt–carbon bond cleavage in cyclohexylcobaloximes by halogens takes place with inversion at the carbon, *e.g.* (17) → (18). The mechanism



(17) (18)

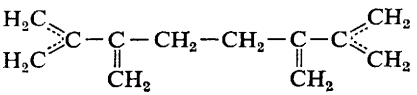
is tentatively assigned as S_E2. Most S_E2 reactions proceed with retention of configuration, but an S_E2 mechanism with inversion, as here, is not unknown. Reaction of s-butylcobaloxime with bromine or iodine also occurs with inversion at the carbon.[23] The bimolecular nucleophilic displacement mechanism for transferring alkyl groups in reactions of the type:

$$[Co^{III}(dmg)_2(py)(Me)] + [Co^{I}(LL)_2(py)]^- \rightleftharpoons [Co^{I}(dmg)_2(py)]^- + [Co^{III}(LL)_2(py)(Me)],$$

where LLH = cyclohexanedione dioxime, has been discussed.[24]

Three examples of mercury(II)-catalysed cobalt–carbon bond breaking in alkylcobaloximes and alkylcobalamins[25] have been mentioned earlier (Part II, Chapter 3, Section 2).

Rhodium.—The formation of rhodium(I) complexes with allenes has been much studied for rhodium(I)–halide compounds. Allenes also react with the diketone complexes $Rh(LL)(C_2H_4)_2$, where LL = acetylacetonato or dibenzoylmethanato, to form rhodium(I)–allene compounds. In this case an *X*-ray crystal structure determination has shown that the product contains the allene tetramer (19) bonded to the rhodium by two π-allyl bonds.[26]



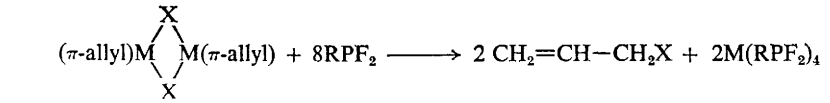
(19)

Iridium.—Examples of iridium–carbon bond formation resulting from intramolecular oxidative addition reactions of phosphine or phosphite complexes are discussed in Chapter 6 of this Part.

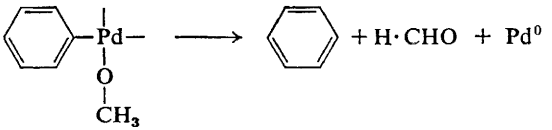
Nickel.—Carbon monoxide is known to promote ligand coupling reactions, which generally involve breaking two metal–ligand bonds and forming one

[23] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1971, **93**, 5283.
[24] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 1371.
[25] A. Adin and J. H. Espenson, *Chem. Comm.*, 1971, 653; G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Letters*, 1971, 275; J.-Y. Kim, N. Imura, T. Ukita, and T. Kwan, *Bull. Chem. Soc. Japan*, 1971, **44**, 300.
[26] G. Pantini, P. Racanelli, A. Immirzi, and L. Porri, *J. Organometallic Chem.*, 1971, **33**, C17.

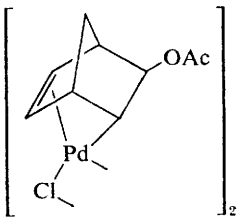
carbon–ligand bond. It has recently been shown that fluorophosphines can also promote ligand coupling, as in the following reaction, where M = Ni or Pd:[27]



Palladium.—A ligand coupling reaction which involves palladium–allyl bond breaking has already been noted in the paragraph on nickel compounds.[27] Reductive cleavage of palladium–carbon bonds can be achieved by use of, for example, methanol [28] or borohydrides.[29] Deuterium-labelling experiments indicate hydrogen (deuterium) transfer from co-ordinated methoxide in the former reductive cleavage:



The recently reported case of reductive cleavage by borohydride concerns norbornenyl and related compounds, such as (20); the mechanism was



(20)

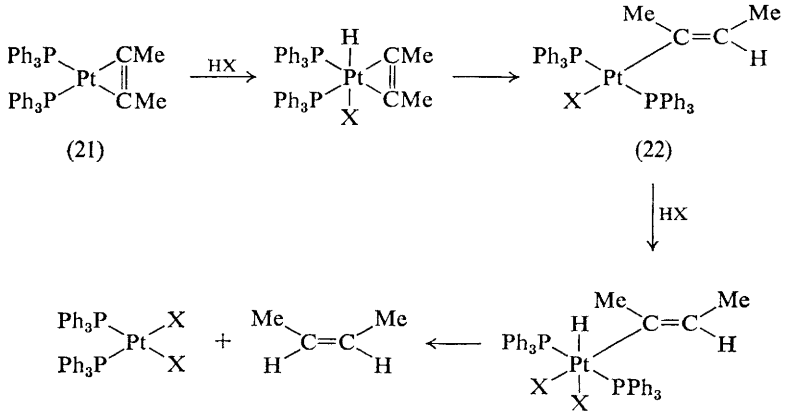
investigated by stereochemical and deuterium-labelling techniques. Radical intermediates of significant lifetime are ruled out by the stereospecificity of the reduction. The most likely mechanism is formation of a palladium hydride species RPdH which undergoes a concerted elimination of RH, leaving palladium metal.[29]

The mechanisms of formation of π-allyl–palladium complexes, both from tetrachloropalladate(II) and allyl alcohol in acidic aqueous solution [30] and from palladium dichloride and alkenes in, for example, dimethylformamide,[31] have been discussed. Allylpalladium halide dimers react

[27] H. T. Dodd and J. F. Nixon, *J. Organometallic Chem.*, 1971, **32**, C67.
[28] D. A. White and G. W. Parshall, *Inorg. Chem.*, 1970, **9**, 2358.
[29] E. Vedejs and M. F. Salomon, *J. Amer. Chem. Soc.*, 1970, **92**, 6965.
[30] R. Pietropaolo, P. Uguagliati, T. Boschi, B. Crociani, and U. Belluco, *J. Catalysis*, 1970, **18**, 338.
[31] F. Conti, M. Donati, G. F. Pregaglia, and R. Ugo, *J. Organometallic Chem.*, 1970, **30**, 421.

with butadiene, with displacement of allyl groups by the diene. The rates of these reactions are proportional to the square root of the concentration of butadiene.[32]

Platinum.—Whereas the bis-triphenylphosphineplatinum–ethylene complex react with acids HX to give $Pt(H)(X)(PPh_3)_2$ plus free ethylene, the corresponding alkyne compounds give $PtX_2(PPh_3)_2$ plus alkene. This reaction of platinum–alkyne complexes has been studied, particularly for the but-2-yne compound (21), with several acids in a range of solvents. The nature and distribution of the organic products can be rationalized according to the mechanism shown in Scheme 2, in which platinum(IV)–hydride

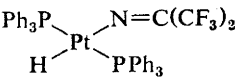


Scheme 2

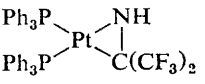
and isolable vinyl intermediates are involved.[33] The reverse of the alkyne to vinyl type of transformation exemplified by (21) → (22) is represented by the ring-closure reaction (23) → (24).[34] This reaction takes place only in the presence of added phosphine, whose role is to promote isomerization of (23) to the *cis*-form. A similar alkyne complex (25), containing cyano-groups, is obtained from the reaction of tetrakis-triphenylphosphineplatinum(0) with dicyanoacetylene. The dicyanoacetylene reacts with the bis-triphenylphosphineplatinum(0) which in solution is present in equilibrium with the tris- and tetrakis-complexes.[35] The platinum(II) complexes *trans*-$[PtClMeL_2]$, with L = PMe_2Ph or $AsPh_3$, react with alkynes in alcohol solutions to produce alkoxycarbene complexes,[36] and react with

[32] V. N. Sokolov, G. M. Khvostic, I. Ya. Poddubnyi, and G. P. Kondratenkov, *J. Organometallic Chem.*, 1971, **29**, 313.
[33] P. B. Tripathy and D. M. Roundhill, *J. Organometallic Chem.*, 1970, **24**, 247; P. B. Tripathy, B. W. Renoe, K. Adzamli, and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1971, **93**, 4406.
[34] B. Cetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215.
[35] G. L. McClure and W. H. Baddley, *J. Organometallic Chem.*, 1970, **25**, 261.
[36] M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 1711.

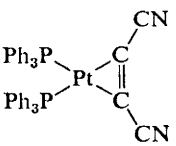
perfluoronitriles to produce cationic imino-ether and nitrile complexes.[37] In both cases carbonium ion intermediates of the type (26), in which the



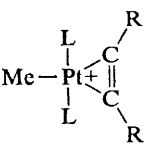
(23)



(24)



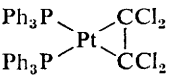
(25)



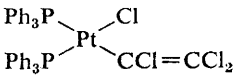
(26)

ion is stabilized by the proximity of the platinum, play an important role.[38]

Whereas the reaction of tetrakis-triphenylphosphineplatinum with chloroalkenes in neutral solvents gives a chloroalkene and then a chlorovinyl compound, for example (27) and (28) respectively from tetra-

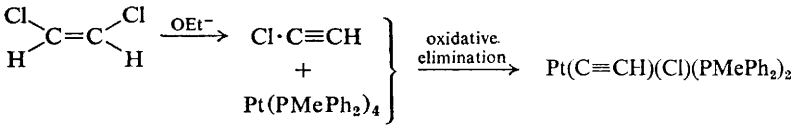


(27)



(28)

chloroethylene,[39] if a similar reaction is carried out in the presence of base, for instance ethoxide ion, then it is possible to produce a σ-acetylide compound. An example of this is illustrated in Scheme 3.[40] The fact

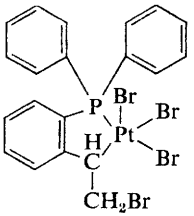


Scheme 3

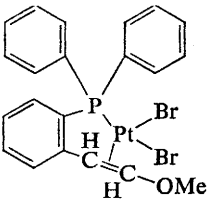
that *trans*-stilbene is produced from the reaction of the σ-alkenyl compound $Pt(CPh{=}CHPh)(Cl)(PPh_3)_2$ with hydrogen chloride indicates either that inversion at carbon accompanies platinum–carbon bond fission, or that there is a *cis* → *trans*-stilbene isomerization subsequent to platinum–carbon bond fission.[41]

[37] H. C. Clark and L. E. Manzer, *Chem. Comm.*, 1971, 387.
[38] M. H. Chisholm, H. C. Clark, and D. H. Hunter, *Chem. Comm.*, 1971, 809.
[39] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278; W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **14**, 201; 1968, **15**, 217.
[40] J. Lewis, B. F. G. Johnson, K. A. Taylor, and J. D. Jones, *J. Organometallic Chem.*, 1971, **32**, C62.
[41] B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc.* (*A*), 1971, 2667.

The compound Pt(LL)(Ph)(PPh_3), with LL = methoxydicyclopentadienyl, has both a platinum–carbon σ-bond and a platinum–alkene bond. Electrophilic reagents, such as mercury(II) chloride, break the platinum–carbon σ-bond; nucleophilic reagents such as methoxide or cyanide break the platinum–alkene bond. Similar reactions of the pyridine analogue Pt(LL)(Ph)(py) are more complicated, because it is easier to replace the pyridine by, for example, chloride at the same time as the electrophilic reagent is attacking the platinum–carbon σ-bonding.[42] Platinum–carbon σ-bonding appears to be changed into platinum–carbon π-bonding during alcoholysis of the compound (29); the product is (30).[43]



(29)



(30)

As a logical extension of the formation of metal–carbon bonds, the following useful preparative route to metal–silicon bond formation may be mentioned:

$$R_3Si{\cdot}NMe_2 + L_nMH \longrightarrow R_3Si{\cdot}ML_n + NHMe_2$$

the mechanism of this reaction varies with the nature of the metal (M), from S_N2 for M = Pt to S_N1cb for M = Group VI metal.[44]

5 Group I

Copper and Silver.—Decomposition of 1-propenyl- and 2-butenyl-copper(I) and -silver(I) compounds to hexa-2,4-dienes occurs with retention of configuration. This indicates a non-radical mechanism, for intermediate vinylic radicals would be of very low configurational stability and would thus lead to extensive isomerization.[45] The decomposition of n-propylcopper(I) gives propene and propane, but no six-carbon molecules. It therefore seems highly unlikely that propyl radicals are intermediates.[46] Perhaps, as in the earlier but very similar report on the absence of eight-carbon molecules from the decomposition of triphenylphosphine-n-butylcopper,[47] the mechanism involves initially the separation of alkene,

[42] G. Carturan, L. Busetto, A. Palazzi, and U. Belluco, *J. Chem. Soc.* (*A*), 1971, 219.
[43] M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *J. Organometallic Chem.*, 1971, **26**, 293.
[44] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1970, 2594.
[45] G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, 1971, **93**, 1379.
[46] K. Wada, M. Tamura, and J. Kochi, *J. Amer. Chem. Soc.*, 1970, **92**, 6656.
[47] G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, *J. Amer. Chem. Soc.*, 1970, **92**, 1426.

leaving a copper(I)–hydride intermediate. However, the autocatalytic nature of the decomposition of n-propylcopper(I) can be attributed to the intermediacy of a dinuclear copper(0) intermediate.[46]

6 Group III

Thallium.—The decomposition of pyridinomethylthallium(III) in aqueous solution in the presence of chloride is a redox reaction since the inorganic products are thallium(I) species, but the important step is S_N2 attack of chloride at the methylene-carbon, with synchronous displacement of the thallium. The determined activation parameters, $\Delta H^{\ddagger} = 28$ kcal mol^{-1} and $\Delta S^{\ddagger} = +14$ cal deg^{-1} mol^{-1} for reaction of $TlCl(CH_2pyH)^{2+}$ with elimination of TlCl, are consistent with an S_N2 mechanism.[12] The decomposition of $RTlX_2$ into TlX + RX, in pyridine solution, also proceeds by nucleophilic attack, by pyridine or halide, at carbon.[48]

General.—The kinetic patterns observed, and mechanisms operating, in transition-metal–carbon bond cleavage and formation are strongly dependent on the strength and stability of the metal–carbon bonding. Until recently it has generally been accepted that π-accepting ligands stabilize metal–carbon σ-bonds by electronic effects. It now appears that the main function of these ligands is to block co-ordination sites on the metal and so inhibit hydride transfer and alkene elimination.[49] Supporting ligands are not always necessary for the isolation of kinetically inert compounds containing metal to alkyl-carbon σ-bonds. Thus if the reaction:

$$M-CH_2CH_2R \longrightarrow MH + CH_2{=}CHR$$

can be prevented by replacing the β-hydrogens by groups which cannot readily be transferred to the metal, then compounds such as $Mo_2(CH_2SiMe_3)_6$ and $Mo_2(CH_2CMe_3)_6$ can be isolated.[50]

[48] M. D. Johnson, *Chem. Comm.*, 1970, 1037.
[49] G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *Chem. Comm.*, 1970, 1369; M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometallic Chem.*, 1970, **25**, C36.
[50] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1971, 1079.

3
Homogeneous Catalysis

BY R. D. W. KEMMITT AND J. BURGESS

1 General

Two reviews deal with the relation between homogeneous and heterogeneous catalysis. One of these reviews is of a general physical and theoretical nature,[1] while the other is concerned with specific classes of compounds — alkenes, alkynes, and fats — and concentrates on their hydrogenation and isomerization.[2] Homogeneous catalysis by ruthenium complexes has been reviewed.[3] The application of molecular orbital symmetry rules, to organic as well as to organometallic reaction mechanisms, has been discussed,[4] and a set of rules similar to, but simpler to apply than, the Woodward–Hoffmann rules has been described.[5]

Two further review articles discuss the factors which determine the catalytic reactivities of transition-metal complexes.[6, 7] The influence of the non-reacting ligands present in the complexes is described in detail, especially from the point of view of being able to tailor certain types of complex to give just the right catalytic properties.[7] A specific example of an investigation of the effects of ligands on catalytic activity is provided in the study of the complexes $MX(CO)L_2$, where M = Rh or Ir, X = Cl, Br, or I, and L = a phosphine or phosphite.[8]

Often in homogeneous catalysis reactions the active catalyst is not the actual transition-metal compound added but some species derived from this by loss of a ligand. For the complex tris-triphenylphosphinerhodium(I) chloride there has been some argument as to the equilibrium position for reaction (1). N.m.r. experiments suggested that the equilibrium lay well

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3 \qquad (1)$$

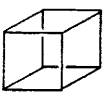
to the left, whereas molecular weight determinations suggested that the equilibrium position was close to complete dissociation. It has now been shown that the molecular weight results are not reliable, since the original experiments were conducted in the presence of oxygen, which has a large

[1] V. A. Tulupov, *Russ. J. Phys. Chem.*, 1970, **44**, 478.
[2] E. N. Frankel and H. J. Dutton, *Topics Lipid Chem.*, 1970, **1**, 161.
[3] B. R. James, *Inorg. Chim. Acta Rev.*, 1970, **4**, 73.
[4] R. G. Pearson, *Chem. Eng. News*, 1970, **48**, 66.
[5] R. G. Pearson, *Accounts Chem. Res.*, 1971, **4**, 152.
[6] A. A. Vlcek, *Chem. listy*, 1970, **64**, 449.
[7] G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1971, **10**, 105.
[8] W. Strohmeier and W. Rehder-Stirnweiss, *Z. Naturforsch.*, 1970, **25b**, 549.

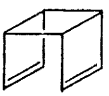
effect on the system.[9] The equilibrium constant for reaction (1) has been determined spectrophotometrically, in benzene solution, and the extent of dissociation of the tris-triphenylphosphine complex is indeed small.[10] Equilibrium ligand dissociation has also been described for the catalyst *trans*-$[PdCl_2(PhCN)_2]$.[11] Vaska's iridium(I) complex $IrCl(CO)(PPh_3)_2$ is reluctant to add a further molecule of triphenylphosphine, but the complex $IrCl(CO)(PMe_2Ph)_2$ readily adds another molecule of phosphine to give the five-co-ordinate complex $IrCl(CO)(PMe_2Ph)_3$.[12]

2 Isomerization

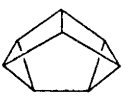
Strained Carbocyclic Systems.—A large number of examples of catalysis of valence isomerization of strained ring compounds by transition-metal complexes has been considered during the period covered by this Report. The most commonly used metal centres are rhodium and silver, and much of the interest in this field is concentrated on determining and accounting for the differences, in effectiveness and in the nature of the products, between rhodium catalysts and silver catalysts. Thus, for instance, in the presence of $[RhCl(nor)]_2$ or $[RhCl(cod)]_2$, cubane (1) isomerizes to the diolefin (2),[13] but in the presence of silver perchlorate cubane isomerizes to cuneane (3).[14]



(1)



(2)



(3)

It has been suggested that the number of *d*-electrons on the metal may be important in determining the mechanism and products of isomerization, but the observation that the d^8 cation palladium(II) also causes the isomerization of cubane to cuneane, like the d^{10} silver(I) but unlike d^8 rhodium(I) complexes, eliminates this idea. The redox properties of the respective complexes may be relevant – rhodium(I) is much readier to undergo oxidative addition than silver(I) or palladium(II).[14] One factor which may be of considerable importance is the relative strengths of metal–carbon bonds. It is energetically much more favourable to insert rhodium(I) into a carbon–carbon bond than to insert silver(I) into such a bond.[15] Though the different courses of isomerizations catalysed by rhodium(I) and silver(I) complexes may be ascribed to the operation of a non-concerted mechanism for the former but

[9] D. D. Lehman, D. F. Shriver, and I. Wharf, *Chem. Comm.*, 1970, 1486.
[10] H. Arai and J. Halpern, *Chem. Comm.*, 1971, 1571.
[11] M. Kubota, B. A. Denechaud, P. M. McKinney, T. E. Needham, and G. O. Spessard, *J. Catalysis*, 1970, **18**, 119.
[12] J.-Y. Chen and J. Halpern, *J. Amer. Chem. Soc.*, 1971, **93**, 4939.
[13] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515.
[14] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 6366.
[15] J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, 1970, **92**, 7499.

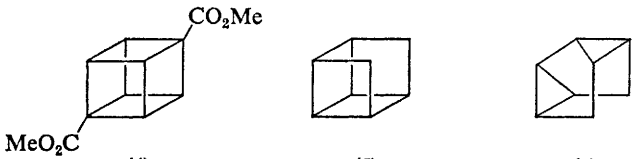
of a concerted mechanism for the latter,[16] the initial step may in each case be similar. This common initial step is suggested to be the interaction of the metal ion with a carbon–carbon bond.[15] If the carbon–carbon bond be a double bond, then interaction as in normal metal–alkene complexes is possible, but even for a formally single bond with only a little π-character there could be enough interaction to initiate reaction.[17] The role of co-ordinate bonding in these isomerizations that are catalysed by transition-metal complexes has been discussed in the light of orbital symmetry requirements.[18]

After these general introductory sentences, we shall mention the numerous specific examples of isomerization that have been reported recently. The reactions detailed are grouped according to the type of organic compound isomerized rather than by the transition metal.

The rate law for the isomerization of cubane (1) to cuneane (3) in the presence of silver perchlorate is:

$$-\mathrm{d[cubane]}/\mathrm{d}t = k[\mathrm{cubane}][\mathrm{AgClO_4}] \qquad (2)$$

Rate constants k have been determined for several substituted cubanes, and their values show that isomerization rates vary greatly with the nature of the substituents. Thus the derivative (4) isomerizes 17 000 times as rapidly as cubane itself.[14] Logarithms of k values correlate linearly with substituent σ^* values.[19] The rate law for isomerization of seco-cubane (5) derivatives in the presence of silver(I) is exactly the same as that for isomerization of cubanes [equation (2) above].[20] The products of isomerization are tetracyclo[3,3,0,$0^{2,8}$,$0^{4,6}$]octanes (6). Copper bronze also forms an effective



(4) (5) (6)

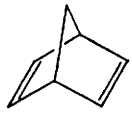
catalyst for isomerization of cubane derivatives; this reaction seems to bear a considerable resemblance to the rhodium(I)- and silver(I)-catalysed reactions.[21]

The isomerization of quadricyclene (7) to norbornadiene (8), catalysed by $[RhCl(CO)_2]_2$, is thought to proceed by a non-concerted mechanism, from the evidence provided by the isolation of new rhodium(I) compounds

[16] L. A. Paquette, *J. Amer. Chem. Soc.*, 1970, **92**, 5765.
[17] L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.
[18] F. D. Mango, *Tetrahedron Letters*, 1971, 505.
[19] G. F. Koser, *Chem. Comm.*, 1971, 388.
[20] L. A. Paquette, R. S. Beckley, and T. McCreadie, *Tetrahedron Letters*, 1971, 775; H. Westberg and H. Ona, *Chem. Comm.*, 1971, 248.
[21] N. B. Chapman, J. M. Key, and K. J. Toyne, *Tetrahedron Letters*, 1970, 5211.



(7)



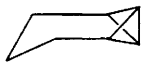
(8)

derived from these compounds. For $[RhCl(nor)]_2$-catalysed conversion of quadricyclene into norbornadiene, the rate law is:

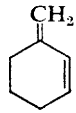
$$-\,d[\text{quadricyclene}]/dt = k[\text{quadricyclene}][\{RhCl(nor)\}_2]$$

The rate of isomerization is not affected by the addition of an excess of norbornadiene, which indicates that equilibrium loss of norbornadiene from the rhodium(I) catalyst is not an essential feature of the mechanism.[22] This same isomerization has been taken as a model reaction for an investigation of the effects of varying the metal centre and the nature of the ligands present on catalytic effectiveness. The initial co-ordination of the quadricyclene to a transition-metal centre can be inhibited by the presence of added ligands such as pyridine; the subsequent isomerization step is under the control of the electronic effects of the other ligands present that are bonded to the transition metal.[23]

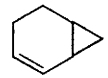
The products of isomerization of tricyclo[4,1,0,$0^{2,7}$]heptane (9) depend on the nature of the catalyst. In the presence of $[RhCl(CO)_2]_2$, compound (10) is produced; in the presence of $RhCl(CO)(PPh_3)_2$, both (10) and (11)



(9)

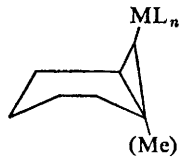


(10)



(11)

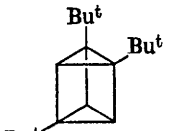
are produced.[24] A more extensive study of isomerization of the tricycloheptane (9) and its 1-methyl derivative, in the presence of one of a group of eleven catalysts, suggests that the transition-metal complexes play a common role in acting as Lewis acids to generate a carbonium ion intermediate of structure (12).[25] This idea of a common initial step in isomerization mechanisms for a variety of transition-metal catalysts has already



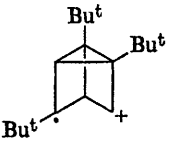
(12)

[22] L. Cassar and J. Halpern, *Chem. Comm.*, 1970, 1082.
[23] J. Manassen, *J. Catalysis*, 1970, **18**, 38.
[24] P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 1971, **93**, 1042.
[25] P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 1971, **93**, 4597.

been mentioned, though in a slightly different guise, in the first paragraph of this section.[15] The possibility of a common initial step of electron transfer to the catalyst acting as a Lewis acid may apply not only to the usual transition-metal catalysts but also to catalysts such as mercury(II) chloride or tin(II) chloride, and to organic electron-acceptors, for example trinitrobenzene. All of these compounds catalyse the isomerization of tri-t-butylprismane (13). The range of products observed, whose natures depend on the catalyst, can all be derived *via* an intermediate prismane radical cation (14), generated by a one-electron transfer to the catalyst.[26] The tricycloheptane (9) isomerizes to *cis,cis*-1,3-cycloheptadiene (15) in the



(13)



(14)


(15)

presence of silver tetrafluoroborate in deuteriochloroform solution.[27] The dependence of the rate of this isomerization on the concentration of tricycloheptane indicates that a silver(I)–tricycloheptane complex is a fairly stable intermediate. Indeed, it proved possible to estimate its formation constant, which is 0.19 in solution.[28]

In the compounds mentioned so far, there have been considerable steric constraints to isomerization imposed by their multiply connected structures. This potential source of complication can be avoided by working with simpler strained cyclic compounds, for example bicyclobutanes (16). In fact, the tricycloheptane (9) forms a link between the two types of compound, for it is a bicyclobutane with an additional trimethylene bridge.[28, 29] This is obvious from a comparison of (16) and (17); the latter

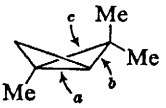

(16)


(17)

is an alternative representation of (9), which brings out this similarity. Most studies of isomerization of bicyclobutanes use di- or tri-methyl derivatives rather than cyclobutane itself, as the methyl groups form convenient labels for monitoring stereochemistry. The products of isomerization are different for the silver(I)-catalysed reaction than for thermal

[26] K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1971, **93**, 1270.
[27] L. A. Paquette, G. R. Allen, and R. P. Henzel, *J. Amer. Chem. Soc.*, 1970, **92**, 7002.
[28] L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, 1971, **93**, 1288.
[29] M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Comm.*, 1971, 486.

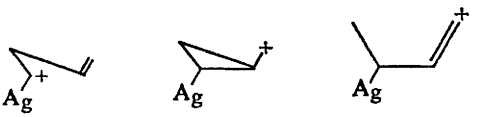
isomerization.[30] They are also different for silver(I) catalysis than for palladium(II) catalysis, which is a different situation from cubane isomerization, where the same product, cuneane, is the result of silver(I) or of palladium(II) catalysis.[29] Even different complexes of the same transition metal can lead to different products, as in palladium(II) catalysis of isomerization of trimethylbicyclobutane (18). In the presence of $PdCl_2$-



(18)

$(PhCN)_2$, bonds *a* and *b* break; in the presence of di-μ-chloro-bis-π-allylpalladium(II), bonds *b* and *c* break.[31] Isomerization catalysed by $[RhCl(CO)_2]_2$ or by $[RuCl_2(CO)_3]_2$ also results in breaking bonds *a* and *b*, but in isomerization catalysed by $[CuC_6F_5]_4$ the third combination of bonds (*a* and *c*) break.[32]

There has been some argument on the nature of intermediates in the silver(I)-catalysed isomerizations of these bicyclobutanes. Evidence has been presented, from the nature and distribution of products from isomerization of tetrasubstituted bicyclobutanes, for the breaking of two strained carbon–carbon bonds, to generate argentocarbonium ions of the type (19).[33] This situation contrasts with rhodium(I) catalysis of isomerization, where only one carbon–carbon bond is thought to be broken, and indeed comparisons of bicyclobutane isomerizations catalysed by silver(I) perchlorate and by bis-benzonitrilepalladium(II) dichloride,[34] and of silver(I)-catalysed isomerizations of bicyclobutanes and of tricycloheptane,[35] are claimed to indicate that only one carbon–carbon bond is broken in forming the argentocarbonium ion intermediate (20). However, it is admitted that (20) may subsequently react further to form (19), or to form (21) instead.



(19) (20) (21)

The product of thermal or of rhodium(I)-catalysed isomerization of bicyclopentane (22) is cyclopentene (23). The thermal reaction occurs at

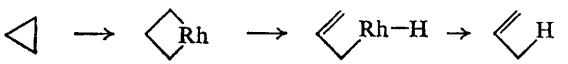
[30] M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 1043.
[31] P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Comm.*, 1971, 842.
[32] P. G. Gassman and F. J. Williams, *Tetrahedron Letters*, 1971, 1409.
[33] L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, 1971, **93**, 2335.
[34] M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 4610.
[35] M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 4611.

ca. 300 °C; in the presence of $[RhCl(CO)_2]_2$, isomerization takes place smoothly at *ca.* 25 °C. In this case only one carbon–carbon bond has to break.[36] The isomerization of the norbornene derivative (24) to (25) is a

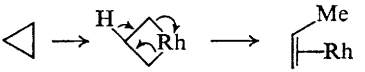


(22) (23) (24) (25)

very similar reaction; it is catalysed by $RhCl(PPh_3)_3$. Deuterium-labelling experiments indicate that here the opening of the cyclopropyl ring involves the mechanism outlined in Scheme 1 rather than that in Scheme 2.[37]

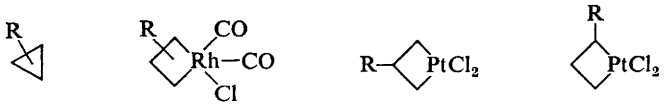


Scheme 1



Scheme 2

Substituted cyclopropanes (26) react in the presence of $[RhCl(CO)_2]_2$ to give alkenes by isomerization and carbonyl compounds by carbonyl insertion. The intermediate (27) is thought to be common to both reactions.[38] Platinum(II) can also insert into cyclopropanes; the stereochemistry of the product, (28) *vs.* (29), is determined by the balance



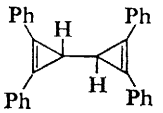
(26) (27) (28) (29)

between the energy needed to break the respective carbon–carbon bonds and the energy regained by the subsequent formation of the two platinum–carbon bonds.[39] The effects of methyl substituents on the stereochemistry of opening of cyclopropyl rings have also been investigated for several methylbicycloheptanes in the presence of a variety of catalysts.[40]

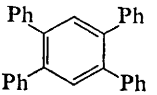
The bicyclopropenyl compound (30) isomerizes in the presence of silver perchlorate to tetraphenylbenzene (31), *via* the Dewarbenzene derivative

[36] P. G. Gassman, T. J. Atkins, and J. T. Lumb, *Tetrahedron Letters*, 1971, 1643.
[37] T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, 1971, **93**, 1049.
[38] K. G. Powell and F. J. McQuillin, *Chem. Comm.*, 1971, 931.
[39] K. G. Powell and F. J. McQuillin, *Tetrahedron Letters*, 1971, 3313.
[40] C. Pinazzi, J. Brossas, J.-C. Brosse, and F. Clouet, *Compt. rend.*, 1971, **272**, *C*, 2131.

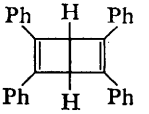
(32). There is no evidence for the intermediacy of either of the suggested thermal isomerization intermediates tetraphenylprismane or 1,2,3,4-tetraphenyl-Dewarbenzene.[41] The isomerization of hexamethyl-Dewarbenzene to hexamethylbenzene is catalysed by the usual transition-metal complex catalysts.[42] In the presence of palladium(II) chloride or of $[RhCl(CO)_2]_2$, methylenecyclobutane (33) does not undergo isomerization, but gives π-allyl complexes of the type (34).[43] This reaction may be



(30)



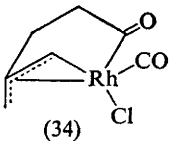
(31)



(32)



(33)

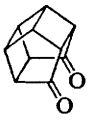


(34)

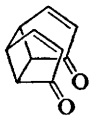
compared with the reaction of substituted cyclopropanes with this same catalyst, mentioned in the previous paragraph, where both insertion and isomerization take place.[38]

The oxidative ring cleavage of cyclopropenes [44] and of cyclobutenes [45] by thallium(III), mercury(II), palladium(II), or lead(IV) bears some resemblance to the isomerizations discussed above. In particular, the first step in the oxidations is probably insertion of the metal into a carbon–carbon bond, as in isomerization.

The preceding discussion has dealt entirely with strained hydrocarbons. There have been one or two extensions to hydrocarbon derivatives. Thus the isomerization of the diketone (35) to the unsaturated diketone (36),



(35)

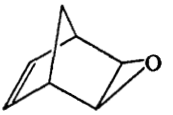


(36)

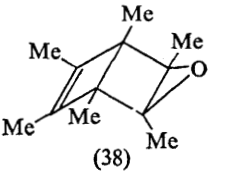
which is catalysed by the rhodium(I) complexes $[RhCl(CO)_2]_2$ or $[RhCl(nor)]_2$,[46] is very closely analogous to hydrocarbon isomerizations

[41] R. Weiss and C. Schlierf, *Angew. Chem. Internat. Edn.*, 1971, **10**, 811.
[42] C. J. Attridge and S. J. Maddock, *J. Organometallic Chem.*, 1971, **26**, C65.
[43] R. Rossi, P. Diversi, and L. Porri, *J. Organometallic Chem.*, 1971, **31**, C40.
[44] T. Shirafuji, Y. Yamamoto, and H. Nozaki, *Tetrahedron Letters*, 1971, 4713.
[45] J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Comm.*, 1971, 40.
[46] P. E. Eaton and S. A. Cerefice, *Chem. Comm.*, 1970, 1494.

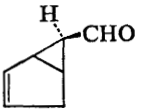
already mentioned. The rearrangements of the epoxides of norbornadiene (37) and of hexamethyl-Dewarbenzene (38), to give the aldehyde (39) and the ketone (40) respectively, represent a greater extension of the hydrocarbon



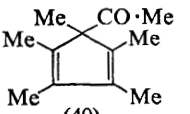
(37)



(38)

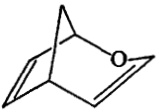


(39)

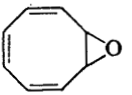


(40)

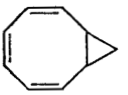
work, for in isomerization of these epoxides it is the heterocyclic ring which is cleaved. Thus norbornadiene epoxide rearranges firstly to (41), before undergoing further reaction to give (39). The first step probably involves insertion of the rhodium into an oxygen–carbon bond.[47] The isomerization of cyclo-octatetraene epoxide (42) takes a different course



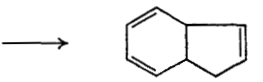
(41)



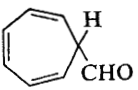
(42)



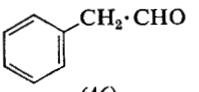
(43)



(44)



(45)

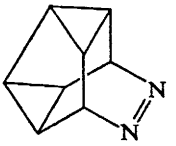


(46)

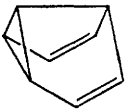
[47] R. Grigg and G. Shelton, *Chem. Comm.*, 1971, 1247.

from that of its hydrocarbon analogue (43). Whereas in the presence of $[RhCl(CO)_2]_2$ (43) isomerizes to the dihydroindene (44), in the presence of the same catalyst the epoxide (42) isomerizes to the cycloheptatriene aldehyde (45), which itself undergoes slow (thermal) rearrangement to the benzene derivative (46).[48]

On heating in the presence of transition-metal catalysts, the diazapentacyclodecene (47) gives cyclo-octatetraene, or cyclo-octatetraene plus the diene (48), depending on the conditions. The key step in the formation of



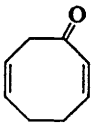
(47)



(48)

the cyclo-octatetraene is the transition-metal-catalysed isomerization of (48).[49]

Two examples have been reported of reactions which are the reverse of the isomerizations described so far, in that they involve a reduction in the number of carbon–carbon π-bonds and an increase in the number of carbon–carbon σ-bonds. Photolysis of cyclo-octa-2,6-dienone (49) in the presence of copper(I) compounds gives the tricyclic ketone (50).[50] The other example is a step in the silver(I)-catalysed benzyne cycloaddition.[51]



(49)

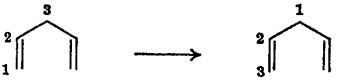


(50)

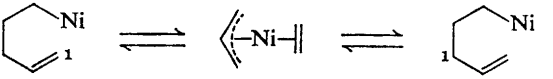
Alkenes.—Kinetic studies of alkene isomerization, catalysed by transition-metal complexes, are rare. One recent example is isomerization of hex-1-ene, catalysed by $Co(N_2)(PPh_3)_3$, where the rate is proportional to the square of the catalyst concentration; this suggests hydrogen migration in a dinuclear intermediate.[52] The activation enthalpy for this isomerization is 10.1 kcal mol^{-1}, the activation entropy being $-$ 21 cal deg^{-1} mol^{-1}. Isomerization

[48] R. Grigg, R. Hayes, and A. Sweeney, *Chem. Comm.*, 1971, 1248.
[49] R. M. Moriarty, Chin-Lung Yeh, and N. Ishibi, *J. Amer. Chem. Soc.*, 1971, **93**, 3085.
[50] R. Noyori, H. Inoue, and M. Kato, *Chem. Comm.*, 1970, 1695.
[51] L. A. Paquette, *Chem. Comm.*, 1971, 1076.
[52] J. Kovaćs, G. Speier, and L. Markó, *Inorg. Chim. Acta*, 1970, **4**, 412.

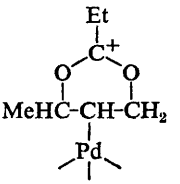
mechanisms are more commonly investigated by labelling experiments and subsequent characterization of products. Positional labelling is usually achieved by replacing hydrogen atoms in the alkene either by deuterium or by methyl groups. Both methods are illustrated by a study of the isomerization of penta-1,4-diene, catalysed by $NiCl_2$–PR_3–$AlClR_2$ catalysts, where both ^2H- and Me-labelling experiments show that isomerization occurs thus:



This is consistent with an isomerization mechanism involving:[53]



Both kinetic and labelling experiments on isomerization of enol propionates and vinyl halides indicate that the normally considered mechanisms of inter- or intra-molecular hydride transfer or of reversible π-allyl complex formation [54] are not applicable here.[55] Rather, in the presence of palladium(II) compounds, the reaction appears to proceed through a 1,3-acetoxonium ion with a palladium–carbon σ-bond, *e.g.* the ion (51).[56]



(51)

The influence of steric factors on reactivity and on selectivity has been discussed for the catalysis, by a variety of phosphine complexes of ruthenium, iridium, and platinum, of the isomerization of 4-vinylcyclohexane.[57] Titanium tetra-(−)-menthoxide plus tri-isobutylaluminium catalyse stereoselective isomerization of racemic alk-1-enes.[58]

[53] R. G. Miller, H. J. Golden, D. J. Baker, and R. D. Stauffer, *J. Amer. Chem. Soc.*, 1971, **93**, 6308.
[54] P. Taylor and M. Orchin, *J. Organometallic Chem.*, 1971, **26**, 389.
[55] P. M. Henry, *J. Amer. Chem. Soc.*, 1971, **93**, 3547.
[56] P. M. Henry, *Chem. Comm.*, 1971, 328.
[57] J. E. Lyons, *J. Org. Chem.*, 1971, **36**, 2497.
[58] C. Carlini, D. Politi, and F. Ciardelli, *Chem. Comm.*, 1970, 1260.

Some recently reported examples of homogeneous catalysis of isomerization of alkenes by transition-metal complexes are listed in Table 1.[59-74]

Table 1 *Homogeneous catalysis of isomerization of alkenes*

Catalyst	*Substrate*	*Ref.*
$W(CO)_4$(cod)	alk-1-enes	59
$M(CO)_6$[a]	stilbenes	60
$[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$[b]	dichlorobutenes	61
$Fe(acac)_3$	dichlorobutenes	61
$RuCl_2(PPh_3)_3$[c]	5-vinylnorbornene	57
$RuCl_2(PPh_3)_3$[c]	alkenes	62
$Ru(H)(NO)(PR_3)_3$	hex-1-ene	63
$Os(H)(NO)(PR_3)_3$	hex-1-ene	63
$Co(H)(CO)_4$	dimethyl maleate	54
$Co(H)(CO)_{4-n}(PR_3)_n$	alkenes	64
$[Co(CO)_2(PR_3)_n]$[b]	alkenes	65
$Co(N_2)(PPh_3)_3$[b]	hex-1-ene	52
$RhCl(PPh_3)_3$	1,2-bis(phenylpropionyl)benzene	66
$Rh(H)(CO)(PPh_3)_3$	heptenes	67
$[RhCl_2(h^5\text{-}C_5Me_5)]_2$	cyclohexadienes	68
$[IrCl(cyclo\text{-}octene)_2]_2$–$PR_3$	alkenes	69
$[Ir(cod)(MeCN)_2]^+$	hex-1-ene	70
trans-$[IrCl(CO)(PPh_3)_2]$	alkenes	57
trans-$[IrCl(CO)(PPh_3)_2]$	cyclododeca-1,5,9-triene	71
$NiCl_2(PR^1{}_3)_2$–$AlClR^2{}_2$	penta-1,4-diene	53
$Ni(P\{O\text{-}o\text{-}tolyl\}_3)_2(C_2H_4)$	dienes	72
$[Ni(H)(P\{OEt\}_3)_4]^+$	penta-1,4-diene	73
Pd^{II} compounds	unsaturated esters, halides	55, 56
$Pt(PPh_3)_4$	dienes	74
$PtCl_2(PPh_3)_2$–$SnCl_2$	alkenes	57

[a] M = Mo or W, and this is photoisomerization; [b] Kinetic data reported; [c] Catalytic activity enhanced by oxygen or hydroperoxides.

[59] Jin-Liang Wang and H. R. Menapace, *J. Catalysis*, 1971, **23**, 144.
[60] M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 3285
[61] G. Henrici-Olivé and S. Olivé, *J. Organometallic Chem.*, 1971, **29**, 307.
[62] J. E. Lyons, *Chem. Comm.*, 1971, 562.
[63] S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 3068.
[64] G. F. Pregaglia, A. Andreetta, G. F. Ferrari, and R. Ugo, *J. Organometallic Chem.*, 1971, **30**, 387.
[65] G. F. Pregaglia, A. Andreetta, G. F. Ferrari, G. Montrasi, and R. Ugo, *J. Organometallic Chem.*, 1971, **33**, 73.
[66] E. Müller, E. Langer, H. Jäkle, H. Muhm, W. Hoppe, R. Graziani, A. Gieren, and F. Brandl, *Z. Naturforsch.*, 1971, **26b**, 305.
[67] W. Strohmeier and W. Rehder-Stirnweiss, *J. Organometallic Chem.*, 1971, **26**, C22.
[68] K. Moseley and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2844.
[69] H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *Chem. Comm.*, 1970, 1694.
[70] M. Green, T. A. Kuc, and S. H. Taylor, *Chem. Comm.*, 1970, 1553.
[71] C. J. Attridge and S. J. Maddock, *J. Chem. Soc.* (*C*), 1971, 2999.
[72] R. G. Miller, P. A. Pinke, R. D. Stauffer, and H. J. Golden, *J. Organometallic Chem.*, 1971, **29**, C42.
[73] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6785.
[74] L. W. Gosser and G. W. Parshall, *Tetrahedron Letters*, 1971, 2555.

A reaction closely related to the above isomerization reactions is that of cyclization of diallyl ether:



This reaction is catalysed by $RhCl_3,3H_2O$, in the presence of a trace of allyl alcohol. The mechanism is thought to include two insertion steps, and the intermediacy of a rhodium–hydride species.[75]

3 Disproportionation

Recent reports of homogeneous catalysis of alkene disproportionation and related reactions are listed in Table 2.[76–83] In the majority of cases there is

Table 2 *Homogeneous catalysis of disproportionation reactions*

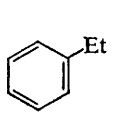
Catalyst	*Substrate*	*Products*	*Ref.*
$WCl_4(py)_2$–$AlEtCl_2$	*cis*-pent-2-ene	but-2-ene + hex-3-ene[a]	78
$W(CO)_5(PPh_3)$–$AlEtCl_2$	pent-2-ene	but-2-ene + hex-3-ene	79
$[M(COR')(CO)_5]^-$–AlR_nCl_{3-n}[b]	pent-1-ene	oct-4-enes + ethylene	80
$ReCl_5$–$SnBu^n_4$	pent-2-ene	but-2-ene + hex-3-ene	81
$Co(NO)(PPh_3)_3$	nitric oxide	$Co(NO_2)(NO)_2(PPh_3)$ + N_2	82
$RhCl_3$–EtOH	4-vinylcyclohexene	ethylbenzene + ethylcyclohexene	76
$[Rh(cod)(MeCN)_2]^+$	cyclohexa-1,3-diene	benzene + cyclohexane	70
$Rh(h^5\text{-}C_5Me_5)(h^4\text{-}C_6H_8)$	cyclohexa-1,3-diene	benzene + cyclohexane	68
trans-$[PtCl_2(PEt_3)_2]$	$Me_3Si\cdot SiHMe_2$	$Me(SiMe_2)_nH$, $1 \leqslant n \leqslant 6$	77

[a] In toluene solution, pent-2-ene in the presence of WCl_6–$AlEtCl_2$ undergoes a Friedel–Crafts reaction with the solvent instead of undergoing the expected disproportionation (see ref. 83); [b] M = Mo or W.

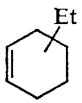
minimal discussion of the mechanism. The disproportionation of 4-vinylcyclohexene to ethylbenzene (52) and ethylcyclohexenes (53), catalysed by rhodium trichloride in ethanol, proceeds mainly through isomerization to (54), which itself subsequently disproportionates to the products (52) and

[75] A. Bright, J. F. Malone, J. K. Nicholson, J. Powell, and B. L. Shaw, *Chem. Comm.*, 1971, 712.
[76] C. J. Attridge and P. J. Wilkinson, *Chem. Comm.*, 1971, 620.
[77] K. Yamamoto, H. Okinoshima, and M. Kumada, *J. Organometallic Chem.*, 1971, **27**, C31.
[78] L. Bencze and L. Markó, *J. Organometallic Chem.*, 1971, **28**, 271.
[79] L. Ramain and Y. Trambouze, *Compt. rend.*, 1971, **273**, *C*, 1409.
[80] W. R. Kroll and G. Doyle, *Chem. Comm.*, 1971, 839.
[81] J. A. Moulijn and C. Boelhouwer, *Chem. Comm.*, 1971, 1170.
[82] M. Rossi and A. Sacco, *Chem. Comm.*, 1971, 694.
[83] V. M. Kothari and J. J. Tazuma, *J. Org. Chem.*, 1971, **36**, 2951.

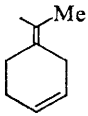
(53).[76] Evidence for a silylene intermediate in the disproportionation of methylsilicon hydrides, catalysed by *trans*-$[PtCl_2(PEt_3)_2]$, has been obtained by trapping the silylene with diphenylacetylene, giving (55).[77]



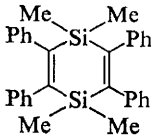
(52)



(53)



(54)



(55)

Symmetry arguments have been advanced to explain why under certain circumstances alkenes in the presence of transition-metal catalysts undergo disproportionation or dismutation, while under other conditions they undergo (cyclo-)addition. The latter often seems favoured by d^8 catalysts; high-spin d^4 and d^6 species should preferentially catalyse dismutation.[84] A discussion of symmetry considerations in heterogeneous catalysis of alkene disproportionation or dismutation contains many observations that are also of relevance to homogeneous systems.[85]

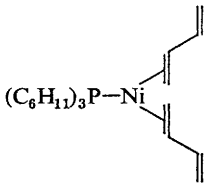
4 Oligomerization

Isolation and characterization of intermediates remain the most widely exploited method for deducing mechanisms of homogeneously catalysed oligomerizations, but a few examples of the usefulness of other methods have appeared. Tracer studies, using deuterium-labelled compounds, provide a means of following the progress of hydrogen atoms. Comparison of dimerization of C_2H_4 and of C_2D_4, catalysed by NiBr-(σ-1-naphthyl)$(PPh_3)_2$, shows that the active catalyst is a nickel hydride species whose hydrogen (deuterium) comes from the ethylene and not from the solvent, the triphenylphosphine, or the naphthyl group.[86] The nature and variation of e.s.r. signals from paramagnetic species can yield information on unstable organic radical intermediates, as in the study of homogeneous polymerization of phenylacetylene catalysed by a range of nickel and platinum complexes, for example *cis*-$[NiBr_2(PPh_3)_2]$ or *cis*-$[Pt(Cl)(H)(PPh_3)_2]$.[87] An example of the investigation of the stereochemistry of homogeneously catalysed polymerization is provided by the observation of a stereoregular propylene polymer from the dissymmetric allene (*R*)-penta-2,3-diene in the presence of π-allylnickel iodide.[88] The

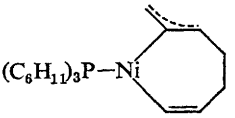
[84] G. L. Caldow and R. A. MacGregor, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 645.
[85] G. S. Lewandos and R. Pettit, *Tetrahedron Letters*, 1971, 789.
[86] K. Maruyama, T. Kuroki, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc Japan*, 1971, **44**, 2002
[87] D. Cordischi, A. Furlani, P. Bicev, M. V. Russo, and P. Carusi, *Gazzetta*, 1971, **101**, 526.
[88] L. Porri, R. Rossi, and G. Ingrosso, *Tetrahedron Letters*, 1971, 1083.

mechanism of stereospecific dimerization of styrene in the presence of π-allylnickel trifluoroacetate has been briefly discussed.[89]

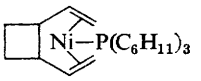
An intermediate isolated from the dimerization of butadiene in the presence of nickel complexes, thought [90] to be (56), has been shown to be the cyclic compound (57); it is quite possible that (56) is a transient precursor of (57).[91] This reassignment of structure may somewhat affect the arguments, based on reactivities of (58) and what was thought to be (56), for a mechanism involving formation of linear polymers followed by cyclization, rather than of concerted cyclo-oligomerization, for cyclopolymerization – at least in the present case of the cyclodimerization of butadiene to divinylcyclobutane (59) and vinylcyclohexene (60).[90] The



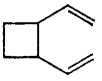
(56)



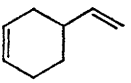
(57)



(58)



(59)



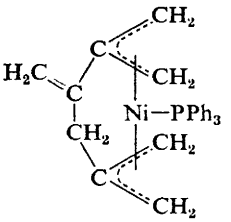
(60)

first step in allene oligomerization, catalysed by nickel–phosphine complexes, is the formation of Ni(allene)$(PPh_3)_2$. This has been characterized; it reacts with further allene molecules to generate linear or cyclic polymers.[92]

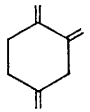
A rather later stage in the cyclo-oligomerization of allene, catalysed by $Ni(cod)_2$, is represented by the characterization of 2,3-bis-(π-allyl)-propenenickel(0), isolated as its triphenylphosphine complex (61). The final product in this reaction is 1,2,4,-trimethylenecyclohexane (62).[93] From a search for intermediates and determination of products, the mechanism of cyclotrimerization of tolan and phenylacetylene, catalysed by $Rh_4(CO)_{12}$, seems to involve the intermediacy of compounds of the type (63).[94] The isolation and characterization of intermediates, for example (64) from *cis*-addition of allylpalladium compounds to norbornadiene,[95] have also yielded much information on palladium-catalysed

[89] F. Dawans, *Tetrahedron Letters*, 1971, 1943.
[90] P. W. Jolly, I. Tkatchenko, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1971, **10**, 328, 329.
[91] J. M. Brown, B. T. Golding, and M. J. Smith, *Chem. Comm.*, 1971, 1240.
[92] R. J. de Pasquale, *J. Organometallic Chem.*, 1971, **32**, 381.
[93] S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Comm.*, 1971, 863.
[94] Y. Iwashita and F. Tamura, *Bull. Chem. Soc. Japan*, 1970, **43**, 1517.
[95] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1971, **30**, C45.

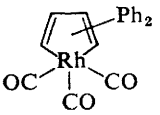
oligomerization of monoenes and dienes.[96] Although platinum(0) complexes have a marked effect on the trimerization of benzyne to triphenylene, it proved impossible to isolate a platinum(0)–benzyne intermediate, *e.g.* (65), analogous to the stable compounds (66).[97]



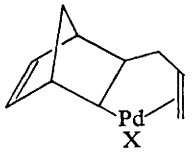
(61)



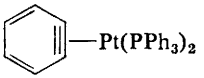
(62)



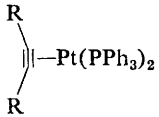
(63)



(64)

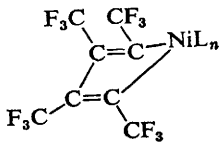


(65)



(66)

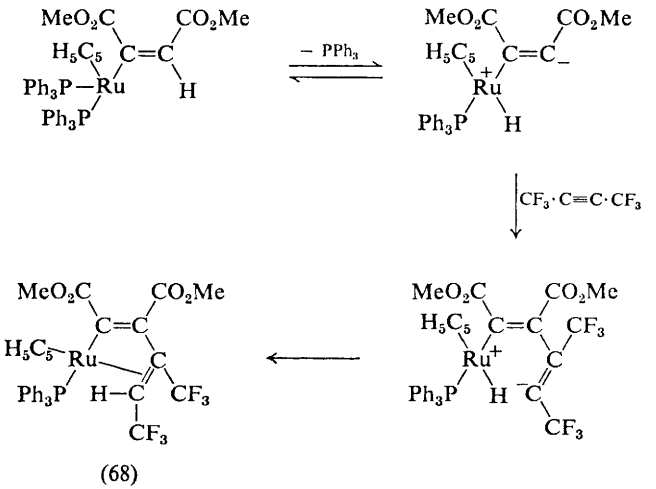
The precise mechanism of many oligomerization reactions remains open to discussion. We have already mentioned the question of whether cyclodimerization of butadiene, catalysed by nickel complexes, is a concerted or a stepwise process, of polymerization and then cyclization. The cyclotrimerization of alkynes is often thought to proceed by co-ordination of three alkyne molecules to the metal catalyst, with a subsequent concerted cyclization step. Recent studies of the cyclotrimerization of hexafluorobut-2-yne in the presence of $Ni(cod)_2$ or of arsine complexes, however, suggest a stepwise process in which an intermediate (67) is formed, to which



(67)

[96] D. Medema and R. van Helden, *Rec. Trav. chim.*, 1971, **90**, 304, 324.
[97] T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *J. Chem. Soc.* (*C*), 1971, 977.

Diels–Alder addition of a third hexafluorobut-2-yne molecule can take place.[98] Here the mechanism may be controlled by the presence of the strongly electronegative groups in the alkyne.[99] An alternative mechanism for cyclo-oligomerization involves a series of insertion reactions. Such a series of reactions is suggested by the sequence shown in Scheme 3. Though



(68)

Scheme 3

this scheme does not correspond to an oligomerization, it is an informative model, for the use of one di-CO_2Me and one di-CF_3 derivative provides stereochemical marking for the course of the reaction. Indeed, the sequence of groups in the product (68) suggests that insertion into carbon–hydrogen rather than into metal–carbon bonding has occurred.[100]

Intermolecular dimerizations of alkynes, catalysed by transition-metal complexes, are often reported; the first examples of intramolecular cyclizations have recently been reported. The cycloalkadiynes 1,7-cyclotridecadiyne (69) and 1,8-cyclotetradecadiyne (70), in the presence of



(69) (70)

[98] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 448.
[99] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981.
[100] T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *Chem. Comm.*, 1971, 852.

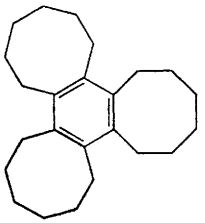
$Co(h^5\text{-}C_5H_5)(CO)_2$, give cyclobutadiene derivatives. The yield is much better from the former diyne, for stereochemical reasons.[101]

In many systems the active catalyst is, as in Scheme 3, generated by the loss of a ligand from the stable complex added. Sometimes the exact composition and nature of catalysts has an important bearing on the mechanism through the number of vacant sites which can become available on the metal. Thus in the presence of $RhBr_3,3H_2O$, diphenylacetylene reacts with methylmagnesium bromide to give stilbenes and condensation products such as 1,2,3-triphenylnaphthalene, but in the presence of $RhBr(PPh_3)_3$, where available sites on the metal are much more restricted, there is no condensation, and the sole product is *trans*-α-methylstilbene, the product of an insertion reaction.[102]

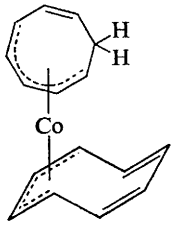
The present state of knowledge concerning homogeneous catalysis of ethylene polymerization by vanadium and by chromium compounds has been reviewed.[103] The relevance of orbital symmetry rules to transition-metal catalysis of [2 + 2] cycloaddition reactions has been discussed.[104]

Examples of oligomerization reactions, catalysed by transition-metal complexes, are given in Table 3.[105–131]

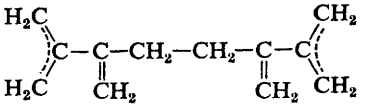
[101] R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 1970, **92**, 6071.
[102] M. Michman and M. Balog, *J. Organometallic Chem.*, 1971, **31**, 395.
[103] G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1971, **10**, 776.
[104] G. L. Caldow and R. A. MacGregor, *J. Chem. Soc.* (*A*), 1971, 1654; F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1971, **93**, 1123.
[105] C. Pinazzi, J. Brossas, J.-C. Brosse, and F. Clouet, *Compt. rend.*, 1971, **272**, *C*, 2131.
[106] H. A. Martin and R. O. de Jongh, *Rec. Trav. chim.*, 1971, **90**, 713.
[107] Y. Uchida, K. Furuhata, and S. Yoshida, *Bull. Chem. Soc. Japan*, 1971, **44**, 1966.
[108] Y. Uchida, K. Furuhata, and H. Ishiwatari, *Bull. Chem. Soc. Japan*, 1971, **44**, 1118.
[109] M. Michman and H. H. Zeiss, *J. Organometallic Chem.*, 1970, **25**, 161.
[110] R. P. A. Sneeden and H. H. Zeiss, *J. Organometallic Chem.*, 1971, **28**, 259.
[111] A. Carbonaro and A. Greco, *J. Organometallic Chem.*, 1970, **25**, 477.
[112] H. Kolshorn, H. Meier, and E. Müller, *Tetrahedron Letters*, 1971, 1469.
[113] J. R. Jones, *J. Chem. Soc.* (*C*), 1971, 1117.
[114] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 285.
[115] C. K. Brown, D. Georgiou, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3120.
[116] R. S. Dickson and H. P. Kirsch, *J. Organometallic Chem.*, 1971, **32**, C13.
[117] D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Comm.*, 1971, 331.
[118] G. Pantini, P. Racanelli, A. Immirzi, and L. Porri, *J. Organometallic Chem.*, 1971, **33**, C17.
[119] T. Ohta, K. Ebina, and N. Yamazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 1321.
[120] J. R. Jones and T. J. Symes, *J. Chem. Soc.* (*C*), 1971, 1124.
[121] M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1971, **10**, 77.
[122] M. Uchino, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1970, **24**, C63.
[123] J. Kiji, K. Masui, and J. Furukawa, *Chem. Comm.*, 1970, 1310.
[124] K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Japan*, 1970, **43**, 3630.
[125] A. Miyake, H. Kondo, and M. Nishino, *Angew. Chem. Internat. Edn.*, 1971, **10**, 802.
[126] F. J. Weigert, R. L. Baird, and J. R. Shapley, *J. Amer. Chem. Soc.*, 1970, **92**, 6630.
[127] T. Sakakibara, S. Nishimura, K. Kimura, S. Fujioka, and Y. Odaira, *Tetrahedron Letters*, 1971, 4719.
[128] K. Dunne and F. J. McQuillin, *J. Chem. Soc.* (*C*), 1970, 2196.
[129] K. Dunne and F. J. McQuillin, *J. Chem. Soc.* (*C*), 1970, 2203.
[130] M. L. H. Green and H. Munakata, *Chem. Comm.*, 1971, 549.
[131] G. Hata, K. Takahashi, and A. Miyake, *J. Org. Chem.*, 1971, **36**, 2116.



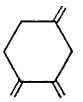
(71)



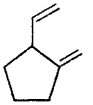
(72)



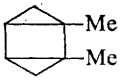
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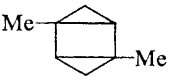
(74)



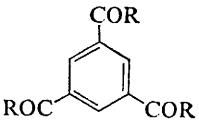
(75)



(76)



(77)



(78)

Table 3 *Homogeneous catalysis of oligomerization by transition-metal complexes*

Catalyst	*Substrate*	*Reaction/products*	*Ref.*
$TiCl_4$–$AlCl_nEt_{3-n}$	methylbicyclo[4,1,0]heptanes	polymerization	105
$Ti(1\text{-Me-allyl})(h^5\text{-}C_5H_5)_2$	alk-1-ynes	*trans*-polyalkenes	106
$Zr(allyl)_4$–$AlCl_nEt_{3-n}$	isoprene	dimerization	107
$VO(OEt)_3$–$AlEt_3$	isoprene	linear oligomers	108
$CrCl_3(THF)_3$–MeMgX	diphenylacetylene	phenylbenzenes, phenylnaphthalenes	109
$Cr(allyl)_3$, $Cr_2(allyl)_4$	but-2-yne	tetra-, penta-, hexa-methylbenzenes	110
WCl_6–$AlCl_nEt_{3-n}$	methylbicyclo[4,1,0]heptanes	polymerization	105
$Fe(but)_2(CO)$, Fe(but)(cot)(CO)	butadiene	dimerization	111
$Fe(CO)_5$	cyclo-octene	trimerization, (71)	112
CoX_2–AlX_nEt_{3-n}	monoenes	dimerization	113
$Co_4(CO)_{12}$	diphenylacetylene	cyclotrimerization	94
(72)	butadiene, diphenylacetylene	oligomerization	114
$RhBr_3,3H_2O$–MeMgBr	diphenylacetylene	oligomerization	102
$Rh_4(CO)_{12}$	diphenylacetylene	cyclotrimerization	94
$Rh(H)(CO)(PPh_3)_3$	alk-1-ynes	polymerization	115
$[Rh(h^5\text{-}C_5H_5)(CO)]_2$	alkynes	cyclization	116
Rh(acac)(cod)	hexafluorobut-2-yne	cyclotrimerization[a]	117
$Rh(acac)(C_2H_4)_2$	allene	tetramer (73)[a]	118
$Ir(H)(CO)(PPh_3)_3$	alk-1-ynes	polymerization	115
$Ir(H)(CO)_2(PPh_3)_2$	alk-1-ynes	polymerization	115
NiX_2–AlX_nEt_{3-n}	monoalkenes	dimerization	113
Ni^0–X^-–PPh_3 or py	butadiene	linear oligomers	119
$Ni(acac)_2$–$AlEt_2(OEt)$	alk-1-enes	linear dimers	120
cis-$[NiBr_2(PBu^n_3)_2]$	phenylacetylene	polymerization	87
cis-$[NiBr_2(PPh_3)_2]$	phenylacetylene	polymerization	87
$Ni(PPh_3)_2$	allene	(cyclo-)oligomerization	92
$Ni(P\{O\cdot C_6H_4\text{-}o\text{-}C_6H_5\}_3)_2$	allene	cyclotrimerization, (74)	121
Ni(Cl)(Ph)(bipy)–AlX_nEt_{3-n}	alk-1-enes	dimerization	122
trans-[NiCl(*o*-tolyl)$(PEt_3)_2$]	butadiene	cyclodimerization, (75)	123
$NiBr(o\text{-tolyl})(PPh_3)_2$	ethylene	dimerization	124
$NiBr(1\text{-naphthyl})(PPh_3)_2$	ethylene	dimerization	86, 124
$Ni(C{\equiv}CPh)_2(PPh_3)_2$	phenylacetylene	polymerization	87
$Ni(\pi\text{-allyl})_2$–$NiCl(\pi\text{-allyl})$	butadiene	cyclopolymerization[b]	125

$NiI(\pi\text{-allyl})$	(*R*)-penta-2,3-diene	polymerization	88
$[Ni(O_2C\cdot CF_3)(\pi\text{-allyl})]_2$	styrene	dimerization	89
$Ni(cod)_2$	allene	(62)	93
$Ni(cod)_2$	hexafluorobut-2-yne	cyclotrimerization	98
$Ni(AsMe_2Ph)_4$	hexafluorobut-2-yne	cyclotrimerization	98
$\{(C_6H_{11})_3P\}_2Ni\cdot N_2\cdot Ni\{P(C_6H_{11})_3\}_2$	butadiene	dimerization	91
$PdCl_2$	1-methylcyclopropene	cyclodimerization, (76), (77)	126
$PdCl_2$–NaOAc	unsaturated ketones	cyclotrimerization, (78)	127
$[PdCl_4]^{2-}$	myrcene, ocimene	dimerization	128
$Pd(PPh_3)_4$	terpenes	dimerization	129
$[Pd(H)(PPr_3)(diphos)]^+$	butadiene	oligomerization	130
$PdCl_2(PPh_3)_2$–OR^- [c]	butadienes	octadienes[c]	131
cis-$[PtCl_2(PPh_3)_2]$ *cis*-$[Pt(H)(Cl)(PPh_3)_2]$ *trans*-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ $[Pt(HC{\equiv}CPh)(PPh_3)_2]$	phenylacetylene	polymerization	87
$[Pt(PPh_3)_4]$	benzyne	triphenylene	97

[a] Remains bonded to the metal; [b] Specifically cyclo-tetra-, -penta-, and -hexa-merization; [c] Reduction and dimerization take place in the presence of active-hydrogen-containing compounds.

5 Co-addition and Co-oligomerization

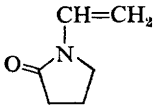
As in the previous section, all the relevant references are listed, arranged by Periodic Table order of catalysts, in tabular form (Table 4 [132–163]), but only those references with significant discussion of reaction mechanism are mentioned in the text. Most such discussion is based on characterization of products and intermediates, but there have been two kinetic investigations of this type of reaction. The cationic nickel hydride $[NiH\{P(OEt)_3\}_4]^+$, whose kinetics of formation are mentioned elsewhere,[132] catalyses the reaction of buta-1,3-diene with ethylene to produce hexadienes. The rate-determining step is in fact ligand dissociation to generate the active catalyst $[NiH\{P(OEt)_3\}_3]^+$. The rate constant for this dissociation is 0.015 s^{-1} in methanol at 25 °C; activation parameters are $\Delta H^{\ddagger} = 17$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10$ cal deg^{-1} mol^{-1}. The subsequent organic addition reaction goes through a π-crotyl complex $[Ni(\pi\text{-}C_4H_7)\{P(OEt)_3\}_3]^+$, which

[132] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 4217.
[133] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6777.
[134] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6785.
[135] D. R. Coulson, *Tetrahedron Letters*, 1971, 429.
[136] H. Hirai and H. Sawai, *Bull. Chem. Soc. Japan*, 1970, **43**, 2208.
[137] K. Kawamoto, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 2512.
[138] K. Kawamoto, A. Tatani, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 1239.
[139] S. Danno, I. Moritani, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc.* (*B*), 1971, 196.
[140] M. E. Vol'pin, L. G. Volkova, I. Ya. Levitin, N. N. Boronina, and A. M. Yurkevich, *Chem. Comm.*, 1971, 849.
[141] S. Danno, I. Moritani, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 3966.
[142] K. Ohno, T. Mitsuyasu, and J. Tsuji, *Tetrahedron Letters*, 1971, 67.
[143] K. Takahashi, A. Miyake, and G. Hata, *Chem. and Ind.*, 1971, 488.
[144] T. Saegusa, Y. Ito, and T. Shimizu, *J. Org. Chem.*, 1970, **35**, 3995.
[145] J. R. Graham and L. H. Slaugh, *Tetrahedron Letters*, 1971, 787.
[146] T. Saegusa, Y. Ito, K. Yonezawa, Y. Inubushi, and S. Tomita, *J. Amer. Chem. Soc.*, 1971, **93**, 4049.
[147] P. Warner, *Tetrahedron Letters*, 1971, 723.
[148] I. U. Khand, G. R. Knox, P. L. Pauson, and W. E. Watts, *Chem. Comm.*, 1971, 36.
[149] A. Takahashi and T. Inukai, *Chem. Comm.*, 1970, 1473.
[150] I. Hashimoto, N. Tsuruta, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, 1970, **35**, 3748.
[151] I. Hashimoto, M. Ryang, and S. Tsutsumi, *Tetrahedron Letters*, 1970, 4567.
[152] R. Noyori, T. Odagi, and H. Takaya, *J. Amer. Chem. Soc.*, 1970, **92**, 5780.
[153] T. C. Shields and W. E. Walker, *Chem. Comm.*, 1971, 193.
[154] P. Heimbach, H. Selbeck, and E. Troxler, *Angew. Chem. Internat. Edn.*, 1971, **10**, 659.
[155] R. Baker, D. E. Halliday, and T. N. Smith, *Chem. Comm.*, 1971, 1583.
[156] K. Suga, S. Watanabe, and K. Hijikata, *Austral. J. Chem.*, 1971, **24**, 197.
[157] R. S. Shue, *Chem. Comm.*, 1971, 1510.
[158] R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, *Chem. Comm.*, 1970, 1293.
[159] T. Mitsuyasa, M. Hara, and J. Tsuji, *Chem. Comm.*, 1971, 345.
[160] K. Ohno and J. Tsuji, *Chem. Comm.*, 1971, 247.
[161] R. M. Manyik, W. E. Walker, K. E. Atkins, and E. S. Hammack, *Tetrahedron Letters*, 1970, 3813.
[162] W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *Tetrahedron Letters*, 1970, 3817.
[163] W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *Tetrahedron Letters*, 1970, 3821.

adds on ethylene.[133] This investigation has been extended to cover reactions with a range of dienes, to establish the importance of structural and electronic factors, and to study catalysis by $[NiD\{P(OEt)_3\}_4]^+$ of the reaction with cyclopentadiene.[134] A preliminary study of the kinetics of addition of ethylene to secondary amines catalysed by rhodium trichloride has established that the reaction is zero-order in piperidine and first-order in catalyst; the order with respect to ethylene has not been found.[135]

The majority of postulated mechanisms refer to catalysis by palladium compounds. From studies of reactions of amides with alkenes, especially of pyrrolidone with ethylene, catalysed by palladium dichloride, it has proved possible to establish the reaction sequence:[136]

(i) co-ordination of ethylene to palladium dichloride;
(ii) replacement of chloride by pyrrolidone;
(iii) insertion of the ethylene into the Pd—N bond;
(iv) Pd—C bond breaking to give the product (79).

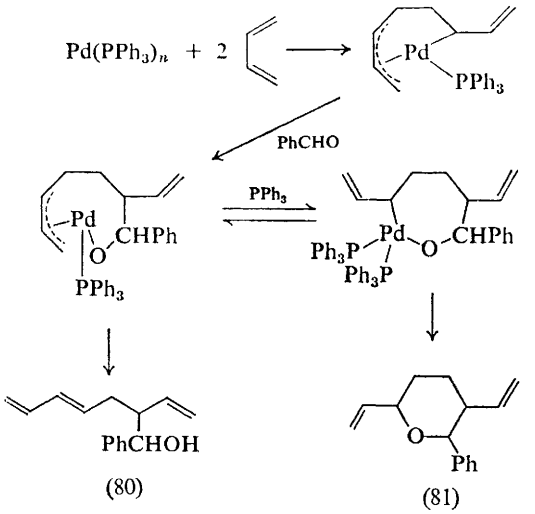


(79)

Solvent effects on, and products from, reaction of styrene with ethylene in the presence of di-μ-chloro-dichlorobis(styrene)dipalladium(II), $[Pd(Ph\cdot CH{=}CH_2)Cl_2]_2$, indicate a mechanism similar to (i) → (iv) above, with the addition of a preliminary equilibrium between the dimer and solvated monomers.[137] The mechanism of reaction of styrene with vinyl compounds, catalysed by the same chloride-bridged dipalladium complex, has been studied using isotopic tracer (H, D) experiments.[138] Palladium-acetate-catalysed reaction of styrene with benzene, also investigated using deuterium tracer experiments, involves no hydride shift,[139] in contrast to the rather closely related Wacker process. The importance of intermediates with palladium–carbon σ-bonds in palladium(II)-catalysed alkylation [140] and arylation [140, 141] of alkenes has been demonstrated.

Reaction of butadiene with aldehydes in the presence of palladium(0)–triphenylphosphine species leads to two products (80) and (81), whose formation can be explained by the mechanism outlined in Scheme 4.[142] Whereas butadiene reacts with active-hydrogen-containing compounds such as α-cyano-esters or β-diketones in the presence of palladium complexes of unidentate phosphines,[131] in the presence of palladium complexes of bidentate phosphines addition of the butadiene to the active-hydrogen compound takes place.[143]

Azides (R^1N_3) do not react with isonitriles (R^2NC) alone, but in the presence of $Fe(CO)_5$ there is a smooth and specific reaction to yield $R^1N{=}C{=}NR^2$ plus dinitrogen; an intermediate containing a nitrene



(80) (81)

Scheme 4

co-ordinated to the iron is conceivable.[144] In the presence of tungsten hexachloride, propylene or pent-1-ene will alkylate benzene, but ethylene reacts with benzene to produce very little ethylbenzene but a large amount of butylbenzenes. As ethylene is less reactive than butenes towards benzene, and as ethylene readily dimerizes under the conditions of this catalytic reaction, the likely sequence is ethylene dimerization followed by reaction of butenes with benzene.[145] The stereoselective addition of α-chloro-ketones, -esters, or -nitriles ($Cl \cdot CH_2 \cdot Y$) to ethylene to produce



(82)

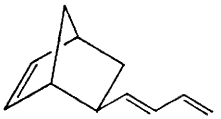
cyclopropane derivatives (82), catalysed by copper(I) oxide plus t-butyl isocyanide, is thought to involve the intermediacy of α-chloro-organocopper isonitriles.[146] The possibility that the monohomotropylium ion may be an intermediate in the silver(I)-catalysed reaction of benzyne with cyclooctatetraene has been discussed.[147]

One example of the reverse of co-addition, a retro-Diels–Alder reaction, has been described. This is the breaking down of norbornadiene in the presence of alkynedicobalt hexacarbonyls into acetylene and cyclopentadiene; the latter remains bonded to the cobalt.[148]

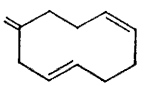
Table 4 *Co-addition and co-oligomerization reactions homogeneously catalysed by transition-metal compounds*

Catalyst	*Reactants*	*Products*	*Ref.*
$MoCl_5$	benzene + ethylene	s-butylbenzene	145
WCl_6	benzene + ethylene	butylbenzenes	145
WCl_6	benzene + propylene	cumene; di- and tri-isopropylbenzene	145
$Fe(CO)_5$	azides + isocyanides	$R^1N{:}C{:}NR^2$	144
$Co(acac)_3$–$AlEt_3$	butadiene + norbornadiene	(83)	149
$RhCl_3,3H_2O$ / $[RhCl(C_2H_4)_2]_2$	ethylene + secondary amines	(see ref.)	135
$IrCl_3,3H_2O$	ethylene + secondary amines	(see ref.)	135
$K_2Ni_2(CN)_6$	acrylonitrile + benzyl bromide	4-phenylbutyronitrile	150
$K_4Ni_2(CN)_6$	*trans*-β-bromostyrene + alkenes	(see ref.)	151
$Ni(acrylonitrile)_2$	methylenecyclopropanes + alkenes	(see ref.)	152
$Ni(acac)_2$–$PR^1R^2{}_2$[a]	butadiene + alcohols	(see ref.)	153
Ni[tri-(2-biphenylyl) phosphite]	butadiene + allenes	mainly (84), (85)	154
$[NiH\{P(OEt)_3\}_4]^+$	butadiene + ethylene	mainly hexa-1,4-diene	133
$[NiH\{P(OEt)_3\}_4]^+$	conjugated acyclic dienes	(see ref.)	134
$Ni(acac)_2$–$P(OPr^i)_2Ph$	butadiene + amines	octadienyl-, butenyl-amines	155
$PdCl_2$	isoprene + acetic acid	isoprene acetates[b]	156
$PdCl_2$	alkenes + amides	*e.g.* (79)	136
$[PdCl_4]^{2-}$	alkenes + methylcobalt compounds	(see ref.)	140
$[Pd(PhCH{=}CH_2)Cl_2]_2$	ethylene + styrene	(see ref.)	137
$[Pd(PhCH{=}CH_2)Cl_2]_2$	vinyl compounds + styrene	(see ref.)	138
$Pd(OAc)_2$	benzene + styrene	(see ref.)	139
$Pd(OAc)_2$[c]	alkenes + aromatics	(see ref.)	157
$Pd(OAc)_2$	alkenes + aromatics	(see ref.)	141
$Pd(OAc)_2$	styrene + ferrocene	*trans*-α-styrylferrocene	158
$Pd(PPh_3)_n$	butadiene + aldehydes	(80) and (81)	142
$PdCl_2(PPh_3)_2$	butadiene + 1-nitropropane	(86) and (87)	159
$Pd(PPh_3)_2$(maleic anhydride)	isoprene + phenyl isocyanate	*cis*- and *trans*-(88)	160
$Pd(acac)_2$–PPh_3	butadiene + aldehydes	(89) and (90)	161
$Pd(acac)_2$–PR_3 or $P(OR)_3$	butadiene + acetic acid	(see ref.)	162
$Pd(acac)_2$–PPh_3	butadiene + ammonia	tri-octa-2,7-dienylamine	159
$Pd(acac)_2$–PPh_3	allyl compounds + amines	(see ref.)	163
Cu_2O–Bu^tNC	alkenes + α-chloro-compounds	substituted cyclopropanes (82)	146
Ag^+	benzyne + cot	(see ref.)	147

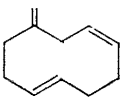
[a] $PR^1R^2{}_2$ must be an alkylarylphosphine; triarylphosphine complexes are not effective catalysts; [b] In non-polar solvents (*e.g.* benzene) isoprene monomer acetates are produced; in polar solvents (*e.g.* tetrahydrofuran) isoprene dimer acetates are produced; [c] Presence of oxygen prevents $Pd^{II}\rightarrow Pd^0$.



(83)



(84)



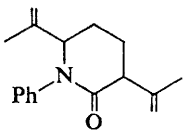
(85)

$CH_2{=}CH(CH_2)_3CH{=}CH{\cdot}CH_2{\cdot}CH(Et)NO_2$

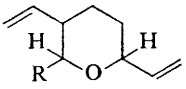
(86)

$\{CH_2{=}CH(CH_2)_3{\cdot}CH{=}CH{\cdot}CH_2\}_2C(Et)NO_2$

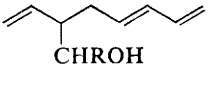
(87)



(88)



(89)



(90)

6 Homogeneous Hydrogenation

This section deals with homogeneous catalysis of hydrogenation reactions, both by direct reaction with molecular hydrogen or by hydrogen transfer from some other compound.

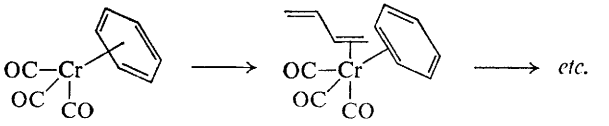
Organic Compounds.—Mechanisms of activation of molecular hydrogen by transition-metal complexes have been reviewed,[164] and similarities between homogeneous and heterogeneous catalysis of hydrogenation discussed.[165] Kinetic hydrogen isotope effects in catalytic hydrogenation of alkenes can be correlated with apparent orders of reaction with respect to the hydrogen.[166]

Titanium. The reaction of $Ti(h^5\text{-}C_5Me_5)_2$ with molecular hydrogen is reversible, but that with carbon monoxide is not, so this titanium compound may be a useful hydrogenation catalyst but will not be a useful catalyst for carbonylation.[167] Hydrogenated Ti(1-methylallyl)$(h^5\text{-}C_5H_5)_2$ catalyses

[164] L. Vaska and M. F. Werneke, *Trans. New York Acad. Sci.*, 1971, **33**, 70.
[165] R. L. Augustine and J. F. van Peppen, *Ann. New York Acad. Sci.*, 1970, **172**, 244.
[166] S. Siegel and D. W. Ohrt, *Chem. Comm.*, 1971, 1529.
[167] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1971, **93**, 2045; R. H. Marvich and H. H. Brintzinger, *ibid.*, p. 2046.

hydrogenation of 1,3-dienes, but not of alk-1-ynes, which are polymerized rather than hydrogenated.[106] The nitrogen-fixation catalysts $TiCl_3$–Mg, $TiCl_2(h^5\text{-}C_5H_5)_2$–sodium naphthalenide, and analogous iron and molybdenum mixtures will hydrogenate cyclohexyl isocyanide and n-butylacetylene.[168] A 'titanocene dimer' $(TiC_{10}H_{10})_2$, thought to be involved in homogeneous hydrogenation both of organic compounds and of molecular nitrogen, has now been shown to be $[Ti(H)(C_5H_5)(C_5H_4)]_2$, with a double hydride bridge.[169]

Chromium. The complexes $Cr(arene)(CO)_3$ are highly selective catalysts for the hydrogenation of dienes to monoenes. A recent study concentrated on the reduction of methyl hexa-2,4-dienoate (sorbate), and the mechanism was found to be similar to that for reaction with iron-carbonyl catalysts. It does not involve rate-determining loss of the arene to give $Cr(CO)_3$ as the active species, as suggested earlier for a different catalytic system, but rather the arene becoming bi- or uni- rather than ter-dentate, so that the diene can be co-ordinated:



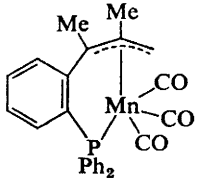
Subsequently, hydrogen co-ordinates to the chromium prior to transfer to, and thus reduction of, the diene.[170] Some preliminary observations on photochemical catalytic hydrogenation of conjugated dienes in the presence of $Cr(CO)_6$ or of $Cr(CO)_4$(nor) have been published.[171] Deuterium tracer experiments have shown that hydrogen (deuterium) transfer from alkylchromium compounds to dienes takes place intermolecularly, from the β-position of the alkyl group.[172]

Molybdenum. Ethylene reacts with molecular deuterium in the presence of $MoCl_5$–$SnCl_2$ in THF. The activation energy[173] for this reduction is 18 kcal mol^{-1}.

Manganese. Some years ago, a π-oxapropenyl complex was suggested as an intermediate in the hydrogenation of $\alpha\beta$-unsaturated carbonyl compounds in the presence of $CoH(CO)_4$.[174] A compound recently prepared

[168] E. E. van Tamelen, H. Rudler, and C. Bjorklund, *J. Amer. Chem. Soc.*, 1971, **93**, 3526.
[169] H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1970, **92**, 6182.
[170] M. Cais and A. Rejoan, *Inorg. Chim. Acta*, 1970, **4**, 509.
[171] J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1971, **27**, C13.
[172] R. P. A. Sneeden and H. H. Zeiss, *J. Organometallic Chem.*, 1971, **27**, 89.
[173] A. P. Krushch and A. E. Shilov, *Kinetika i Kataliz*, 1970, **11**, 86 (*Chem. Abs.*, 1970, **72**, 125 425k).
[174] R. W. Goetz and M. Orchin, *J. Amer. Chem. Soc.*, 1963, **85**, 2782.

from $MnMe(CO)_5$ and *o*-styryldiphenylphosphine probably has a similar structure (91), and thus is an analogous model compound.[175]



(91)

Iron. The kinetics of hydrogenation of methyl sorbate, catalysed by $Fe(CO)_3$(diene) and $Fe(CO)_4$(monoene) complexes, have been studied, with varying catalyst, solvent, and pressure of hydrogen. Ligand exchange and double-bond positional change accompany hydrogenation; the kinetic pattern is consistent with a common intermediate for all three processes. Features of the proposed mechanism include pseudorotation in the five-co-ordinate iron species and the generation of $Fe(CO)_4$ and of $Fe(CO)_3$-(unidentate diene) species (compare chromium, above).[176] Homogeneous hydrogenation of cyclo-octadienes can be achieved by hydrogen transfer from *o*- or *p*-dihydroxybenzene, in the presence of catalytic amounts of $MX_2(PPh_3)_2$ [M = Fe^{II} (best), Co^{II}, or Ni^{II} and X = Cl, Br, or I]. The active catalyst is thought to be $MX_2(PPh_3)$.[177] Dienes may also be hydrogenated by hydrogen transfer from iron–alkyl compounds.[172] The kinetics and mechanism of catalysis by iron(III) chloride and bromide of homogeneous hydrogenation of alkynes have been discussed.[178]

Ruthenium. The hydrido-nitrosyl compounds $Ru(H)(NO)(PPh_3)_3$, $Ru(H)(NO)(PPh_2Pr^i)_3$, and $Ru(H)(NO)(PPh_2\{C_6H_{11}\})_3$ are all good catalysts for hydrogenation of styrene.[63] The complex $RuCl_2(AsPh_3)_3$ catalyses the hydrogenation of maleic acid; a full report on kinetics and mechanism is promised later.[179] The similar compound $RuCl_2(PPh_3)_3$ catalyses hydrogen transfer to $\alpha\beta$-unsaturated carbonyls. For example, in its presence 1-phenylbut-1-en-3-one (benzalacetone) and benzyl alcohol react to give 1-phenylbutan-3-one and benzaldehyde. Ruthenium–hydride and ruthenium–carbonyl (from the unsaturated ketone) intermediates seem likely; again, a full kinetic and mechanistic study of the reaction is in progress and will be reported at some later date.[180] Dimeric ruthenium and rhodium acetates catalyse homogeneous hydrogenation of olefins. Some initial rates of hydrogenation, mainly in dimethylformamide solution, have been

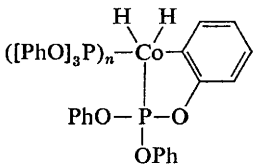
[175] M. A. Bennett and R. Watt, *Chem. Comm.*, 1971, 95.
[176] M. Cais and N. Maoz, *J. Chem. Soc.* (*A*), 1971, 1811.
[177] T. Nishiguchi and K. Fukuzumi, *Chem. Comm.*, 1971, 139.
[178] D. V. Sokol'skii, S. S. Segizbaeva, and Ya. A. Dorfman, *Trudy Inst. khim. Nauk, Akad. Nauk. Kazakh. S.S.R.*, 1970, **30**, 54 (*Chem. Abs.*, 1970, **73**, 134 332a),
[179] M. M. Taqui Khan, R. K. Andal, and P. T. Manoharan, *Chem. Comm.*, 1971, 561.
[180] Y. Sasson and J. Blum, *Tetrahedron Letters*, 1971, 2167.

measured.[181] A variety of ruthenium, rhodium, and iridium compounds are effective mediators for reduction of alkenes and alkynes by hydrogen transfer from formates.[182]

Homogeneous catalysis of hydrogenation by complexes of ruthenium has been reviewed.[183]

Cobalt. Hydrogenation of intermolecular anhydrides (*e.g.* acetic) in the presence of $Co_2(CO)_8$ produces an acid and an aldehyde, of intramolecular anhydrides (*e.g.* succinic) produces an aldehydo-carboxylic acid ($OHC \cdot R \cdot CO_2H$). The effects of pressures of hydrogen and of carbon monoxide on hydrogenation rates are similar to those reported for other reactions catalysed by $Co_2(CO)_8$, so presumably the mechanism is also similar.[184] $CoH(CO)_4$ catalyses the hydrogenation of butadiene to butenes;[185] the intermediates *syn-* and *anti*-1-methyl-π-allylcobalt tricarbonyl have been isolated.[186] In the presence of $CoH(CO)_4$, there is predominantly 1,4-addition of hydrogen to fumarate, whereas 1,2-addition predominates for maleate.[54] In the presence of $Co(\sigma\text{-allyl})(CO)_3(PBu_3)$, cyclododeca-1,5,9-triene is selectively hydrogenated to cyclododecene; reduction in the presence of $Co(\pi\text{-allyl})(CO)_3(PBu_3)$ is not selective.[187]

The importance of metal–hydrogen bonds in homogeneous catalysis has been discussed generally, with particular emphasis on experimental work on hydrogenation (deuteriation) of ethylene, but-1-ene, and deuteriated derivatives thereof. The mechanistic scheme set out for hydrogenation of ethylene to ethane, catalysed by $CoH(P[OPh]_3)_4$, features ligand-to-metal hydride transfer to generate the intermediate (92).[188] A



(92)

catalyst mixture consisting of $Co(acac)_2$, $Cr(acac)_3$, and Al_2Et_6 is more effective for alkene hydrogenation than simply $Co(acac)_2$–Al_2Et_6. The best results were obtained for a cobalt to chromium ratio of 1 : 1. The relative redox properties of the two metals may be important in determining

[181] B. C. Hui and G. L. Rempel, *Chem. Comm.*, 1970, 1195.
[182] M. E. Vol'pin, V. P. Kukolev, V. O. Chernyshev, and I. S. Kolomnikov, *Tetrahedron Letters*, 1971, 4435.
[183] B. R. James, *Inorg. Chim. Acta, Rev.*, 1970, **4**, 73.
[184] H. Wakamatsu, J. Furukawa, and N. Yamakami, *Bull. Chem. Soc. Japan*, 1971, **44**, 288.
[185] F. Ungvary and L. Markó, *Acta Chim. Acad. Sci. Hung.*, 1969, **62**, 425.
[186] W. Rupilius and M. Orchin, *J. Org. Chem.*, 1971, **36**, 3604.
[187] I. Ogata, *Tokyo Kogyo Shikensho Hokoku*, 1970, **64**, 89 (*Chem. Abs.*, 1970, **73** 102 428v).
[188] R. A. Schunn, *Inorg. Chem.*, 1970, **9**, 2567.

reactivity; whatever the reason, this is an interesting approach to tailoring catalysts.[189] Contrary to earlier reports, alkyl-lithium compounds are as effective cocatalysts as alkylaluminiums — and the former are easier to handle. The use of alkyl-lithiums has been investigated in some detail for hydrogenation of cobalt 2-ethylhexanoate. The variation of hydrogenation rates with conditions and concentrations is described.[190]

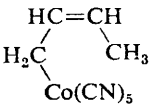
The newly characterized compounds $CoH(CO)_n(PBu^n_3)_{4-n}$ [64] and $[Co(CO)_2(PR_3)]_n$ [65] are effective catalysts for the hydrogenation of mono- and of di-enes.

A great deal of work has been done on the use of cobalt–cyanide complexes as catalysts for homogeneous hydrogenation, as is evinced by the citation of 144 references in a recent review of this subject.[191] Basic to the behaviour of $[Co(CN)_5]^{3-}$ as a hydrogenation catalyst is its reaction with molecular hydrogen. The latest contribution to the study of the mechanism of this reaction concludes that it is concerted and is not, as are the reactions with hydrogen peroxide and alkyl halides, a stepwise process with free-radical intermediates. Whether this concerted mechanism involves a termolecular reaction according to the stoicheiometry:

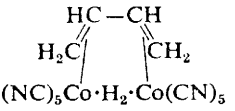
$$2[Co(CN)_5]^{3-} + H_2 \longrightarrow 2[Co(H)(CN)_5]^{3-}$$

or pre-equilibrium formation of the dimer $[Co_2(CN)_{10}]^{6-}$, which itself reacts with molecular hydrogen, has not been established.[192]

The results of a study of the kinetics and product distribution of the hydrogenation of butadiene in the presence of $[Co(CN)_5]^{3-}$ in water and in a range of aqueous organic mixed solvents can best be accommodated by a reaction intermediate (93) for production of the main products but-1-ene and *cis*-but-2-ene. The *trans*-but-2-ene also found amongst the products might conceivably appear by way of a transition state (94) derived from a



(93)



(94)

dimeric catalyst species, rather than simply by way of a π-allyl–cobalt bonded intermediate. In any case, the variations observed with variation in solvent strongly suggest two different active cobalt–cyanide–hydrogen reducing species.[193]

[189] F. K. Shmidt, S. M. Krasnopol'skaya, and V. G. Lipovich, *Izvest. Nauch.-Issled. Inst. Nefte-Uglekhim. Sin. Irkutsk. Univ.*, 1970, **12**, 24 (*Chem. Abs.*, 1971, **75**, 53 727x).
[190] J. C. Falk, *J. Org. Chem.*, 1971, **36**, 1445.
[191] J. Hanzlik, *Chem. listy*, 1971, **65**, 454 (*Chem. Abs.*, 1971, **75**, 53 718v).
[192] J. Halpern and M. Pribanić, *Inorg. Chem.*, 1970, **9**, 2616.
[193] T. Funabiki and K. Tarama, *Bull. Chem. Soc. Japan*, 1971, **44**, 945; *Chem. Comm.*, 1971, 1177; *Tetrahedron Letters*, 1971, 1111.

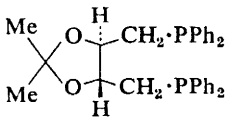
Other substrates whose kinetics of hydrogenation, catalysed by $[Co(CN)_5]^{3-}$, have been reported include muconic acid,[194] methacrylic acid,[195] cinnamic acid,[196] sorbic acid,[196] and chlorobutenes.[197] Dimethylglyoxime–cobalt complexes are also effective catalysts for hydrogenation of cinnamic, muconic, and sorbic acids; here the kinetics and reaction mechanism are more complicated.[196] Alkenes containing electron-withdrawing substituents, unsaturated nitrogen-containing compounds (for example nitrobenzene and azobenzene), α-diketones, and α-keto-acids, are all hydrogenated at atmospheric pressure in the presence of $Co(dmgH)_2$. The relative reactivities of these substrates have been qualitatively estimated by determining reduction times.[198] When an optically active amine complex of $Co(dmgH)_2$ is used as catalyst, then asymmetric hydrogenation is observed. For instance, when the amine is quinine, hydrogenation of benzil yields predominantly (*S*)-(+)-benzoin; the degree of stereoselectivity depends on the solvent.[199] In the presence of Co(salen), chloroform or 1,1,1-trichloroethane, but not *gem*-dichlorides or monochloro-alkanes, are reduced by $NaBH_4$. The kinetic pattern suggests that Co^I–salen and RCl_2-C·Co·salen species are important intermediates.[200]

Rhodium. $RhCl(PPh_3)_3$ is a useful catalyst for homogeneous hydrogenation of alkenes and polyenes, for one gets hydrogenation and no disproportionation.[201] The rates of uptake of hydrogen by $RhCl(PPh_3)_3$ and by $RhBr(PPh_3)_3$ are very similar; the rate of uptake is reduced by adding extra triphenylphosphine.[202] Relative rates of hydrogenation of eleven alkenes and alkynes in the presence of $RhCl(PPh_3)_3$ and of its iridium analogue $IrCl(PPh_3)_3$ have been measured in toluene at 25 °C. In almost all cases uptake is ten to a hundred times faster in the presence of the rhodium complex, but in the case of *trans*-hept-3-ene the catalytic activity of the rhodium complex is marginally less than that of its iridium analogue.[203] For catalysts $M(H)(CO)(PPh_3)_3$, hydrogenation rates are always greater for M = Rh than for M = Ir.[204] Rates of homogeneous hydrogenation of a range of alkenes and alkynes have been measured in the presence of catalysts $RhX(CO)L_2$. The effectiveness of the catalysts decreases in the order X = Cl > Br > I > SCN for alkenes and phenylacetylene (the order varies somewhat for cyclo-octadiene and unsaturated

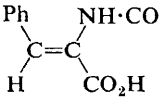
[194] L. Simandi and E. Budo, *Acta Chim. Acad. Sci. Hung.*, 1970, **64**, 125 (*Chem. Abs.*, 1970, **73**, 39 105v).
[195] A. Zakhariev, V. Ivanova, and D. Shopov, *Doklady Bolg. Akad. Nauk*, 1970, **23**, 679 (*Chem. Abs.*, 1970, **73**, 91 901r).
[196] L. Simandi, B. E. Zahonyi, and F. Nagy, *Kem. Kozlem*, 1971, **35**, 129 (*Chem. Abs.*, 1971, **75**, 53 742y).
[197] T. Funabiki and K. Tarama, *Bull. Chem. Soc. Japan*, 1970, **43**, 3965.
[198] Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Japan*, 1971, **44**, 283.
[199] Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Japan*, 1971, **44**, 583.
[200] I. Ya. Levitin, M. Dvolaitzky, and M. E. Vol'pin, *J. Organometallic Chem.*, 1971, **31**, C37.
[201] A. J. Birch and K. A. M. Walker, *Austral. J. Chem.*, 1971, **24**, 513.
[202] W. Strohmeier and R. Endres, *Z. Naturforsch.*, 1971, **26b**, 362.
[203] W. Strohmeier and R. Endres, *Z. Naturforsch.*, 1971, **26b**, 730.
[204] W. Strohmeier and S. Hohmann, *Z. Naturforsch.*, 1970, **25b**, 1309.

esters), and in the order L = PPh_3 > $P(C_6H_{11})_3$ > $P(OPh)_3$ for all substrates.[205] A different kinetic pattern has been reported for hydrogenation of hept-1-ene and dimethyl maleate in toluene solution, compared with that for hex-1-ene and dec-1-ene in benzene, in the presence of $Rh(H)(CO)(PPh_3)_3$; the active catalyst is presumably $Rh(H)(CO)(PPh_3)_2$, since added PPh_3 inhibits the reaction.[206] Hydrogenation in the presence of catalysts $RhCl(CO)(Ph_2P\{CH_2\}_nCH{=}CH_2)_2$, with n = 0, 1, 2, or 3, is a two-step process. The first step is reversible addition of hydrogen. Rates depend greatly on the value of n, probably for steric reasons, with maximum rate for n = 2.[207] A qualitative report has appeared of two new hydrogenation catalysts for alkenes: $Rh(H)(Cl)_2(PBu^tPr^n_2)_2$, which requires the presence of base, for example sodium isopropoxide in isopropyl alcohol solution, and $Rh(H)_2(Cl)(PBu^t_3)_2$, which is very active even in the absence of base.[208]

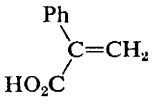
Asymmetric hydrogenation can be achieved by the use of rhodium complexes of chiral phosphines as catalysts. The chiral diphosphine species $Rh^I(Cl)$(diphosphine)(solvent), generated *in situ* from $[RhCl(cyclooctene)_2]_2$ and the diphosphine (95), is a stereoselective catalyst: α-acetamidocinnamic acid (96) is reduced with an optical purity yield of 72%, atropic acid (97) is reduced with 63% optical purity.[209] These results



(95)



(96)



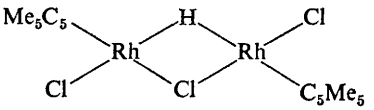
(97)

represent a considerable improvement on earlier asymmetric hydrogenations using a rhodium–methylpropylphenylphosphine catalyst, where the maximum optical purity achieved was 28%. While it seems most appropriate that the chiral centre in asymmetric homogeneous hydrogenation catalysts should be as close to the rhodium as possible, *i.e.* the adjacent phosphorus atom, it has been found that phosphine complexes in which the chiral centre is at carbon can also be efficiently stereoselective. Thus a neomenthyldiphenylphosphine–rhodium(I) catalyst promotes a very asymmetric hydrogenation of β-methylcinnamic acid to 3-phenylbutanoic acid.[210] Asymmetric hydrogenation has also been reported for catalysts $[RhCl_2(py)_2(amide)]^+$, when the amide is optically active.[211] For the catalyst with amide = dimethylformamide, the variation of rates of

[205] W. Strohmeier and W. Rehder-Stirnweiss, *Z. Naturforsch.*, 1971, **26b**, 61.
[206] W. Strohmeier and W. Rehder-Stirnweiss, *Z. Naturforsch.*, 1971, **26b**, 193.
[207] G. E. Hartwell and P. W. Clark, *Chem. Comm.*, 1970, 1115.
[208] C. Masters, W. S. McDonald, G. Raper, and B. L. Shaw, *Chem. Comm.*, 1971, 210.
[209] T. P. Dang and H. B. Kagan, *Chem. Comm.*, 1971, 481.
[210] J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Amer. Chem. Soc.*, 1971, **93**, 1301.
[211] P. Abley and F. J. McQuillin, *J. Chem. Soc.* (*C*), 1971, 844.

hydrogenation with structure for a series of cycloalkenes has been discussed in terms of the effect of co-ordination on the bonding in the cyclohexene, and of heats of hydrogenation.[212] Another active rhodium(I) catalyst which is cationic and contains co-ordinated solvent is $[Rh(cod)(MeCN)_2]^+$, which catalyses hydrogenation of hex-1-ene to hexane and of cyclo-octa-1,5-diene to cyclo-octene.[70]

A mixture of rhodium(II) dimer (Rh_2^{4+}), acetate, triphenylphosphine, and methanol provides a catalytic system for the hydrogenation of alkenes and alkynes. A qualitative report on this system [213] has been followed by a comparative study of hydrogenation rates catalysed by rhodium(I) carboxylates $Rh(O_2C\cdot R)(PPh_3)_3$ (prepared from Rh_2^{4+}, the stoicheiometric quantity of triphenylphosphine, and an excess of the lithium salt RCO_2Li) and the catalyst $RhCl(PPh_3)_3$. The carboxylate catalysts with R = Me or Et are much less effective than $RhCl(PPh_3)_3$, and the carboxylate catalysts with other R groups are ineffective.[214] The failure to detect any paramagnetic species during hydrogenation of dec-1-ene in the presence of the rhodium(II) dimer $[Rh(O_2CMe)_2]_2$ suggests that this dimer, and not a derived monomeric species, is the active catalyst.[181] The dichloro-bridged dimer $[RhCl_2(h^5\text{-}C_5Me_5)]_2$ also catalyses hydrogenation of alkenes. Here one chloro-bridge appears to be broken and substituted, to give the chloro-hydrido-bridged species (98) as an active intermediate.[215] $[RhCl(CO)_2]_2$



(98)

is a very efficient catalyst for the reduction of azobenzene specifically to hydrazobenzene (no aniline is produced) by lithium aluminium hydride.[216]

The reaction of nitrobenzene and substituted analogues with carbon monoxide and water in the presence of rhodium carbonyl derivatives and tertiary amines is one of homogeneous reduction:

$$PhNO_2 + 3CO + H_2O \longrightarrow PhNH_2 + 3CO_2$$

There are a few mechanistic comments; phenyl isocyanate intermediates are not consistent with the available evidence.[217]

Iridium. Whereas $RhCl(PPh_3)_3$ is a good catalyst for homogeneous hydrogenation, its iridium analogue $IrCl(PPh_3)_3$ is usually very much less

[212] P. Abley, I. Jardine, and F. J. McQuillin, *J. Chem. Soc.* (*C*), 1971, 840.
[213] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 3322.
[214] R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3224.
[215] C. White, D. S. Gill, J. W. Kang, H. B. Lee, and P. M. Maitlis, *Chem. Comm.*, 1971, 734.
[216] M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *Chem. Comm.*, 1971, 661.
[217] A. F. M. Iqbal, *Tetrahedron Letters*, 1971, 3385.

effective,[203] indeed in many systems it is completely ineffective.[69] However, mixtures of $[IrCl(cyclo\text{-}octene)_2]_2$ and triphenylphosphine, especially at an iridium : phosphine ratio of 1 : 2, in other words of composition equivalent to $IrCl(PPh_3)_2$, are active hydrogenation catalysts.[69] The group of compounds $IrX(CO)L_2$ are also active hydrogenation catalysts. The rates of hydrogen uptake by compounds $IrX(CO)L_2$, and equilibrium constants for the reactions:

$$IrX(CO)L_2 + H_2 \rightleftharpoons Ir(H)_2X(CO)L_2$$

depend primarily on the nature of X, and to a lesser extent on the π-acceptor strengths of the ligands L.[218] Rates of hydrogenation in the presence of $IrX(CO)L_2$ obviously depend on the nature of X and on the nature of L.[219] Attempts have been made to find a consistent reactivity pattern for hydrogenations promoted by this group of catalysts. Generally, rates decrease in the order X = Cl > Br > I, independently of the nature of the unsaturated compound, but no correlation could be established between reaction rates and π-acceptor properties of phosphine ligands L.[220] The effect of steric factors in controlling the reactivity of this type of catalyst is at present not fully understood.*

The slowness of hydrogenation reactions catalysed by many iridium compounds is an advantage when reaction mechanisms are under investigation. Thus for hydrogenation of ethylene in the presence of $Ir(H)(CO)(PPh_3)_3$ it is possible to study not only the kinetics of the overall reduction of the ethylene but also of establishment of the equilibrium:

$$Ir(H)(CO)(PPh_3)_3 + H_2 \rightleftharpoons Ir(H)_3(CO)(PPh_3)_2 + PPh_3$$

This equilibrium is in fact a composite of equilibrium loss of PPh_3 from $Ir(H)(CO)(PPh_3)_3$ followed by equilibrium addition of hydrogen to the active intermediate $Ir(H)(CO)(PPh_3)_2$.[221] Rates of hydrogenation of a variety of alkenes, alkynes, and unsaturated esters in the presence of $Ir(H)(CO)(PPh_3)_3$ have been reported.[204] The chloro-bridged dimer $[IrCl_2(h^5\text{-}C_5Me_5)]_2$ catalyses hydrogenation of a range of alkenes,[215] as does the $[Ir(cod)(MeCN)_2]^+$ cation.[70] The complex $IrHCl_2(DMSO)_3$ may be the active catalyst in iridium(III)-catalysed hydrogen transfer between isopropyl alcohol and cyclic ketones in DMSO solution in the presence of chloride, though it is possible that $[IrHCl(DMSO)_3]^+$ is in fact the active species.[222]

The crystal structure has been reported for an intermediate in the hydrogenation of the unsaturated ketone benzylideneacetophenone,

[218] W. Strohmeier, *J. Organometallic Chem.*, 1971, **32**, 137.
[219] W. Strohmeier and R. Fleischmann, *J. Organometallic Chem.*, 1971, **29**, C39.
[220] W. Strohmeier, R. Fleischmann, and T. Onoda, *J. Organometallic Chem.*, 1971, **28**, 281.
[221] M. G. Burnett and R. J. Morrison, *J. Chem. Soc.* (*A*), 1971, 2325.
[222] M. Gulotti, R. Ugo, and S. Colonna, *J. Chem. Soc.* (*C*), 1971, 2652.

* There is, however, some recent information on the role of steric factors in determining the affinity of iridium(I) cations for molecular oxygen (G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758).

catalysed by $[Ir(Cl)_4(DMSO)_2]^-$. The stability of the isolated intermediate arises from chelation of the iridium.[223]

Nickel. The anion $[Ni_2(CN)_6]^{4-}$ bears some resemblance to the much-studied $[Co(CN)_5]^{3-}$. Hence kinetics of reduction of butadiene in aqueous solution in the presence of the former anion have been investigated. The first step is slow formation of the complex $[Ni_2(CN)_6(\pi\text{-}C_4H_6)]^{4-}$. This intermediate then gives rise to species containing π-1-methylallyl or π-butadienyl complexes of nickel cyanide which are the immediate precursors of the reduction process. Two precursors with two subsequent reduction paths are needed to accommodate observations of different product distributions under different experimental conditions.[224] Rates of hydrogenation of styrene and of phenylacetylene depend on solvent and on composition for mixed Ni^{2+}–acac–$AlEt_3$ catalysts.[225]

Palladium. α-Diethylenic glycols, *e.g.* (99) or *C*-alkyl derivatives thereof, can be reduced to α-diethylenic alcohols, *e.g.* (100), in the presence of

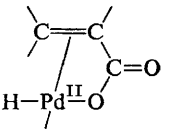
$CH_2{=}CH{-}CH(OH){-}CH(OH){-}CH{=}CH_2$

(99)

$CH_2{=}CH{-}CH_2{-}CH(OH){-}CH{=}CH_2$

(100)

trans-$[PdCl_2(PPh_3)_2]$ in formamide. The nature of the solvent is critical for specific reduction in this manner.[226] Palladium dichloride catalyses hydrogen transfer from saturated aliphatic acids to aromatic compounds, *via* the intermediate (101).[227] The determined rate law and stereochemistry



(101)

suggest an oxypalladation–deoxypalladation mechanism for hydrogen–deuterium exchange between enol acetates and acetic acid, catalysed by $PdCl_2$–LiCl mixtures.[228]

Platinum. Rate laws have been determined for homogeneous hydrogenation of ethylene and acetylene in the presence of platinum(II)–tin(II) catalysts. This kinetic evidence and ancillary results from deuterium tracer experiments suggest a mechanism in which the molecular hydrogen is split heterolytically to give a Pt—H bond plus H^+; ethylene or acetylene then

[223] M. McPartlin and R. Mason, *J. Chem. Soc.* (*A*), 1970, 2206.
[224] D. Bingham and M. G. Burnett, *J. Chem. Soc.* (*A*), 1971, 1782.
[225] N. F. Noskova, N. I. Marusich, and D. V. Sokol'skii, *Trudy Inst. khim. Nauk, Akad. Nauk Kazakh. S.S.R.*, 1970, **30**, 3 (*Chem. Abs.*, 1971, **74**, 6837c).
[226] Y.-L. Pascal and F. Quetier, *Compt. rend.*, 1971, **272**, *C*, 490.
[227] T. Sakakibara, S. Nishimura, K. Kimura, I. Minato, and Y. Odaira, *J. Org. Chem.*, 1970, **35**, 3884.
[228] P. M. Henry, *J. Amer. Chem. Soc.*, 1971, **93**, 3853.

co-ordinate to the Pt—H intermediate and react with this hydride and with H^+.[229] Acyl chlorides react with triethylsilane in the presence of, for example, *cis*-$[PtCl_2(PPh_3)_2]$ to produce aldehydes. This hydrogen transfer is achieved *via* an oxidative-addition–reductive-elimination mechanism.[230]

Dinitrogen.—The reductive fixation of nitrogen under mild conditions has been reviewed in two articles, one of which concentrates on titanium-based catalysts,[231] the other mentioning compounds of several of the later transition metals, such as molybdenum, iron, and ruthenium.[232] In catalyst systems containing titanium compounds, the dinitrogen is generally reduced to ammonia;[168, 233] discussion of the mechanisms of these complicated reactions continues.[234] E.s.r. spectroscopy is a useful technique for searching for intermediates, as has been illustrated for vanadium-based [235] as well as for titanium-based catalyst mixtures. The drawback with e.s.r. investigations is that it is difficult to tell whether the detected paramagnetic species are intermediates in the major reaction pathway or whether they are part of some minor pathway or side-reaction.[234] Whereas titanium and vanadium complexes in the presence of the appropriate reducing agents are efficient reductants for molecular nitrogen, similar complexes of zirconium, for example $ZrCl_2(h^5\text{-}C_5H_5)$, are ineffective.[236]

Catalysts based on titanium generally favour the production of ammonia from molecular nitrogen, whereas catalysts in which the transition-metal component is provided by iron or molybdenum result in hydrazine formation. Titanium compounds in the presence of molybdenum compounds also favour hydrazine formation, as do chromium(II)– and vanadium(II)–molybdenum catalysts. Indeed, vanadium(II) itself [in the presence of some magnesium(II)] rapidly reduces molecular nitrogen to hydrazine; the vanadium(II) here acts both as activator and reductant.[237]

A dinuclear iron complex of molecular nitrogen has been isolated from mixtures of iron(III) chloride, triphenylphosphine, isopropylmagnesium chloride, and molecular nitrogen in ether solution. Addition of hydrochloric acid to this complex produces some hydrazine.[238] However,

[229] I. Yasumori and K. Hirabayashi, *Trans. Faraday Soc.*, 1971, **67**, 3283.
[230] S. P. Dent, C. Eaborn, and A. Pidcock, *Chem. Comm.*, 1970, 1703.
[231] E. E. van Tamelen, *Accounts Chem. Res.*, 1970, **3**, 361.
[232] G. I. Likhtenshtein and A. E. Shilov, *Russ. J. Phys. Chem.*, 1970, **44**, 474.
[233] M. E. Volpin, A. A. Belyi, V. B. Shur, N. A. Katkov, I. M. Nekaeva, and R. V. Kudryavtsev, *Chem. Comm.*, 1971, 246; M. E. Volpin, M. A. Ilatovskaya, and V. B. Shur, *Kinetika i Kataliz*, 1970, **11**, 333 (*Chem. Abs.*, 1970, **73**, 39 054c).
[234] E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *J. Amer. Chem. Soc.*, 1970, **92**, 5251.
[235] T. P. M. Beelen and W. van Erk, *Rec. Trav. chim.*, 1971, **90**, 1197.
[236] D. R. Gray and C. H. Brubaker, *Inorg. Chem.*, 1971, **10**, 2143.
[237] N. T. Denisov, O. N. Efimov, N. I. Shuvalova, A. K. Shilova, and A. E. Shilov, *Russ. J. Phys. Chem.*, 1970, **44**, 1693; A. E. Shilov, N. T. Denisov, O. N. Efimov, N. Shuvalov, N. I. Shuvalova, and A. K. Shilova, *Nature*, 1971, **231**, 460.
[238] Yu. G. Borodko, M. O. Broitman, L. M. Kachapina, A. E. Shilov, and L. Yu. Ukhin, *Chem. Comm.*, 1971, 1185; M. O. Broitman, N. T. Denisov, N. I. Shuvalov, and A. E. Shilov, *Kinetika i Kataliz*, 1971, **12**, 504 (*Chem. Abs.*, 1971, **75**, 80 759r).

mixtures of iron(II) sulphate, sodium molybdate, 2-aminoethanol, and sodium borohydride reduce molecular nitrogen not to hydrazine but to ammonia.[239] In this, as in several recent reports, use of ^{15}N tracers provides positive proof that the source of the ammonia, or hydrazine, produced by the reductive fixation process is indeed the molecular nitrogen introduced into the system.

7 Hydrogen Exchange

Hydrogen (deuterium) exchange reactions which are subject to homogeneous catalysis by transition-metal compounds are listed in Table 5,

Table 5 *Hydrogen exchange with organic compounds, catalysed by transition-metal compounds*

Catalyst	*Substrate*	*Mechanism*	*Ref.*
$TaH_3(h^5\text{-}C_5H_5)_2$	aromatic hydrocarbons	oxidative addition of C—H	242
$Fe(CO)_3$(diene)	(diene ligand)	Michael addition–elimination	243
$RhCl(PPh_3)_3$	cycloalkenes	rhodium–alkyl intermediates	244
$IrH_5(PR_3)_2$	aromatic hydrocarbons	reductive elimination of H_2 then oxidative addition of C—H	242
$NiX_2(PPh_3)_2$	ethylene	nickel–σ-ethyl intermediate	245
$PtCl_4^{2-}$–CH_3CO_2H	alkanes	oxidative-addition–reductive-elimination	246
$PtCl_4^{2-}$–CH_3CO_2H	alkylbenzenes	π-arene ⇌ π-allyl	247

which is arranged in Periodic Table order of the metals. The main points of interest in the exchange mechanisms are briefly indicated in this Table. E.s.r. spectroscopy can be a useful technique in elucidating the nature of intermediates in these reactions;[240] its application to platinum-catalysed exchange has been described.[241]

8 Homogeneous Dehydrogenation

Dehydrogenation of formic acid is catalysed by the cobalt(I) compounds $Co(H)(CO)_x(PBu^n_3)_{4-x}$, where $x = 1$, 2, or 3; the compound with $x = 2$ is the most effective catalyst. Rates of dehydrogenation vary with the solvent used, being greatest in the most polar media.[248] Some of the

[239] R. E. E. Hill and R. L. Richards, *Nature*, 1971, **233**, 114.
[240] K. P. Davis, J. L. Garnett, and J. H. O'Keefe, *Chem. Comm.*, 1970, 1672.
[241] K. P. Davis and J. L. Garnett, *J. Phys. Chem.*, 1971, **75**, 1175.
[242] E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 1970, **92**, 5234.
[243] H. W. Whitlock, C. R. Reich, and R. L. Markezich, *J. Amer. Chem. Soc.*, 1970, **92**, 6665.
[244] J. G. Atkinson and M. O. Luke, *Canad. J. Chem.*, 1970, **48**, 3580.
[245] N. Ando, K. Maruya, T. Mizoroki, and A. Ozaki, *J. Catalysis*, 1971, **20**, 299.
[246] R. J. Hodges, D. E. Webster, and P. B. Wells, *Chem. Comm.*, 1971, 462; *J. Chem. Soc. (A)*, 1971, 3230.
[247] J. L. Garnett and R. S. Kenyon, *Chem. Comm.*, 1971, 1227.
[248] L. Marangoni, A. Andreetta, G. Ferrari, and G. Pregaglia, *Chimica e Industria*, 1970, **52**, 862 (*Chem. Abs.*, 1971, **74**, 6890q).

hydrogen-transfer reactions mentioned in the previous section might also be considered as homogeneous dehydrogenation with respect to one component — for example, the hydrogen transfer from saturated aliphatic acids to aromatic compounds, which is catalysed by palladium(II) chloride.[227] The coupling of benzene derivatives, for example of toluene or xylenes, which is catalysed by palladium(II) acetate and is thought to proceed by a radical mechanism,[249] is also related to homogeneous dehydrogenation in that such oxidative coupling formally involves the removal of one hydrogen atom from each molecule of substrate.

9 Homogeneous Oxidation

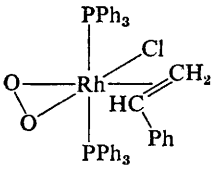
Two ruthenium compounds have proved effective catalysts for homogeneous oxidation of cyclohexane, to cyclohex-2-en-1-one, cyclohex-2-en-1-ol, and cyclohexene oxide, and oxidation of triphenylphosphine. Kinetic studies of oxygen uptake in systems containing $RuCl_2(PPh_3)_3$ show that the active catalyst is in fact $RuCl_2(PPh_3)_2$.[250] The activation parameters for oxidation of triphenylphosphine, catalysed by $Ru(NCS)(NO)(O_2)(PPh_3)_2$, are $\Delta H^{\ddagger} = 21.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7.1$ cal deg^{-1} mol^{-1}. The mechanism involves rate-determining transfer of both atoms of the co-ordinated oxygen molecule to two molecules of co-ordinated triphenylphosphine in an intermediate $Ru(NCS)(NO)(O_2)(PPh_3)_3$.[251]

The relative catalytic activities of a series of cobaloximes and of aquocobalamine for homogeneous oxidation of formaldehyde have been qualitatively assessed. Vitamin B_{12a} is by far the most effective; the rate law for the process is complicated.[252] The effect of these catalysts on decomposition of the formic acid produced was also studied.[253] Somewhat simpler cobalt complexes catalyse the oxidation of alkylbenzenes. Thus cobalt(II) acetate in hydrochloric acid is a good catalyst for the oxidation of *p*-xylene or *p*-toluic acid to terephthalic acid.[254] $Co(acac)_3$ catalyses oxidation of toluene,[255] and a cobalt stearate complex catalyses the oxidation of isopropylbenzene.[256]

Evidence has been obtained for a hydroperoxide intermediate in rhodium(I)–cyclo-octene-catalysed homogeneous oxidation. This intermediate may arise from hydrogen transfer from co-ordinated cyclo-octene to co-ordinated oxygen.[257] The product of oxidation of styrene in the presence of

[249] H. Itatani and H. Yoshimoto, *Chem. and Ind.*, 1971, 674.
[250] S. Cenini, A. Fusi, and G. Capparella, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3576.
[251] B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, *Chem. Comm.*, 1970, 1272.
[252] Y. Hohokabe and N. Yamazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 2142.
[253] Y. Hohokabe and N. Yamazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 2145.
[254] H. D. Holtz, *Chem. Comm.*, 1971, 1166.
[255] M. Nakai, S. Sato, and Y. Fujimura, *Chubu Kogyo Daigaku Kyo*, 1969, **5**, 151 (*Chem. Abs.*, 1970, **73**, 7723d).
[256] V. A. Tulupov and A. V. Uvarov, *Russ. J. Phys. Chem.*, 1970, **44**, 1684.
[257] B. R. James and E. Ochiai, *Canad. J. Chem.*, 1971, **49**, 975.

$RhCl(PPh_3)_3$ depends on the solvent. In polar solvents such as dioxan, the carbon–carbon double bond cleaves and the products include benzaldehyde; in protic solvents such as ethanol, the product is acetophenone; in toluene, both benzaldehyde and acetophenone are produced. The mechanism involves loss of one triphenylphosphine ligand from the rhodium, followed by co-ordination of oxygen and styrene to give the intermediate (102).[258]



(102)

Low-oxidation-state phosphine complexes, particularly of rhodium and of iridium, catalyse the oxidation of cyclohexene, by an autocatalytic free-radical mechanism.[259] The isolation of $[IrCl(C_2H_4)(O_2)(PPh_3)_2],C_6H_6$ is claimed to furnish the first model intermediate for homogeneous oxidation of alkenes.[69] The reactions of iridium(I) complexes with molecular oxygen are related to this topic of homogeneous oxidation; these reactions are dealt with in the chapter on oxidative addition (Chapter 6 of Part IV).

During 1970 it was suggested that palladium-catalysed autoxidation of hydrocarbons was initiated *via* formation of a palladium–molecular oxygen complex, $Pd(O_2)(PR_3)_2$.[260] Now a kinetic study of palladium(0) compounds as catalysts for cumene autoxidation shows that the catalytic initiation should be ascribed to $Pd(PPh_3)_4$-catalysed decomposition of hydroperoxides still present in the cumene, and that invocation of a $Pd(O_2)(PPh_3)_2$ complex is not necessary.[261] Palladium(I) species are sometimes proposed as reactive intermediates in homogeneous catalysis. One such species, $[Pd_2(C_6H_8)(OAc)_2],\frac{1}{2}HOAc$, has now been isolated from reaction mixtures that contain palladium(II) acetate, cyclohexa-1,4-diene, and oxygen in acetic acid.[262] Palladium(II) acetate in acetic acid solution catalyses oxidation and autoxidation of cyclohexene and of cyclohexa-1,3- and -1,4-dienes. The mechanism is complicated by heterogeneous catalysis by palladium metal, generated during the reaction.[263] A comprehensive investigation of the products, stoicheiometry, tracer behaviour, and solvolysis of intermediates of palladium(II)-catalysed oxidation of alkenes has been directed

[258] K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 3898.
[259] A. Fusi, R. Ugo, F. Fox, A. Pasini, and S. Cenini, *J. Organometallic Chem.*, 1971, **26**, 417.
[260] E. W. Stern, *Chem. Comm.*, 1970, 736.
[261] R. A. Sheldon, *Chem. Comm.*, 1971, 788.
[262] J. M. Davidson, *Chem. Comm.*, 1971, 1019.
[263] R. G. Brown and J. M. Davidson, *J. Chem. Soc.* (*A*), 1971, 1321.

at elucidating the roles, if any, of σ- and π-allyl intermediates and of oxypalladation adducts in the mechanism of oxidation.[264]

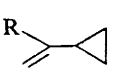
An ambiguity in the assignment [265] of mechanism of oxidation of triphenylphosphine, catalysed by $Pt(PPh_3)_3$, has been resolved, though there remain some details to be settled.[266] The rate of oxidation of carbon monoxide by iron(III) in the presence of hydrido–carbonyl–halide complexes of platinum(II) is proportional to the concentration of carbon monoxide and proportional to the concentration of platinum(II); added chloride inhibits the reaction.[267]

The conversion of amines into aldehydes or ketones in the presence of $[MoBr(h^5\text{-}C_5H_5)(SMe_2)]^+PF_6^-$ in aqueous solution is not catalytic, since the final molybdenum species is different from the starting material, but the suggested mechanism, of ligand replacement and β-elimination steps, is of interest in relation to mechanisms of homogeneous catalysis of oxidation.[268]

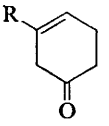
10 Hydration, Carbonylation, and Hydroformylation

Group VIII Metals.—The majority of catalysts reported for homogeneous hydration, carbonylation, and hydroformylation are compounds of these nine metals, particularly of cobalt, rhodium, and palladium.

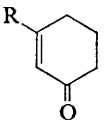
Iron. Alk-1-enes, ethyl acrylate, ethyl crotonate, ethyl but-3-enoate, and styrene are all carbonylated by carbon monoxide in the presence of $K[FeH(CO)_4]$ or $K_2[Fe(CO)_4]$.[269] Vinylcyclopropanes (103) are carbonylated in the presence of $Fe(CO)_5$ or $Fe_2(CO)_9$, under irradiation. The initial product is (104), which can isomerize to (105).[270] The reaction of alkenes



(103)



(104)



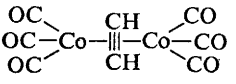
(105)

with carbon monoxide plus carbon tetrachloride, which is catalysed by $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$ and other dinuclear carbonyls, is an extension of carbonylation; the products include acyl chlorides. A mechanism has been proposed in the light of kinetic results obtained under a variety of experimental conditions.[271]

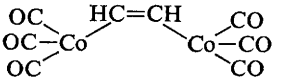
[264] P. M. Henry and G. A. Ward, *J. Amer. Chem. Soc.*, 1971, **93**, 1494; S. Wolfe and P. G. C. Campbell, *ibid.*, pp. 1497, 1499.
[265] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491.
[266] J. Halpern and A. L. Pickard, *Inorg. Chem.*, 1970, **9**, 2798.
[267] N. K. Eremenko, K. I. Matveev, L. N. Rachkovskaya, S. K. Katanakhova, and L. F. Mel'gunova, *Kinetika i Kataliz*, 1971, **12**, 147 (*Chem. Abs.*, 1971, **74**, 103 495x).
[268] F. W. S. Benfield and M. L. H. Green, *Chem. Comm.*, 1971, 1274.
[269] H. Masada, M. Mizuno, S. Suga, Y. Watanabe, and Y. Takegami, *Bull. Chem. Soc. Japan*, 1970, **43**, 3824.
[270] R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Letters*, 1970, 4253.
[271] T. Susuki and J. Tsuji, *J. Org. Chem.*, 1970, **35**, 2982.

Ruthenium. Cyclic secondary amines, including morpholine and piperidine, can be carbonylated to give *N*-formyl derivatives in the presence of ruthenium carbonyl compounds $[Ru(O_2CMe)(CO)_2]_n$ or $Ru_3(CO)_{12}$. With the former catalyst it is possible to isolate an intermediate $[Ru(O_2CMe)(amine)(CO)_2]_m$, where *m* is probably 2.[272]

Cobalt. The rate law for carbonylation of Schiff bases, catalysed by $Co_2(CO)_8$, has been reported.[273] Dicobalt octacarbonyl also catalyses reaction between aldehydes, for instance formaldehyde or acetaldehyde, amides, for example acetamide or benzamide, and carbon monoxide. The products are *N*-acyl-amino-acids.[274] The main product from the reaction of acetylene with carbon monoxide in the presence of $CoH(CO)_4$ is ethyl acrylate. Characterization of the intermediates permits suggestions to be made as to the mechanism of this reaction. Initial reactions between the acetylene and two molecules of catalyst may give (106), in equilibrium with its isomer (107); the carbon monoxide inserts into the cobalt–carbon bonds of the latter.[275] Further information about $Co_2(CO)_8$-catalysed hydroformylation of acrylonitrile [276] and of 3-methyl[3-^{2}H]hex-1-ene [277] has led



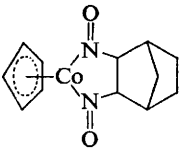
(106)



(107)



(108)



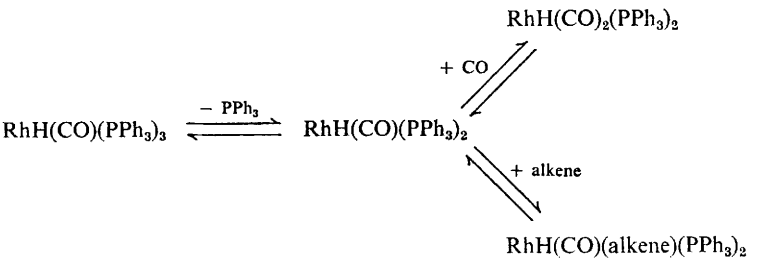
(109)

to minor modifications of the mechanisms proposed in earlier discussions of these systems. Reactions of alkenes with carbon monoxide have been much studied; reactions of alkenes with nitric oxide represent a very similar but rarely studied situation. The reaction of the cyclic alkene (108) with nitric oxide in the presence of a nitric-oxide-bridged dicobalt dicyclopentadienyl catalyst results in the formation of the compound (109).[278]

Rhodium. The determination of the rates of conversion of alkenes to aldehydes under hydroformylation conditions, using $RhH(CO)(PPh_3)_3$ as

[272] J. J. Byerley, G. L. Rempel, N. Takebe, and B. R. James, *Chem. Comm.*, 1971, 1482.
[273] T. Joh, N. Hagihara, and S. Murahashi, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 1970, **27**, 99 (*Chem. Abs.*, 1970, **73**, 39 112v).
[274] H. Wakamatsu, J. Uda, and N. Yamakami, *Chem. Comm.*, 1971, 1540.
[275] Y. Iwashita, F. Tamura, and H. Wakamatsu, *Bull. Chem. Soc. Japan*, 1970, **43**, 1520.
[276] Y. Ono, S. Sato, M. Takesada, and H. Wakamatsu, *Chem. Comm.*, 1970, 1255.
[277] C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, 1971, **93**, 1280.
[278] H. Brunner and S. Loskot, *Angew. Chem. Internat. Edn.*, 1971, **10**, 515.

catalyst and varying the pressures of hydrogen and of carbon monoxide, and the concentrations of catalyst, alkene, and added phosphine, shows that several equilibria are involved in the reaction mechanism. In the initial stages carbon monoxide and the alkene are complexed to the rhodium (Scheme 5). Subsequently there is hydrogen transfer to the alkene to give



Scheme 5

an alkyl-rhodium species, carbonyl insertion into this alkyl–rhodium bond, and oxidative addition of hydrogen to regenerate the rhodium–hydrogen bond of the original form of the catalyst.[279]

Hydroformylation of PhCH=CHMe in the presence of $RhCl(PPh_3)_3$ produces $PhCH(CHO)\cdot CH_2\cdot CH_3$ and $PhCH_2\cdot CH(CHO)\cdot CH_3$, as well as some $PhCH_2\cdot CH_2\cdot CH_3$.[280] Both $Rh_4(CO)_{12}$ [281] and mixed carbonyl–phosphine complexes derived from $Rh_4(CO)_{12}$ and from $Rh_6(CO)_{16}$ [282] are active catalysts for hydroformylation of alkenes. Acyl-rhodium intermediates may be important when $Rh_4(CO)_{12}$ is the catalyst, for $[Rh(CO)_2(O_2CR)]_2$ dimers have been isolated [281] from alkene hydroformylations in which this polynuclear carbonyl has been the catalyst. $Rh_4(CO)_{12}$ also catalyses the reaction between ethylene and carbon monoxide, which produces several products, including octane-3,6-dione, undecane-3,6,9-trione, and tetradecane-3,6,9,12-tetraone. The products obtained indicate a mechanism in which addition of ethylene to rhodium and insertion of carbon monoxide into a rhodium–carbon bond alternate.[283]

The mechanism of reaction of allyl alcohol in the presence of $[IrCl(cod)]_2$, which is mainly dehydration to diallyl ether, has been discussed.[284]

Iridium. The isolation and some reactions have been described for possible intermediates in hydroformylation of aliphatic alk-1-ynes in the presence of $IrH(CO)(PPh_3)_3$ or $IrH(CO)_2(PPh_3)_2$.[285]

[279] C. K. Brown and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 2753.
[280] R. Laï and E. Ucciani, *Compt. rend.*, 1971, **273**, *C*, 1369.
[281] B. Heil, L. Markó, and G. Bor, *Chem. Ber.*, 1971, **104**, 3418.
[282] B. L. Booth, M. J. Else, R. Fields, and R. N. Haszeldine, *J. Organometallic Chem.*, 1971, **27**, 119.
[283] Y. Iwashita and M. Sakuraba, *Tetrahedron Letters*, 1971, 2409.
[284] G. Pannetier, R. Bonnaire, and P. Fougeroux, *J. Organometallic Chem.*, 1971, **30**, 411.
[285] C. K. Brown and G. Wilkinson, *Chem. Comm.*, 1971, 70.

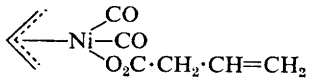
Nickel. Cinnamoylation of alkenes can be performed by allowing them to react with *trans*-β-bromostyrene and nickel carbonyl.[151] Nickel-carbonyl-catalysed carbonylation of aryl halides is thought to have the following reactions as initial stages:

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO \quad (3)$$

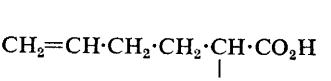
$$Ni(CO)_3 + RI \rightleftharpoons Ni(RI)(CO)_3 \quad (4)$$

To provide further information on this carbonylation, the stoicheiometric reactions of aryl halides with nickel carbonyl [equations (3) and (4)] have been investigated.[286]

Allyl halides can be carbonylated in the presence of $Ni(CO)_4$. The mechanism suggested includes formation of a π-allylnickel intermediate (110), which undergoes a double intramolecular insertion (see Chapter 4 of Part IV). The final product is but-3-enylsuccinic acid (111).[287]

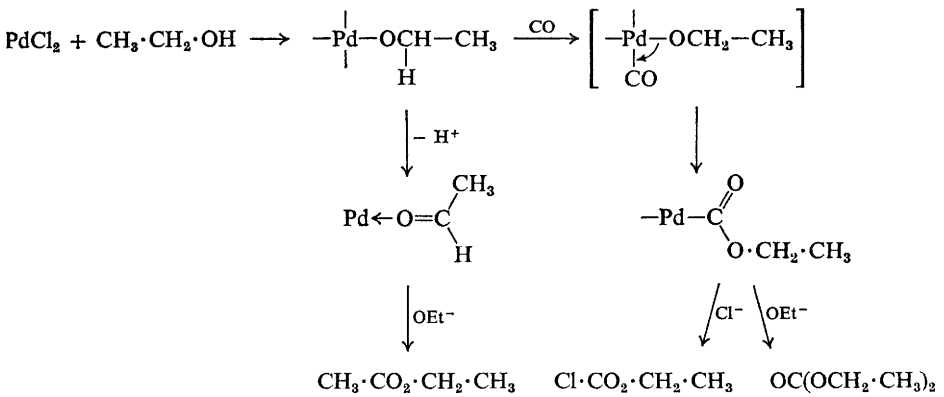


(110)



(111)

Palladium. Ethanol can be carbonylated in the presence of palladium chloride. The product distribution suggests the mechanism outlined in Scheme 6; this is supported by the isolation of a very labile palladium–



Scheme 6

carbonyl intermediate.[288] Palladium chloride also catalyses the carbonylation of conjugated dienes [289] and the formation of α-diketones from

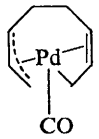
[286] M. Nakayama and T. Mizoroki, *Bull. Chem. Soc. Japan*, 1971, **44**, 508.
[287] G. P. Chiusoli and S. Merzoni, *Chem. Comm.*, 1971, 522.
[288] M. Graziani, P. Uguagliati, and G. Carturan, *J. Organometallic Chem.*, 1971, **27**, 275.
[289] S. Hosaka and J. Tsuji, *Tetrahedron*, 1971, **27**, 3821.

reaction of allyl halides with water.[290] π-Allyl-palladium complexes are important intermediates in the latter reaction, and such complexes are also effective catalysts for the carbonylation of allyl chloride to vinylacetyl chloride.[291]

Palladium acetate plus triphenylphosphine catalyse the dimerization and carbonylation of butadiene. The major product is octa-2,7-dien-1-ol, formed by dimerization of the butadiene on the palladium to form (112),



(112)



(113)

reaction with carbon monoxide to form (113), and subsequent insertion of carbon monoxide into a palladium–carbon bond.[292]

The effect of pH on the rate of hydration of acetylene, catalysed by palladium sulphate–iron(II) sulphate, has been traced to the stage $L_nPd{\cdot}CH{:}CHOH \rightarrow CH_2{:}CHOH + PdL_n$.[293]

Platinum. Further comments have been offered concerning the mechanism of $PtCl_6^{2-}$–$SnCl_2$ catalysis of homogeneous carbonylation of alkenes.[294]

Other Catalysts.—Copper(II) alkoxides can be carbonylated, giving dialkyl carbonates, by insertion of carbon monoxide into the copper–alkoxide-oxygen bond.[295] The first well-characterized copper(I)–carbonyl compounds are [CuCl(CO)(en)] and $[(en)Cu(\mu\text{-}CO)_2Cu(en)]Cl_2$.[296] The effects of pH on rates of hydration of acetylene have been compared for the three catalysts Cu_2SO_4–$CuSO_4$, $HgSO_4$, and $PdSO_4$–$Fe_2(SO_4)_3$.[293] Alkyl and aryl halides can be carbonylated in the presence of ethanol, antimony pentachloride, and liquid sulphur dioxide:[297]

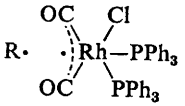
$$RX + CO + EtOH \longrightarrow RCO_2Et + HX$$

11 Decarbonylation

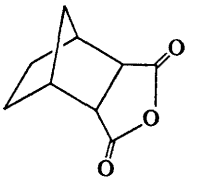
The rhodium(I) complex $RhCl(PPh_3)_3$ catalyses decarbonylation of substituted cyclopropylaldehydes [298] and of allylic alcohols.[299] For the former

[290] R. Jira and J. Sedlmeier, *Tetrahedron Letters*, 1971, 1227.
[291] H. C. Volger, K. Vrieze, J. W. F. M. Lemmers, A. P. Praat, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta*, 1970, **4**, 435.
[292] K. E. Atkins, W. E. Walker, and R. M. Manyik, *Chem. Comm.*, 1971, 330; W. E. Billups, W. E. Walker, and T. C. Shields, *ibid.*, p. 1067.
[293] D. V. Sokol'skii, Ya. A. Dorfman, S. S. Segizbaeva, I. A. Kazantseva, and B. Yu. Nogerbekov, *Zhur. priklad. Khim.*, 1970, **43**, 502 (*Chem. Abs.*, 1970, **73**, 39 102s).
[294] L. J. Kehoe and R. A. Schell, *J. Org. Chem.*, 1970, **35**, 2846.
[295] T. Saegusa, T. Tsuda, and K. Isayama, *J. Org. Chem.*, 1970, **35**, 2976.
[296] G. Rucci, C. Zanzottera, M. P. Lachi, and M. Camia, *Chem. Comm.*, 1971, 652.
[297] M. Nojima, K. Tatsumi, and N. Tokura, *Bull. Chem. Soc. Japan*, 1971, **44**, 2001.
[298] H. M. Walborsky and L. E. Allen, *J. Amer. Chem. Soc.*, 1971, **93**, 5465.
[299] A. Emery, A. C. Oehlschlager, and A. M. Unrau, *Tetrahedron Letters*, 1970, 4401.

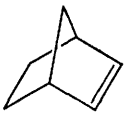
series of compounds a radical-pair intermediate (114) is suggested. $Ni(CO)_2(PPh_3)_2$ catalyses the loss of both carbon monoxide and carbon dioxide from acid anhydrides, for example the anhydride (115) gives (116); the first step is insertion of the nickel into a carbon–oxygen bond, giving



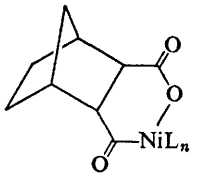
(114)



(115)



(116)



(117)

(117).[300] The decomposition of formic acid to give carbon dioxide and hydrogen is catalysed by rhodium or iridium iodocarbonyls in the presence of hydrogen iodide. The reactions involved may be:[301]

$$[M(CO)_xI_4]^- + HCO_2H \longrightarrow [M(CO)_xI_2]^- + 2HI + CO_2\uparrow$$

$$[M(CO)_xI_2]^- + 2HI \longrightarrow [M(CO)_xI_4]^- + H_2\uparrow$$

12 Hydrosilylation

The most extensive recent kinetic study of hydrosilylation has been concerned with a variety of substrates and with cobalt, rhodium, and platinum catalysts. Reactions studied are listed in Table 6. In most cases relative rates were determined, which showed amongst other things that the reactivities of silanes increased as the ionic character of the silicon–hydrogen

Table 6 *Summary of hydrosilylation reactions for which rates are available (from ref.* 302)

Alkene	*Silane*	*Catalyst*
Hept-1-ene	$Et_nCl_{3-n}SiH$	$PtCl_6^{2-}$
Hex-1-ene	$(MeO)_nPr^n{}_{3-n}SiH$	$PtCl_6^{2-}$
Ethylene	$PhMe_2SiH$, $(p\text{-}Cl\cdot C_6H_4)Me_2SiH$, $(p\text{-}MeO\cdot C_6H_4)Me_2SiH$	$PtCl_6^{2-}$, $Co_2(CO)_8$, or $RhCl(PPh_3)_3$

[300] B. M. Trost and F. Chen, *Tetrahedron Letters*, 1971, 2603.
[301] D. Forster and G. R. Beck, *Chem. Comm.*, 1971, 1072.

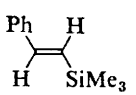
bond decreased. The four most fully studied reactions were found all to be first-order in ethylene.[302]

$Pt(PPh_3)_4$ catalyses the hydrosilylation of alk-1-enes, with no concurrent isomerization.[303] $Pt(C_2H_4)(PPh_3)_2$ also catalyses hydrosilylation of alkenes.[304] The first examples of asymmetric homogeneous hydrosilylation of alkenes employed platinum–chiral phosphine complexes as catalysts. *cis*-Dichloro(ethylene)[(*R*)-benzylmethylphenylphosphine]platinum(II) gave a reasonable optical yield; the analogous complex of methylphenyl-n-propylphosphine was much less stereospecific.[305] Later it was reported that similar nickel complexes, for example *trans*-dichlorobis-[(*R*)-benzylmethylphenylphosphine]nickel(II), were superior to the platinum(II) complexes.[306] Square-planar $NiCl_2(PBu^n_3)_2$ proves a better catalyst than tetrahedral $NiBr_2(PPh_3)_2$ for the reaction of styrene with trichlorosilane; $Ni\{P(OPh)_3\}_4$ is a very good catalyst for this reaction. The mechanisms of these and analogous platinum(II)-catalysed hydrosilylations have been discussed.[307] Hydrosilylation of hex-1-ene by trichlorosilane is catalysed by a variety of palladium complexes, including $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2$ plus PPh_3, and Pd metal plus PPh_3.[308]

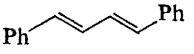
The compound $[Co(H)_2(PPh_3)_3\{Si(OEt)_3\}]$, formed by oxidative elimination between $[Co(H)(N_2)(PPh_3)_3]$ and the appropriate silane, is itself a catalyst for hydrosilylation and for *O*-silylation.[309]

Hydrogermylation is an obvious sequel to hydrosilylation. An investigation of the reaction of phenylacetylene with optically active germanes, for example methyl-1-naphthylphenylgermane, catalysed by $PtCl_6^{2-}$, $RhCl(PPh_3)_3$, or *cis*-$[PtCl_2(PPh_3)_2]$, shows retention of configuration at the germanium.[310]

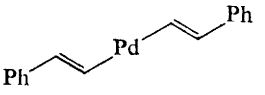
One mechanistic study of desilylation has been reported; β-trimethylsilylstyrene (118) reacts with palladium(II) chloride in methanol to give *trans*-1,4-diphenylbuta-1,3-diene (119). The reaction sequence involves co-ordination of the β-trimethylsilylstyrene to the palladium, followed by



(118)



(119)



(120)

[302] M. Čapka, P. Svoboda, V. Bažant, and V. Chvalovsky, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2785.
[303] W. Fink, *Helv. Chim. Acta*, 1971, **54**, 1304.
[304] K. Yamamoto, T. Hayashi, and M. Kumada, *J. Organometallic Chem.*, 1971, **28**, C37.
[305] K. Yamamoto, T. Hayashi, and M. Kumada, *J. Amer. Chem. Soc.*, 1971, **93**, 5301.
[306] K. Yamamoto, Y. Uramoto, and M. Kumada, *J. Organometallic Chem.*, 1971, **31**, C9.
[307] E. W. Bennett and P. J. Orenski, *J. Organometallic Chem.*, 1971, **28**, 137.
[308] M. Hara, K. Ohno, and J. Tsuji, *Chem. Comm.*, 1971, 247.
[309] N. J. Archer, R. N. Haszeldine, and R. V. Parish, *Chem. Comm.*, 1971, 524.
[310] R. J. P. Corriu and J. J. E. Moreau, *Chem. Comm.*, 1971, 812.

elimination of trimethylchlorosilane and reaction with a second molecule of the β-trimethylsilylstyrene to give a bis-styrylpalladium(II) intermediate (120). Oxidative coupling of the two styryl groups, with reductive elimination of palladium(0), completes the reaction.[311]

[311] W. P. Weber, R. A. Felix, A. K. Willard, and K. E. Koenig, *Tetrahedron Letters*, 1971, 4701.

4
Insertion Reactions

BY R. D. W. KEMMITT AND J. BURGESS

The title of this chapter covers a variety of reactions, in some of which the insertion in question is more apparent than real. Thus in the classic example, the reaction of methylmanganese pentacarbonyl with carbon monoxide:

$$MnMe(CO)_5 + CO \rightarrow Mn(COMe)(CO)_5$$

the incoming carbon monoxide is not incorporated into the acyl group. The acyl-carbonyl is in fact derived from one of the carbon monoxide ligands already bonded to the manganese at the start of the reaction. This reaction is thus an alkyl migration or 1,2-shift, rather than a true insertion. On the other hand, there are reactions which result in direct insertion of an incoming molecule into a metal–ligand bond, though the detailed mechanism may consist of several stages. Examples of both types of 'insertion', and of insertion reactions of undetermined mechanism, are all collected together in this chapter, which is subdivided according to the nature of the inserted molecule.

1 Alkenes and Alkynes

Several examples of the insertion of alkenes and alkynes into metal–carbon and metal–hydrogen bonds have been mentioned incidentally in the previous chapter, on homogeneous catalysis. In this section we concentrate on reactions in which the mechanistic interest centres on the insertion process.

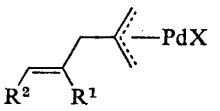
The mechanism of insertion of an alkene, for example ethylene, into a platinum–hydrogen bond in a platinum(II)–hydride complex, *e.g.*:

$$trans\text{-}[Pt(Cl)(H)(PEt_3)_2] + C_2H_4 \rightarrow Pt(Et)(Cl)(PEt_3)_2$$

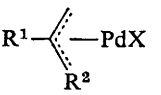
was originally suggested to include a five-co-ordinate intermediate in which the alkene and the hydrogen were both bound, separately, to the platinum.[1] Evidence has now been presented that under certain conditions, of which perhaps the presence of a silver salt which can remove halide efficiently is the most significant, insertion can proceed by a dissociative reaction and a cationic intermediate, for example *trans*-$[Pt(H)(PMePh_2)_2(OCMe_2)]^+$ for the reaction of *trans*-$[Pt(Br)(H)(PMePh_2)_2]$ with ethylene in acetone solution containing $AgPF_6$.[2]

[1] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.
[2] H. C. Clark and H. Kurosawa, *Chem. Comm.*, 1971, 957.

1,3-Dienes and allenes (*i.e.* 1,2-dienes) insert into palladium–allyl bonds to give, for example, (1) from allene itself and the allyl compound (2). The



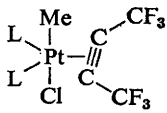
(1)



(2)

mechanism of this reaction appears to be a two-step process in which co-ordination of the diene to the palladium precedes the actual insertion. The latter is the rate-determining step.[3] The insertion of allene into bis-μ-acetato-2,2′-bis-π-allyldipalladium has been probed by isotopic labelling experiments, using [$^2H_4$]allene. The reaction is much faster than that of allene insertion into the analogous acetylacetone–palladium dimer, for there is steric strain in the acetato-compound.[4]

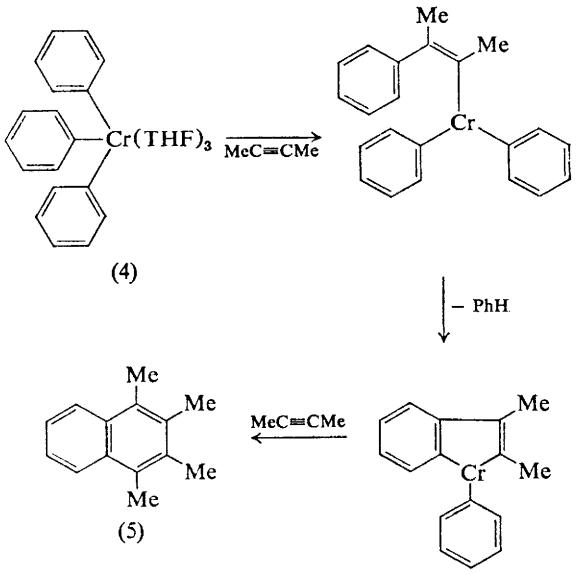
Several insertion reactions of perfluoro-alkenes and -alkynes have been described. Insertion into the manganese–tin bond of $Me_3Sn \cdot Mn(CO)_5$ and into the iron–Group IV element (M) bond of $Me_3M \cdot Fe(CO)_2(h^5\text{-}C_5H_5)$ appears to involve a four-centred transition state.[5] The stability of intermediate π-complexes is thought to govern rates of insertion of tetrafluoroethylene and of hexafluorobut-2-yne into the platinum–carbon bonds of *cis*-[$PtMe_2L_2$] or of *trans*-[$PtXMeL_2$], where L is a phosphorus or arsenic base.[6] In certain cases it has proved possible to isolate and characterize these intermediates, which from spectroscopic evidence are deemed to have the structure (3), with the alkyne carbons coplanar with the PtL_2 portion of the molecule.[7]



(3)

Triphenyltris-(tetrahydrofuran)chromium(III) (4) reacts with but-2-yne to give 1,2,3,4-tetramethylnaphthalene (5). From deuterium labelling and kinetic isotope effects, and from the isolation of intermediates, it proved possible to propose the mechanism shown in Scheme 1. The sequence is insertion, then cyclization of the styrylchromium intermediate to a benzchromole, followed by reaction with a second molecule of but-2-yne.[8]

[3] R. P. Hughes and J. Powell, *Chem. Comm.*, 1971, 275.
[4] T. Okamoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 1353.
[5] R. E. J. Bichler, M. R. Booth, and H. C. Clark, *J. Organometallic Chem.*, 1970, **24**, 145.
[6] H. C. Clark and R. J. Puddephat, *Inorg. Chem.*, 1970, **9**, 2670.
[7] H. C. Clark and R. J. Puddephat, *Inorg. Chem.*, 1971, **10**, 18.
[8] G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 1970, **92**, 5625.



Scheme 1

Mono- and di-substituted acetylenes react with $Zr(Cl)(H)(h^5\text{-}C_5H_5)_2$ by insertion into the zirconium–hydride bond.[9]

Two or three further examples of alkene and alkyne insertion are mentioned in the section on cyclization and ring expansion at the end of this chapter.

2 Other Carbon Compounds

Carbon Monoxide.—Some examples of carbon monoxide insertion (alkyl migrations) have been mentioned in the discussion of carbonylation and hydroformylation reactions in the previous chapter (Part IV, Chapter 3, Section 10). The remaining reports will be treated here in Periodic Table order.

Molybdenum. ω-Bromoallenes, *e.g.* (6), react with the $[Mo(CO)_3(h^5\text{-}C_5H_5)]^-$ anion, in tetrahydrofuran solution, to produce the new series

$$Br\cdot CH_2\cdot CH_2\cdot CR^1{=}C{=}CHR^2$$

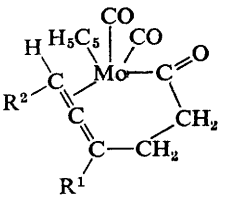
(6)

of allene complexes (7). The mechanism of formation of these complexes is thought to involve the formation of $MoR(h^5\text{-}C_5H_5)(CO)_2$, where R is $-CH_2\cdot CH_2\cdot CR^1{=}C{=}CHR^2$, with a subsequent carbonyl insertion (*i.e.*

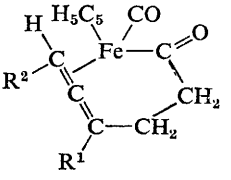
[9] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometallic Chem.*, 1971, **27**, 373.

R migration) step, and finally bonding of the allene moiety to the molybdenum. The last step can be prevented by addition of a phosphine, which bonds to the metal to prevent co-ordination of the allene double-bond.[10]

Iron. The mechanism of formation of the compounds (8) is analogous to that outlined for the molybdenum series (7) above.[10]



(7)



(8)

An extensive kinetic study of the carbonyl insertion, or alkyl migration, reaction

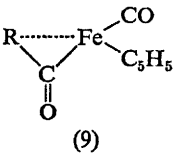
$$Fe(R)(CO)_2(h^5\text{-}C_5H_5) + PMe_2Ph \rightarrow Fe(COR)(CO)(h^5\text{-}C_5H_5)(PMe_2Ph)$$

in acetonitrile included the determination of the activation parameters for three compounds (Table 1). The activation enthalpies are in the order

Table 1 *Activation parameters for the reaction of* $Fe(R)(CO)_2(h^5\text{-}C_5H_5)$ *with dimethylphenylphosphine, in acetonitrile solution (from ref.* 11)

R	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
Me	18.2	− 19
Et	14.4	− 30
Pr^i	12.5	− 33

expected from iron–alkyl bond strengths; the activation entropies can be correlated with steric effects of the groups R. The dependence of rate on concentration of phosphine is not linear, which suggests competition for an active intermediate. The large negative values of the activation entropies suggest a highly organized transition state, for which the structure (9) is suggested.[11]



(9)

Oxidative addition of methyl iodide to *trans*-$[Fe(CO)_3(PMe_3)_2]$ gives ultimately $Fe(Me)(I)(CO)_2(PMe_3)_2$, but the reaction scheme includes the

[10] J. Benaïm, J. Y. Mérour, and J. L. Roustan, *Tetrahedron Letters*, 1971, 983.
[11] M. Green and D. J. Westlake, *J. Chem. Soc.* (*A*), 1971, 367.

participation of $Fe(COMe)(I)(CO)_2(PMe_3)_2$, the product of a carbonyl insertion reaction.[12] An i.r. study has shown the formation of propoxide species in the heterogeneously catalysed reaction of ethylene and carbon monoxide at an iron surface. This is thought to represent the first example of an insertion reaction, taking place at a metal surface, which is a direct analogue of homogeneously catalysed insertion processes.[13]

Iridium. Both the kinetics[14] and the stereochemistry[15] of the carbonyl insertion reaction

$$IrCl_2(R)(CO)_2L + L' = IrCl_2(COR)(CO)(L)(L')$$

have been thoroughly investigated, for R = Me or Et; L and L′ are arsines. Some of the kinetic parameters are reported in Table 2. They

Table 2 *Kinetic results for reaction of* $IrCl_2(R)(CO)_2L$ *with* $AsPh_3$ *(from ref.* 14); *ε is the dielectric constant of the solvent*

R	L	*Solvent* (ε)	$10^5k^a/s^{-1}$	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}
Et	$AsPh_3$	cyclohexanone (18.3)	4.2	—	—
		1,2-dichloroethane (10.4)	15.0	—	—
		tetrahydrofuran (7.7)	5.8	25.0	+ 1.8
		chlorobenzene (5.6)	11.0	22.5	− 5.0
Et	$AsMe_2Ph$	tetrahydrofuran	24.4	22.7	− 4.7
		chlorobenzene	37.9	21.4	− 5.9
Me	$AsPh_3$	chlorobenzene	1.6	23.0	− 6.7

[a] At 40 °C.

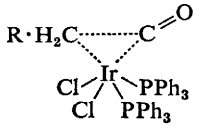
show that solvent assistance, which is thought to be of great importance in carbonyl insertion reactions, cannot be of much significance in these particular systems. The rate-determining step is thought to be (non-solvent-assisted) formation of a five-co-ordinated acyl species.[14] The stereochemical study suggested that the geometry of this five-co-ordinated species is probably square-pyramidal, with the acyl group apical. In other words, the vacant site is opposite the group with the largest *trans*-effect.[15]

The reaction

$$IrCl_2(CO\cdot CH_2R)(PPh_3)_2 \longrightarrow IrCl_2(CH_2R)(CO)(PPh_3)_2$$

where R = C_6H_5, C_6F_5, *p*-$NO_2\cdot C_6H_4$, *p*-$Me\cdot C_6H_4$, or *p*-$MeO\cdot C_6H_4$, is of interest as the reverse of carbonyl insertion. In this reaction electron-releasing substituents promote migration of CH_2R, but electron-withdrawing groups retard it. This trend suggests that iridium to carbonyl-carbon bond formation is an important element in generating the transition state (10).[16]

[12] M. Pańkowski and M. Bigorgne, *J. Organometallic Chem.*, 1971, **30**, 227.
[13] A. J. Goodsel and G. Blyholder, *Chem. Comm.*, 1970, 1122.
[14] R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 331.
[15] R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 1971, **5**, 317.
[16] M. Kubota, D. M. Blake, and S. A. Smith, *Inorg. Chem.*, 1971, **10**, 1430.

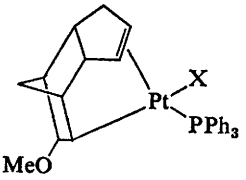


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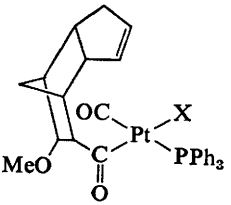
Platinum. The carbonyl insertion reaction:

$$PtClEt(CO)(AsPh_3) + AsPh_3 \longrightarrow PtCl(COEt)(AsPh_3)_2$$

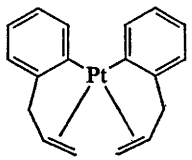
occurs at a rate that is independent of the concentration of the arsine. In a series of six solvents, the rate decreases as the donor strength of the solvent increases. These two observations indicate that the formation of the COEt ligand takes place without assistance either from the incoming ligand or from the solvent. This state of affairs is very unusual, except for the iridium case mentioned above, for carbonyl insertion reactions. The difference in mechanism between these platinum and iridium reactions and 'normal' carbonyl insertions is further underlined by the very different activation entropies for the two sets of compounds.[17] Other examples of carbonyl insertion reactions of platinum(II) complexes include the reactions of *cis*-$[PtMe_2L_2]$ and of *trans*-$[PtXMeL_2]$, where L is a phosphorus or arsenic base, with carbon monoxide,[6] and the reaction of the compound (11) with carbon monoxide. The final product of the latter is (12), produced *via* carbon monoxide insertion into the platinum–carbon σ-bond of (11), followed by displacement of the π-bonded olefinic part of the organic ligand



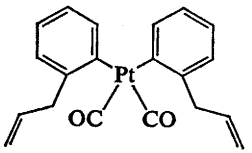
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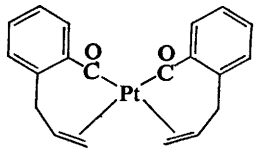
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(13)



(14)

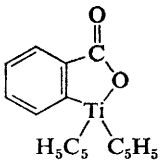


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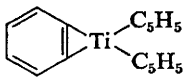
[17] R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 854.

from the platinum by a second molecule of carbon monoxide.[18] Intramolecular carbonyl insertion forms the second step in the reaction of (13) with carbon monoxide in benzene, for the intermediate (14) is converted into the product (15) on standing in benzene.[19]

Carbon Dioxide.—The sole example of carbon dioxide insertion into a transition-metal–carbon bond is afforded by the reaction of $Ti(h^5\text{-}C_5H_5)_2Ph_2$ with carbon dioxide, which produces (16). The suggested mechanism is



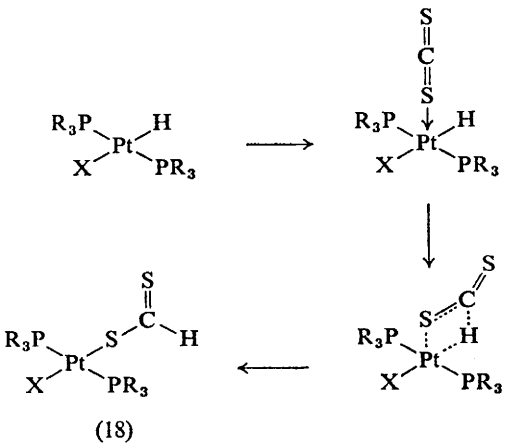
(16)



(17)

via reaction of (17), a suggested intermediate in the thermal decomposition of $Ti(h^5\text{-}C_5H_5)_2Ph_2$, with the carbon dioxide.[20]

Carbon Disulphide.—The kinetics of reaction of *trans*-$[Pt(X)(H)(PR_3)_2]$, where R = Et or Ph, with carbon disulphide in methanol indicate at least two stages in the reaction. The first step has a dependence of rate on the concentration of the platinum complex and of the carbon disulphide; the rate of the second step is independent of carbon disulphide concentration, suggesting an intramolecular process. The whole sequence proposed is shown in Scheme 2.[21] Whereas the product (18) of this reaction is thought

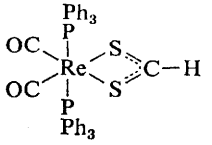


(18)

Scheme 2

[18] G. Carturan, M. Graziani, and U. Belluco, *J. Chem. Soc.* (*A*), 1971, 2509.
[19] M. Aresta and R. S. Nyholm, *Chem. Comm.*, 1971, 1459.
[20] I. S. Kolomnikov, T. S. Lobeeva, V. V. Gorbachevskaya, G. G. Aleksandrov, Yu. T. Struckhov, and M. E. Vol'pin, *Chem. Comm.*, 1971, 972.

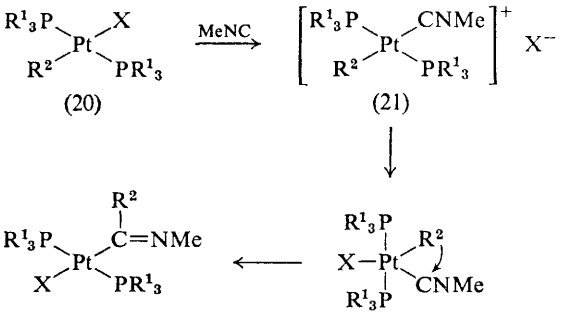
to contain a unidentate CS_2H^- ligand, the product (19) of the reaction of carbon disulphide with $ReH(CO)_2(PPh_3)_3$ has been shown by crystal



(19)

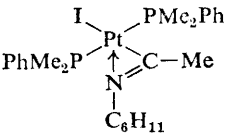
structure determination to contain bidentate CS_2H^-.[22] The first example of carbon disulphide insertion into a metal–carbon bond is provided by the reaction of $M(R)(CO)_5$ (M = Mn or Re) with carbon disulphide.[23]

Isocyanides.—The proposed mechanism for insertion of isocyanides into platinum–alkyl and –aryl bonds, as in (20), is shown in Scheme 3. The



Scheme 3

ionic intermediate (21) has been isolated.[24] Isocyanides also insert into the platinum–carbon bond of the very similar iodo-compounds $Pt(I)(Me)(PR_3)_2$ (ref. 25) and into the palladium–carbon bond of the analogous compounds $Pd(I)(Me)(PMe_2Ph)_2$.[26] In these latter systems it has been proposed, on the basis of n.m.r. evidence, that the products contain five-co-ordinated platinum or palladium, as in for example (22). The mechanism of insertion



(22)

[21] A. Palazzi, L. Busetto, and M. Graziani, *J. Organometallic Chem.*, 1971, **30**, 273.
[22] V. G. Albano, P. L. Bellon, and G. Ciani, *J. Organometallic Chem.*, 1971, **31**, 75.
[23] E. Lindner, R. Grimmer, and H. Weber, *Angew. Chem. Internat. Edn.*, 1970, **9**, 639.
[24] P. M. Treichel and R. W. Hess, *J. Amer. Chem. Soc.*, 1970, **92**, 4731.
[25] Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 1873.
[26] Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1970, **43**, 3634.

of cyclohexyl isocyanide into molybdenum–benzyl bonds, in Mo(benzyl)-(h^5-C_5H_5)$(CO)_3$ and its derivatives, has been compared with that for sulphur dioxide insertion.[27]

Carbenes.—Attempts to insert $:CF_2$ into several metal–metal bonds failed, because the difluorocarbene precursor $Me_3Sn(CF_3)$ underwent exchange reactions at one of the metals, *e.g.*:[28]

$$Me_3Sn\cdot Mn(CO)_5 + Me_3Sn(CF_3) \longrightarrow (CF_3)Me_2Sn\cdot Mn(CO)_5 + Me_4Sn$$

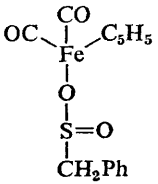
Consequently, examples of carbene insertion reactions reported over the period covered by this Report are restricted to bonds between non-transition elements. Reactions of $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ with $PhHgCBr_3$, $PhHgCBr_2Cl$, or $PhHgCBrCl_2$ involve two successive carbene insertions, the first into a mercury–silicon or –germanium bond, the second into the mercury–carbon bond thus formed.[29] The kinetics of insertion of :CHCl into silicon–hydrogen bonds,[30] and the stereochemistry of insertion of $:CBr_2$ into silicon–hydrogen and germanium–hydrogen, of $:CH\cdot CO_2Et$ into silicon–hydrogen,[31] and of $:CCl_2$ into benzyl-carbon–hydrogen[32] bonds have been studied. The retention of configuration observed in the last system is consistent with a concerted process, or at least hydride abstraction in a tight ion-pair, rather than with a mechanism involving solvent-separated ion-pairs.

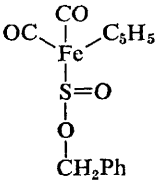
3 Sulphur Dioxide and Sulphide Trioxide

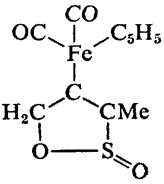
Sulphur Dioxide.—Insertion reactions of sulphur dioxide into transition-metal–alkyl bonds [33] and into metal–carbon bonds [34] have been the subject of review articles.

N.m.r. and i.r. spectroscopy, and chemical evidence, all suggest that the mechanism of insertion of sulphur dioxide into metal–carbon bonds in such compounds as Fe(h^5-C_5H_5)(R)$(CO)_2$, Mo(h^5-C_5H_5)(R)$(CO)_3$, and $MnR(CO)_5$ involves initial formation of an *O*-bonded sulphinate, *e.g.* (23), followed by rearrangement to the stable *S*-bonded product, *e.g.* (24).[35] The reaction of sulphur dioxide with 2-alkynyl compounds of transition metals was first considered to produce allenyl(oxy)sulphinyl compounds $MS(O)\cdot OC(R)=C=CH_2$.[36] Later, the products were said to be allenyl-*O*-sulphinates, $MOS(O)\cdot C(R)=C=CH_2$.[37] Now the available evidence

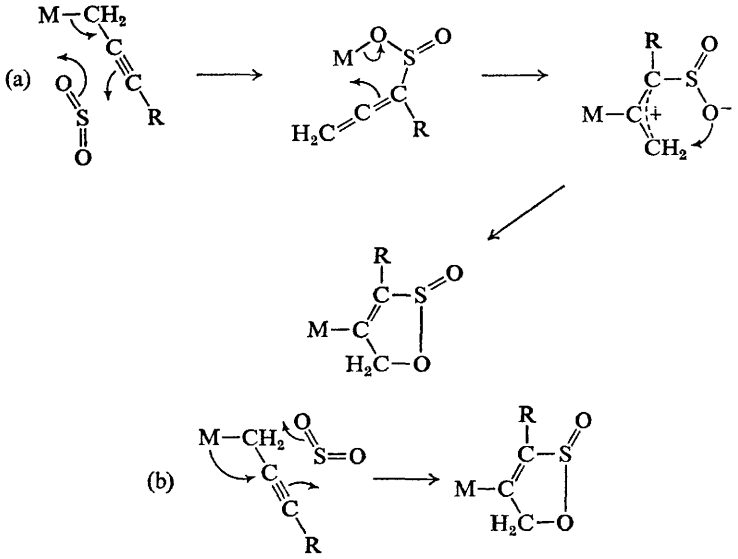
[27] Y. Yamamoto and H. Yamazaki, *J. Organometallic Chem.*, 1970, **24**, 717.
[28] H. C. Clark and B. K. Hunter, *J. Organometallic Chem.*, 1971, **31**, 227.
[29] D. Seyferth, E. M. Hanson, B. Prokai, and R. J. Cross, *J. Organometallic Chem.*, 1970, **24**, 33.
[30] Y.-N. Tang, S. H. Daniel, and N.-B. Wong, *J. Phys. Chem.*, 1970, **74**, 3148.
[31] A. G. Brook, J. M. Duff, and D. G. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 7567.
[32] D. Seyferth and Ying Ming Cheng, *J. Amer. Chem. Soc.*, 1971, **93**, 4072.
[33] A. Wojcicki, *Accounts Chem. Res.*, 1971, **4**, 344.
[34] W. Kitching and C. W. Fong, *Organometallic Chem. Rev.*, 1970, **A5**, 281.
[35] S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Chem. Comm.*, 1971, 1526.
[36] J. E. Thomasson and A. Wojcicki, *J. Amer. Chem. Soc.*, 1968, **90**, 2709.
[37] J.-L. Roustan and C. Charrier, *Compt. rend.*, 1969, **268**, *C*, 2113.


(23)


(24)


(25)

strongly contra-indicates an allenic product, particularly in that an *X*-ray crystal structure determination of the iron product (25) shows that it is vinylic, containing a sultine ring.[38] For this and similar reactions of sulphur dioxide there appear to be two mechanisms consistent with the available data;[39] these are shown in Scheme 4. These mechanisms, like most others

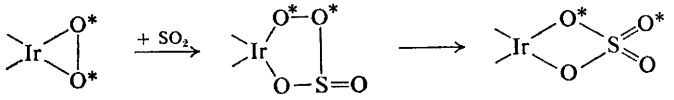

Scheme 4

proposed for sulphur dioxide insertion, rest on product characterization evidence. The kinetics of insertion of sulphur dioxide into $Fe(h^5\text{-}C_5H_5)(R)(CO)_2$ have been investigated in liquid sulphur dioxide.[40] The reaction of *threo*-$[Fe(h^5\text{-}C_5H_5)(CHD\cdot CHD\cdot CMe_3)(CO)_2]$ with sulphur dioxide proceeds with inversion of configuration at the α-carbon.[41]

[38] M. R. Churchill, J. Wormald, D. A. Ross, J. E. Thomasson, and A. Wojcicki, *J. Amer. Chem. Soc.*, 1970, **92**, 1795; M. R. Churchill and J. Wormald, *ibid.*, 1971, **93**, 354.
[39] J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, 1971, **10**, 2130.
[40] S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, 1971, **93**, 2535.
[41] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1971, **93**, 1529.

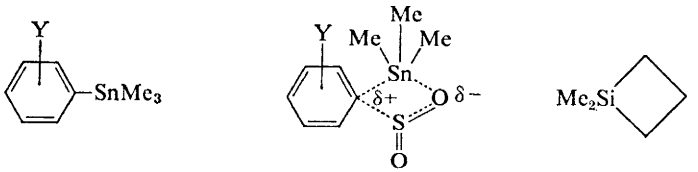
Other, qualitative, studies of sulphur dioxide insertion into metal–carbon bonds include reactions involving $Fe(h^5\text{-}C_5H_5)(R)(CO)L$, where L = PPh_3, PBu^n_3, or $AsPh_3$, and R = Me or benzyl;[42] and σ-allyl compounds of iron, molybdenum, and tungsten.[43] The crystal structure of $Fe(h^5\text{-}C_5Me_5)(CO)(SO_2\cdot CH_2\cdot CH{=}CHPh)$ has been determined in connection with the investigation of the mechanism of sulphur dioxide insertion into iron–allyl and manganese–allyl bonds. The products of insertion of sulphur dioxide into $Fe(h^5\text{-}C_5H_5)(CO)_2(CH_2\cdot CH{=}CMe_2)$ are thought to include both $Fe(h^5\text{-}C_5H_5)(CO)_2(SO_2\cdot CH_2\cdot CH{=}CMe_2)$ and $Fe(h^5\text{-}C_5H_5)(CO)_2(SO_2\cdot CMe_2\cdot CH{=}CH_2)$.[44]

Sulphur dioxide inserts into palladium–oxygen bonds. When a solution of palladium chloride in an alcohol is treated with sulphinato-complex is produced, presumably by insertion into a palladium–alkoxide bond.[45] The reaction of sulphur dioxide with molecular oxygen complexes of platinum and of iridium, producing sulphato-complexes, involves insertion of sulphur dioxide into one of the metal–oxygen links, as shown in Scheme 5.[46]



Scheme 5

The first kinetic study of sulphur dioxide insertion into a transition-metal–carbon bond, mentioned above, indicated an electrophilic mechanism.[40] Such a mechanism is also indicated by the first kinetic study of sulphur dioxide insertion into tin–carbon bonds. For insertion into the substituted phenyltrimethyltin compounds (26), the variation of second-order rate constant with the nature of the substituent Y gave a reasonable Hammett



(26) (27) (28)

plot, with a reaction constant of $\rho = -1.87$. For the unsubstituted compound (26; Y = H), activation parameters for sulphur dioxide insertion were determined as $\Delta H^{\ddagger} = 7.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -31$ cal deg^{-1} mol^{-1}. From these kinetic results, and from the solvent variation of rate

[42] M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, 1970, **4**, 347.
[43] J.-Y. Merour, *Compt. rend.*, 1970, **271**, *C*, 1397.
[44] M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1971, **10**, 572.
[45] M. Graziani, R. Ros, and G. Carturan, *J. Organometallic Chem.*, 1971, **27**, C19.
[46] R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, 1970, **9**, 2367; J. Valentine, D. Valentine, and J. P. Collman, *ibid.*, 1971, **10**, 220.

constants, the most plausible transition state is (27).[47] A qualitative description of insertion of sulphur dioxide into the tin–carbon bond of Ph_3SnCl is accompanied by some brief mechanistic speculation.[48] Sulphur dioxide inserts easily into tin–carbon and lead–carbon bonds, and one case of its insertion into a germanium–carbon bond is known. Now the first example of its insertion into a silicon–carbon bond, in (28), has been reported.[49] The insertion of sulphur dioxide into metal–alkyl bonds in compounds of the Group III elements aluminium, gallium, and indium has been described.[50]

Sulphur Trioxide.—Investigation of sulphur trioxide insertion into *sp*-element–carbon bonds has now been extended to mercury, as in the reaction with dimethylmercury.[51] Sulphur trioxide insertion reactions have been reviewed.[34]

4 Miscellaneous Compounds

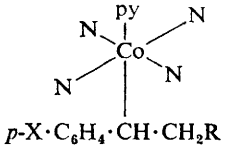
***sp*-Element Halides.**—The kinetics of the reaction of tin(II) chloride or of tin(II) bromide with the $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$ dimer indicate that insertion of the tin into the iron–iron bond is a two-stage process. The first step is reversible breaking of one of the two carbonyl bridges, for which the activation energy is *ca.* 32 kcal mol^{-1}. The second step is nucleophilic attack by the tin halide.[52] In contrast, the reaction of the $[Ni(h^5\text{-}C_5H_5)(CO)]_2$ dimer with tin(II) chloride or with tin(II) bromide is a simple bimolecular reaction. In tetrahydrofuran solution the activation parameters are $\Delta H^{\ddagger} = 19.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.8$ cal deg^{-1} mol^{-1} for the reaction with tin(II) bromide, and $\Delta H^{\ddagger} = 22.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.0$ cal deg^{-1} mol^{-1} for the reaction with tin(II) chloride.[53] The difference in behaviour between the iron and nickel dimeric compounds might be due simply to the greater number of ligands around, and consequent greater difficulty of approach of tin halide to, the iron.

The trichlorides and tribromides of arsenic and of antimony react with $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$ by insertion of MX_3, or of MX_2^+ arising from the self-ionization $2MX_3 \rightleftharpoons MX_2^+ + MX_4^-$, into the iron–iron bond.[54]

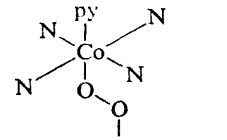
Indium(I), as In_2Br_4, inserts into carbon–bromine and into carbon–iodine bonds,[55] and into metal–metal and metal–halide bonds as in $Mn_2(CO)_{10}$, $MnCl(CO)_5$, or $AuCl(PPh_3)$.[56]

[47] C. W. Fong and W. Kitching *J. Amer. Chem. Soc.*, 1971, **93**, 3791.
[48] R. C. Edmondson, D. S. Field, and M. J. Newlands, *Canad. J. Chem.*, 1971, **49**, 618.
[49] J. Dubac, P. Mazerolles, M. Joly, W. Kitching, C. W. Fong, and W. H. Atwell, *J. Organometallic Chem.*, 1970, **25**, C20.
[50] J. Weidlein, *J. Organometallic Chem.*, 1970, **24**, 63.
[51] K. A. R. Salib and J. B. Senior, *Chem. Comm.*, 1970, 1259.
[52] P. F. Barrett and K. K. W. Sun, *Canad. J. Chem.*, 1970, **48**, 3300.
[53] P. F. Barrett and R. R. Clancy, *Canad. J. Chem.*, 1971, **49**, 2627.
[54] W. R. Cullen, D. J. Patmore, J. R. Sams, M. J. Newlands, and L. K. Thompson, *Chem. Comm.*, 1971, 952.
[55] L. Waterworth and I. J. Worrall, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 403.
[56] A. T. T. Hsieh and M. J. Mays, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 223.

Oxygen.—$[Os(H)(NO)_2(PPh_3)_2]^+$ reacts with oxygen to form $[Os(OH)(NO)_2(PPh_3)_2]^+$, apparently by an insertion reaction, with the consequent hydroperoxo-intermediate $[Os(OOH)(NO)_2(PPh_3)_2]^+$, for which there is a precedent in the chemistry of the $[Co(H)(CN)_5]^{3-}$ anion.[57] A preliminary communication concerning the insertion of oxygen into the cobalt–carbon bond of cobaloximes (29) to produce (30), wherein R = H, Me, or OH and



(29)



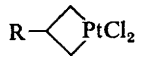
(30)

X = H, OMe, or a halogen, promises a later report on a study of the mechanism of this reaction.[58]

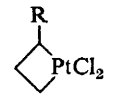
Metals.—The stereochemical course of the reaction between substituted cyclopropanes (31) and platinum(II) chloride, which could give (32) or (33), characterized as their pyridine adducts (34), depends on the balance



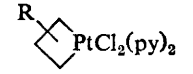
(31)



(32)



(33)



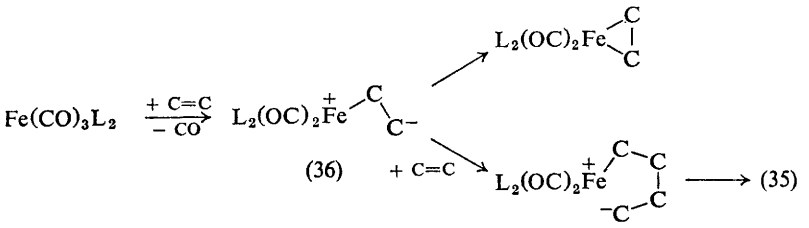
(34)

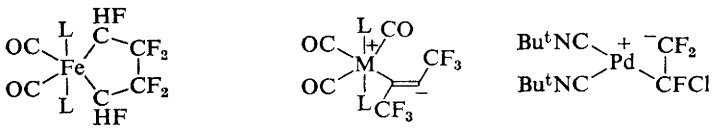
between the energy needed for breaking the appropriate carbon–carbon bond and the energy regained by forming the platinum–carbon bonds.[59] A similar situation obtains in reactions of substituted cyclopropanes with, for example, the $[RhCl(CO)_2]_2$ dimer.[60]

5 Ring Formation and Expansion

Irradiation of hexane solutions containing *trans*-$[M(CO)_3L_2]$, where M = Fe or Ru and L is a phosphine or phosphite, and fluoro-alkenes usually results simply in the formation of a fluoro-alkene complex, but reaction of *trans*-$[Fe(CO)_3\{P(OEt)_3\}_2]$ with $CF_2{=}CFH$ produces the compound (35). Both reactions can be explained by formation of a common ionic intermediate (36), as shown in Scheme 6.[61] A similar situation prevails for reactions of hexafluorobut-2-yne with these complexes *trans*-$[M(CO)_3L_2]$. Here the suggested ionic intermediate is the species (37).[62] A

[57] K. R. Grundy, K. R. Laing, and W. R. Roper, *Chem. Comm.*, 1970, 1500.
[58] K. N. V. Duong, C. Fontaine, C. Giannotti, and A. Gaudemer, *Tetrahedron Letters*, 1971, 1187.
[59] K. G. Powell and F. J. McQuillin, *Tetrahedron Letters*, 1971, 3313.
[60] K. G. Powell and F. J. McQuillin, *Chem. Comm.*, 1971, 931.
[61] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975.
[62] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981.



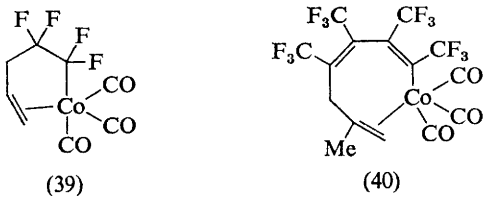


(35) (37) (38)

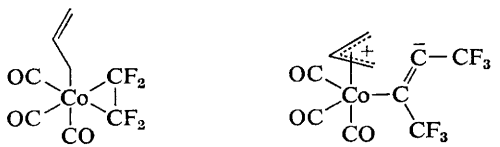
Scheme 6

similar ionic intermediate (38) is proposed in the reaction of $Pd(CNBu^t)_2$ with $CF_2{=}CFCl$, which produces *trans*-$[Pd(CNBu^t)_2(Cl)(CF{=}CF_2)]$.[63]

$Co(\pi\text{-allyl})(CO)_3$ and its π-2-methylallyl analogue react with tetrafluoroethylene or hexafluoropropene to produce cyclic compounds of the type (39). Reaction with hexafluorobut-2-yne involves two insertions, to produce the similar compound (40). There is insufficient evidence to pro-



(39) (40)



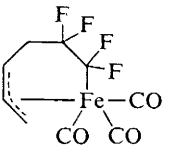
(41) (42)

pose an unequivocal mechanism for these reactions, but it is fairly certain that the π-allyl group and the unsaturated fluorocarbon are both coordinated in adjacent positions to the cobalt in an intermediate. Whether this intermediate is a d^6 species, such as (41), or an ionic equivalent, *e.g.*

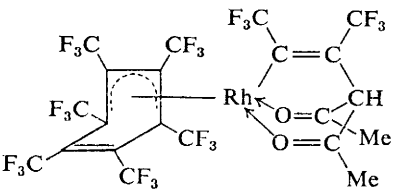
[63] *H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, J. Chem. Soc. (A), 1971, 3472.*

(42), is not known, but the latter seems more likely, particularly for the hexafluorobut-2-yne reaction.[64]

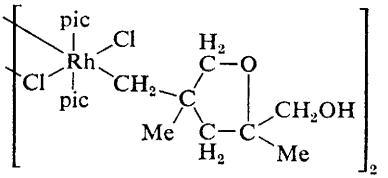
Tetrafluoroethylene reacts with $Fe(CO)_3$(butadiene) by a two-step oxidative addition process to give (43).[65] The reaction of the rhodium(I) complex Rh(acac)(cod) with hexafluorobut-2-yne results both in trimerization of this alkyne, and either its insertion into a γ-bonded acetylacetonate intermediate or a concerted addition to the acetylacetonate ring, to produce (44).[66] $RhCl_3,3H_2O$ reacts with 2-methylallyl alcohol, in the presence of 4-methylpyridine (pic), probably *via* two insertion reactions, to



(43)

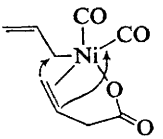


(44)

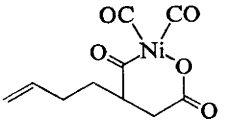


(45)

give the compound (45), which contains a substituted tetrahydrofuran ring methylene-bonded to the rhodium. The product dimer (45) was characterized by *X*-ray crystallographic techniques.[67] The carbonylation of allyl halides by nickel tetracarbonyl has an extraordinary mechanism, whose penultimate step is claimed to be the simultaneous insertion of an alkene grouping into two nickel–carbon bonds, as indicated in (46), to produce (47).[68]



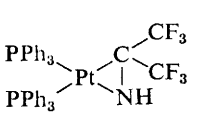
(46)



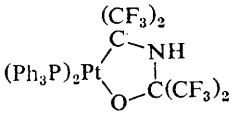
(47)

[64] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3476.
[65] A. Bond, M. Green, B. Lewis, and S. F. W. Lowrie, *Chem. Comm.*, 1971, 1230.
[66] D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Comm.*, 1971, 331.
[67] J. A. Evans, D. R. Russell, A. Bright, and B. L. Shaw, *Chem. Comm.*, 1971, 841.
[68] G. P. Chiusoli and S. Merzoni, *Chem. Comm.*, 1971, 522.

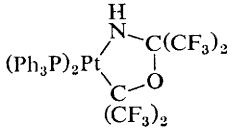
The reaction of (48) with an excess of hexafluoroacetone in ether gives either (49) or (50). The mechanism of this insertion and ring-expansion reaction may involve oxidative addition of the hexafluoroacetone to (48) to give the platinum(IV) intermediate (51).[69] A similar mechanism probably



(48)

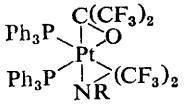


(49)

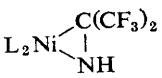


(50)

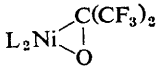
operates for the similar reactions of nickel complexes, of the compound (52) in which L = t-butyl isocyanide with hexafluoroacetone, and of the complementary reaction of (53) with $(CF_3)_2C{=}NH$. Both reactions produce both (54) and (55); the isomer distribution in the products gives some



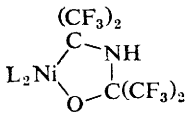
(51)



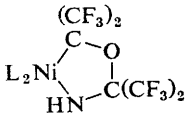
(52)



(53)



(54)

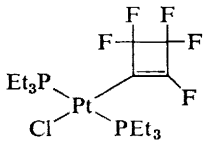


(55)

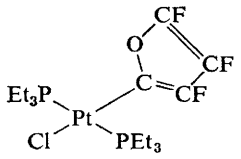
indication of the lifetime and possible intramolecular rearrangement of the oxidative addition intermediates.[70] The mechanism of reaction of $Ni(Bu^tNC)_4$ with hexafluoroacetone and $(CF_3)_2C{=}NH$ has also been discussed.[71]

The mechanism for the conversion of the perfluorocyclobutenyl group on platinum in (56) to a furyl group (57) may involve attack of water at the perfluorocyclobutenyl-carbon bonded to the platinum, conversion into an

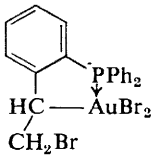
[69] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3161.
[70] M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2828.
[71] A. Greco, M. Green, S. K. Shakshooki, and F. G. A. Stone, *Chem. Comm.*, 1970, 1374.



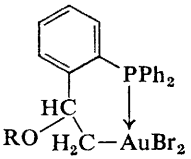
(56)



(57)



(58)



(59)

acyclic ketone, and subsequent ring closure to incorporate the oxygen.[72] Heating the gold(III) compound (58) in methanol, ethanol, or aqueous acetone not only solvolyses the *C*-bromine but also results in ring expansion. The product (59) probably results from a Wagner–Meerwein reaction.[73]

[72] W. J. Cherwinski and H. C. Clark, *J. Organometallic Chem.*, 1971, **29**, 451.
[73] M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, R. Mason, P. B. Hitchcock, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 1971, **93**, 4592.

5
Reactions of Co-ordinated Ligands

BY R. D. W. KEMMITT AND J. BURGESS

1 Carbonyls and Nitrosyls

Carbonyls.—The possibility of nucleophilic attack at the carbonyl-C rather than at the metal atom of metal carbonyl complexes is by now a well-established reaction route, particularly for nitrogen-containing nucleophiles. Thus azide ion reacts with the Group VI hexacarbonyls, $M(CO)_6$, by attack at carbon. However, with Group VII carbonyls and carbonyl halides, azide ion may react either at the carbonyl-C or at the metal to displace carbon monoxide or another ligand directly. An example of the latter course of reaction is that of $MnBr(CO)_5$ with sodium azide in aqueous ethanol, where the product is the tris-μ-azido-compound $Mn_2(CO)_6(N_3)_3$.[1] Azide ion attacks at the carbonyl-C of $[Fe(h^5\text{-}C_5H_5)(C_2H_4)(CO)_2]^+$, but cyanate or cyanide ions displace the ethylene.[2] Cyanate ion reacts with $[Fe(h^5\text{-}C_5H_5)(CO)_3]^+$ by direct displacement of carbon monoxide as a result of nucleophilic attack at the metal, not at the carbonyl-C.[3] Various other examples of nucleophilic attack at carbonyl-C atoms have been described [4–7] and are collected in the Table. Kinetic results are available for reactions of $W(CO)_6$ or $W(CO)_5(PPh_3)$ with Grignard reagents,[8] $[Fe(h^5\text{-}C_5H_5)(CO)_2L]^+$ with azide ion,[9] and *trans*-$[PtCl(CO)(PPh_3)_2]$ with alcohols.[10]

The converse reaction, of attack of carbon monoxide at, for instance, co-ordinated azide, is also observed. Thus carbonylation of $Pt(NCO)(N_3)(PPh_3)_2$ in ethanol gives some $Pt(NCO)_2(PPh_3)_2$,[11] and $Mo(h^5\text{-}C_5H_5)(N_3)(CO)(PPh_3)_2$ reacts with carbon monoxide when irradiated to give

[1] R. Mason, G. A. Rusholme, W. Beck, H. Englemann, K. Joos, B. Lindenberg, and H. S. Smedal, *Chem. Comm.*, 1971, 496.
[2] L. Busetto, A. Palazzi, R. Ros, and U. Belluco, *J. Organometallic Chem.*, 1970, **25**, 207.
[3] L. M. Charley and R. J. Angelici, *Inorg. Chem.*, 1971, **10**, 868.
[4] W. Beck and B. Lindenberg, *Angew. Chem. Internat. Edn.*, 1970, **9**, 735.
[5] J. T. Moelwyn-Hughes, A. W. B. Garner, and A. S. Howard, *J. Chem. Soc.* (*A*), 1971, 2370.
[6] J. T. Moelwyn-Hughes, A. W. B. Garner, and A. S. Howard, *J. Chem. Soc.* (*A*), 1971, 2361.
[7] A. E. Kruse and R. J. Angelici, *J. Organometallic Chem.*, 1970, **24**, 231.
[8] D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, 1971, **5**, 247.
[9] M. Graziani, L. Busetto, and A. Palazzi, *J. Organometallic Chem.*, 1971, **26**, 261.
[10] J. E. Byrd and J. Halpern, *J. Amer. Chem. Soc.*, 1971, **93**, 1634.
[11] W. Beck, M. Bauder, G. La Monica, S. Cenini, and R. Ugo, *J. Chem. Soc.* (*A*), 1971, 113.

Table *Reactions whose mechanism involves nucleophilic attack at carbonyl-C rather than at metal centres; compounds arranged by Periodic Table order of metals*

Carbonyl compound	*Nucleophile*	*Products*	*Ref.*
$M(CO)_6$ [a]	hydroxylamine	$[M(NCO)(CO)_5]^-$	4
$W(CO)_6$	$PhCH_2MgCl$		8
$W(CO)_5(PPh_3)$	$PhCH_2MgCl$		8
$Mn(Br)(CO)_3(PMe_2Ph)_2$	hydrazine	$Mn(NCO)(CO)_2(N_2H_4)(PMe_2Ph)_2$	5
$Re(X)(CO)_3(PR_3)_2$ [b]	hydrazine	$Re(NCO)(CO)_2(N_2H_4)(PR_3)_2$	6
$[Fe(h^5\text{-}C_5H_5)(C_2H_4)(CO)_2]^+$	azide ion	$Fe(h^5\text{-}C_5H_5)(NCO)(CO)(C_2H_4)$	2
$[Fe(h^5\text{-}C_5H_5)(CO)_2L]^+$ [c]	azide ion	$Fe(h^5\text{-}C_5H_5)(NCO)(CO)L$	9
$[Ru(h^5\text{-}C_5H_5)(CO)_3]^+$	azide ion	$Ru(h^5\text{-}C_5H_5)(NCO)(CO)_2$	7
	hydrazine	carbazoyl derivative	7
	primary amines	carbamoyl derivatives	7
trans-$[PtCl(CO)(PPh_3)_2]^+$	alcohols	alkoxycarbonyl compounds	10

[a] M = Cr, Mo, or W; [b] similar reactions for several tetracarbonyl analogues (ref. 6); [c] L = C_2H_4, CO, or PPh_3.

$Mo(h^5\text{-}C_5H_5)(NCO)(CO)(PPh_3)_2$.[12] Moreover, this carbon monoxide plus azide reaction can take place as an intramolecular reaction of co-ordinated ligands, for the complex $Mo(h^5\text{-}C_5H_5)(N_3)(CO)_2(PPh_3)$ reacts with triphenylphosphine to give $Mo(h^5\text{-}C_5H_5)(NCO)(CO)(PPh_3)_2$. In the latter two reactions the mechanism may not involve direct attack of carbon monoxide on an intact azide ligand, but might rather proceed *via* a nitrene intermediate which picks up carbon monoxide.[12]

In mixed complexes containing carbonyl and thiocarbonyl ligands, nucleophilic attack at co-ordinated carbon could take place either at carbonyl-C or at thiocarbonyl-C. $[Fe(h^5\text{-}C_5H_5)(CO)_2(CS)]^+$ reacts with, for example, azide ion or hydrazine by attack of the nucleophile at the thiocarbonyl-C.[13] On the other hand, methoxide ion attacks $[Ir(CO)_2(CS)(PPh_3)_2]^+$ at the carbonyl-C.[14]

Nitrosyls.—A product characterization and ^{15}N-tracer study of the reaction of *trans*-$[RuCl(NO)(diars)_2]^{2+}$ with nitrogen bases, for example hydrazine, indicates nucleophilic attack at the nitrosyl-N.[15] Similarly, the reaction of azide ion with $[RuCl(NO)(bipy)_2]^{2+}$ is thought to involve attack at the nitrosyl-N. The rate law for this reaction is first order in each reactant.[16] Varying degrees of nitrosyl-protonation are involved in the following reactions of metal nitrosyl compounds with hydrogen chloride:[17]

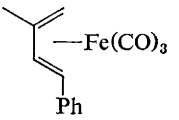
$$OsCl(CO)(NO)(PPh_3)_2 \longrightarrow OsCl_2(CO)(HNO)(PPh_3)_2$$

$$Os(NO)_2(PPh_3)_2 \longrightarrow OsCl_2(NHOH)(NO)(PPh_3)_2$$

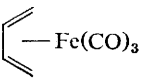
$$Ir(NO)(PPh_3)_3 \longrightarrow IrCl_3(NH_2OH)(PPh_3)_2$$

2 Alkenes and Alkynes

Linear Alkenes and Alkynes.—N.m.r. studies of protonation and deuteriation of the iron-diene compound (1), which is easier to work with than the



(1)



(2)

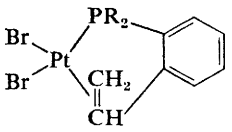
simpler parent compound (2), give convincing proof that the earlier assumption that the proton takes up its position on the ligand on the side close to the metal is correct.[18] Both acids (*i.e.* H^+) and sulphur dioxide react with

[12] A. T. McPhail, G. R. Knox, C. G. Robertson, and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 205.
[13] L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, 1971, **10**, 78.
[14] M. J. Mays and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1971, 2747.
[15] P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, 1971, **93**, 84.
[16] F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, 1971, **93**, 1294.
[17] K. R. Grundy, C. A. Reed, and W. R. Roper, *Chem. Comm.*, 1970, 1501.
[18] T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, 1971, **93**, 5296.

$Mn(prop\text{-}2\text{-}ynyl)(CO)_4(PPh_3)$, by electrophilic attack at the propynyl-C atom remote from the manganese.[19]

The rate-determining step in the reaction of $Ph_3SnCH_2CH{=}CHR$, where R = H, Me, or Ph, with iodine is thought to be unimolecular decomposition of a π-complex between the organotin compound and the iodine. Kinetic parameters and product distributions have been obtained for this reaction in a variety of solvents, in some cases with the addition of iodide ion to the reaction mixture. In acetone or acetonitrile the mechanism is said to involve attack at the carbon atom γ to the tin, but in the more polar solvents methanol and dimethyl sulphoxide there is also some direct electrophilic attack by iodine or iodide ion at the tin.[20]

The vinylphenylphosphine complex (3), with R = Ph, undergoes a complicated oxidative-addition reaction with bromine, but the analogous

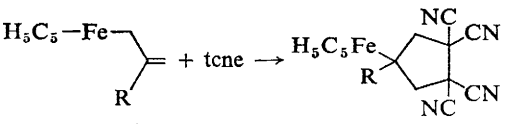


(3)

complex with R = *o*-vinylphenyl reacts with bromine simply at the two non-co-ordinated vinyl groups without oxidation of the metal to platinum(IV).[21]

Strongly basic amines (alkylamines, pK_b 3—6) react with *syn,syn*-1,5-dimethylpentadienyliron tricarbonyl to give *cis,trans*-dienylamines, but weakly basic amines (arylamines, pK_b *ca.* 10) react with inversion to give *trans,trans*-dienylamines. The best explanation of this difference is that product control is kinetic for the strong bases, thermodynamic for the weak ones.[22]

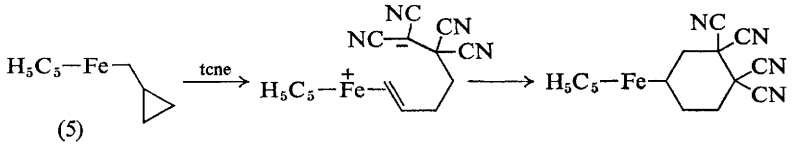
The mechanism of reactions of $Fe(h^1\text{-allyl})(h^5\text{-}C_5H_5)$ (4) or $Fe(h^5\text{-}C_5H_5)(h^1\text{-cyclopropylmethyl})$ (5) with electrophiles, such as tetracyanoethylene or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, *e.g.*



(4)

[19] W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. L. Loader, *J. Chem. Soc.* (*A*), 1971, 930.
[20] R. M. G. Roberts, *J. Organometallic Chem.*, 1970, **24**, 675.
[21] D. I. Hall and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, 1491.
[22] G. Maglio, A. Musco, and R. Palumbo, *J. Organometallic Chem.*, 1971, **32**, 127.

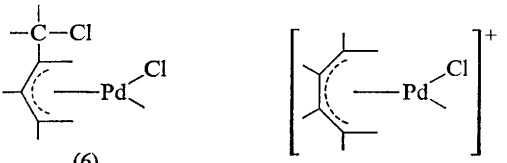
may be concerted, or may involve a dipolar intermediate, *e.g.*



(5)

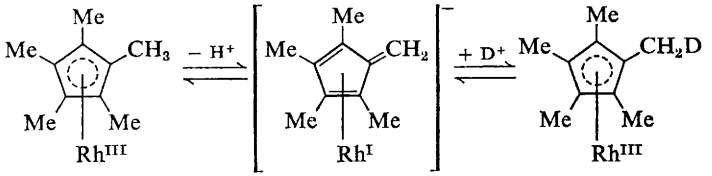
The latter mechanism seems intuitively more likely.[23]

The abstraction of chloride ion by strong acids from chloroalkyl-π-allylpalladium species (6) produces the stable tetrahapto-carbonium ion complex (7). This is in effect a model S_N1 transition state.[24]

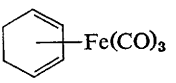


(6) (7)

Cyclic Alkenes.—The $[\{Rh(h^5\text{-}C_5Me_5)\}_2(OH)_3]^+$ cation undergoes hydrogen–deuterium exchange in D_2O–OD^- solution, not only with the hydroxide protons but also with the pentamethylcyclopentadienyl ligands. The mechanism suggested has as its principal feature the deprotonation of a methyl group to give a formally rhodium(I) intermediate:[25]



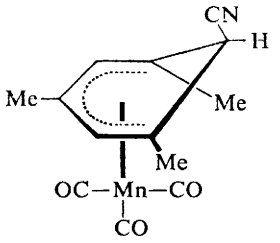
There have been two investigations of protonation of cyclohexa-1,3-dieneiron tricarbonyl (8) and its methoxy-derivatives.[18, 26] Protonation occurs on the side of the cyclic diene ligand which is closer to the metal.[18]



(8)

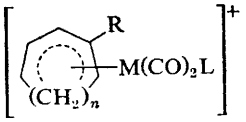
[23] W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **93**, 5299.
[24] J. Lukas and P. A. Kramer, *J. Organometallic Chem.*, 1971, **31**, 111.
[25] J. W. Kang and P. M. Maitlis, *J. Organometallic Chem.*, 1971, **30**, 127.
[26] A. J. Birch and M. A. Haas, *J. Chem. Soc.* (*C*), 1970, 2465.

The reaction of $[Mn(arene)(CO)_3]^+$ with cyanide ion was thought to proceed through an ionic intermediate, but now the intermediate has been isolated and its chemical and spectroscopic properties are not consistent with an ionic formulation. Rather, the cyanide appears to have added to one carbon of the arene ring giving, for arene = mesitylene, the compound (9).[27]



(9)

The kinetics of reactions of the cyclohexadienyl and cycloheptatrienyl compounds of iron and osmium (10) with acetylacetone or dimedone have been determined in acetonitrile solution. The rate law suggests that the

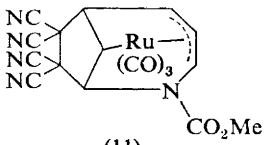


M = Fe or Os
R = H or OMe
L = CO or PPh_3
n = 1 or 2

(10)

mechanism involves a pre-equilibrium between the β-diketone and its deprotonated anion, followed by rate-determining attack of the reactive carbanion at the co-ordinated cycloalkene ring. The cycloheptadienyl compounds are slightly less susceptible than the cyclohexadienyl compounds to nucleophilic attack.[28]

Crystal-structure determination of the respective products show that tcne adds in 1,3-positions to cycloheptatriene co-ordinated to $Fe(CO)_3$, and in 1,6-positions to *N*-methoxycarbonylazepine co-ordinated to $Ru(CO)_3$, giving (11). These results show the difference caused by



(11)

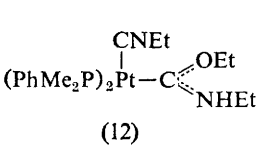
[27] P. J. C. Walker and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 404.
[28] L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1971, 1602.

co-ordination, for tcne adds 1,4 to *N*-ethoxycarbonylazepine—1,6-addition is thermally forbidden for the unco-ordinated azepine.[29]

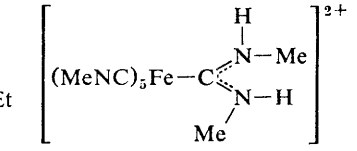
Products of electrophilic substitution and of addition reactions of cyclo-octatetraene co-ordinated to $Fe(CO)_3$ have been studied.[30]

3 Other Ligands

The reactions of co-ordinated isocyanide in $Pt(CNEt)_2(PMe_2Ph)_2$ with ethanol, aniline, benzyl mercaptan, or similar compounds occur by 1,2-*cis*-addition to the carbon–nitrogen bond, to give carbene compounds of the type (12).[31] Addition of methylamine to co-ordinated methyl isocyanide in $[Fe(CNMe)_6]^{2+}$ is thought to occur by attack of methyl-amine-N at isocyanide-C, to give initially (13).[32]



(12)

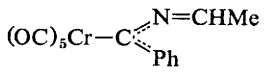


(13)

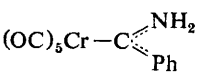
There have been three reports of reactions involving $Cr(CO)_5$(carbene) compounds. The rate law for reaction of $Cr(CO)_5\{C(OMe)Ph\}$ with primary amines in a variety of solvents is

$$+\ d[Cr(CO)_5\{C(NHR)Ph\}]/dt = k[Cr(CO)_5\{C(OMe)Ph\}][RNH_2][HY][Z]$$

Here HY is a proton donor and Z is a proton acceptor—in most cases these roles are performed by the amine and/or the solvent. All these reactions have a *negative* activation energy, and all the experimental observations can be accommodated by the mechanism shown in the Scheme.[33] The same carbene complex, $Cr(CO)_5\{C(OMe)Ph\}$, reacts with aminoethanol in two ways, to produce (14) and (15). Both are formed by attack at the carbene-C; (14) arises from attack by HN=CHMe (aminoethanol minus the elements of water), and (15) from attack by NH_3 (aminoethanol minus the elements of acetaldehyde).[34] The compound $Cr(CO)_5${acetoxy-(2-furyl)carbene} reacts with hydrazoic acid to give $Cr(CO)_5$(2-furonitrile).

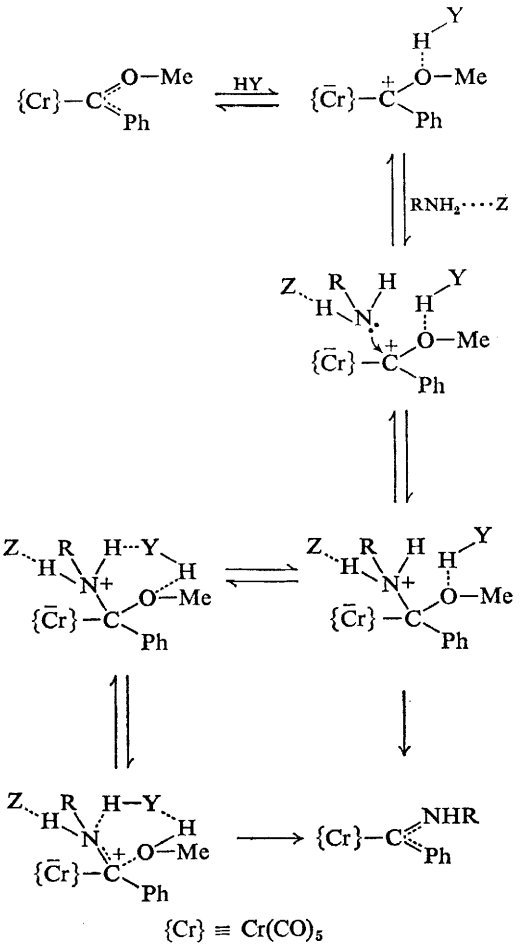


(14)



(15)

[29] M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *Chem. Comm.*, 1971, 222.
[30] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc.* (*A*), 1971, 422.
[31] H. C. Clark and L. E. Manzer, *J. Organometallic Chem.*, 1971, **30**, C89.
[32] J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, 1971, **93**, 4613.
[33] H. Werner, E. O. Fischer, B. Heckl, and C. G. Kreiter, *J. Organometallic Chem.*, 1971, **28**, 367.
[34] L. Knauss and E. O. Fischer, *J. Organometallic Chem.*, 1971, **31**, C68.



$\{Cr\} \equiv Cr(CO)_5$

Scheme

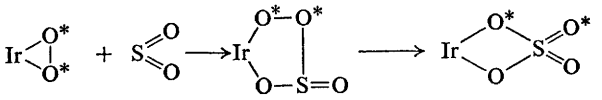
The first step is attack at the carbene-C to form $Cr(CO)_5\{C(N_3)$-2-furyl$\}$. This can lose dinitrogen and rearrange either in a concerted or a two-stage manner. The latter would have a transient nitrene intermediate. As the authors had no success in trapping any such nitrene the former, concerted, mechanism is preferred.[35]

Hydrogen exchange with the α-carbon-protons of the co-ordinated amino-acids in $[Mo(h^5\text{-}C_5H_5)_2$(amino-acid)$]^+$ could involve a carbanion or an oxazolonium ion intermediate.[36] Whereas benzyl thiocyanate

[35] J. A. Connor and E. M. Jones, *J. Chem. Soc.* (*A*), 1971, 3368.
[36] E. S. Gore and M. L. H. Green, *J. Chem. Soc.* (*A*), 1970, 2315.

isomerizes very slowly to benzyl isothiocyanate, benzyl thiocyanate co-ordinated to $Cr(CO)_3$ isomerizes to the isothiocyanate rapidly. The $Cr(CO)_3$ moiety may stabilize the benzyl cation, thus facilitating loss and subsequent return and rearrangement of the thiocyanate ion in an intermolecular mechanism of isomerization.[37]

The reaction of molecular oxygen complexes of iridium or platinum with sulphur dioxide to produce sulphato-complexes involves both insertion into a metal–oxygen bond and bond formation between the sulphur and the leaving oxygen, with subsequent rearrangement of the peroxo-sulphite intermediate thus generated:[38]



Interestingly, both $Ir(SC_6F_5)(O_2)(CO)(PPh_3)_2$ plus sulphur dioxide and $Ir(SC_6F_5)(SO_2)(CO)(PPh_3)_2$ plus oxygen give the *same* sulphato-complex of iridium.[39] It could be argued that many other insertion (or migration) reactions of organometallic compounds are in reality reactions of co-ordinated ligands, but the reader is referred to Part IV Chapter 4 for discussion of these reactions. We have also, as in the previous volume of this Report, omitted references to reactions of co-ordinated compounds, particularly of cyclopentadiene and its derivatives in ferrocenes, where the primary appeal appears to be to organic chemists.

[37] A. Ceccon, *J. Organometallic Chem.*, 1971, **29**, C19.
[38] R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, 1970, **9**, 2367; J. Valentine, D. Valentine, and J. P. Collman, *ibid.*, 1971, **10**, 220.
[39] M. H. B. Stiddard and R. E. Townsend, *J. Chem. Soc.* (*A*), 1970, 2179.

6
Oxidative Addition and Reductive Elimination

BY R. D. W. KEMMITT AND J. BURGESS

1 Introduction

This chapter deals with references concerning oxidative addition reactions of transition-metal complexes, the closely related reaction of oxidative elimination, and the converse reaction, which is reductive elimination. Oxidative addition is simply what the name implies, *e.g.*

$$\textit{trans}\text{-}[Ir^{I}Cl(CO)(PPh_3)_2] + XY \longrightarrow Ir^{III}(Cl)(X)(Y)(CO)(PPh_3)_2$$

In oxidative elimination the addition of the oxidant is accompanied, or more usually preceded, by the loss of one or more ligands from the transition-metal complex, *e.g.*

$$Pt^{0}(PPh_3)_4 + XY \longrightarrow Pt^{II}(X)(Y)(PPh_3)_2 + 2PPh_3$$

Oxidative additions are particularly common for square-planar complexes; the electronic configuration of the metal changes from d^8 to d^6. Oxidative eliminations are common for d^{10} complexes, which give d^8 products. Oxidations of d^6 centres to d^4 are less common, though a recent example will be found in the section on ruthenium below. Indeed, for ruthenium, both $d^6 \rightarrow d^4$, *i.e.* ruthenium(II) to ruthenium(IV), and $d^8 \rightarrow d^6$, *i.e.* ruthenium(0) to ruthenium(II), processes are possible. Again, for platinum, $d^8 \rightarrow d^6$, corresponding to platinum(II) to platinum(IV), and $d^{10} \rightarrow d^8$, corresponding to platinum(0) to platinum(II), oxidative additions or eliminations are encountered.

Although in this chapter we shall be restricting coverage to reactions of transition-metal complexes, the phenomenon of oxidative addition is not confined to this type of compound. Such reactions are also well established for non-transition metals—a recently reported example [1] concerns the oxidative addition of methyl bromide to indium(I) bromide to give $InBr_2Me$—and for non-metals, as in the reaction of phosphorus trichloride with chlorine, to cite a very familiar example. Likewise, reductive eliminations are known and studied outside the area of transition-metal complexes. One example has been mentioned in Chapter 1 of Part II of this volume, namely the elimination of alkyl halides from the thallium(III) compounds $TlRX_2$.[2]

[1] L. Waterworth and I. J. Worrall, *Chem. Comm.*, 1971, 569.
[2] M. D. Johnson, *Chem. Comm.*, 1970, 1037.

Sometimes the reactions of oxidative addition and reductive elimination are coupled, in the sense of the latter following the former. This situation arises particularly in platinum chemistry, where a platinum(II) compound may react with a molecule of the type associated with oxidative addition to give another platinum(II) compound, *via* the formation of a transient platinum(IV) intermediate. This sequence of reactions is often encountered in homogeneous catalysis (see Chapter 3 of this Part).

Oxidative addition has been the subject of one general, concise review.[3]

2 Oxidative Addition: Group VIII Elements

Iron.—Iron pentacarbonyl undergoes an oxidative elimination reaction with hexamethylditin, in which one molecule of carbon monoxide is lost per molecule of pentacarbonyl. The product is the octahedral iron(II) compound $Fe(SnMe_3)_2(CO)_4$.[4] Alkyl halides also react with the iron(0) carbonyls $Fe(CO)_3(PR_3)_2$ and $Fe(CO)_4(PR_3)$ as well as $Fe(CO)_5$, but these are not simple oxidative eliminations. Thus methyl iodide does react with $Fe(CO)_3(PMe_3)_2$ to produce the iron(II) compound $Fe(I)(Me)(CO)_2(PMe_3)_2$, but the reaction goes through the formation of an acetyl derivative $Fe(I)(COMe)(CO)_2(PMe_3)_2$, with subsequent loss of carbon monoxide and a 'reverse methyl migration' step.[5] In another report of reactions of alkyl halides, this time specifically the bromides RBr, with $Fe(CO)_5$, the product of the oxidative addition step was suggested to be $[Fe(R)(CO)_4]^-$, which subsequently isomerized to $[Fe(COR)(CO)_3]^-$. In the presence of triphenylphosphine and acid this latter anion can react further to produce an aldehyde. Overall this reaction sequence represents the conversion of RBr to RCHO.[6]

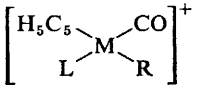
Ruthenium.—The oxidative addition of quinones to d^8 and to d^{10} metal centres is well documented. Now the oxidative addition of *o*-quinones to the d^6 complex $RuCl_2(PPh_3)_3$ has been reported.[7] The reactions of ruthenium and iron cyclopentadienyl carbonyl dimers with azobenzene are described later (see manganese and rhenium).

Osmium.—Earlier studies on oxidative elimination reactions of iron(0) and ruthenium(0) compounds with unsaturated organic compounds containing electronegative substituents have been complemented by an investigation of the reactions of *trans*-$[Os(CO)_3\{P(OMe)_3\}_2]$ and of *trans*-$[Os(CO)_3(PMe_2Ph)_2]$ with tetrafluoroethylene, trifluoroethylene, and chlorotrifluoroethylene.[8]

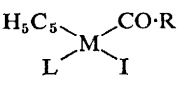
Cobalt.—A detailed kinetic study of oxidative addition of alkyl iodides to the compounds $M(h^5\text{-}C_5H_5)(CO)L$, where M = Co, Rh, or Ir, and L = a

[3] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.
[4] E. W. Abel and S. Moorhouse, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 905.
[5] M. Pańkowski and M. Bigorgne, *J. Organometallic Chem.*, 1971, **30**, 227.
[6] M. P. Cooke, *J. Amer. Chem. Soc.*, 1970, **92**, 6080.
[7] A. L. Balch and Y. S. Sohn, *J. Organometallic Chem.*, 1971, **30**, C31.
[8] M. Cooke, M. Green, and T. A. Kuc, *J. Chem. Soc.* (*A*), 1971, 1200.

tertiary phosphine, has been reported. The dependence of rates on the nature of the metal, the nature of the phosphine L, the nature of the alkyl iodide (methyl *vs.* ethyl), and the solvent, has been established. The mechanism proposed to account for all these observations is of initial attack by the metal atom at the α-carbon of the alkyl iodide. The resultant ionic species (1) is in fact the final product for M = Ir, but for M = Co or Rh it is a transient intermediate which co-ordinates iodide and undergoes an alkyl-migration step to give the product (2).[9]



(1)

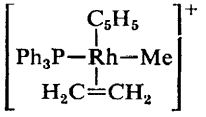


(2)

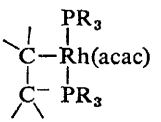
Triethoxysilane reacts with the cobalt(I) complex $CoH(N_2)(PPh_3)_3$ to give the cobalt(III) derivative $Co(H)_2\{Si(OEt)_3\}(PPh_3)_3$ with elimination of molecular nitrogen.[10]

Rhodium.—The kinetics of reaction of $Rh(h^5\text{-}C_5H_5)(CO)(PR_3)$ with alkyl[9] and with benzyl [11] halides indicate a second-order rate law and nucleophilic attack by the rhodium at the α-carbon of the alkyl or benzyl halide. The kinetics of reaction of the above rhodium complex with PR_3 = PPh_3 with allyl halides suggest a more complicated mechanism.[11]

The ionic intermediate (3) is suggested in the reaction of $Rh(h^5\text{-}C_5H_5)(C_2H_4)(PPh_3)$ with methyl iodide.[12] Oxidative addition of perfluoroalkyl iodides to $Rh(h^5\text{-}C_5H_5)(C_2H_4)_2$ gives rhodium(III) derivatives, for example $Rh(h^5\text{-}C_5H_5)(C_2H_4)(C_3F_7)(I)$ from C_3F_7I.[13] Perfluoro-organic halides and fluoroalkenes add oxidatively to $Rh(acac)(PR_3)_2$ compounds; ionic intermediates, of the type (4), have also been suggested here.[14] Several oxidative



(3)



(4)

addition reactions of $Rh(h^5\text{-}C_5H_5)(CO)_2$ have been described.[15] Although oxidative additions to neutral rhodium compounds have frequently been reported, it is only in the past couple of years that oxidative additions to

[9] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.
[10] N. J. Archer, R. N. Haszeldine, and R. V. Parish, *Chem. Comm.*, 1971, 524.
[11] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1653.
[12] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1165.
[13] A. J. Mukhedkar, V. A. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3158.
[14] A. J. Mukhedkar, V. A. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3166.
[15] J. W. Kang and P. M. Maitlis, *J. Organometallic Chem.*, 1971, **26**, 393.

cationic rhodium compounds have been carried out. The first reports dealt with the cations $[Rh\{P(OR)_3\}_4]^+$, with R = Me, Et, or Pr^i, and $[Rh\{P(OR)_3\}_5]^+$, with R = Me or Et.[16] Subsequently, oxidative additions to $[Rh(CNR)_4]^+$, $[Rh(CNR)_2(PPh_3)_2]^+$, and $[Rh(CNR)_3(PPh_3)_2]^+$ were achieved. The mechanism of reaction of the last named five-co-ordinate cation includes both oxidative elimination and electrophilic attack by, for instance, the iodide of an alkyl iodide, to produce a transient dicationic species.[17]

The reaction of *trans*-$[RhCl(CO)_2L]$, where L = SEt_2, $SeEt_2$, or $TeEt_2$, with hydrogen chloride in pentane gives $RhCl_3(CO)L_2$. The mechanism of this reaction is thought to involve two oxidative additions of hydrogen chloride to the rhodium compound. $RhCl_3(CO)L_2$ can also be generated directly by the addition of chlorine itself to $RhCl(CO)_2L$.[18]

Iridium.—A kinetic study of oxidative addition of alkyl iodides to $Ir(h^5\text{-}C_5H_5)(CO)(PR_3)$ has been mentioned under cobalt (*q.v.*).[11] There is evidence for a transitory ionic intermediate $[IrMe(h^5\text{-}C_5Me_5)(CO)_2]^+I^-$ in the reaction of $Ir(h^5\text{-}C_5Me_5)(CO)_2$ with methyl iodide.[19] This suggestion parallels a similar one for oxidative addition to the analogous rhodium(I) compound $Rh(h^5\text{-}C_5H_5)(CO)_2$.[15]

Stereochemistry. Past and current discussions on the stereochemical course of oxidative addition reactions are centred on iridium(I) compounds, though several stereochemical studies at other metal centres, especially cobalt(I), have been conducted.

Inversion of configuration was reported for the oxidative addition of *trans*-1-bromo-2-fluorocyclohexane to *trans*-$[IrCl(CO)(PMe_3)_2]$, in dichloromethane.[20] Recently an attempt to confirm this observation failed, and it was claimed that there was no reaction between these two compounds.[21] This is not very surprising in the light of the generally low reactivity of other acyclic halides towards iridium(I) compounds.

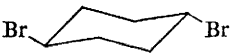
Retention of configuration at the carbon centre has been reported for the reaction of ethyl α-bromopropionate with a range of iridium(I) compounds *trans*-$[IrX(CO)L_2]$, where X = Cl, I, or SCN, and L = PPh_3 or PPh_2Me. These reactions were thought to take place by a one-step concerted process.[22] There is, unfortunately, one weak link in the argument which leads to the proposal of retention of configuration at carbon in the oxidative addition process. A subsequent iridium–carbon bond cleavage by halogen is assumed to take place with retention of configuration, whereas evidence from similar reactions of cobalt and iron compounds suggests

[16] L. M. Haines, *J. Organometallic Chem.*, 1970, **25**, C85; *Inorg. Chem.*, 1971, **10**, 1693.
[17] J. W. Dart, M. K. Lloyd, J. A. McCleverty, and R. Mason, *Chem. Comm.*, 1971, 1197.
[18] F. Faraone, R. Pietropaolo, and S. Sergi, *J. Organometallic Chem.*, 1970, **24**, 797.
[19] R. B. King and A. Efraty, *J. Organometallic Chem.*, 1971, **27**, 409.
[20] J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Comm.*, 1970, 612.
[21] F. R. Jensen and B. Knickel, *J. Amer. Chem. Soc.*, 1971, **93**, 6339.
[22] R. W. Johnson and R. G. Pearson, *Chem. Comm.*, 1970, 986; R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5519.

that inversion may well occur.[21] Thus the stereochemical changes observed in a reaction cycle starting from, and finishing at, $[Co(dmgH)_2py]^-$ and (−)-1-methylheptyl bromide, strongly suggest inversion at carbon in cobalt–carbon bond cleavage by bromine.[23] Cobalt–carbon bond cleavage, by, for example, bromine in dichloromethane, in cyclohexylcobaloximes, (5) → (6), also takes place with inversion at the carbon.[24]



(5)



(6)

Iron–carbon bond cleavage in the reaction of $Me_3C{\cdot}CHD{\cdot}CHD{\cdot}Fe(h^5\text{-}C_5H_5)(CO)_2$ with bromine also takes place predominantly with inversion of configuration at the carbon.[25] Thus it would seem more likely that the correct interpretation of the stereochemistry of α-bromopropionate addition to iridium(I) is that this reaction involves inversion at the carbon atom, but at the time of writing none of the evidence available gives unequivocal support to this hypothesis. Reaction of silanes with *trans*-$[IrCl(CO)(PPh_3)_2]$ seems to involve retention of configuration at silicon.[26]

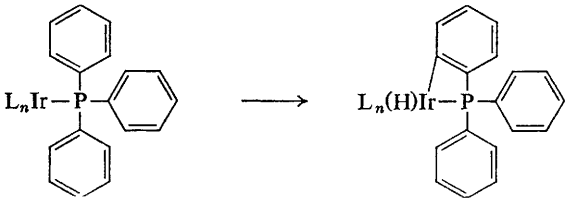
Addition of Oxygen. Rate constants for the forward and reverse reactions, and activation parameters for the forward reaction, have been determined for the equilibria

$$\textit{trans}\text{-}[IrCl(CO)L_2] + O_2 \rightleftharpoons IrCl(O_2)(CO)L_2$$

where L = one of eight phosphines or triphenylarsine. Equilibrium constants have been calculated from the ratios of the forward and reverse rate constants; there is a fair correlation between the equilibrium constants and the respective forward and reverse rate constants. For compounds containing the phosphines $P(C_6H_4X\text{-}p)_3$, where X = H, Cl, Me, or OMe, there is a correlation of logarithms of the rate constants for the forward reaction with Hammett σ values of the substituents. This suggests a connection between the basicity of the phosphines and the reactivity of their respective iridium(I) complexes towards molecular oxygen.[27] Thermodynamic data for addition of oxygen, sulphur dioxide, hydrogen, or ethylene to iridium(I) and rhodium(I) complexes have been compared with kinetic data in an attempt to describe the role of the metal in activating these adduct molecules.[28] The effect of steric factors in determining the affinity of four-co-ordinate iridium cations for oxygen has been assessed.[29]

[23] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 571.
[24] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1971, **93**, 5283.
[25] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 1971, **93**, 1529.
[26] L. H. Sommer, J. E. Lyons, and H. Fujimoto, *J. Amer. Chem. Soc.*, 1969, **91**, 7051.
[27] L. Vaska and L. S. Chen, *Chem. Comm.*, 1971, 1080.
[28] L. Vaska, *Inorg. Chim. Acta*, 1971, **5**, 295.
[29] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758.

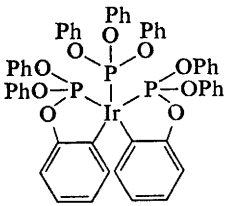
Intramolecular Oxidative Addition. This type of oxidative addition is commonly encountered with phosphine and phosphite complexes of iridium(I). It involves insertion of the iridium into a phenyl-carbon–hydrogen bond, resulting in iridium–carbon bond formation:



A recent example of this type of orthometallation is provided by the second stage of the reaction of IrCl(cyclo-octene) with triphenylphosphite.[30] Some iridium(I)–phosphite complexes react to form not just one but two or three iridium–carbon bonds per molecule. The reaction sequence then involves hydrogen elimination between intramolecular oxidative additions:[31]

$$L_nIr(H)\{P(OPh)_3\} \longrightarrow L_nIr(H)_2\{P(OPh)_2(OC_6H_4)\}$$
$$\longrightarrow L_nIr\{P(OPh)_2(OC_6H_4)\} + H_2$$
$$\longrightarrow \text{second intramolecular cyclization, } \textit{etc.}$$

In the particular case of the reaction of $Ir(H)(Cl)\{P(OPh)_3\}$ in boiling decalin, an *X*-ray crystal-structure determination of the product (7)



(7)

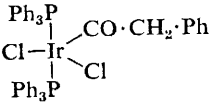
confirms the formation of two iridium–phenyl-carbon bonds in this instance.[32] These oxidative addition orthometallations are even easier for phosphite complexes than for phosphine complexes, for the iridocyclic ring is five-membered from the former, four-membered from the latter.

Miscellaneous Examples. Recent preparative papers dealing with oxidative addition include those concerning *trans*-$[IrCl(CO)(PPh_3)_2]$ with the thiophenols C_6H_5SH and C_6F_5SH,[33] $Ir(h^5\text{-}C_5H_5)(CO)(PPh_3)$,[34] $Ir(h^5\text{-}C_5Me_5)(CO)_2$,[15] $Ir(C{\equiv}CR)(CO)(PPh_3)_2$, and $Ir(C{\equiv}CR)(CO)(PPh_3)_3$, which coexist

[30] M. A. Bennett and R. Charles, *Austral. J. Chem.*, 1971, **24**, 427.
[31] E. W. Ainscough, S. D. Robinson, and J. J. Levison, *J. Chem. Soc.* (*A*), 1971, 3413.
[32] J. M. Guss and R. Mason, *Chem. Comm.*, 1971, 58.
[33] M. H. B. Stiddard and R. E. Townsend, *J. Chem. Soc.* (*A*), 1970, 2719.
[34] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2653.

in equilibrium,[35] and *trans*-[IrCl(CO)(PPh_3)$_2$] with R_3SnH.[36] This last reaction is discussed in relation to the recently described analogous oxidative addition of R_3GeH, and the well-established oxidative addition of R_3SiH. Several cases of oxidative addition reactions of silanes to transition-metal complexes occur in the reaction schemes for hydrosilylation of organic substrates mentioned in Part IV, Chapter 3, Section 12.

Whereas the normal oxidative addition reactions of four-co-ordinate iridium(I) complexes produce octahedral iridium(III) complexes, the reaction of *trans*-[IrCl(N_2)(PPh_3)$_2$] with acyl chlorides is one of oxidative elimination, to produce a five-co-ordinate iridium(III) compound, *e.g.* (8),



(8)

with liberation of molecular nitrogen. Benzoyl chloride reacts only with compounds *trans*-[IrCl(CO)(PR_3)$_2$] which contain fairly strongly basic phosphines; oxidative addition occurs for PR_3 = $PMePh_2$, but not for PR_3 = PPh_3.[37]

Oxidative addition to cationic iridium(I) species is illustrated by reaction of $[Ir(CNR)_4]^+$ or $[Ir(CNR)_2(PPh_3)_2]^+$ with, for instance, iodine or alkyl halides.[17] The five-co-ordinate cation $[Ir(CNR)_3(PPh_3)_2]^+$ undergoes oxidative elimination reactions,[17] as do members of the $[Ir(CO)_x(PMe_2Ph)_{5-x}]^+$ series of cations.[38] The reaction of $[Ir(CO)_2(PMe_2Ph)_3]^+$ with mercury(II) iodide in methanol is thought to go through the doubly charged cation $[Ir(HgX)(CO)_2(PMe_2Ph)_3]^{2+}$, which then undergoes nucleophilic attack.[38] The neutral five-co-ordinate compound [IrCl(CO)$(PMe_2Ph)_3$] reacts with molecular hydrogen more rapidly than does [IrCl(CO)$(PMe_2Ph)_2$].[39]

An example of photo-induced oxidative addition is that of *trans*-[IrCl(CO)(PPh_3)$_2$] with 9,10-phenanthraquinone; the iridium(I) complex effectively acts as a trap for excited quinone molecules.[40]

Whereas *trans*-[IrCl(CO)(PPh_3)$_2$] and related compounds react by oxidative addition, the nitrosyl analogue $Ir(NO)(PPh_3)_3$ reacts by oxidative elimination to give a five-co-ordinate product. Thus the nitrosyl compound is behaving formally as a d^{10} complex of the NO^+ ligand rather than a d^8 complex of NO^-. But in contrast to $Pt(PPh_3)_4$, and to a lesser extent

[35] C. K. Brown, D. Georgiou, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3120.
[36] M. F. Lappert and N. F. Travers, *J. Chem. Soc.* (*A*), 1970, 3303.
[37] M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, 1971, **93**, 1368.
[38] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 3356.
[39] J.-Y. Chen and J. Halpern, *J. Amer. Chem. Soc.*, 1971, **93**, 4939.
[40] J. S. Valentine and D. Valentine, *J. Amer. Chem. Soc.*, 1970, **92**, 5795.

$Pt(PPh_3)_3$, $Ir(NO)(PPh_3)_3$ is very reluctant to undergo loss of one PPh_3 ligand.[41]

Nickel.—Phosphine and phosphite complexes of nickel(0) react with strong acids to produce complexes $[NiHL_4]^+$.[42] Reaction with weak acids may proceed further, with attack of the anion at the nickel. Thus the complex $Ni(LL)_2$, where LL = 1,4-bis(diphenylphosphino)butane, reacts with hydrogen cyanide to form firstly a hydride, which reacts quickly with cyanide to give the bimolecular intermediate $Ni_2(CN)_2(LL)_3$. The ultimate products are the nickel(II) monomer $Ni(CN)_2(LL)_2$ and dimer $[Ni(CN)_2(LL)]_2$.[43] $Ni(PPh_3)_4$ undergoes normal oxidative elimination reactions with aryl halides to produce the new nickel(II) complexes $Ni(aryl)(X)(PPh_3)_2$.[44]

Palladium.—Reactivity trends for reaction of $Pd(PPh_3)_4$ with aryl halides are:

$$PhI > PhBr > PhCl$$

$$p\text{-}O_2N\cdot C_6H_4\cdot Cl > p\text{-}NC\cdot C_6H_4\cdot Cl > p\text{-}Ph\cdot CO\cdot C_6H_4\cdot Cl > PhCl$$

These trends indicate a close resemblance between the mechanism of oxidative addition here and bimolecular nucleophilic displacement from an aromatic carbon centre. Carbon–halogen bond breaking therefore seems implicated in the rate-determining step of the oxidative addition.[45]

Platinum.—Compounds both of platinum(0) and of platinum(II) undergo oxidative addition or elimination reactions. These will be treated separately.

Platinum(0) *to Platinum*(II). Oxidative additions in which the molecule being added to the metal complex undergoes carbon–carbon bond cleavage are rare, but can be arranged by suitable choice of organic compound. Thus both CN^- and $C(CN)_3^-$ are relatively stable anions, and indeed the compound $MeC(CN)_3$, which could act as a source of either of these anions by carbon–carbon bond cleavage, undergoes oxidative elimination with $Pt(PPh_3)_4$ to give $Pt(CN)\{CMe(CN)_2\}(PPh_3)_2$.[46] Another example of oxidative elimination involving carbon–carbon bond breaking, again with CN^- as one of the moieties added to the platinum, is that of trialkylphosphine complexes of platinum(0) with aryl nitriles. Trialkylphosphine complexes are much more reactive than their triaryl analogues; tris(triethylphosphine)platinum(0) readily adds hydrogen to give a five-co-ordinate hydride $PtH_2(PEt_3)_3$.[47]

[41] C. A. Reed and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 3054.
[42] *E.g.*, C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 4217.
[43] C. Corain, P. Rigo, and G. Favero, *Inorg. Chem.*, 1971, **10**, 2329.
[44] M. Hidai, T. Kashiwagi, T. Ikeuchi, and Y. Uchida, *J. Organometallic Chem.*, 1971, **30**, 279.
[45] P. Fitton and E. A. Rick, *J. Organometallic Chem.*, 1971, **28**, 287.
[46] J. L. Burmeister and L. M. Edwards, *J. Chem. Soc.* (*A*), 1971, 1663.
[47] D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 3543.

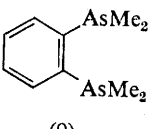
3,3,3-Trifluoroprop-1-yne reacts readily with $Pt(PPh_3)_4$ to give a π-compound, $Pt(PPh_3)_2(CF_3 \cdot C{\equiv}CH)$. On long standing and in the presence of an excess of the trifluoropropyne, a bis-σ-fluoroacetylide of platinum(II) is produced. The obvious deduction is that the π-compound is an intermediate in the oxidative addition reaction that yields the bis-acetylide.[48] Oxidative elimination reactions of platinum(0)–phosphine complexes with protonic acids, HX, which give $Pt(H)(X)(PR_3)_2$, have been discussed in relation to the relative strengths of the acids HX.[49]

Examples of oxidative addition and elimination reactions of principally preparative interest include those of $[Pt(PPh_3)_3]$ with diazonium salts to produce salts of $[Pt(N{=}N \cdot C_6H_4 \cdot R\text{-}p)(PPh_3)_3]^+$,[50] of $Pt(PPh_3)_4$ with methyldichlorosilane,[51] of $Pt(CNBu^t)_2(PPh_3)_2$ with iodine, methyl iodide, or trifluoromethyl iodide, to produce the platinum(II) salts $[Pt(CNBu^t)_2(PPh_3)_2R]^+I^-$,[52] of $Pt(PhC{\equiv}CPh)(PPh_3)_2$ with tetrachloro-*o*-benzoquinone,[53] and of $Pt(PPh_3)_4$, $Pt(C_2H_4)(PPh_3)_2$, or $Pt(O_2)(PPh_3)_2$ with acyl or aroyl azides.[54] Oxidative additions to $Pt(PPh_3)_2$ are conveniently performed by reaction of the oxidative addition reagent with $Pt(PPh_3)_2(CO_3)$ in ethanol. In the absence of the oxidant the product of refluxing $Pt(PPh_3)_2(CO_3)$ in ethanol in the dark is $Pt(PPh_3)_2$ in a moderately stable dimeric form.[55] The chemistry of $Pt(PPh_3)_2$ has been investigated with respect to its role in oxidative elimination reactions.[56]

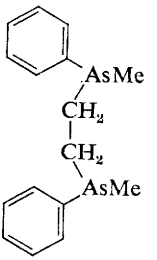
Oxidative addition steps are an important feature in the mechanisms of reactions of $Pt(alkyne)(PPh_3)_2$ complexes with protonic acids (*cf.* Scheme 2 in Chapter 2),[57] of reaction of $Pt(PMePh_2)_4$ with chloroalkenes to give platinum(II) acetylides,[58] and of $Pt(PPh_3)_4$ with nitromethane, in benzene–ethanol–water solvent, which provides a safe route to the fulminato-complex $Pt(CNO)_2(PPh_3)_2$.[59]

Platinum(II) *to Platinum*(IV). The stereochemistry of oxidative addition to the platinum(II) complexes $[PtMe_2(LL)]$ has been determined for LL = the bidentate arsenic ligands (9) and (10). The oxidative addition of methyl halides gives the 1,2,3-or *fac*-trimethylplatinum(IV) compound (11); it is not possible to choose between *cis* and *trans* addition from this observation.

[48] W. R. Cullen and F. L. Hou, *Canad. J. Chem.*, 1971, **49**, 3404.
[49] D. M. Roundhill, P. B. Tripathy, and B. W. Renoe, *Inorg. Chem.*, 1971, **10**, 727.
[50] S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 3441.
[51] W. Fink and A. Wenger, *Helv. Chim. Acta*, 1971, **54**, 2186.
[52] G. A. Larkin, R. Mason, and M. G. H. Wallbridge, *Chem. Comm.*, 1971, 1054.
[53] D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Comm.*, 1971, 199.
[54] W. Beck, G. La Monica, S. Cenini, and R. Ugo, *J. Chem. Soc.* (*A*), 1971, 113.
[55] D. M. Blake and R. Mersecchi, *Chem. Comm.*, 1971, 1045.
[56] R. Ugo, G. La Monica, F. Cariati, S. Cenini, and F. Conti, *Inorg. Chim. Acta*, 1970, **4**, 390.
[57] P. B. Tripathy and D. M. Roundhill, *J. Organometallic Chem.*, 1970, **24**, 247; P. B. Tripathy, B. W. Renoe, K. Adzamli, and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1971, **93**, 4406.
[58] J. Lewis, B. F. G. Johnson, K. A. Taylor, and J. D. Jones, *J. Organometallic Chem.*, 1971, **32**, C62.
[59] W. Beck, K. Schorpp, and F. Kern, *Angew. Chem. Internat. Edn.*, 1971, **10**, 66.

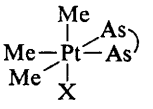


(9)

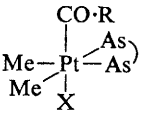


(10)

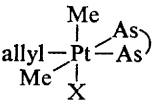
The oxidative addition of acyl halides (R·COX) gives the *cis*-dimethyl compounds (12), and hence the R·COX addition has been *trans*. In contrast, allyl halides add in a *cis* fashion, to give the products (13). The



(11)



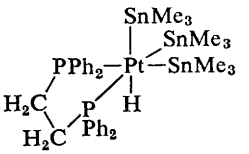
(12)



(13)

steric courses of oxidative additions to platinum(II) here are the same as those established for iridium(I) compounds.[60]

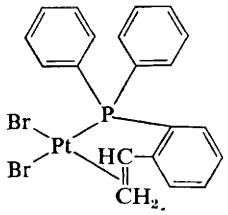
There is evidence for the formation of nitrogen-bridged diplatinum intermediates in the reaction of *cis*-$[Pt(NO_2)_2(NH_3)_2]$ with hydrogen bromide.[61] The reaction of $[Pt(SiMe_3)_2(LL)]$, where LL = the chelating diphosphine $Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh_2$, with hydrogen is first-order in platinum compound and first-order in hydrogen, with a second-order rate constant of approximately 5×10^{-2} l mol^{-1} s^{-1} at 25 °C.[62] Reactions of platinum(II) complexes with metal hydrides are generally considered to involve oxidative addition as the first step, but it is rarely possible to isolate the platinum(IV) product. Recently, several reactions in which Group IV hydrides react with platinum(II) complexes have been found from which platinum(IV) compounds can be isolated.[63] For example, the reaction of trimethyltin hydride with $[Pt(SnMe_3)_2(Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh_2)]$ gives the compound (14).[63]



(14)

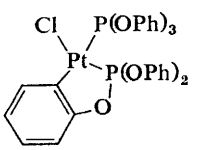
[60] A. J. Cheney and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3545, 3549.
[61] G. S. Muraveiskaya and I. I. Antokol'skaya, *Russ. J. Inorg. Chem.*, 1971, **16**, 106.
[62] A. F. Clemmitt and F. Glockling, *J. Chem. Soc.* (*A*), 1971, 1164.
[63] A. F. Clemmitt and F. Glockling, *Chem. Comm.*, 1970, 705; J. E. Bentham, S. Cradock, and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1971, 587.

The reaction of [Pt(methoxydicyclopentadienyl)(Ph)(PPh_3)] with hydrogen chloride or mercury(II) chloride, in which the platinum–carbon σ-bond to the dicyclopentadienyl ligand is broken, involves oxidative addition.[64] The *o*-vinylphenylphosphine complex (15) undergoes oxidative addition with bromine to yield a platinum(IV) dimer.[65]

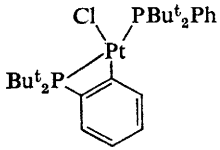


(15)

Intramolecular orthometallation reactions of iridium(I)–phosphine or –phosphite complexes, discussed earlier in this chapter, are oxidative addition reactions. Platinum(II)–phosphine and –phosphite complexes undergo similar orthometallation reactions, but in their case oxidative addition to give a platinum(IV) species is generally followed by reductive elimination to give a platinum(II) product. Thus, when *cis*-[$PtCl_2${$P(OPh)_3$}$_2$] is heated in boiling decalin, the product is the platinum(II) compound (16).[66] This type of reaction is facilitated by bulky groups in the phosphine or phosphite ligands. Thus *trans*-[$PtCl_2(PBu^t_2Ph)_2$] reacts readily to give (17). It is even possible to induce an analogous cyclization



(16)



(17)

by platinum–carbon bond formation from complexes of phosphines containing alkyl groups by this steric inducement, for example from *trans*-[$PtCl_2(PBu^t_2Pr^n)_2$].[67]

3 Oxidative Addition: Other Elements

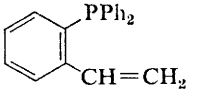
Chromium.—Photochemical reactions of, for example, $Cr(C_6H_6)(CO)_3$ with silanes in hydrocarbon solvents give the silyl–transition-metal hydrides (18). The mechanism is thought to be dissociative, with loss of one carbon

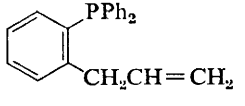
[64] G. Carturan, L. Busetto, A. Palazzi, and U. Belluco, *J. Chem. Soc.* (*A*), 1971, 219.
[65] D. I. Hall and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, 1491.
[66] E. W. Ainscough and S. D. Robinson, *Chem. Comm.*, 1971, 130.
[67] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

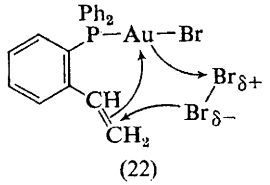
$$\rightarrow\!\!\!

the mechanism of electrophilic metallation of a benzene ring suggested for this palladium chloride reaction seems unlikely for the above carbonyls of low-oxidation-state metals. A more likely mechanism is initial displacement of carbon monoxide followed by co-ordination of metal to nitrogen, in turn followed by insertion of the metal carbonyl moiety into a phenyl-carbon–hydrogen bond, with final elimination of hydrogen from the hydride so produced.[71]

Gold.—The products of the reaction between bromine and the gold(I) complexes AuBrL, where L = compound (20) or (21), or their dimethylarsine


(20)


(21)


(22)

analogues, are gold(III) compounds containing a σ-bond between the gold and a carbon atom of the phosphorus or arsenic ligand. Concerted attack is proposed, as outlined in (22).[72]

4 Reductive Elimination

The kinetics of reductive elimination of hydrogen from iridium(I) have been investigated, mainly in chloroform solution:

$$[Ir(H)_2(CO)_2L^1_2]^+ + L^2 \longrightarrow Ir(CO)_2L^1_2L^2 + H_2$$

In this equation L^1 = a tertiary phosphine or arsine, and L^2 = trimethyl or triphenyl phosphite, methyldiphenylphosphine, or carbon monoxide. The need to employ a displacing ligand L^2, and the production of a five-co-ordinate iridium(I) compound, means that this reaction is not quite the reverse of the normal and much-studied oxidative addition to four-co-ordinate iridium(I).* The suggested mechanism for the reductive elimination is rate-determining loss of hydrogen followed by rapid reaction with the incoming ligand L^2. For $L^1 = PMePh_2$ and $L^2 = P(OMe)_3$, the activation parameters are $\Delta H^{\ddagger} = 20.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5$ cal deg^{-1} mol^{-1}. Reaction rates are fairly insensitive to solvent variation, at least for the one case investigated, $L^1 = PEt_3$ and $L^2 = P(OMe)_3$.[73]

[71] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3204.
[72] M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 1971, **93**, 4591.
[73] M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 3000.

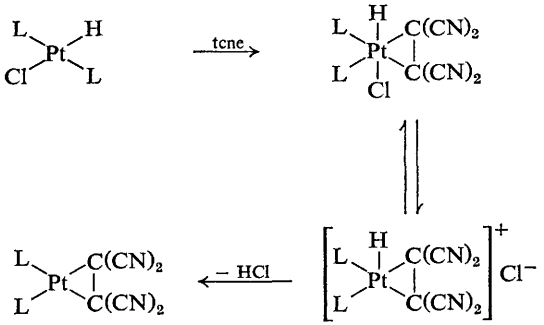
* A few examples of oxidative elimination reactions of five-co-ordinate iridium(I) species have been described (*e.g.*, refs. 17, 38, and 39).

The mechanism of reductive elimination of triphenylsilane from the d^4 manganese(III) hydride complex (23) by the action of triphenylphosphine,

$$\underset{(23)}{Ph_3Si\cdot Mn(H)(h^5\text{-}C_5H_5)(CO)_2} + PPh_3 \longrightarrow Mn(h^5\text{-}C_5H_5)(CO)_2(PPh_3)_2 + Ph_3SiH$$
(24)

has been examined by kinetic and deuterium-labelling experiments. The initial reaction is rate-determining loss of the silane, for which $\Delta H^{\ddagger} = 29.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = +16.3$ cal deg^{-1} mol^{-1} in n-heptane. This step is reversible; the reaction is forced to go to completion by the added triphenylphosphine trapping the manganese(I) intermediate as (24). The crystal structure of (23) shows that the hydride hydrogen is at the normal bonded distance from the manganese, and that it is also fairly near the silicon. This suggests that the mechanism may involve lengthening of the manganese–hydrogen and shortening of the silicon–hydrogen distances during formation of the transition state.[74]

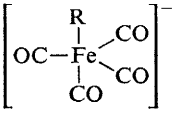
The mechanism shown in the Scheme is suggested [75] for the reaction of hydridoplatinum(II) complexes with tetracyanoethylene,[76] which involves reductive elimination of hydrogen chloride from the platinum.



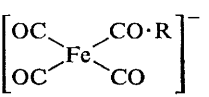
Scheme

The synthesis of *trans*-[IrCl(CS)(PPh$_3$)$_2$] from iridium(I) and carbon disulphide involves oxidative addition followed by reductive elimination.[77] The reaction of alkyl bromides (RBr) with $[Fe(CO)_4]^{2-}$ involves oxidative addition to give (25), which isomerizes to (26). Further reactions of (26), including addition of a hydrogen to the metal, are followed by reductive

[74] A. J. Hart-Davis and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1971, **93**, 4388.
[75] H. C. Clark and R. J. Puddephat, *Inorg. Chem.*, 1971, **10**, 416.
[76] W. H. Baddley, *Inorg. Chim. Acta Rev.*, 1968, **2**, 7.
[77] M. Kubota and C. R. Carey, *J. Organometallic Chem.*, 1970, **24**, 491.



(25)



(26)

elimination of the organic product (R·CHO).[78] This sequence of oxidative addition followed by reductive elimination, illustrated by the above two preparative examples, is also found in some intramolecular reactions of phosphine and phosphite complexes of platinum(II) (see, for example, refs. 66 and 67 of this chapter), and in some homogeneous catalysis systems (see Chapter 3 of this part).

[78] M. P. Cooke, *J. Amer. Chem. Soc.*, 1970, **92**, 6080.

7

Isomerization; Intramolecular Processes

BY R. D. W. KEMMITT AND J. BURGESS

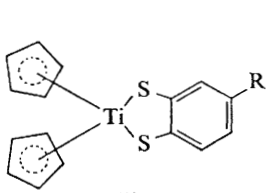
The investigation of intramolecular rearrangements of organometallic derivatives of the transition metals by n.m.r. techniques has been reviewed.[1] A new system of nomenclature for such processes has been proposed,[2] and the application of matrix representations [3] and group theory [4] to these systems discussed.

1 Group IV

Titanium.—The elucidation of the crystal structure of $Ti(C_5H_5)_4$ has shown that each titanium has two monohapto-C_5H_5 and two pentahapto-C_5H_5 groups bonded to it.[5] Low-temperature ^1H n.m.r. spectra suggest fluxional behaviour of the monohapto-C_5H_5 groups; the spectra were too poor for the kinetic parameters to be determined. At higher temperatures (− 30 to + 60 °C) there is monohapto ⇌ pentahapto interconversion taking place, with an activation energy of 16.1 kcal mol^{-1} and log A of 13.5 in toluene solution.[6] These reports amplify a preliminary communication on these intramolecular processes in $Ti(C_5H_5)_4$.[7] The ^1H n.m.r. spectra of the cyclopentadienyldithiolato-complexes of titanium (1) and (2) are temperature dependent. The intramolecular rearrangement process responsible is thought to be inversion at the two sulphur atoms, (2) ⇌ (3), with a free energy of activation of between 14 and 15 kcal mol^{-1} at 10—20 °C.[8]

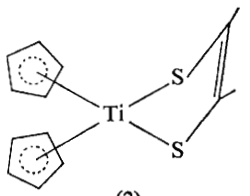
Zirconium and Hafnium.—In the compounds $Zr(\beta\text{-diketonate})_3(h^5\text{-}C_5H_5)$ the metal is formally nine-co-ordinated, though these compounds can also be regarded as approximating to a trigonal-bipyramidal structure with the cyclopentadienyl ligand in one of the axial positions (4). Two kinetic

[1] K. Vrieze and P. W. N. M. van Leeuwen, in 'Progress in Inorganic Chemistry', vol. 14, ed. S. J. Lippard, Wiley–Interscience, New York, 1971.
[2] G. Binsch, E. L. Eliel, and H. Kessler, *Angew. Chem. Internat. Edn.*, 1971, **10**, 570.
[3] M. Gielen, *Bull. Soc. chim. belges*, 1971, **80**, 9.
[4] J. Brocas and M. Gielen, *Bull. Soc. chim. belges*, 1971, **80**, 207.
[5] J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, 1971, **93**, 3592.
[6] J. L. Calderon, F. A. Cotton, and J. Takats, *J. Amer. Chem. Soc.*, 1971, **93**, 3587.
[7] J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, 1970, **92**, 3801.
[8] H. Köpf, *Angew. Chem. Internat. Edn.*, 1971, **10**, 134.

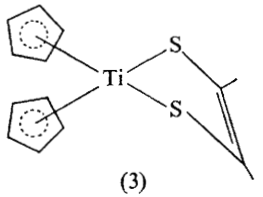


(1)

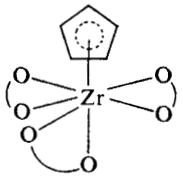
R = H or Me



(2)



(3)



(4)

processes can be monitored for these compounds. In the faster process the environments of the non-equivalent terminal groups of the equatorial diketonate ligands are averaged; in the slower process there is interchange between the di-equatorial and the axial-equatorial ligand environments. The former process is intramolecular, but the latter process may be intermolecular, since the rate is not independent of concentration of added β-diketone. Activation parameters for the two processes in $Zr(hfac)_3(h^5\text{-}C_5H_5)$ in di-isopropyl ether solution are $\Delta H^{\ddagger} = 15.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = +5$ cal deg^{-1} mol^{-1} for the former process, and $\Delta H^{\ddagger} = 26.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = +17$ cal deg^{-1} mol^{-1} for the latter.[9]

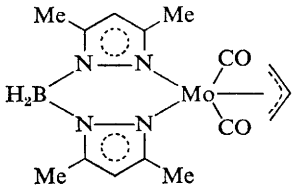
Kinetics of rearrangement of the eight-co-ordinate complexes $Zr(acac)_2(h^5\text{-}C_5H_5)Cl$, $Hf(acac)_2(h^5\text{-}C_5H_5)Cl$, and $Zr(acac)_2(h^5\text{-}C_5H_5)Br$ have also been studied by n.m.r. techniques. In these compounds there is only one rearrangement process apparent; this is intramolecular, but may be a twist or may involve intermediates containing unidentate acac. Rate constants and activation parameters are reported for the reactions in benzene solution.[10]

[9] J. J. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.*, 1970, **92**, 7342.
[10] T. J. Pinnavaia and A. L. Lott, *Inorg. Chem.*, 1971, **10**, 1388.

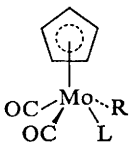
2 Group VI

Molybdenum and Tungsten.—Whereas $Ti(C_5H_5)_4$ undergoes two types of intramolecular rearrangement, both fluxional behaviour of the two mono-hapto-cyclopentadienyl groups and $h^1 \rightleftharpoons h^5$ interconversion, the molybdenum analogue, also of formula $Mo(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2$, shows no signs of undergoing $h^1 \rightleftharpoons h^5$ rearrangement at accessible temperatures.[11] However, the mixed-ligand complex $Mo(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)(NO)(S_2CNMe_2)$ shows fluxional behaviour of the $h^1\text{-}C_5H_5$ group at moderately low temperatures, and there is evidence for $h^1 \rightleftharpoons h^5$ rearrangement at higher temperatures.[12]

Stereochemical non-rigidity of the eight-co-ordinate compounds $MoH_4(PR_3)_4$, typically where PR_3 = $PMePh_2$, has been probed by ^1H and by ^{31}P n.m.r. spectroscopy. No kinetic results are presented in this preliminary communication, but the mechanism of rearrangement is discussed on the assumption that the molecules have T_d symmetry, or in other words consist of interlocking concentric tetrahedra whose apices are defined by the four hydrogen and by the four phosphorus atoms respectively. The two forms of motion discussed are the so-called 'tetrahedral tunnelling' of hydrogen atoms, originally proposed for the similar six-co-ordinate iron complexes $FeH_2[P(OEt)_3]_4$, and a 'breathing' distortion of the T_d ground state giving a D_{2d} transition state.[13] Stereochemical non-rigidity has also been observed for the 1-pyrazolyl derivative of molybdenum shown in formula (5).[14]



(5)

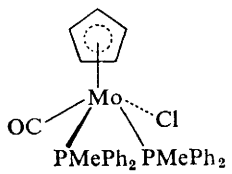


(6)

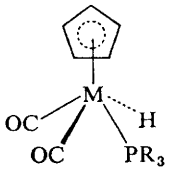
Kinetic studies by ^1H n.m.r. spectroscopy of *cis–trans* isomerization of the formally seven-co-ordinate molybdenum compounds (6), with L = a phosphine or phosphite and R = H, D, Me, $PhCH_2$, Cl, Br, or I, show that the kinetic parameters of this intramolecular process vary to a small extent as L varies, but vary greatly as R varies. Thus the activation energies for the compounds (6) with R = H or D are between 12 and 14 kcal mol^{-1}, but for compounds with R = halide, activation energies are in the range 22—26 kcal mol^{-1}. The most probable transition state for these isomerizations is described as approximating to a trigonal bipyramid with the

[11] J. L. Calderon and F. A. Cotton, *J. Organometallic Chem.*, 1971, **30**, 377.
[12] W. G. Kita, M. K. Lloyd, and J. A. McCleverty, *Chem. Comm.*, 1971, 420.
[13] J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.*, 1971, **93**, 5263.
[14] S. Trofimenko, *Inorg. Chem.*, 1970, **9**, 2493.

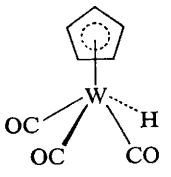
cyclopentadienyl ring occupying one apical site and either R or L the other. As rate constants for both directions of these *cis–trans* equilibria have been determined, equilibrium constants can be determined from the ratios of the respective rate constants.[15] In fact the *cis*-form of (6) has two enantiometric forms, whose interconversion can also be monitored by ^{1}H n.m.r. spectroscopy. For the cyclopentadienyl compounds (6) the barrier for *cis–cis'* interconversion is much lower than for *cis–trans*, but for analogous π-indenyl complexes the two types of barrier are of comparable size.[16] Replacing one of the carbonyls of (6) by a phosphine, to give a compound of the type (7), results in a much faster rate of *cis–trans* isomerization.[17] Kinetic results have been reported for *cis–trans* isomerization of both molybdenum and tungsten compounds (8) containing a hydride ligand rather than the halide ligand of compounds (6) and (7). For the tungsten



(7)



(8)



(9)

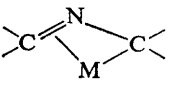
compounds, intramolecularity of isomerization can be demonstrated by the persistence of tungsten–hydrogen coupling. Some correlation between the kinetic and thermodynamic parameters has been found for these isomerizations.[18] Isomerization of the similar tungsten compound (9) in the nematic phase has been studied.[19]

A ^{1}H n.m.r. study of the dithiocarbamate compounds $Mo(NO)(S_2CNMe_2)_3$ and $Mo(NO)_2(S_2CNMe_2)_2$, and the tungsten analogue of the latter, indicated a free energy of activation of about 21 kcal mol^{-1} for intramolecular rearrangement of the dinitrosyl compounds, and of about 18 kcal mol^{-1} for the mononitrosyl compound. An intramolecular mechanism involving partial dissociation of a thiocarbamato-ligand is suggested.[20]

An n.m.r. study of aza-allyl derivatives of molybdenum and of tungsten of formula $M(h^1\text{-}C_5H_5)(CO)_2(Y_2CNCY_2)$, where $Y = p\text{-}Me\cdot C_6H_4$, represents an extension of studies on the usual palladium-allyl series of compounds. The low-temperature n.m.r. spectra of the molybdenum and

[15] J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 5852.
[16] J. W. Faller, A. S. Anderson, and A. Jakubowski, *J. Organometallic Chem.*, 1971, **27**, C47.
[17] G. Wright and R. J. Mawby, *J. Organometallic Chem.*, 1971, **29**, C29.
[18] P. Kalck, R. Prince, R. Poilblanc, and J. Roussel, *J. Organometallic Chem.*, 1970, **24**, 445.
[19] M. C. McIvor, *J. Organometallic Chem.*, 1971, **27**, C59.
[20] R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 994.

tungsten compounds are consistent with the σ-π structure (10). On raising the temperature of the sample to about 10 °C, the metal to carbon–nitrogen-π-bond is broken, permitting free rotation about the adjacent carbon–nitrogen single bond. At about 70 °C, epimerization starts to take place.[21]

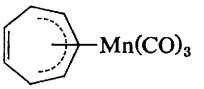


(10)

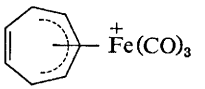
The compounds $MX_2(dam)_2(CO)_2$, where M = Mo or W, are seven-co-ordinate, containing one uni- and one bi-dentate diarsenic ligand per molecule. A number of intramolecular rearrangement processes are conceivable for such compounds; these are discussed in the light of the observed n.m.r. spectra over a range of temperatures.[22]

3 Group VII

Manganese.—The pentahapto-cycloheptatrienyl compound (11) is fluxional. The activation energy for fluxional rearrangement is several kcal mol^{-1} higher than for the analogous, but charged, iron compound (12). The



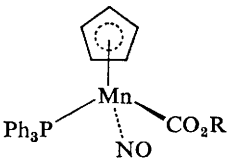
(11)



(12)

increased rate of fluxional motion in the cationic compound suggests that back-bonding is a significant controlling factor, with stronger back-bonding in the manganese compound causing the slower rate.[23]

The kinetics of racemization of the pseudo-tetrahedral compound (13) have been studied by ^1H n.m.r. and polarimetric techniques. Racemization



(13)

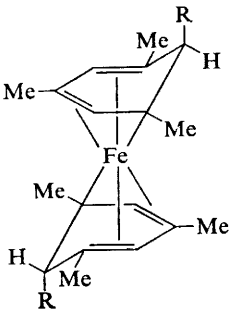
is a first-order process, whose rate depends slightly on the nature of the solvent, and slightly on the nature of the alkyl group R. The rate-determining step is loss of the phosphine ligand; for loss of PPh_3 the enthalpy of

[21] H. R. Keable and M. Kilner, *Chem. Comm.*, 1971, 349.
[22] M. W. Anker, R. Colton, and C. J. Rix, *Austral. J. Chem.*, 1971, **24**, 1157.
[23] T. H. Whitesides and R. A. Budnik, *Chem. Comm.*, 1971, 1514.

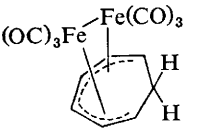
activation is 31.1 kcal mol^{-1}.[24] ^{19}F N.m.r. spectra of the compounds $Mn(CO)_{4-x}(NO)(PF_3)_x$, with $0 \leqslant x \leqslant 3$, indicate fast intramolecular rearrangement.[25]

4 Group VIII

Iron.—*Fluxional Molecules.* The newly prepared compounds bis-(6-phenyl- and bis-(6-t-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) (14) exhibit a sort of fluxional behaviour in which a rocking or twisting motion of the cyclohexadienyl rings interconverts σ- and π-bonds to the iron. The barriers to this motion are very similar for the phenyl and t-butyl com-



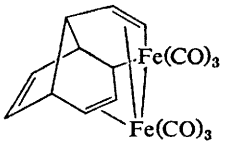
(14) R=Ph or Bu^t



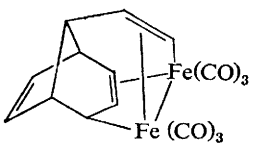
(15)

pounds.[26] Fluxional behaviour has also been reported for the cyclo-octatriene ligands in the cations $[Fe_2(C_8H_9)(CO)_6L]^+$, where L = py or PPh_3,[27] but, perhaps surprisingly, not for the di(irontricarbonyl) derivative of cycloheptatriene (15).[28]

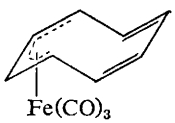
The kinetic parameters for valence isomerization of diferratricyclododecatriene, (16) $\rightleftharpoons$ (17), are $\Delta G^{\ddagger} = 16.2$ kcal mol^{-1}, $\Delta H^{\ddagger} = 10.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -18.5$ cal deg^{-1} mol^{-1}, in deuteriobenzene solution.[29]



(16)



(17)

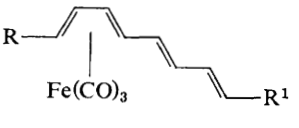


(18)

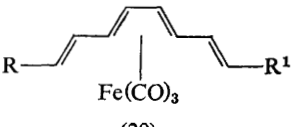
[24] H. Brunner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 249; H. Brunner and H.-D. Schindler, *Chem. Ber.*, 1971, **104**, 2467.
[25] C. A. Udovich and R. J. Clark, *J. Organometallic Chem.*, 1970, **25**, 199.
[26] J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, 1970, **92**, 7209.
[27] R. Aumann and S. Winstein, *Angew. Chem. Internat. Edn.*, 1970, **9**, 638.
[28] F. A. Cotton, B. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, 1971, **93**, 5069.
[29] R. Aumann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 560.

There is wide-line n.m.r. evidence for fluxional behaviour even in the solid state, as, for example, for the cyclo-octatetraene complex (18) and the di-iron species $Fe_2(C_8H_8)(CO)_5$.[30]

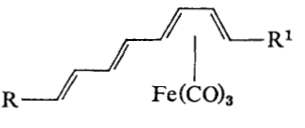
Isomerization of Polyene Compounds. Intramolecular rearrangement of $Fe(CO)_3$(polyene) compounds are somewhat similar to the fluxional behaviour described above. Though one is concerned with acyclic rather than cyclic polyenes, and with π-bonding rather than σ-bonding changes, the shift isomerizations (19) ⇌ (20) ⇌ (21) could be considered analogues



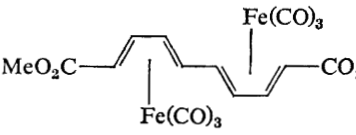
(19)



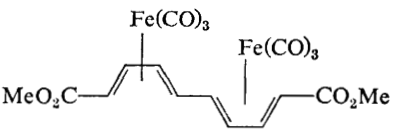
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(21)



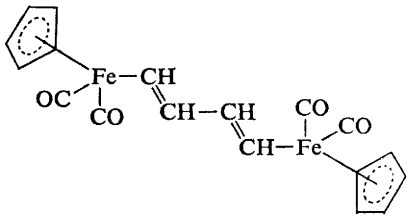
(22)



(23)

of fluxional movements. A kinetic study for various groups R and R^1 has elucidated the electronic effects of substituents on isomerization rates.[31] The closely related compounds $Fe_2(CO)_6$(polyene) can exist in *meso* (22) or optically active (23) forms. Racemization of such compounds could involve the $Fe(CO)_3$ groups exchanging positions, or could involve just one $Fe(CO)_3$ group and its associated carbon atoms. Kinetic and stereochemical evidence favours the latter.[32] The mechanisms of shift isomerization and of racemization in this type of compound have been compared.[33] Valence tautomerism was suggested for the compound *trans,trans*-1,4-bis-(dicarbonyl-h^5-cyclopentadienyliron)buta-1,3-diene (24) on the basis of

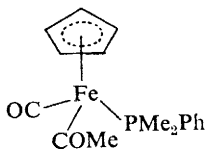
[30] A. J. Campbell, C. A. Fyfe, and E. Maslowsky, *Chem. Comm.*, 1971, 1032.
[31] H. W. Whitlock, C. Reich, and W. D. Woessner, *J. Amer. Chem. Soc.*, 1971, **93**, 2483.
[32] R. L. Markezich and H. W. Whitlock, *J. Amer. Chem. Soc.*, 1971, **93**, 5291.
[33] H. W. Whitlock and R. L. Markezich, *J. Amer. Chem. Soc.*, 1971, **93**, 5290.



(24)

^{1}H n.m.r. spectra at various temperatures.[34] More detailed investigations,[35] especially at 251 MHz,[36] show that the compound is in fact static. The line broadening apparent at 60 MHz can be resolved into lines separated by a very small but temperature-independent chemical shift.

Other Racemizations and Isomerizations. N.m.r. studies of (25) show that its isomerization is slow, on the n.m.r. time-scale, up to 100 °C. It is thus

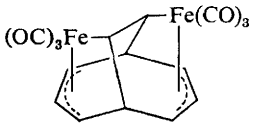


(25)

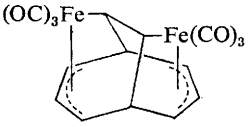
configurationally more stable than its manganese analogue (13).[37] Three isomers, with two interconversion processes, are reported for the hexacarbonyldi-iron complex with the allene trimer 1,2,4-trimethylenecyclohexane.[38] The kinetics and mechanism of intramolecular rearrangement in $FeH_2[P(OEt)_3]_4$, briefly reported in earlier communications,[39] have now been fully described and discussed.[40]

Miscellaneous. The barrier to the molecular rearrangement process (26) ⇌ (27) in the bis-tricarbonyliron complex of tetracyclo[4,4,0,$0^{5,7}$,$0^{2,10}$]-deca-3,8-diene is 15.9 kcal mol^{-1} at 33 °C in methylene chloride.[41] The effect of adjacent ferrocenyl groups on inversion at pyramidal nitrogen has

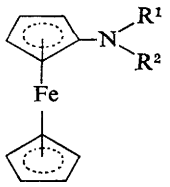
[34] C. H. Campbell and M. L. H. Green, *Chem. Comm.*, 1970, 1009.
[35] W. P. Giering, *Chem. Comm.*, 1971, 4.
[36] F. A. L. Anet and O. J. Abrams, *Chem. Comm.*, 1970, 1611.
[37] H. Brunner, H.-D. Schindler, E. Schmidt, and M. Vogel, *J. Organometallic Chem.*, 1970, **24**, 515.
[38] S. Otsuka, A. Nakamura, and K. Tani, *J. Chem. Soc.* (*A*), 1971, 154.
[39] F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 1068; P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, p. 3432.
[40] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1971, **93**, 4701.
[1] R. Aumann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 189.



(26)



(27)



(28)

been probed for four compounds of the type (28). Unfortunately, as three of the compounds investigated were amides, it was not possible to disentangle restricted rotation about amide-carbon–nitrogen bonds from inversion at the nitrogen, so there is a certain inconclusive air to the discussion.[42]

Variable-temperature n.m.r. spectra of $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}SiMe_2)_2Fe(CO)_3$ indicate an activation energy of 9 kcal mol^{-1} for molecular rearrangement of this molecule in the mixed solvent CF_2Cl_2–CH_2Cl_2. Breaking of the carbonyl or $SiMe_2$ bridges is possible.[43]

Ruthenium and Osmium.—There have been three reports of n.m.r. studies of intramolecular rearrangement processes of hydrido-complexes of these elements. There is a low barrier to rearrangement of the complexes $[MH(PF_3)_4]^-$, where M = Ru or Os, in $CHClF_2$ solution. A Berry 'pseudorotation' seems unattractive here, both since the geometry of these molecules deviates markedly from trigonal bipyramidal, and since the Berry mechanism would in this case necessitate moving the hydride through an equatorial position, an unfavourable process that would lead to a high barrier to rearrangement.[44] For the series $M(H)(NO)(PR_3)_3$, where M = Ru or Os, there is a range of behaviour from one extreme, with M = Ru and $PR_3 = PPr^iPh_2$ or M = Os and $PR_3 = PPh_3$, where any intramolecular rearrangement is slow on the n.m.r. scale, to the other extreme, for M = Ru and $PR_3 = PMePh_2$, where there is fast intramolecular rearrangement even at the lowest temperature accessible. That rearrangement is indeed intramolecular in the latter case has been confirmed by experiments in which an excess of phosphine was added to the solution of the complex. The single n.m.r. peak from the complex was unshifted, and the added phosphine gave a separate, sharp, resonance.[45] Rapid intramolecular tautomerization is also reported for the hydrogens in $Ru_4H_4(CO)_{4-x}[P(OMe)_3]_x$.[46]

The variation of the n.m.r. spectrum of $Ru(\pi\text{-allyl})_2(CO)_2$ with temperature reveals two kinetic processes. At high temperatures the *syn–anti*

[42] R. Damrauer, *J. Organometallic Chem.*, 1971, **32**, 121.
[43] D. Kummer and J. Furrer, *Z. Naturforsch.*, 1971, **26b**, 162.
[44] P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1971, **93**, 1797.
[45] S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 3068.
[46] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4594.

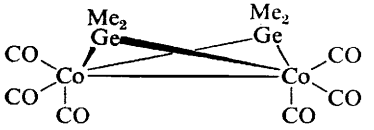
rearrangement can be monitored. At low temperatures the π-allyl methylene groups exchange environments. An intramolecular twisting mechanism is suggested for the latter process.[47]

Tautomerization of ruthenium carbonylmesoporphyrin-IX dimethyl ester, 29) $\rightleftharpoons$ (30), is dissociative in mechanism, with a free energy of activation of 18.3 kcal mol^{-1} at 64 °C.[48]

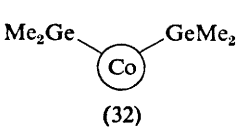


(29) (30)

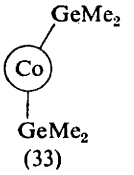
Cobalt.—The dimethylgermyl-bridged dicobalt compound (31) undergoes an intramolecular rearrangement process with an activation energy of 15 kcal mol^{-1}. The process is thought to be that illustrated by (32) $\rightleftharpoons$ (33) $\rightleftharpoons$ (34), which involves the conversion of one square-pyramidal configuration into another at the cobalt, through a trigonal-bipyramidal transition state. This is in a sense the opposite of the usual Berry pseudorotation for five-co-ordinate molecules.[49]



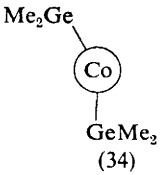
(31)



(32)



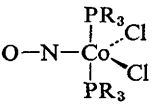
(33)



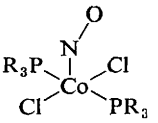
(34)

The nitrosyl compounds $CoX_2(NO)(PR_3)_2$ have two ν(N—O) bands in their solution i.r. spectra. The relative intensities of these bands vary with the nature of PR_3. These observations have been interpreted in terms of a novel intramolecular redox process involving compounds containing NO^+ and NO^-, with the former in a trigonal-bipyramidal structure (35) with

[47] M. Cooke, R. J. Goodfellow, M. Green, and G. Parker, *J. Chem. Soc.* (*A*), 1971, 16.
[48] J. W. Faller and J. W. Sibert, *J. Organometallic Chem.*, 1971, **31**, C5.
[49] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 1970, **92**, 5003.



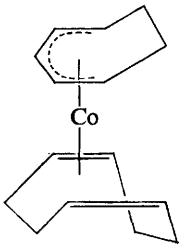
(35)



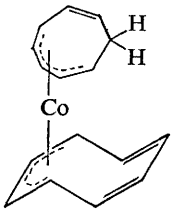
(36)

collinear Co—N—O, and the latter with the nitrosyl group at the apical position of a square pyramid (36), with bent Co—N—O.[50]

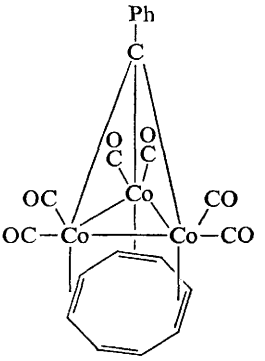
h^5-Cycloheptadienyl-π-cyclo-octa-1,5-dienecobalt (37) exhibits fluxional behaviour, with an energy barrier of about 14 kcal mol^{-1} in toluene, but π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt is not fluxional, at least up to 60 °C.[51] h^5-Cyclo-octatrienyl-1,2,3,4-h^4-cyclo-octatetraenecobalt (38) is



(37)



(38)

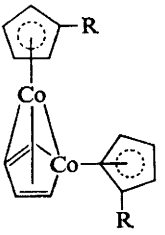


(39)

also fluxional, though experimental difficulties prevented an estimation of its barrier to fluxional rearrangement.[52] Fluxional behaviour is exhibited by the cyclo-octatetraene derivative of methylidynetricobalt enneacarbonyl (39).[53] Rearrangement is thought to involve 1,2-shifts. It is difficult to estimate the kinetic parameters because more than two spins are exchanging.[54]

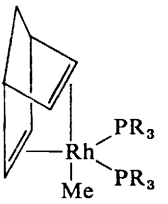
A slightly different example of fluxional behaviour, in which metal–metal as well as metal–carbon bonding seems to be involved, is afforded by the compounds (40). The activation parameters are $\Delta H^{\ddagger} = 25.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 8.6$ cal deg^{-1} mol^{-1} for (40) with R = H, and $\Delta H^{\ddagger} = 24.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 8.6$ cal deg^{-1} mol^{-1} for (40) with R = CO_2Me, in *o*-dichlorobenzene.[55]

[50] J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, 1971, **93**, 1788.
[51] S. Otsuka and T. Taketomi, *J. Chem. Soc.* (*A*), 1971, 583.
[52] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 285.
[53] M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *Chem. Comm.*, 1971, 72.
[54] B. H. Robinson and J. Spencer, *J. Organometallic Chem.*, 1971, **33**, 97.
[55] M. Rosenblum, W. P. Giering, B. North, and D. Wells, *J. Organometallic Chem.*, 1971, **28**, C17.



(40)

Rhodium.—Low-temperature n.m.r. spectra of $MeRh(cod)L_2$, where L = a phosphine or arsine, and similar compounds with nor replacing cod, suggest a structure based on a trigonal bipyramid (41). N.m.r. spectra at higher temperatures suggest two types of isomerization behaviour. For



(41)

the cyclo-octadiene complexes and for $RhMe(nor)(PPh_3)_2$ there is an *intermolecular* process involving equilibrium loss of a phosphine or arsine ligand. The intermolecularity of these reactions is indicated by the loss of coupling to the ligand. A square-planar transition state or intermediate seems more likely than a tetrahedral. For all the other norbornadiene complexes there is *intramolecular* rearrangement at higher temperatures; these complexes [56] behave like the previously described $IrR(cod)(PR_3)_2$ series.[57]

Intramolecular rearrangement in $RhH(PF_3)_4$, in $RhH[P(OEt)_3]_4$, and in $IrH(PF_3)_4$, is similar in nature to that described above for ruthenium and osmium analogues of these compounds.[44] The cations $[RhH_2(PR_3)_4]^+$ have a *cis*-configuration and do not undergo ready intramolecular rearrangement, in contrast to the uncharged iron complexes $FeH_2[P(OEt)_3]_4$ and related compounds.[58]

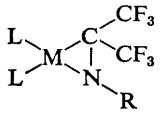
The barrier to ethylene rotation in $Rh(h^5\text{-}C_5Me_5)(C_2H_4)_2$ is slightly higher than that in $Rh(h^5\text{-}C_5H_5)(C_2H_4)_2$; there is no rotation of the ethylene with respect to the iridium–ethylene bonding in analogous iridium complexes, at least up to 80 °C.[59] The co-ordinated ethylene, but not the

[56] D. P. Rice and J. A. Osborn, *J. Organometallic Chem.*, 1971, **30**, C84.
[57] J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, 1970, **92**, 6976.
[58] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 2397.
[59] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

co-ordinated tetrafluoroethylene, can rotate in $Rh(h^1\text{-}C_5H_5)(C_2H_4)(C_2F_4)$.[60] The determination of the crystal structure of the closely related compound $Rh(acac)(C_2H_4)(C_2F_4)$ shows that the tetrafluoroethylene is closer, and thus more strongly bonded, to the rhodium than is the ethylene.[61]

Iridium.—The five-co-ordinated iridium(I) complexes $IrR^1(cod)(PR^2_3)_2$, which have a trigonal-bipyramidal structure [62] [*cf.* the rhodium compounds (41) above], undergo molecular rearrangement on the n.m.r. time-scale. The ^1H resonances of the alkyl group R^1, the phosphine PR^2_3, and the cyclo-octadiene, were monitored. The rearrangement process is intramolecular, and may well take place by a Berry pseudorotation mechanism, though a diene twist is also consistent with the observations.[63] Both pseudorotation and, at high temperatures, *syn–anti* rearrangement can be monitored by n.m.r. spectroscopy for compounds $Ir(allyl)(CO)(PPh_3)_2$.[64]

Nickel and Platinum.—The surprising equivalence of geminal CF_3 shifts in the compounds (42), with M = Ni or Pt, L = PPh_3 or $PMePh_2$, R = H or Me, could be due to rapid inversion metal at the nitrogen, facilitated by orbital interactions with the metal.[65]



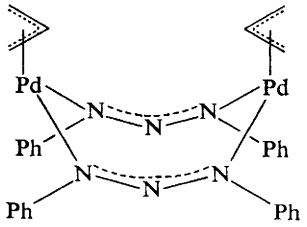
(42)

Palladium.—The compounds of palladium whose isomerization has been most widely studied are allyl derivatives, both mononuclear and bridged dinuclear series. In order to elucidate molecular rearrangements in mono-palladium-allyl compounds, some stereochemical labelling is required. The two most convenient ways of arranging this are to use a complex containing an asymmetric amine or phosphine ligand, or to study a derivative of an asymmetrically substituted allyl group. Both approaches were used in a detailed n.m.r. study of 1,1-dimethylallyl- and 1,3-dimethylallyl-[(*S*)-α-phenylethylamine]chloropalladium, to show that isomerization and epimerization take place through a σ- (or h^1-) bonded intermediate. Both a 1,3-h^2-flip process, in which the allyl group and the palladium are coplanar in the transition state, and an h^2-alkene-intermediate route, were eliminated.[66] Further evidence for the route *via* a σ- (or h^1-) bonded intermediate has been provided by a similar study of unsymmetrical allyl-phosphine-palladium chlorides and acetates. 2-Isopentyl- and 2-isobutyl-substituted allyl compounds do not undergo rearrangement; presumably

[60] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.
[61] J. A. Evans and D. R. Russell, *Chem. Comm.*, 1971, 197.
[62] M. R. Churchill and S. A. Bezman, *J. Organometallic Chem.*, 1971, **31**, C43.
[63] J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, 1970, **92**, 6976.
[64] C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 850.
[65] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3161.
[66] J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, 1971, **93**, 2642.

steric hindrance is too great.[67] *Syn–anti* rearrangement in allylpalladium dichlorides also appears to involve a σ-bonded intermediate.[68] The temperature dependence of the n.m.r. spectra of allyl- and methylallylpalladium complexes $Pd(allyl)(PPh_2R)(SnCl_3)$ suggests both inter- and intra-molecular rearrangements, involving the five-co-ordinated species $Pd(allyl)Cl(PPh_2R)(SnCl_2)$ as an intermediate.[69]

In the monomeric species $Pd(allyl)(OAc)(PMe_2Ph)$, *syn–anti* rearrangement goes *via* a σ-bonded allyl intermediate, but the isomers of the carboxylato-bridged dimers $[Pd(allyl)(CO_2R)]_2$ interconvert by inversion of the $Pd(\mu\text{-}CO_2R)_2Pd$ section of the molecule rather than by $\pi \rightarrow \sigma \rightarrow \pi$ rearrangements of the palladium-allyl groups.[70] However, rearrangements in chloride-bridged analogues do involve the allyl groups and, as in the monomeric compounds mentioned in the preceding paragraph, involve σ-bonded intermediates.[71] $[Pd(allyl)(triazene)]_2$ dimers, *e.g.* (43), are rigid,



(43)

with no inversion of the $Pd(\mu\text{-triazene})_2Pd$ unit, in contrast to the allylpalladium acetate dimers above.[72]

[67] P. W. N. M. van Leeuwen, A. P. Praat, and M. van Diepen, *J. Organometallic Chem.*, 1971, **29**, 433.
[68] D. J. S. Guthrie, R. Spratt, and S. M. Nelson, *Chem. Comm.*, 1971, 935.
[69] M. Sakakibara, Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometallic Chem.*, 1971, **27**, 139.
[70] J. Powell, *J. Chem. Soc.* (*A*), 1971, 2233.
[71] C. W. Alexander, W. R. Jackson, and R. Spratt, *J. Amer. Chem. Soc.*, 1970, **92**, 4990; P. W. N. M. van Leeuwen, A. P. Praat, and M. van Diepen, *J. Organometallic Chem.*, 1970, **24**, C31.
[72] T. Jack and J. Powell, *J. Organometallic Chem.*, 1971, **27**, 133.

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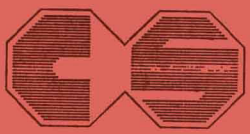
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