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Foreword

This Report deals with kinetics and mechanisms of reactions of inorganic compounds in solution — in water, in non-aqueous and mixed solvents, and extremely briefly, in molten salts. Journals scanned have included those received in the authors' libraries between January 1969 and August 1970. Coverage of primary journals over this period is intended to be fairly complete, though fully comprehensive coverage is, even with the assistance of *Chemical Abstracts* and other secondary sources, not humanly possible. Our policy of trying to mention all significant papers means that such mention must often be cursory; we regret the consequent loss of subtlety and only hope that misrepresentation by oversimplification is minimal. Mention of review articles is restricted to those which are readily accessible to the majority of readers.

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.

The arrangement of this Report, basically by type of reaction and type of compound, should be clear from the list of contents. The one drawback to the arrangement adopted is that references to the role of solvents are scattered throughout the text. To remedy this dispersion a short chapter devoted to the role of the solvent has been included in the section on substitution; references cited in this chapter are generally also mentioned at the appropriate point elsewhere in the volume. We have refrained from writing a general introductory survey of the major advances in the field in the hope that *Annual Reports*, now freed from the duty of mentioning as many references as possible, will provide just such a broad periodic survey.

The dividing line between inorganic and organic chemistry is always difficult to define, and has been drawn rather arbitrarily and erratically for the present volume. Thus several references to organo-sulphur, -phosphorus, and -silicon chemistry have been included as they seemed to supplement usefully the discussion of substitution at these atoms. However, in the organometallic section discussion is limited almost entirely to compounds of the transition metals, with only scant reference to such compounds as the organomercurials.

The Senior Reporter would like to acknowledge the help and advice of Professor C. W. Rees in inaugurating this report, and his debt to the admirable annual surveys entitled 'Organic Reaction Mechanisms', edited by Capon, Perkin, and Rees. All the authors are grateful for helpful comments from their colleagues; we are particularly indebted to Dr. A. G. Sykes and Dr. G. Davies for their thorough perusal of much of the manuscript and their perceptive comments thereon. We would warmly welcome comments from readers both on the general organisation and arrangement of this Report, and on specific details. J. B.

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Part I

ELECTRON TRANSFER PROCESSES

Introduction

Electron transfer processes involving metal ions are being increasingly studied and the role of metal complexes, together with the dramatic effects which the co-ordinated ligands can have on the reaction rates, are being considered. New and modified techniques enable investigators to examine a larger and more varied range of metal-ion oxidants and reductants. Such is the number of papers currently appearing on these topics that a degree of selection has had to be imposed, but an attempt has been made to cover fairly comprehensively all the areas where studies are being undertaken. Photochemical oxidations have been generally excluded, together with electrochemical processes occurring at electrode–solution interfaces. A number of recent conferences have dealt with several aspects of the subject, and the Faraday Society Discussion on Homogeneous Catalysis with special reference to Hydrogenation and Oxidation has now been published [1] together with the Proceedings of the Eleventh Co-ordination Chemistry Conference.[2] The Plenary lectures at this meeting are also available, and include an article by Halpern on Co-ordination Compounds in Homogeneous Catalysis.[3] Two reports on mechanisms of reaction in solution have also appeared.[4, 5]

In the case of reactions involving two metal ions, redox processes generally involve a single electron transfer step. In 'inner sphere' systems where ligand bridging has been known to take place between the metal centres,[6] the recent emphasis has been to attempt to formulate more precisely the nature of the precursor complexes formed in the initial stages of the reactions.[7, 8] In this context, the most favoured reactants have been the cobalt(III)- and ruthenium(III)-ammine complexes with the strongly reducing chromium(II) or vanadium(II) ions.

Reactions of the type

$$M(H_2O)_x^{n+} + L \rightleftharpoons M(H_2O)_{x-1}L^{n+} \longrightarrow M^{(n-1)+} + P$$

will take place as written if accompanied by a decrease in free energy, and the stability of any complex ion with respect to an intramolecular redox

[1] *Discuss. Faraday Soc.*, 1968, No. 46, The Faraday Society, London.
[2] 'Proceedings in Co-ordination Chemistry,' ed. M. Cais, Elsevier, Amsterdam, 1968.
[3] J. Halpern, *Pure & Applied Chem.*, 1969, **20**, 59.
[4] J. Burgess, *Ann. Reports* (*A*), 1969, **66**, 411.
[5] S. B. Brown and P. Jones, *Ann. Reports* (*A*), 1969, **66**, 107.
[6] A. G. Sykes, *Chem. in Britain*, 1970, 159.
[7] R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, 1970, **9**, 23.
[8] W. G. Movius and R. G. Linck, *J. Amer. Chem. Soc.*, 1970, **92**, 2677.

reaction will be dependent on several factors. If the ligand (L) has a low electron affinity, then it will be oxidised. Unlike metal ions, which may undergo changes in oxidation state in single-electron steps without the formation of highly reactive intermediates, ligands acting as reducing agents frequently require two-electron changes to reach a new stable state. The role of metal complexes in metal ion oxidations has recently been discussed for a number of transition metal species,[9] as has the question of intermediates in oxidations.[10] If a transient complex is formed in the course of the reaction, there are three possible rate-controlling factors:

(a) rate of formation of the intermediate
(b) rate of electron transfer within the complex ion
(c) rate of breakdown of the complex.

Reviews on the aquated cobalt(III)[11] and manganese(III)[12] ions as oxidants discuss the various pathways involved in the interactions of these species with both organic and inorganic substrates.

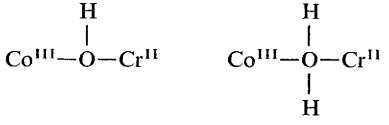
The catalytic activity of co-ordination compounds in oxidations continues to be examined and, together with the Faraday Society Discussion,[1] other aspects of this area of investigation have been the subject of recent reviews.[13, 14] Redox reactions involving bipyridyl and *o*-phenanthroline complexes of transition metals have been discussed[15] and catalytic oxidations of complexes of manganese, cobalt, copper, and palladium have also been surveyed.[16] Reviews are also available of ruthenium ammine chemistry,[17] and redox reactions involving molybdenum complexes,[18] together with an account of catalase and peroxidase reactivity of copper(II) complexes.[19]

[9] A. McAuley, *Co-ord. Chem. Revs.*, 1970, **5**, 245.
[10] J. Halpern, *J. Chem. Educ.*, 1968, **45**, 374.
[11] G. Davies and B. Warnqvist, *Co-ord. Chem. Revs.*, 1970, **5**, 349.
[12] G. Davies, *Co-ord. Chem. Revs.*, 1969, **4**, 199.
[13] M. I. Siling and A. I. Gel'bshtein, *Uspekhi Khim.*, 1969, **38**, 479.
[14] M. Matusek, F. Jaros, and A. Tockstein, *Chem. Listy*, 1969, **63**, 188.
[15] W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. and Radiochem.*, 1969, **12**, 153.
[16] T. Yasui, *Kogyo Kagaku Zasshi*, 1969, **72**, 1615.
[17] P. C. Ford, *Co-ord. Chem. Rev.*, 1970, **5**, 75.
[18] J. T. Spence, *Co-ord. Chem. Rev.*, 1969, **4**, 475.
[19] H. Sigel, *Angew. Chem. Internat. Edn.*, 1969, **8**, 167.

1
Reactions Between Two Metal Complexes

1 Reducing Agents

Chromium(II).—Many reactions have been studied using this reductant and with inert oxidants such as the cobalt(III) ammine complexes it is possible to characterise more fully the 'inner sphere' route in redox systems. Any precursor complexes formed in these reactions would greatly affect the energetics of these systems. The Cr^{II} reactions with various $Co\,en_2ACl^{2+}$ complexes have been studied[7] where A = Cl^-, F^-, OH_2, py, and NH_3. The rates are relatively insensitive to the ligand A but several of these reactions have apparently negative activation energies, the situation being described in terms of influence of the rapid formation and dissociation of precursor complexes on the overall reaction rates. Evidence for similar complexes has also been found in the corresponding reactions with *trans*-Co-(*trans*-14-diene)$(H_2O)_2^{3+}$ and *trans*-Co tet-a $(OH_2)_2^{3+}$.[20] These macrocyclic complexes are exceptionally acidic (pK_a = 4·02 and 2·70 at 25 °C respectively) so that significant concentrations of the oxidant are present as the aquohydrocomplexes and the hydroxy-bridged path is considered to be very reactive. From pH-dependence studies, it is suggested that precursor complexes involving the two metal centres of the form Co^{III}–X–Cr^{II} are sufficiently long-lived to participate in acid–base equilibria, and species (1) is considered to have a longer lifetime than its protonated analogue (2).



(1) (2)

The mechanism for these reactions may thus be written as

$$M_1L_6^{2+} + M_2L_5X^{3+} \rightleftharpoons L_5M_1^{II}\text{–}X\text{–}M_2^{III}L_5 + L \qquad (1)$$

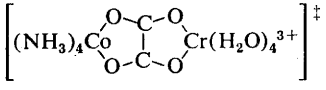
$$L_5M_1^{II}\text{–}X\text{–}M_2^{III}L_5 \rightleftharpoons L_5M_1^{III}\text{–}X\text{–}M_2^{II}L_5 \qquad (2)$$

$$L_5M_1^{III}\text{–}X\text{–}M_2^{II}L_5 \overset{+L}{\rightleftharpoons} M_1L_5X^{3+} + M_2L_6^{2+}$$

[20] M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, 1969, **91**, 3982.

where M_1 and M_2 refer to the two metal atoms and X to the bridging ligand. In the case of outer-sphere oxidations, no evidence has been found for the formation of precursor complexes.

In the reactions with *cis*- and *trans*-Co $en_2(HCO_2)_2^+$ complexes,[21] double bridging is considered to occur, and protonation decreases the rate of reduction of the *cis* complex, but increases the activity of the *trans* complex. Also with the *cis* species single and double ligand bridges are formed with the transfer of one or two formate groups to the chromium. Multiple bridging has also been postulated in the reduction of the corresponding oxalatotetrammine complex,[22] the quantitative formation of $Cr(ox)^+$ suggesting the symmetrical transition state:



The effect of the co-ordinating group on the rate of the reaction has been investigated in an interesting comparison of the rates of reaction of the mercaptoacetato bisethylenediamine cobalt(III) complex and its glycollato analogue.[23] The rate of reduction of Co $en_2(SCH_2COO)^+$ is $\sim 2 \times 10^3$ faster than for Co $en_2(OCH_2COO)^+$. The reactions are considered inner sphere and the increase in reactivity may be due to less steric hindrance of the larger thiolate group with the methylene, and a lower bond strength and greater covalency of the Co–S bond. The reduction of the linkage isomers (3) and (4), which are N- and O-bonded, respectively, also shows

$(NH_3)_5Co(NH_2CHO)^{3+}$ (3) $\qquad$ $(NH_3)_5Co(OCHNH_2)^{3+}$ (4)

marked effects.[24] Isomer (3) is a moderately strong acid and the rate law exhibits an inverse hydrogen ion dependence suggestive of the reactivity of a conjugate base. Reduction proceeds with ligand transfer to yield the O-bonded chromium(III) complex, whereas with (4) no ligand transfer takes place, the hexa-aquochromium(III) ion being produced at a considerably slower rate. Studies have been made with fumarato-cobaltammine complexes, the rates being fairly insensitive to oxidant[25] and close to those found for the acetate complexes.

In an investigation of electron transfer through structural units, it has been shown that the reduction of some pyridinepentamminocobalt(III) derivatives proceeds *via* an outer-sphere mechanism,[26] the rates for the 3- and 4-methyl derivatives being similar to the pyridine complex itself whereas the 2-methyl and quinoline species react about 100 times faster.

[21] J. R. Ward and A. Haim, *J. Amer. Chem. Soc.*, 1970, **92**, 475.
[22] C. Hwang and A. Haim, *Inorg. Chem.*, 1970, **9**, 500.
[23] R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, 1970, **92**, 1089.
[24] R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, 1970, **92**, 1533.
[25] H. Diaz and H. Taube, *Inorg. Chem.*, 1970, **9**, 1304.
[26] Y. Wang and E. S. Gould, *J. Amer. Chem. Soc.*, 1969, **91**, 4998.

In this case there may be steric hindrance between the organic ligand and the *cis* ammonias, and it may be that a large part of the activation energy for these outer sphere systems is involved in the stretching of the Co^{III}–N bonds.

Reactions involving ruthenium(III) complexes have also demonstrated the existence of precursor species. In the reduction of *cis*-$Ru^{III}(NH_3)_4Cl_2^+$,[27] there is no adherence to a normal second-order rate law and a reversible electron transfer prior to the rate-determining step is proposed. The intermediate has been observed spectrally and the mechanism may be written as

$$Cr^{II} + \textit{cis}\text{-}Ru(NH_3)_4Cl_2^+ \underset{}{\overset{K}{\rightleftharpoons}} [Ru(NH_3)_4Cl_2Cr^{II}]^{3+}$$

$$[Ru(NH_3)_4Cl_2Cr^{II}]^{3+} \xrightarrow{k} Ru^{II} + Cr^{II}.$$

The K value of 460 l mol^{-1} is considered too large for the assignment (5), the species (6) being preferred. There may be equilibrium between (5) and

$$[Ru^{III}(NH_3)_4Cl_2Cr^{II}]^{3+} \qquad [Ru^{II}(NH_3)_4Cl_2Cr^{III}]^{3+}$$
$$(5) \qquad\qquad (6)$$

(6) (presumably rapidly established) and the slow step leading to formation of products is one which involves substitution on the ruthenium(II),

$$(6) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CrCl^{2+} + Ru(NH_3)_4(H_2O)_2^{2+} + Cl^-$$

where $k_3 \sim 150$ s^{-1}. The equilibrium constant for the formation of the chloride bridged binuclear intermediate

$$Ru(NH_3)_5H_2O^{2+} + Cr(H_2O)_5Cl^{2+} \rightleftharpoons (NH_3)_5RuClCr(H_2O)_5^{4+} + H_2O$$

has been shown [8] to be $\sim 4 \times 10^{-5}$ l mol^{-1}. Inner-sphere intermediates have also been identified in the reduction of carboxylatopentammine complexes,[28] the rates and activation parameters indicating that the decomposition takes place through ruthenium(II) hydrolysis with ligand transfer to the chromium(III). For the corresponding halogenopentammine complexes [28] the rate law may be expressed as

$$\frac{-d[Ru^{III}]}{dt} = k_1[Ru^{III}]\,[Cr^{II}]$$

except for the iodide species where the reaction is strongly autocatalytic due to the aquation of the iodide complex:

$$(NH_3)_5RuI^{2+} + (NH_3)_5Ru(OH_2)^{2+} \longrightarrow (NH_3)_5RuI^+ + Ru(NH_3)_5(OH_2)^{3+}$$

$$H_2O + Ru(NH_3)_5I^+ \longrightarrow (NH_3)_5RuOH_2^{2+} + I^-$$

[27] W. G. Movius and R. G. Linck, *J. Amer. Chem. Soc.*, 1969, **91**, 5934.
[28] J. A. Stritar and H. Taube, *Inorg. Chem.*, 1969, **8**, 2281.

Variation of the rate of dissociation of intermediates of the type $[Ru^{II}ClCr^{III}]^{4+}$ with decreasing acidity suggests the equilibrium [29]

$$[Ru^{II}ClCr^{III}]^{4+} + H_2O \rightleftharpoons [Ru^{II}ClCr(OH)]^{3+} + H^+$$

followed by

$$[Ru^{II}ClCr^{III}(OH)]^{3+} \begin{cases} \nearrow Ru^{II} + Cr(OH)Cl^+ \\ \searrow RuCl^+ + CrOH^{2+} \end{cases}$$

Addition of vanadium(II) also causes an increase in the rate of decomposition of the binuclear species.

Reductions of monosubstituted iron(III) complexes have been studied,[30] the reactions being inner sphere with rates in the order $Br^- > Cl^- > F^-$ in contrast to the corresponding europium(II) systems. The order does, however, parallel that for the Cr^{II} reduction of pentammine-cobalt(III) halide complexes. Reactions with platinum(IV) complexes have been studied,[31] and in the case of $[Pt(NH_3)_5Cl]^{3+}$ and $[Pt(NH_3)_5OH]^{3+}$ a two-electron change is involved with intermediate formation of Cr^{IV} and subsequent production of dimeric Cr^{III} complexes:

$$Cr^{II} + Pt^{IV} \xrightarrow{2e} Pt^{II} + Cr^{IV}$$

$$Cr^{IV} + Cr^{II} \longrightarrow (Cr^{III})_2$$

The reduction of anionic species has also been examined.[32–34] In the case of hexachloroiridate(IV),[33] there is evidence for both inner- and outer-sphere paths. Path k_4 may make a small contribution but was not detected in this study; see Scheme 1.

$$Cr^{II} + IrCl_6^{2-} \xrightarrow[\text{(outer)}]{k_1} Cr^{III} + IrCl_6^{3-}$$

$$\text{(inner)}\ \downarrow k_2$$

$$[CrClIrCl_5] \begin{cases} \xrightarrow{k_3} CrCl^{2+} + IrCl_5(H_2O)^{2-} \\ \xrightarrow{k_4} Cr^{3+} + IrCl_6^{3-} \end{cases}$$

Scheme 1

[29] D. Seewald, N. Sutin, and K. O. Watkins, *J. Amer. Chem. Soc.*, 1969, **91**, 7307.
[30] D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 599.
[31] J. K. Beattie, Proceedings of the 157th Meeting of the American Chemical Society, Minneapolis, April 1969, paper INORG. 145.
[32] R. N. F. Thorneley and A. G. Sykes, *Chem. Comm.*, 1969, 331.
[33] A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc.* (*A*), 1970, 232.
[34] R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 862.

The spectrum of the dinuclear intermediate involved in the inner-sphere route has been derived (Figure 1). Using thermodynamic data for

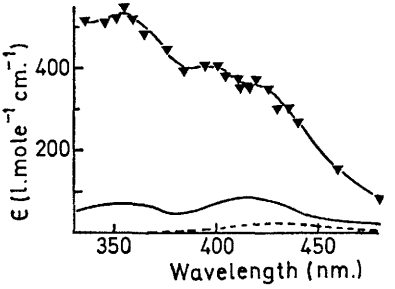


Figure 1 *A comparison of the spectrum of the intermediate* $[(H_2O)_5CrClIrCl_5]$ *(triangles) with spectra of the related mononuclear complexes,* $Cr(H_2O)_5Cl^{2+}$ *(dashed line), and* $IrCl_6^{3-}$ *(full line).*

comparable inner-sphere and outer-sphere complex formation, it has been shown that for the redox processes the enthalpy terms favour the outer sphere whereas the entropies of activation favour the inner-sphere mechanism. The difference in enthalpies of activation for the inner and outer routes is 5·7 kcal mol^{-1}. Dinuclear complexes are also formed in the reduction of hexacyanoferrate. Two products are formed,[34] one of which may be

$$[(H_2O)_5Cr^{III}—N{\equiv}C—Fe^{II}(CN)_5]^-$$

whilst the other is considered to be a protonated species with different bonding of the bridge. As in the case of $IrCl_6^{2-}$, the reaction is rapid, with $k \sim 5 \times 10^6$ l mol^{-1} s^{-1}. In the chromium(II) reduction of perchlorate,[29] however,

$$8Cr^{II} + ClO_4^- + 8H^+ \longrightarrow CrCl^{2+} + 7Cr^{III} + 4H_2O$$

the reaction is catalysed by ruthenium(II), the rate law being independent of the chromous species. A mechanism consistent with the data may be written as

$$Ru^{II} + ClO_4^- \longrightarrow Ru^{IV} + ClO_3^-$$

$$ClO_3^- + 6Cr^{II} \xrightarrow{\text{fast}} CrCl^{2+} + 5Cr^{III}$$

$$Ru^{IV} + 2Cr^{II} \xrightarrow{\text{fast}} Ru^{II} + 2Cr^{III}$$

the first step being rate determining. Electrochemical techniques have been used to study the oxidation of chromium(II) in the presence of chloride and

bromide ions[35] and thiocyanate.[36] The data suggest that the anions adsorbed on the electrode surface act as a bridge for electrode transfer and so facilitate the reaction:

$$Hg + X^- \rightleftharpoons HgX^-(\text{adsorbed})$$

$$HgX^-(\text{ads}) + Cr^{II} \longrightarrow Hg + Cr^{III}X^{2+} + e^-$$

In the case of thiocyanate[36] product studies have demonstrated the existence of multiple ligand bridges.

Vanadium(II).—An interesting feature of many vanadium(II) redox reactions is the similarity of kinetic data (k, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) to those for V^{2+} substitutions and the possibility that these processes are substitution controlled. The reaction with the oxalatotetramminecobalt(III) complex has been studied,[22] the rate law being

$$-d[Co^{III}]/dt = k_2[V^{II}][Co^{III}]$$

and here the rate-determining step may be substitution controlled. The reduction of monosubstituted pentacyanocobaltate(III) ions[37, 38] may also be controlled by loss of a water molecule from the inner co-ordination sphere of the reductant. The reactions

$$Co(CN)_5X^{3-} + V^{II} + 5H^+ \longrightarrow Co^{II} + V^{III} + X^- + 5HCN$$

where X = Cl^-, Br^-, I^-, SCN^-, N_3^-, and H_2O, proceed *via* ion-pairing with the formation of cobalt(II) intermediates (Figure 2), and in the case

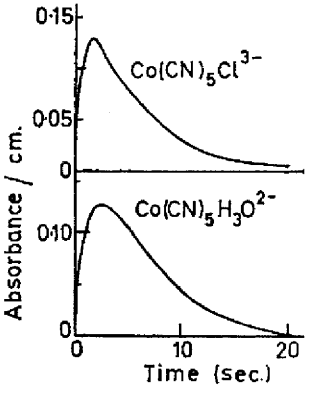


Figure 2 *Observed absorbance–time traces showing formation and decomposition of intermediate* $Co(CN)_5^{3-}$ *at* λ = 280 nm *for the reaction of* $Co(CN)_5X^{3-}$ *with* V^{2+} *at* 25·0 °C *and* μ = 1·00 mol l^{-1}. *Upper curve* 5 × 10^{-5}M-$Co(CN)_5Cl^{3-}$, 0·0105M-V^{2+}; *lower curve* 7 × 10^{-5}M-$Co(CN)_5OH_2^{2-}$, 0·0053M-V^{2+}

[35] J. J. Ulrich and F. C. Anson, *Inorg. Chem.*, 1969, **8**, 195.
[36] D. J. Barclay, E. Passeron, and F. C. Anson, *Inorg. Chem.*, 1970, **9**, 1024.
[37] K. M. Davies and J. H. Espenson, *Chem. Comm.*, 1969, 111.
[38] K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 3093.

of the azido and thiocyanate complexes, the oscilloscope traces point to an inner-sphere mechanism with formation of the corresponding mono-substituted vanadium(III) complexes; see Scheme 2. Rates have also been

$$V^{II} + Co(CN)_5N_3^{3-} \rightleftharpoons [V^{II}.Co(CN)_5N_3^{3-}]$$

$$Co(CN)_5^{2-} + VN_3^{3+}$$

$$\downarrow +5H^+ \qquad \downarrow +H^+$$

$$Co^{II} + 5HCN \qquad V^{III} + HN_3$$

Scheme 2

compared for the reductions of chloropentamminecobalt(III) complexes with the dinuclear species μ-amido[aquotetrammine cobalt(III)]-[chloro-tetrammine cobalt(III)].[39] The reaction

$$V^{II} + \left[(NH_3)_4Co\begin{matrix}NH_2\\OH_2\end{matrix}Co(NH_3)_4\begin{matrix}\\Cl\end{matrix}\right]^{4+} \xrightarrow{H^+} Co(NH_3)_5H_2O^{3+} + V^{III} + Co^{II} + 4NH_4^+$$

is followed by a slower reduction of the pentammine-aquo complex, whereas the rate constant for the reaction of $(NH_3)_5CoCl^{2+}$ is almost identical to that for the dinuclear complex. Because the activation parameters do not fall in the V^{2+} substitution-controlled range, the reactions would appear to be outer sphere. It is suggested that the chloride ligand is an active site to explain the similarity of kinetic data for the reactions of the two chloro-complexes.

The reduction of ruthenium complexes has been examined. In the case of the ruthenium(III) pentammine- and tetrammine-halogeno-complexes [8] reactions follow both inner- and outer-sphere paths and there is no parallel in the trend observed with the corresponding Co^{III} species. The reductions of ruthenium(III) ammine carboxylato-complexes are so fast that they cannot involve substitution by a bridging group into a normal co-ordination site in the reducing agent.[28] The reduction of $Ru(H_2O)_5Cl^{2+}$ has been studied,[29] the rate being invariant of acidity in the range 0·1—1·0 mol l^{-1}.

In reactions with other metal complexes, vanadium(II) acts as reductant in several ways. There is evidence for both one-electron and two-electron exchange paths in the reaction with mercury(II),[40] activation parameters being measured for both reactions. In the one-electron route, mercury(I)

[39] R. S. Taylor, R. N. F. Thorneley, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 856
[40] M. Green and A. G. Sykes, *Chem. Comm.*, 1970, 241.

is formed as an intermediate:

$$V^{II} + Hg^{II} \longrightarrow V^{II} + Hg^{I}$$

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

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

whereas in the two-electron path the products are vanadium(IV) and mercury(0) with subsequent rapid reaction of the latter species as described. The distinction between the mechanistic paths is based on variations in the final concentrations of V^{III} and V^{IV}, the two-electron process being considered as inner sphere. A one-electron transfer takes place in the reaction with copper(II),[41] the only significant product being Cu^{I}. From a comparison of the rate constant and thermodynamic parameters it is concluded that in this case the redox process is again substitution controlled. The rate of reduction of vanadium(V) is acidity dependent,[42] the products being V^{III} and V^{IV}. In the reaction with neptunium(IV) [43] the rate law

$$-\mathrm{d}[Np^{IV}]/\mathrm{d}t = \{k_a + k_b/(H^+) + k_c/(H^+)^2\}[Np^{IV}][V^{II}]$$

is observed, the data being consistent with an outer-sphere mechanism, although the rate constant k_a has a value close to that for the substitution of the primary co-ordination sphere of V^{II}.

Studies on the one-equivalent reduction of hexachloroiridate(IV) [44] show the rate to be very fast ($k > 4 \times 10^6$ l mol^{-1} s^{-1}) and that for the corresponding vanadium(III) reaction, in which VOH^{2+} appears to be the reactant,

$$V^{III} + IrCl_6^{2-} \longrightarrow V^{IV} + IrCl_6^{3-} + 2H^+$$

is too fast to be inner sphere [45] there being little ion-pairing between the vanadium and hexachloroiridate(IV).

Europium(II).—Reductions of monosubstituted iron(III) complexes have been investigated in acidic solutions,[30] the reaction rates being in the order $F^- > Cl^- > Br^-$ in contrast to the reverse order shown by chromium(II). Indirect evidence suggests that reactions are inner sphere, but no ligand transfer is observed owing to the greater lability of the Eu^{III} ion. The reactions with pentammineruthenium(III) carboxylato-complexes are almost identical to the corresponding vanadium(II) reductions.[28] The reaction kinetics may be explained by consecutive second- and first-order reactions:

$$(NH_3)_5RuO_2CR^{2+} + Eu^{II} \xrightarrow{k_2} \text{intermediate} \xrightarrow{k_1} \text{products}$$

(where R = H, Me, and CF_3). The first step is considered to involve the electron transfer, the reaction being too slow to be limited by the substitution of the reductant. The first-order decay observed to yield the products

[41] O. J. Parker and J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 185.
[42] J. H. Espenson and L. A. Krug, *Inorg. Chem.*, 1969, **8**, 2633.
[43] M. J. Burkhart and T. W. Newton, *J. Phys. Chem.*, 1969, **73**, 1741.
[44] R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1036.
[45] B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, 1967, **6**, 1948.

is due to the hydrolysis of the ruthenium(II) complex formed. The reaction

$$Eu^{2+} + VO^{2+} + 2H^+ \longrightarrow Eu^{3+} + V^{3+} + H_2O$$

has been studied,[46] the subsequent reduction of the vanadium(III) occurring much more slowly. The reaction rate is increased by the addition of SCN^-, N_3^-, and Cl^- possibly owing to the interaction of the reductant with vanadium(IV) complexes and at concentrations > 0·1M-SCN^-, the complex $VNCS^{2+}$ is detectable as a product in the stopped-flow apparatus so that the mechanism here may be inner sphere. In the above reaction the transition state is considered to be $[VOEu^{4+}]‡$, the reactions with the protons being presumed to be fast subsequent steps.

Iron(II).—The kinetics and mechanism of the reaction with oxalatotetramminecobalt(III) have been studied,[22] the rate law

$$\frac{-\,d[Co^{III}]}{dt} = k_2[Fe^{II}][Co^{III}]$$

being established. The rate is independent of acidity, the electron transfer step being considered rate determining. Comparison has been made between the reaction with thiocyanatopentamminecobalt(III) ions and related species.[47] In this system the reaction proceeds in two stages,

$$(NH_3)_5CoSCN^{2+} + Fe^{2+} \xrightarrow[5H^+]{k_1} FeNCS^{2+} + Co^{2+} + 5NH_4^+$$

$$FeNCS^{2+} \xrightarrow{k_2} Fe^{3+} + SCN^-$$

the formation of the intermediate confirming that the reaction is inner sphere. The corresponding vanadium(II) reaction is also considered to take place *via* an inner-sphere mechanism. It is of interest that in the reductions of chromium(III) and cobalt(III) complexes of this type using V^{II}, Fe^{II}, and Cr^{II} in all cases the sulphur-bonded complex is reduced faster than those bonded through nitrogen.[47, 48] In four systems compared, the ratio of the rate constants k_{SCN}/k_{NCS} for the reduction of the *S*- and *N*-bonded thiocyanato-species is $\sim 10^4$ except in the case of V^{II} where the value is 10^2 but for this reductant the rate of substitution of water at the vanadium may play an important part.

Two recent studies have been made[49, 50] on the iron(II)–chromium(VI) reaction. Rosseinsky and Nicol[49] investigated the system at low (micromolar) concentrations of ferrous ion using platinum electrode polarography and found the rate equation to be

$$\frac{-\,d[Fe^{II}]}{dt} = k_{1H}[H^+][HCrO_4^-][Fe^{II}] + k_{2H}\frac{[H^+]^3[HCrO_4^-][Fe^{II}]^2}{[Fe^{III}]}$$

[46] J. H. Espenson and R. J. Christensen, *J. Amer. Chem. Soc.*, 1969, **91**, 7311.
[47] D. P. Fay and N. Sutin, *Inorg. Chem.*, 1970, **9**, 1291.
[48] J. H. Espenson, *Inorg. Chem.*, 1965, **4**, 121.
[49] D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc.* (*A*), 1969, 2887.
[50] J. H. Espenson, *J. Amer. Chem. Soc.*, 1970, **92**, 1880.

with $k_{1H} = 2{\cdot}34 \times 10^2\ l^2\ mol^{-4}\ s^{-1}$ and $k_{2H} = 6{\cdot}92 \times 10^8\ l^4\ mol^{-4}\ s^{-1}$, at 20 °C. This rate law differs from that previously described [51] and it appears that at low iron(II) concentrations the additional pathway first order in $[Fe^{II}]$ becomes important. The k_{1H} path may be considered to proceed *via* the reaction of an Fe^{II}–$HCrO_4^-$ ion pair with a proton, or by direct reaction between Fe^{II} and H_2CrO_4. The fact that the slow step for the Fe^{II}–Cr^{VI} path first order in hydrogen ion concentration differs from that for the $[H^+]^3$ reaction (where the rate-determining step is considered to involve Fe^{II} and Cr^V) is attributed to the variation in reactivity of the relevant protonated chromium species. The primary step in the chromium(VI)–iron(II) reaction has also been shown to be first order in both reactants,[50] with a rate dependence close to second order in hydrogen ion. Evidence for the formation of a binuclear intermediate during the course of the reaction has been given in that the absorbance plots pass through a maximum in the range 270—300 nm. Neither iron(III) nor iron(II) appears to react with the intermediate which may decay in one of two ways, either

$$Fe(HCrO_4)^{2+} + H^+ \xrightarrow{k_1} Fe^{III} + H_2CrO_4$$

or

$$Fe\text{–}O\text{–}Cr^{4+} + H^+ \xrightarrow{k_1} Fe^{III} + CrOH^{2+}$$

the value of k_1 ($\sim 20\ l\ mol^{-1}\ s^{-1}$) being compatible with both these reactions. Intermediate formation has also been postulated in the reaction [52] between vanadium(V) and $Fe(CN)_6^{4-}$ which proceeds at least partly *via* an inner-sphere route. The rate law for the redox step

$$\frac{-\,d[V^V]}{dt} = k_{ox}[Fe^{II}][V^V]$$

is consistent with the mechanism

$$VO_2^+ + Fe(CN)_6^{4-} \underset{\longleftarrow}{\overset{k_{ox}}{\longrightarrow}} Fe^{III}\text{–}V^{IV} \qquad (3)$$

$$Fe^{III}\text{–}V^{IV} \xrightarrow{k_0} Fe^{III} + V^{IV} \qquad (4)$$

reaction (3) providing an example of an inner-sphere reaction where the bridging ligand is supplied by the reductant rather than by the oxidising agent. The value of $\sim 34\ s^{-1}$ for k_0 reaction (4) is independent of all concentrations of vanadium(V) when it is present in excess. In the case of the Fe^{II} reduction of hexachloroiridate(IV), however,[44] there is no evidence for dinuclear intermediate formation, the fast reaction being considered as outer sphere.

The influence of organic π-electron systems on the rate of the Tl^{III}–Fe^{II} reaction in perchloric acid has also been investigated.[53]

[51] J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, 1963, **85**, 3328.
[52] J. P. Birk, *Inorg. Chem.*, 1970, **9**, 125; *J. Amer. Chem. Soc.*, 1969, **91**, 3189.
[53] J. Ulstrup, *Acta Chem. Scand.*, 1969, **23**, 3091.

Copper(I).—Copper(I) has been prepared in non-complexing perchlorate media in a metastable form by the reduction of copper(II) by vanadium(II) and chromium(II), the solutions ($\sim 10^{-3}$ mol l^{-1}) being stable for some hours if maintained in an oxygen-free atmosphere out of contact of metallic surfaces. The reduction of cobaltammine complexes has been investigated:[54]

$$Cu^{+} + 5H^{+} + Co(NH_3)_5X^{2+} \longrightarrow Co^{2+} + Cu^{2+} + 5NH_4^{+} + X^{-}$$

the spread of rates for the series of complexes being very substantial, *e.g.* the rate constant for the reduction of *trans*-Co $en_2Cl_2^{+}$ being $> 1 \times 10^{7}$ l mol^{-1} s^{-1} whereas for Co en_3^{3+} the value is $\leqslant 4 \times 10^{-4}$ l mol^{-1} s^{-1}. The reactions generally show mixed second-order rate expressions and may be inner sphere although the high lability of the copper(II) produced precluded examination of the ligands involved in the inner co-ordination sphere after the electron transfer took place. The reactions do, however, resemble those for other reducing species and the transition state is considered to involve a Co^{III}–X–Cu^{I} linkage. The decomposition of this species is governed largely by the relative rates of substitution of the Cu^{II} and Co^{II} complexes. In the copper(II) catalysis of the oxidation of vanadium(III) to vanadium(IV) by cobalt(III) complexes such as $(NH_3)_5CoCl^{2+}$ and *trans*-Co $en_2Cl_2^{+}$,[55] the rate-determining step is considered to be the rapid reaction of V^{3+} by Cu^{2+} followed by a fast oxidation of the copper(I) produced by the pentammine cobaltic complex, *i.e.*

$$V^{III} + Cu^{II} \rightleftharpoons V^{IV} + Cu^{I}$$

$$Cu^{I} + Co^{III} \longrightarrow Cu^{II} + Co^{II}$$

Provided the cobalt(III) complex is in excess the rate law

$$\frac{-\,d[V^{III}]}{dt} = k_0[Cu^{II}]_0[V^{III}]$$

applies where

$$k_0 = k_\alpha + k_\beta/[H^{+}]$$

In this study it has been possible to evaluate the rate constants for the copper(II)–vanadium(III) reaction and from the hydrogen ion dependences it is seen that the mechanism in terms of the activation processes for the forward and reverse reactions are

$$V^{III} + Cu^{II} + H_2O \longrightarrow [V(OH)Cu^{4+}]^{\ddagger} + H^{+}$$

$$VO^{2+} + Cu^{I} + H^{+} \longrightarrow [V(OH)Cu^{4+}]^{\ddagger}$$

[54] O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 1968.
[55] O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, 1969, **91**, 1313.

Also for the reaction

$$VOH^{2+} + Cu^{II} \longrightarrow [V(OH)Cu^{4+}]^{\ddagger}$$

the rate constant $k \sim 3 \times 10^6$ l mol^{-1} s^{-1} is much greater than that for the the vanadium(III) substitution so that a bridge mechanism between V^{3+} and $CuOH^+$ is not considered. The reaction

$$Fe^{3+} + Cu^{I} \longrightarrow Fe^{2+} + Cu^{2+}$$

has been shown to be quantitative in acid solution,[56] the rate law being first order in each metal ion and inverse in hydrogen ion concentration suggesting a transition state of the type

$$FeOH^{2+} + Cu^{I} \longrightarrow [Fe(OH)Cu^{3+}]^{\ddagger}$$

The hydrolysed iron(III) species is considered to react by an inner-sphere mechanism, being more reactive than $Fe(H_2O)_6^{3+}$ by a factor of $\sim 5 \times 10^3$ probably due to the bridging nature of the hydroxy-group. The corresponding reaction involving the $CuOH^+$ species is discounted since the rate constant calculated exceeds that for the diffusion-controlled value in water at 25 °C.

Tin(II).—Several studies have been made using this reductant. In the reaction with copper(II),[57] the mechanism

$$Cu^{II} + Sn^{II} \rightleftharpoons Cu^{I} + Sn^{III}$$

$$Cu^{II} + Sn^{III} \longrightarrow Cu^{I} + Sn^{IV}$$

involving the formation of a tin(III) intermediate being postulated. The reaction rate is sensitive to chloride ions and it may be that a Cu^{II}–$SnCl_3^-$ complex species is involved. With vanadium(V) [58] the reaction

$$Sn^{II} + 2V^{V} \longrightarrow Sn^{IV} + 2V^{IV}$$

is slower in perchloric acid than in hydrochloric. The rate law

$$\frac{-\mathrm{d}[V^{V}]}{\mathrm{d}t} = [Sn^{II}][V^{V}]\{k_0 + k_1[V^{V}]\}$$

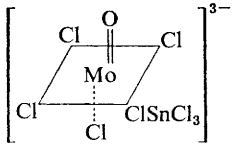
indicates two activated complexes possibly of the type $[V^{V}$–$Sn^{II}]^{\ddagger}$ and $[V^{V}{}_2$–$Sn^{II}]^{\ddagger}$ the latter being formed either by reaction of a dimeric vanadium species with tin(II) or by a rapid interaction of V^{V} with the other activated species. The reduction of molybdenum(V) in concentrated hydrochloric acid solutions has been investigated.[59] The process involves a two-electron equivalence in stoicheiometry for both reagents. The kinetics are complex, with the rate law:

$$\frac{-\mathrm{d}[Sn^{II}]}{\mathrm{d}t} = \frac{-\mathrm{d}[Mo^{V}]}{\mathrm{d}t} = \frac{k_a[Mo^{V}][Sn^{II}]}{k_b + k_c[Mo^{V}] + k_d[Sn^{II}] + k_e[Mo^{III}]}$$

[56] O. J. Parker and J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 1523.
[57] T. L. Nunes, *Inorg. Chem.*, 1970, **9**, 1325.
[58] N. A. Daugherty and B. Scheifelbein, *J. Amer. Chem. Soc.*, 1969, **91**, 4328.
[59] A. A. Bergh and G. P. Haight jun., *Inorg. Chem.*, 1969, **8**, 189.

No intermediates were detected in the visible or u.v. and molybdenum(III) inhibits the reaction whereas Sn^{IV} does not suggesting that the molybdenum(III) in its final form of $MoCl_6^{3-}$ or $MoCl_5H_2O^{2-}$ is produced whereas $SnCl_6^{2-}$ is formed in a subsequent step. A two-electron transfer step is postulated, the negative entropy of activation (− 24 e.u.) being consistent with a mechanism of the type involving charge repulsion of the negative ions.

$$MoOCl_5^{2-} + SnCl_3^- \longrightarrow$$



Other Univalent Metal Ions.—The reductions of cobalt(III) complexes by univalent zinc, cadmium, and nickel ions have been studied in aqueous solutions,[60] using pulse radiolysis techniques. Radiolysis of aqueous solutions of bivalent metal salts and cobalt(III) complexes involve reactions of the type (5)—(7). When the cobaltic complex concentrations are

$$e_{aq}^- + M^{2+} \longrightarrow M^+ \quad (5)$$

$$e_{aq}^- + Co^{III} \longrightarrow Co^{II} \quad (6)$$

$$M^+ + Co^{III} \longrightarrow Co^{II} + M^{2+} \quad (7)$$

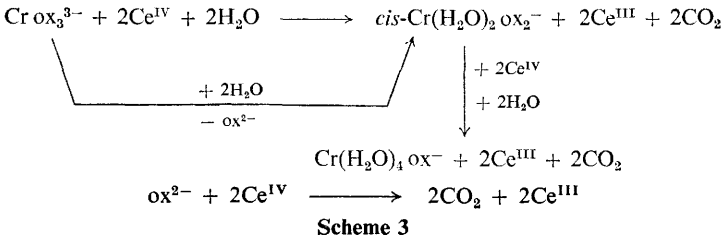
sufficiently low, to avoid a contribution from (6) compared to (5), it is possible to investigate reaction (7) by monitoring the disappearance of M^+. For complexes of the type $Co(NH_3)_5X^{2+}$ where $X = N_3^-$, Cl^-, Br^-, F^-, the order of reactivities observed is $Zn^+ \geqslant Cd^+ > Ni^+$, this order having previously been found for other oxidants.[61] For bisethylenediamine complexes $Co\,en_2XY^{n+}$, however, where X is as above and $Y = NH_3$, H_2O, F^-, Cl^-, or NO_2^-, the order of reactivities is $Cd^+ \geqslant Zn^+ > Ni^+$ with the exception of $Co\,en_3^{3+}$ and $Co\,en\,F(H_2O)^{2+}$. From the results it is considered that Zn^+ is a very strong reductant *via* the outer-sphere mechanism, in view of the high rates of reaction with $Co\,en_3^{3+}$ and $Co(NH_3)_6^{3+}$ ($k > 2 \times 10^8\,l\,mol^{-1}\,s^{-1}$). For Cd^+ there may be contributions from both the inner- and outer-sphere routes in its mode of reaction whilst for Ni^+, although the reaction rates are high, the large effect of the ligands (changing the rates by several orders of magnitude) suggests that it is an inner-sphere reductant.

2 Oxidising Agents

Cerium(IV).—The reactions with trisoxalatochromate(III) and trisoxalatorhodate(III) have been investigated [62] in aqueous sulphuric acid, the stepwise oxidation of the co-ordinated oxalate yielding the bisoxalato species. The

[60] D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1969, **73**, 1091.
[61] D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1968, **72**, 784.
[62] M.-W. Hsu, H. G. Kruszyna, and R. M. Milburn, *Inorg. Chem.*, 1969, **8**, 2201.

evaluation of rate constants for the chromium(III) reaction involves consideration of the consecutive and competing processes shown in Scheme 3.



Scheme 3

The rate behaviour suggests that although the activated complexes for the initial reactions are similar they are not identical, the suggested mechanism being

$$M^{III}ox_3^{3-} + Ce^{IV} \underset{\text{slow}}{\rightleftharpoons} M ox_3^{2-} + Ce^{III} \quad (8)$$

$$M ox_3^{2-} + Ce^{IV} \xrightarrow{\text{fast}} M^{III} ox_2(H_2O)_2^- + Ce^{III} + 2CO_2 \quad (9)$$

with some reversibility in reaction (8) when M = Rh. In the case of Cr^{III}, reaction (8) is seen as an overall process which can be further broken down into a series of steps with the intermediate formation of a cerium(IV) complex.

The iodide-catalysed reaction with arsenic(III) has been studied in sulphuric acid [63] and the oxidation of antimony(III) in perchlorate medium.[64] In the latter investigation, the reaction

$$Sb^{III} + 2Ce^{IV} \longrightarrow Sb^{V} + 2Ce^{III}$$

has the rate law

$$\frac{-\,d[Ce^{IV}]}{dt} = \frac{2[Ce^{IV}][Sb^{III}](k_2[H^+] + k_3K_2)}{[H^+] + k_2}$$

the mechanism involving $Ce(OH)_2^{2+}$ as the reactive oxidising agent together with $Ce(OH)_3^+$. The intermediate Sb^{IV} is postulated, the large increase in rate (~ 3500 times faster) compared with that observed in sulphuric acid being explained on the basis of an atom-transfer mechanism. The reaction with vanadium(IV) has also been studied in perchloric [65] and sulphuric acid [66, 67] media. The iridium-catalysed reduction of cerium(IV) by mercury(I) has also been investigated.[68]

[63] P. A. Rodriguez and H. L. Pardue, *Analyt. Chem.*, 1969, **41**, 1369.
[64] S. K. Mishra and Y. K. Gupta, *J. Chem. Soc.* (*A*), 1970, 260.
[65] G. N. Rao, *Current Sci.*, 1969, **38**, 541.
[66] M. Matusek, *Sb. Ved. Praci, Vysoka Skola, Chem.-Technol., Pardubice*, 1969, **18**, 379 (*Chem. Abs.*, 1970, **72**, 25,467g).
[67] A. Tockstein and M. Matusek, *Coll. Czech. Chem. Comm.*, 1969, **34**, 27.
[68] K. B. Yatsimirskii, L. P. Tikhonova, and I. P. Svarkovskya, *Zhur. neorg. Khim.*, 1969, **14**, 2982.

Chromium(VI).—The oxidation of vanadium(III) has been studied in aqueous perchloric acid.[69] Three one-equivalent redox steps are involved [reactions (10)—(12)], the first of which is rate determining, any two-electron transfer

$$V^{III} + Cr^{VI} \rightleftharpoons Cr^{V} + V^{IV} \quad (10)$$

$$V^{III} + Cr^{V} \rightleftharpoons V^{IV} + Cr^{IV} \quad (11)$$

$$V^{III} + Cr^{IV} \rightleftharpoons V^{IV} + Cr^{III} \quad (12)$$

processes being excluded since no vanadium(v) was detected. Evidence for the presence of Cr^{V} was derived from the oxidation of iodide induced by the Cr^{VI}–V^{III} reaction, the scavenging effect of I^- towards Cr^{V} being demonstrated. For substitution labile species, reactions of type (11) are considered the rate-determining steps in Cr^{VI} oxidations whereas for substitution inert complexes, reaction (10) is the slow process. The mechanism for vanadium(III) is considered outer sphere, the lability of the V^{III} species being too low for a ligand-bridging mechanism. The first step in the corresponding reaction with vanadium(IV) has also been investigated,[70] using vanadium(III) to scavenge the vanadium(v) produced. The rate law

$$\frac{-\,d[Cr^{VI}]}{dt} = k_1[VO^{2+}][HCrO_4^-]$$

indicates an activated complex of the type $[(VOHCrO_4^+) + mH_2O]^{\ddagger}$ since no hydrogen ion dependence was observed. The primary steps in the reaction with iron(II) have also been studied.[49, 50] The kinetics of the arsenic(III) oxidation have been investigated in dihydrogen phosphate–hydrogen phosphate buffer solutions,[71] the two-term rate law being first order in total Cr^{VI} and As^{III} with a complex dependence on buffer concentration. The first term is assigned to the direct oxidation of As^{III} by the complex ion $HCrPO_7^{2-}$, the second term involving either the use of $CrPO_7^{3-}$ as an oxidant or the reaction of $HCrPO_7^{2-}$ with $As(OH)_2O^-$. As no evidence was found for association between As^{III} and HPO_4^{2-} or $H_2PO_4^-$, the assumption is made that the chromium(VI) species form reactive complexes.

Miscellaneous Oxidants.—The cobaltic ion oxidation of silver(I) has been examined in perchlorate media.[72] The following mechanism

$$Co^{III} + Ag^{I} \underset{}{\overset{K_2}{\rightleftharpoons}} Co^{II} + Ag^{II} \quad (13)$$

$$2Ag^{II} \overset{K}{\rightleftharpoons} Ag^{I} + Ag^{III}$$

$$Ag^{III} + H_2O \overset{K_1}{\rightleftharpoons} AgO^+ + 2H^+$$

$$AgO^+ \xrightarrow{k} Ag^+ + \tfrac{1}{2}O_2$$

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[70] K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, 1970, **92**, 1889.
[71] J. G. Mason, A. D. Kowalak, and R. M. Tuggle, *Inorg. Chem.*, 1970, **9**, 847.
[72] D. J. Cowley, D. Mason, and L. H. Sutcliffe, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1709.

yields the rate law

$$\frac{-\mathrm{d}[Co^{III}]}{\mathrm{d}t} = \frac{-\mathrm{d}[Ag^{II}]}{\mathrm{d}t} = \frac{kKK_1K_2^2[Co^{III}]^2[Ag^I]}{[Co^{II}]^2[H^+]^2}$$

with the deduction that the equilibrium (13) is rapidly established. The value for K_2 is considered to be $\sim 3 \pm 2 \times 10^{-2}$ although a precise evaluation is difficult due to the oxidising nature of both Ag^{II} and Co^{III}. Experimentally, however, it has been shown that silver(II) in perchloric acid decays according to a second-order rate law with $\Delta H^{\ddagger} \sim 11$ kcal mol^{-1} and combination of this value with the rate of disappearance of cobalt(III) in the presence of silver(I), using the above rate law, gives K_2 values in good agreement with those derived potentiometrically and spectrophotometrically. For reaction (13), $\Delta H^{\circ} \sim 0{\cdot}0 \pm 2$ kcal mol^{-1} and $\Delta S^{\circ} \sim -7$ cal deg^{-1} mol^{-1}.

The oxidation of Ti^{III} by Fe^{III} [73] and the reaction between Tl^{III} and Sn^{II} [67] have been studied using flow and potential–time dependences. An investigation has also been made [74] of the Ag^{II}–Ce^{III} reaction. Polarographic studies of planar Schiff base complexes of Co^{II}, Ni^{II}, and Cu^{II} have shown well-defined oxidation waves [75] and in some chelates the two-electron oxidation $Co^{II} \rightarrow Co^{IV}$ is postulated. Kinetic studies have also been made on the oxidation of cobalt(II) dipyridyl complexes by copper(II) and iron(III) perchlorates [76] in anhydrous acetonitrile. Solvent effects have also been investigated in redox reactions of tetrahalogenoplatinum(IV) complexes of the type PtL_2X_4.[77]

Table 1 *Rate constants and thermodynamic parameters for redox reactions involving two metal ions (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 of* $\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1})

Oxidant	*Reduction* k_{25} °C	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Chromium(II)					
cis-Co en$_2$ClNH$_3^{2+}$	$2{\cdot}4 \times 10^5$	—	−2	−41	7
cis-Co en$_2$ClH$_2$O^{2+}	$4{\cdot}2 \times 10^5$	—	1·4	−29	7
cis-Co en$_2$Cl py^{2+}	$9{\cdot}4 \times 10^5$	—	8	−3	7
cis-Co en$_2$Cl$_2^+$	$7{\cdot}7 \times 10^5$	—	−6	−51	7
cis-Co en$_2$ClF$^+$	$8{\cdot}9 \times 10^5$	—	−10	−65	7
trans-Co en$_2$Cl$_2^+$	40×10^5	—	−8	−53	7
trans-Co en$_2$F$_2^+$	$4{\cdot}3 \times 10^5$	—	−0·1	−33	7
trans-Co en$_2$F(H$_2$O)$^{2+}$	$1{\cdot}4 \times 10^5$	—	0	−34	7
trans-Co(NH$_3$)$_5$(HCO$_2$)$^{2+}$	7·2	1·0	8·3	−27	21
trans-Co en$_2$(HCO$_2$)$_2^+$	5·1	1·0	5·1	−38	21
cis-Co en$_2$(HCO$_2$)$_2^+$	50	1·0	7·9	−25	21[a]
cis-Co en$_2$(HCO$_2$)$_2^+$	434	1·0	3·7	−35	21[b]

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Table 1 (*cont.*)

Oxidant	*Reduction* k_{25} °C	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
cis-$Co(NH_3)_4$ ox^{+}	2×10^5	1·0	—	—	22
cis-Co en$_2$(HOCH$_2$COO)$^{2+}$	38	1·0	—	—	23
cis-Co en$_2$(OCH$_2$COO)$^{+}$	$9{\cdot}9 \times 10^2$	1·0	—	—	23
cis-Co en$_2$(SCH$_2$COO)$^{+}$	2×10^6	1·0	—	—	23
cis-$Co(NH_3)_5(NH_2CHO)^{3+}$	1·74	—	12·0	− 17	24
cis-$Co(NH_3)_5(OCHNH_2)^{3+}$	$8{\cdot}5 \times 10^{-3}$	—	10·7	− 32	24[c]
cis-$Co(NH_3)_5(FuOH)^{2+}$	1·32	—	6·7	− 36	25[d]
cis-Co en$_2$(H_2O)(FuOH)$^{2+}$	9·10	—	7·4	− 29	25[d]
cis-$Co(NH_3)_4(H_2O)(FuOH)^{2+}$	60·7	—	5·1	− 33	25[d]
$Co(NH_3)_5$ py^{3+}	$4{\cdot}1 \times 10^3$	1·30	—	—	26[e, f]
$Co(NH_3)_5$(2-Mepy)$^{3+}$	$1{\cdot}90 \times 10^5$	1·30	—	—	26[e, f]
$Co(NH_3)_5$(3-Mepy)$^{3+}$	$4{\cdot}5 \times 10^3$	1·30	—	—	26[e, f]
$Co(NH_3)_5$(4-Mepy)$^{3+}$	$1{\cdot}6 \times 10^3$	1·30	—	—	26[e, f]
$Co(NH_3)_5$(4-Etpy)$^{3+}$	$2{\cdot}6 \times 10^3$	1·30	—	—	26[e, f]
$Co(NH_3)_5$(3,5-Lu)$^{3+}$	$2{\cdot}2 \times 10^3$	1·30	—	—	26[e, f, g]
$Co(NH_3)_5$(Quin)$^{3+}$	$2{\cdot}5 \times 10^5$	1·30	—	—	26[e, f, h]
$Ru(NH_3)_5Cl^{2+}$	460	0·1	—	—	8[i]
cis-$Ru(NH_3)_4Cl_2^{+}$	154	0·1	—	—	8[i]
cis-$Ru(NH_3)_4Cl(H_2O)^{2+}$	117	0·1	—	—	8[i]
trans-$Ru(NH_3)_4Cl_2^{+}$	126	0·1	—	—	8[i]
$Ru(NH_3)_5(O_2C_2F_3)^{2+}$	$1{\cdot}6 \times 10^3$	0·11	1·3	− 39	28[k]
$Ru(NH_3)_5(O_2CPhOH)^{2+}$	4×10^3	0·11	—	—	28[j, k]
$Ru(NH_3)_5(O_2CPh)^{2+}$	$5{\cdot}8 \times 10^3$	0·11	1·4	− 35	28[k]
$Ru(NH_3)_5(O_2CH)^{2+}$	$1{\cdot}7 \times 10^5$	0·11	—	—	28[j, k]
$Ru(NH_3)_5(O_2C_2CH_3)^{2+}$	$3{\cdot}2 \times 10^4$	0·11	1	− 34	28[k]
$Ru(NH_3)_5(O_2CC_6H_4CO_2Me)^{2+}$	$6{\cdot}6 \times 10^3$	0·11	—	—	28[j, k]
$Fe(H_2O)_6^{3+}$	$2{\cdot}3 \times 10^3$	1·0	5·2	− 28	30
$Fe(OH)^{2+}$	$3{\cdot}3 \times 10^6$	1·0	4·6	− 13	30
FeN_3^{2+}	2×10^7	1·0	—	—	30[l]
$Fe(CNS)^{2+}$	2×10^7	1·0	—	—	30[l]
FeF^{2+}	$7{\cdot}6 \times 10^5$	1·0	—	—	30[l]
$Fe(NCO)^{2+}$	$7{\cdot}2 \times 10^5$	1·0	2·9	− 22	30
$IrCl_6^{2-}$	10^6	1·0	—	—	33[m]
$IrCl_6^{2-}$	10^6	1·0	—	—	33[n]
$IrCl_6^{2-}$	$4{\cdot}3 \times 10^{-2}$	1·0	21·8	8·4	33[i, o]
$Fe(CN)_6^{3-}$	5×10^6	1·0	—	—	34
Vanadium(II)					
$Co(NH_3)_4$ ox^{+}	45·5	1·0	12·3	− 9·8	22
$Co(NH_3)_5Cl^{2+}$	10·2	2·0	7·5	− 28·8	39
$Co(NH_3)_5(H_2O)^{3+}$	0·94	2·0	—	—	39
$(NH_3)_4(H_2O)Co$ ·NH_2·$CoCl(NH_3)_4^{4+}$	9·4	2·0	7·8	− 27·8	39
cis-$Ru(NH_3)_4Cl_2^{+}$	9800	0·1	—	—	8
trans-$Ru(NH_3)_4Cl_2^{+}$	830	0·1	—	—	8
trans-$Ru(NH_3)_4(OH_2)Cl^{2+}$	1420	0·1	—	—	8
$Ru(NH_3)_5(O_2CMe)^{2+}$	560	0·1	—	—	28
$Ru(NH_3)_5(O_2CH)^{2+}$	$4{\cdot}1 \times 10^3$	0·5	—	—	28
$Ru(NH_3)_5(O_2CCF_3)^{2+}$	$2{\cdot}9 \times 10^3$	0·5	—	—	28
$RuCl^{2+}$	$1{\cdot}88 \times 10^3$	1·0	—	—	29
Hg^{2+}	1·32	2·0	15·2	− 7·2	40[p]

Table 1 (*cont.*)

Oxidant	*Reduction* k_{25} °C	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Hg^{2+}	1·85	2·0	10·9	− 20·6	40[q]
$HgOH^{+}$	3·2 × 10^{4}	2·0	7·9	− 11·5	40[q]
Cu^{II}	26·6	1·0	11·4	− 13·8	41
VO_2^{+}	2·58 × 10^{3}	1·0	1·9	− 36·8	42
Np^{IV}	2·53	2·0	—	—	43
Europium(II)					
FeN_3^{2+}	1·2 × 10^{7}	1·0	—	—	30[l]
$Fe(CNS)^{2+}$	6·4 × 10^{5}	1·0	4·4	− 17·3	30
FeF^{2+}	1·9 × 10^{7}	1·0	—	—	30[l]
$FeOH^{2+}$	6·0 × 10^{6}	1·0	—	—	30[l]
$Ru(NH_3)_5Cl^{2+}$	2·4 × 10^{4}	0·11	—	—	28
$Ru(NH_3)_5Br^{2+}$	1·34 × 10^{4}	0·11	1·0	− 37	28
$Ru(NH_3)_5(O_2CMe)^{2+}$	1·7 × 10^{5}	0·10	—	—	28
$Ru(NH_3)_5(O_2CH)^{2+}$	4·3 × 10^{5}	0·10	—	—	28
$Ru(NH_3)_5(O_2CCF_3)^{2+}$	6·9 × 10^{5}	0·10	—	—	28
VO^{2+}	2·64 × 10^{3}	1·0	2·8	− 33·4	46
$Co(NH_3)_4\,ox^{+}$	4·16 × 10^{4}	1·0	18·5	− 12·1	22
$Co(NH_3)_5SCN^{2+}$	0·12	1·0	—	—	47
$Co(NH_3)_5NCS^{2+}$	3 × 10^{6}	1·0	—	—	48
$IrCl_6^{2-}$	3·1 × 10^{6}	1·0	2·3	− 28	44
V^{V}	1·2 × 10^{6}	0·5	—	—	52[r]
Copper(I)					
trans-$Co\,en_2Cl_2^{+}$	1 × 10^{7}	0·20	—	—	54
$Co(NH_3)_5Br^{2+}$	4·46 × 10^{5}	0·20	$3{\cdot}8_6$	− 19·8	54
$Co(NH_3)_5Cl^{2+}$	4·9 × 10^{4}	0·20	5·3	− 19·4	54
cis-$Co\,en_2Cl_2^{+}$	2·13 × 10^{4}	0·20	—	—	54
$Co(NH_3)_5N_3^{2+}$	1·5 × 10^{3}	0·20	5·4	− 25·8	54
$Co(NH_3)_5OH^{2+}$	3·8 × 10^{2}	0·20	—	—	54
$Co(NH_3)_5NCS^{2+}$	1	0·20	—	—	54
$Co(NH_3)_5F^{2+}$	1·1	0·20	12·4	− 16·6	54
trans-$Co(NH_3)_4(OH_2)CN^{2+}$	0·47	0·20	—	—	54
$Co(NH_3)_5CN^{2+}$	3·3 × 10^{-3}	0·2	—	—	54
$Co(NH_3)_5OH_2^{3+}$	1 × 10^{-3}	0·2	—	—	54
$Co\,en_3^{3+}$	4 × 10^{-4}	0·2	—	—	54
$FeOH^{2+}$	9·8 × 10^{7}	1·0	2·2	− 14·8	56
Zinc(I)					
$Co(NH_3)_6^{3+}$	8·4 × 10^{8}	0·08	—	—	60[s]
$Co(NH_3)_5F^{2+}$	8·2 × 10^{8}	0·08	—	—	60[s]
$Co(NH_3)_5Br^{2+}$	2·6 × 10^{9}	0·08	—	—	60[s, t]
$Co\,en_3^{3+}$	2·5 × 10^{8}	0·08	—	—	60[s]
$Co\,en_2FH_2O^{2+}$	4·7 × 10^{8}	0·08	—	—	60[s]
$Co\,en_2CO_3^{+}$	4·7 × 10^{8}	0·08	—	—	60[s]
trans-$Co\,en_2Cl_2^{+}$	2·3 × 10^{9}	0·08	—	—	60[s]
Cadmium(I)					
$Co(NH_3)_6^{3+}$	1·7 × 10^{8}	0·08	—	—	60[s]
$Co(NH_3)_5F^{2+}$	5·4 × 10^{8}	0·08	—	—	60[s]

Table 1 (*cont.*)

Oxidant	k_{25} °C	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
	Reduction				
$Co(NH_3)_5Br^{2+}$	$2{\cdot}5 \times 10^9$	0·08	—	—	60[s, t]
Co en_3^{3+}	$1{\cdot}6 \times 10^7$	0·08	—	—	60[s]
Co $en_2FH_2O^{2+}$	$4{\cdot}1 \times 10^8$	0·08	—	—	60[s]
Co $en_2CO_3^{+}$	$6{\cdot}7 \times 10^8$	0·08	—	—	60[s]
trans-Co $en_2Cl_2^{+}$	$2{\cdot}6 \times 10^9$	0·08	—	—	60[s]
Nickel(II)					
$Co(NH_3)_6^{3+}$	5×10^6	0·08	—	—	60[s]
$Co(NH_3)_5F^{2+}$	5×10^6	0·08	—	—	60[s]
$Co(NH_3)_5Br^{2+}$	$1{\cdot}05 \times 10^9$	0·08	—	—	60[s, t]
Co en_3^{3+}	5×10^6	0·08	—	—	60[s, t]
Co $en_2FH_2O^{2+}$	5×10^6	0·08	—	—	60[s]
Co $en_2NH_3NO_2^{2+}$	$3{\cdot}3 \times 10^8$	0·08	—	—	60[s]
trans-Co $en_2Cl_2^{+}$	$8{\cdot}3 \times 10^8$	0·08	—	—	60[s]
Vanadium(III)					
Cu^{II}	$1{\cdot}8 \times 10^{-2}$	1·0	21·3	5·2	55
Cu^{II}	$1{\cdot}7 \times 10^2$	1·0	9·4	− 16	55[u]
$IrCl_6^{2-}$	52	1·0	12·4	− 9	44[v]
	Oxidations				
Reductant					
Cerium(IV)					
Cr ox_3^{3-}	4×10^{-2}	1·0	17·6	—	62[w]
Rh ox_3^{3-}	6×10^{-4}	1·0	35	—	62[w]
Sb^{III}	3×10^2	2·0	—	—	64
V^{IV}	$1{\cdot}03 \times 10^3$	1·0	—	—	66
Chromium(VI)					
V^{III}	$3{\cdot}86 \times 10^2$	1·00	—	—	69
V^{IV}	$1{\cdot}86 \times 10^2$	1·00	—	—	70
Iron(III)					
Ti^{III}	25	2·0	—	—	73
Fe $bipy_3^{3+}$					
Co^{II}-edta	$3{\cdot}3 \times 10^4$	0·5	7	− 15	224
Co^{II}-cydta	$6{\cdot}7 \times 10^4$	0·5	5	− 19	224
Co^{II}-hydta	$1{\cdot}7 \times 10^4$	0·5	4	− 26	224
Co^{II}-edta	$9{\cdot}1 \times 10^4$	0·5	—	—	224[x]
Co^{II}-edta	$7{\cdot}9 \times 10^5$	1·0	—	—	224[y]

[a] Single-bridged path. [b] Double-bridged path. [c] T = 26 °C. [d] $FuOH^-$ = fumarate ion. [e] H^+ = 1·00 mol l^{-1}. [f] Outer-sphere reaction. [g] 3,5-Lu = 3,5-Lutidine. [h] Quin = Quinoline. [i] Rate constants in s^{-1}. [j] T = 10 °C. [k] H^+ = 0·11 mol l^{-1}. [l] T = 1·6 °C. [m] Inner-sphere reaction. [n] Outer-sphere reaction. [o] Breakdown of binuclear complex. [p] One-electron reaction. [q] Two-electron reaction. [r] Reductant is $Fe(CN)_6^{4-}$, T = 8 °C. [s] Solutions contain 0·02M$^{II}SO_4$, 1 × 10^{3}M-MeOH and pH 5–6. [t] pH = 4·0. [u] Reductant is VOH^{2+}. [v] Rate law involves term in $[H^+]^{-1}$, k in s^{-1}. [w] $[H^+]$ = 1·0M-H_2SO_4. [x] Oxidant = Fe $phen_3^{3+}$. [y] T = 5 °C, I = 1·0 mol l^{-1} oxidant is Ru $bipy_3^{3+}$.

Lanthanides and Actinides.—The spectra and M^{II}–M^{III} oxidation potentials of lanthanides and actinides have been measured in aqueous solution [78] and the expected reducing ability should be in the sequence

	Tm^{II} >	Sm^{II} >	Yb^{II} >	Eu^{II}
E^{o}(V) M^{II}/M^{III}	2·2	1·55	1·15	0·43

and for the actinides the sequence

$$Cf^{II} > Es^{II} > Md^{II}$$

is proposed. The reversible neptunium(VII)/(VI) couple in sodium hydroxide solutions has been shown from hydroxide ion dependence to be [79]

$$e + NpO_5^{3-} + H_2O \rightleftharpoons NpO_4^{2-} + 2OH^-$$

with $E^{o} = 0{\cdot}582$ V in 1M-NaOH.

The potential for the uranium(III)/(IV) couple in perchloric acid is 0·63 V so that the tervalent species is a very powerful reductant. Recently [80] the first kinetic study using this species has been made, reactions of the type

$$(NH_3)_5CoX^{2+} + U^{3+} + 5H^+ \longrightarrow Co^{II} + U^{IV} + 5NH_4^+ + X^-$$

showing 1 : 1 stoicheiometry. An inner-sphere mechanism is proposed based on the different reactivity of the azido-complexes compared with the corresponding isothiocyanato-species (see Table 2). Reactions with the

Table 2 *Redox reactions of actinides*

	k_{25} °C	I (mol l^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Uranium(III) reductions					
$Co(NH_3)_5N_3^{2+}$	8×10^5	0·20	—	—	80
$Co(NH_3)_5F^{2+}$	$3{\cdot}8 \times 10^5$	0·20	—	—	80
$Co(NH_3)_5Cl^{2+}$	$3{\cdot}2 \times 10^4$	0·20	—	—	80
$Co(NH_3)_5OAc^{2+}$	$1{\cdot}5 \times 10^4$	0·20	—	—	80
$Co(NH_3)_5Br^{2+}$	$1{\cdot}4 \times 10^4$	0·20	—	—	80
$Co(NH_3)_5CN^{2+}$	$3{\cdot}5 \times 10^3$	0·20	—	—	80
$Co(NH_3)_5NCS^{2+}$	18	0·20	—	—	80
$Co(NH_3)_6^{3+}$	1·2	0·20	—	—	80
UO_2^{2+}	$5{\cdot}5 \times 10^4$	1·00	4·3	− 22·3	82
Neptunium(III) reductions					
U^{VI}	39	1·00	2·6	− 42·6	82
Np^{VI}	$1{\cdot}05 \times 10^5$	1·00	1·0	− 32	82
Plutonium(III) reductions					
Np^{VI}	35·5	1·00	3·5	− 39·7	81
Pu^{VI}	2·7	1·00	4·8	− 40·4	82
Neptunium(VII) oxidation					
Tl^{I}	4·46	—	7·7	—	83

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[79] A. J. Zielen and D. Cohen, *J. Phys. Chem.*, 1970, **74**, 394.
[80] J. H. Espenson and R. T. Wang, *Chem. Comm.*, 1970, 207.

penta-aquochromium(III) halides show two paths, the conjugate base $(H_2O)_4Cr(OH)(X)^+$ being considered a highly reactive oxidant in this case. Reductions of VO^{2+}, Cr^{3+}, V^{3+}, Cu^{2+}, Fe^{3+}, and UO_2^{2+} by U^{3+} all proceed at a measurable rate.

The oxidation of plutonium(III) by neptunium(VI) has been investigated [81] at varying acidities, and the following reactions were identified:

$$NpO_2^{2+} + Pu^{3+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pu^{IV} + NpO_2^+$$

$$NpO_2^{2+} + Pu^{3+} + H_2O \xrightarrow{k_3} [Pu.OH.NpO_2^{4+}]^{\ddagger} + H^+$$

The reaction rate is also sensitive to chloride ion concentration.

The overall reaction between neptunium(III) and uranium(VI)

$$2Np^{3+} + UO_2^{2+} + 4H^+ \longrightarrow 2Np^{4+} + U^{4+} + 2H_2O$$

takes place in three separate steps:[82]

$$Np^{3+} + UO_2^{2+} \rightleftharpoons Np^{4+} + UO_2^+$$

$$Np^{3+} + UO_2^+ + 4H^+ \longrightarrow Np^{4+} + U^{4+} + 2H_2O$$

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

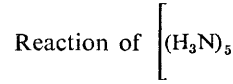
The oxidation of thallium(I) by neptunium(VII) has been investigated,[83] an acidity dependence of the rate constant being observed.

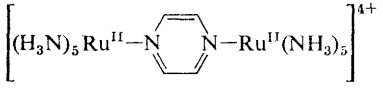
Electron Exchange Reactions.—Several studies are reported of the interaction between Cr^{II} and Cr^{III} complexes.[25, 84, 85, 86] Medium effects have been investigated [84] in the exchange of penta-aquochlorochromium(III) by Cr^{II}, using the rate of exchange of ^{51}Cr measured at varying temperatures. The reaction was also studied in dioxan–water mixtures, the activated complex $[(H_2O)_5CrClCr(H_2O)_5^{4+}]^{\ddagger}$ being postulated. Chromium(II) catalyses the aquations of one oxalato-group from $Cr\,ox_3^{3-}$ and the *trans–cis* isomerisation of $Cr\,ox_2(H_2O)_2^-$ the rate law for the Cr^{II}-catalysed path in both instances being

$$\frac{-\,d[Cr^{III}]}{dt} = k[Cr^{II}][Cr^{III}]$$

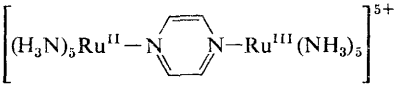
and in the exchange reaction it is considered that two oxalato groups act as bridges.[85] Bridging ligands are also invoked in the exchange with fumaratochromium(III).[25] A direct approach to measuring the Franck–Condon barrier to electron transfer between metal ions using ruthenium

[81] R. B. Fulton and T. W. Newton, *J. Phys. Chem.*, 1970, **74**, 1661.
[82] T. W. Newton, *J. Phys. Chem.*, 1970, **74**, 1655.
[83] R. C. Thompson and J. C. Sullivan, 159th Meeting of the American Chemical Society, Houston, Texas, 1970, paper PHYS. 114.
[84] R. V. James and E. L. King, *Inorg. Chem.*, 1970, **9**, 1301.
[85] D. H. Huchital, *Inorg. Chem.*, 1970, **9**, 486.
[86] T. Spinner and G. M. Harris, Paper INOR-36, 156th Meeting of the American Chemical Society, Atlantic City, New Jersey, September 1968.

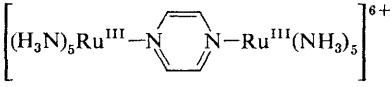
complexes has been investigated.[87] Reaction of  with $(H_3N)_5Ru(OH_2)^{2+}$ yields the complex ion (7). A one-electron oxidation of (7) by cerium(IV) or persulphate produces (8) and further oxidation yields the complex (9). Only (8) shows a strong peak in the near i.r. at



(7)



(8)



(9)

~ 1500 nm, the absorption being considered due to the transition [(II)–(III)] → [(III)–(II)]* (see Figure 3). In this case, the transition energy is

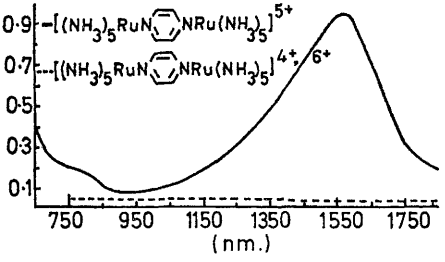
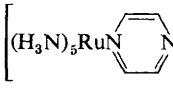
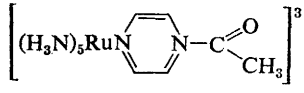


Figure 3 *Near-i.r. spectrum of* (8) *in* D_2O. *Concentration of* (8) = 1·5 × 10^{-4} mol l^{-1}; 1-cm *path length. (Dashed line is actually the blank, but accurately indicates the spectra of* (7) *and* (9) *in this range above* 750 nm *at this concentration level)*

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a measure of the Franck–Condon barrier and a self-exchange rate for internal transfer of ~ 3 × 10^9 s^{-1} is computed for ion (8). The rate constant for the reaction between  and  is 1 × 10^6 m^{-1} s^{-1}.

[87] C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, 1969, **91**, 3988.

Reactions of the type

$$Fe(CN)_6^{4-} + Fe(CN)_5NH_3^{2-} \rightleftharpoons Fe(CN)_6^{3-} + Fe(CN)_5NH_3^{3-}$$

have been investigated [88] and by variation of the neutral or anionic groups replacing the cyano-groups in the oxidant it is possible to vary the overall charge of the ion from -2 to -4. A common feature of these systems is that $\Delta H^{\ddagger} \sim 3$ kcal mol^{-1} and $\Delta S^{\ddagger}$ ranges from -25 to -30 e.u. (Table 3).

Table 3 *Rates and thermodynamic parameters for electron exchange reactions* [k_{25} *is the second-order rate constant* (*in* l mol^{-1} s^{-1}) *at* 25 °C, *the units of* $\Delta H^{\ddagger}$ *and* $\Delta S^{\ddagger}$ *being* kcal mol^{-1} *and* cal deg^{-1} mol^{-1}, *respectively*]

System	k_{25}	I (M)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Cr^{II}–$CrCl^{2+}$	2·8	0·20	7·99	− 27·1	84[a]
Cr^{II} + $Cr\,ox_3^{3-}$	0·129	2·0	8·2	− 35·1	85
Cr^{II} + *trans*-$Cr\,ox_2(H_2O)_2^-$	0·108	2·0	11·9	− 23·2	85
Cr^{II} + *cis*-$Cr\,ox_2(H_2O)_2^-$	0·17	2·0	—	—	85
Cr^{II} + $Cr\,ox\,(H_2O)_4^+$	0·13	—	10·8	− 26·4	86
Cr^{II} + $CrFuOH^{2+}$	1·72	—	6·3	− 35	25[b]
$Fe(CN)_6^{4-}$ + $Fe\,bipy_3^{3+}$	10^8	0·05	—	—	88
$Fe(CN)_6^{4-}$ + $Fe\,bipy\,(CN)_4^-$	8×10^6	0·05	—	—	88
$Fe(CN)_6^{4-}$ + $Fe(CN)_5P(Ph)_3^{2-}$	8×10^4	0·05	3·3	− 25	88
$Fe(CN)_6^{4-}$ + $Fe(CN)_5NH_3^{2-}$	7×10^3	0·05	3·3	− 32	88
$Fe(CN)_6^{4-}$ + $Fe(CN)_5OH_2^{2-}$	1×10^3	0·05	3·2	− 33	88
$Fe(CN)_6^{4-}$ + $Fe(CN)_6^{3-}$	5×10^3	0·05	4·0	− 32	88
$Fe(CN)_5N_3^{4-}$ + $Fe(CN)_6^{3-}$	8×10^4	0·05	1·8	− 30	88
$Fe\,bipy\,(CN)_4^{2-}$ + $Fe(CN)_6^{3-}$	2×10^4	0·05	—	—	88
$Mn(CNBu^t)_6^+$ − $Mn(CNBu^t)_6^{2+}$	4×10^4	—	—	—	90[c]
$Mn(CNEt)_6^+$–$Mn(CNEt)_6^{2+}$	$5{\cdot}5$—16×10^5	—	—	—	90[c, d]
Tl^I–Tl^{III}	$4{\cdot}5 \times 10^{-4}$	—	—	—	91
Tl^I–$TlOAc^{2+}$	$2{\cdot}2 \times 10^{-5}$	—	—	—	—
Tl^I–$TlO_2CCH_2Cl^{2+}$	$6{\cdot}8 \times 10^{-5}$	—	—	—	91
Tl^I–$TlO_2CCHCl_2^{2+}$	$2{\cdot}50 \times 10^{-4}$	—	—	—	91
Tl^I–TlO_2CCCl_3	$6{\cdot}2 \times 10^{-4}$	—	—	—	91
$Co\,phen_3^{2+}$–$Co\,phen_3^{3+}$	16	—	—	—	94
V^{2+}–VO_2^+	2·58	1·0	1·9	− 36·8	42
$Ta_6Br_{12}^{2+}$–$Ta_6Br_{12}^{4+}$	$6{\cdot}8 \times 10^7$	0·04	—	—	97

[a] $T = 0$ °C. [b] $T = 10$ °C, $FuOH^-$ = fumarate. [c] $T = 7$ °C. [d] Values quoted are in various solvents, see text.

Using the Marcus theory, allowance was made for the different free energies of each reaction and, incorporating known rate data, the isotopic exchange rate constants for the complexes were shown to increase in the order

$$Fe(CN)_5N_3^{4-/3-} < Fe(CN)_6^{4-/3-} < Fe(CN)_5NH_3^{3-/2-} \sim Fe(CN)_5P(Ph)_3^{3-/2-} < Fe\,bipy\,(CN)_4^{2-/1-} < Fe\,bipy_3^{2+/3+}$$

The reaction involving $Fe(CN)_5CNS^{4-}$ led to the formation of intermediates. The observations may be accounted for if the iron(II) thiocyanate

[88] R. Stasiw and R. G. Wilkins, *Inorg. Chem.*, 1969, **8**, 156.

complex is *N*-bonded and the rapid (and complete) oxidation yields a transient *N*-bonded species [$Fe(CN)_5NCS^{3-}$] which slowly rearranges to give the blue isomer $Fe(CN)_5SCN^{3-}$. The electron exchange between Fe^{II}–Fe^{III} in formamide has been investigated [89] and ^{55}Mn n.m.r. line-broadening has been used to study the electron transfer processes in manganese-(I) and -(II) isonitrile complexes in acetonitrile, ethanol, and DMSO.[90] There is little variation in rate on changing solvent, and the $\Delta S‡$ values of -20 to -25 e.u. are similar to others for simple electron transfer systems. The possibility of either $Mn(CNR)_6^+$ or $Mn(CNR)_6^{2+}$ losing an isonitrile ligand, with subsequent electron exchange involving a pentaco-ordinate manganese species, cannot be rigorously excluded but is deemed unlikely since in this case the rate would be expected to be slower. Studies of the Tl^I–Tl^{III} exchange [91] in solutions of chloroacetic acids have been made, the rate of reaction being dependent on the degree of substitution of the acid. For this system, in the presence of $NaClO_4$–$HClO_4$ mixtures,[92] it has been shown that there is no rate variation with pH.

Among several studies involving cobalt complexes which have been undertaken are the Co^{II}–Co^{III} exchange with 1,2-diaminopropane and 2,3-diaminobutane as complexing agents.[93] The system

$$(+)\ Co\ phen_3^{3+} + Co\ phen_3^{2+} \rightleftharpoons Co\ phen_3^{2+} + Co\ phen_3^{3+}$$

has been investigated in aqueous polyelectrolyte solutions,[94] powerful catalytic action being exhibited by sodium polyvinylsulphonate. Asymmetry induction in an outer-sphere reaction has been shown to take place in the system.[95]

$$Co\ phen_3^{3+} + Cr\ phen_3^{2+} \rightleftharpoons Co\ phen_3^{2+} + Cr\ phen_3^{3+}$$

When *l*-$Co\ phen_3^{3+}$ is used to oxidise the chromium(II) complex the product is dextrorotatory and when the *d*-form of the oxidant is used it yields a laevorotatory species. Since, at the time of mixing the reagents, there are equal proportions of the *d*- and *l*-Cr^{II} complex ions, the preferential generation of one optical isomer must mean that the redox reaction is substantially slower than the inversion of the $Cr\ phen_3^{2+}$ so that the isomer of reductant which is oxidised more rapidly is constantly replenished. It thus appears that the electron transfer occurs more rapidly if the configurations of the oxidising and reducing agents are mirror images, so lowering the configurational restrictions on collisions leading to electron

[89] I. Ruff and E. Rendek, *Acta Chim. Acad. Sci. Hung.*, 1969, **60**, 57.
[90] D. S. Matteson and R. A. Bailey, *J. Amer. Chem. Soc.*, 1969, **91**, 1975.
[91] R. G. McGregor and D. R. Wiles, *J. Chem. Soc.* (*A*), 1970, 323.
[92] W. J. Gelsema, C. L. de Ligny, H. A. Blijleven, and E. J. Hendricks, *Rec. Trav. chim.*, 1969, **88**, 110.
[93] H. Bartlett and H. Skilandat, *Electroanalyt. Chem. and Interfacial Electrochem.*, 1969, **24**, 207.
[94] S. Brückner, V. Crescenzi, and F. Quadrifoglio, *J. Chem. Soc.* (*A*), 1970, 1168.
[95] J. H. Sutter and J. B. Hunt, *J. Amer. Chem. Soc.*, 1969, **91**, 3107.

transfer. The Pu^{III}–Pu^{VI} exchange has been investigated [82] and the oxidation of vanadium(II) by vanadium(V) gives the rate law [12]

$$\text{Rate} = \{k_\alpha + k_\beta(H^+)\}[V^{II}][V^V]$$

with evidence for a side reaction between V^V and the vanadium(III) produced. The evaluation of fast electron-exchange rates using electrochemistry and reflection spectroscopy has recently been demonstrated.[96, 97] For the reaction A + C $\rightleftharpoons$ 2B the equilibrium constant will be related to the redox potentials of the individual reactions. Mechanistically, A is transformed to C at an electrode at a diffusion-controlled rate and as C diffuses to the bulk solution it encounters A with the resultant attainment of equilibrium. Using an optically transparent electrode, the effect of perturbing the optically monitored species due to the chemical reaction is observed. The method is applicable to reaction times of < 1 ms and the reaction

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

has been examined using this technique.[97]

[96] N. Winograd and T. Kuwana, *Electroanalyt. Chem. and Interfacial Electrochem.*, 1969, **23**, 333.

[97] N. Winograd and T. Kuwana, *J. Amer. Chem. Soc.*, 1970, **92**, 224.

2
Metal Ion–Ligand Redox Reactions

In this chapter the reactions between metal ions in a high oxidation state and inorganic and organic substrates are discussed in detail. Many mechanistic data have been derived from these investigations, and it is now clear that many of these reactions take place *via* an inner-sphere mechanism with, in some cases, evidence for the formation of well-characterised transient intermediates.[98] Inner-sphere complex formation is more likely to take place where neutral or negatively charged substrates are involved rather than with cationic reductants, and three cases of the mechanism:

$$M^{n+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML^{n+}$$

$$ML^{n+} \xrightarrow{k_2} \text{products}$$

have been considered (see ref. 11, Introduction);

(*a*) if $k_{-1} > k_2$, both formation and decomposition of any intermediate complex may be observed,

(*b*) if ML is in a steady state, then the observed rate constant will be a function of k_1, k_2, and k_{-1}, and activation parameters will be composite quantities,

(*c*) if $k_2 \gg k_1$, then $k_{obs} = k_1$, and the rate of the redox process will be limited to the rate of formation of the complex. In several systems, notably those involving aquo-complexes of vanadium(II), ruthenium(II), manganese(III), and cobalt(III), evidence has accumulated which suggests that some redox reactions may indeed proceed by a substitution-controlled mechanism.

The modes of interaction of various metal oxidants are discussed. In general, however, systems which involve cationic species have been more fully investigated than those of anionic reactants.

1 Manganese(III)

The properties and reactions of manganese(III) in aqueous solution have been reviewed by Davies (see ref. 12, Introduction) who has described in detail the equilibria and kinetics in perchlorate media. The potential of the

[98] A. McAuley and J. Hill, *Quart. Rev.*, 1969, **23**, 18.

Mn^{II}–Mn^{III} couple in 3M perchloric acid has recently been evaluated [99] using gold electrodes and a hydrogen half-cell with total manganese concentrations in the range 0·01—0·10 mol l^{-1}. Assuming the formation of Mn^{III} species only, $E^0 = 1{\cdot}541_5 \pm 0{\cdot}0003$ V, a value close to those derived previously.[100] The reactions with hydrazine and the methylhydrazines have been examined,[101] the mechanism being consistent with the formation of protonated hydrazoyl radicals as the rate-determining step. No nitrogen was produced in any of the reactions studied. $MnOH^{2+}$ is more reactive than Mn^{III}, and hydrogen atom transfer is suggested as the dominant oxidation mechanism. As methylation of the hydrazine was increased, the rate of reaction decreased (Table 1). Two studies have been reported of the reaction with hydroquinone,[102, 103] where again the reactions are in the stopped-flow range and the sole product is *p*-benzoquinone:

$$2Mn^{III} + p\text{-}C_6H_4(OH)_2 \longrightarrow 2Mn^{II} + p\text{-}C_6H_4O_2 + 2H^+$$

These studies differ in that, whereas Wells and co-workers [103] have spectrally characterised an intermediate and suggested from the data that the substitution rate for Mn^{III} is 5×10^6 l mol^{-1} s^{-1} (*cf.* the recent study by Diebler [104] on the formation of fluoride species), since it should lie between that for the chromium(II) species and the oxidation rate for the Mn^{III}–hydroquinone complex, Davies and Kustin [102] postulate in the acid range 0·6—3·60 mol l^{-1} an inner-sphere mechanism with hydrogen atom transfer as the predominant mode of reaction for $MnOH^{2+}$, with rates not too different from those derived from studies on other systems (Table 1). The reaction is first-order in each reactant and the observed second-order rate constant is invariant with $[Mn^{III}]_0$, $[H_2Q]$, and $[Mn^{II}]$. A mechanism consistent with intermediate formation may be written:[103]

$$Mn^{3+}{}_{aq} \rightleftharpoons MnOH^{2+} + H^+$$

$$Mn^{3+} + H_2Q \overset{\beta_1}{\rightleftharpoons} MnQH_2{}^{3+}$$

$$MnOH^{2+} + H_2Q \rightleftharpoons MnQH^{2+}$$

$$MnQH_2{}^{3+} \xrightarrow{k_1} Mn^{II} + QH^{\bullet} + H^+ \qquad (1)$$

$$MnQH^{2+} \xrightarrow{k_2} Mn^{II} + QH^{\bullet} \qquad (2)$$

$$Mn^{III} + QH^{\bullet} \xrightarrow{k_3} Mn^{II} + Q + H^+ \qquad (3)$$

where $k_2 \gg k_1$ and both are much slower than k_3. Reaction (1) is considered rate-determining. Using this scheme and assuming

[99] L. Ciavatta and M. Grimaldi, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3071.
[100] H. Diebler and N. Sutin, *J. Phys. Chem.*, 1964, **68**, 174.
[101] G. Davies and K. Kustin, *J. Phys. Chem.*, 1969, **73**, 2248.
[102] G. Davies and K. Kustin, *Trans. Faraday Soc.*, 1969, **65**, 1630.
[103] C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc.* (*A*), 1970, 676.

$\beta_1[QH_2]_0(1 + K_1[H^+]^{-1}) \ll 1$ with $K_h \sim 1$ then:

$$\frac{-\,d[Mn^{III}]_0}{dt} = \frac{2(k_1 + k_2 K_1[H^+]^{-1})\beta_1[Mn^{III}]_0[H_2Q]_0}{1 + K_h[H^+]^{-1} + \beta_1[H_2Q]_0(1 + K_1[H^+]^{-1})}$$

so that the second-order rate constant, k_{obs}, is given by the equation:

$$k_{obs}(1 + K_h[H^+]^{-1}) = 2\beta_1(k_1 + k_2 K_1[H^+]^{-1})$$

In the reactions with hydroxylamine and its methyl derivative and with nitrous acid[104] there is no evidence for complex formation,[105] and six

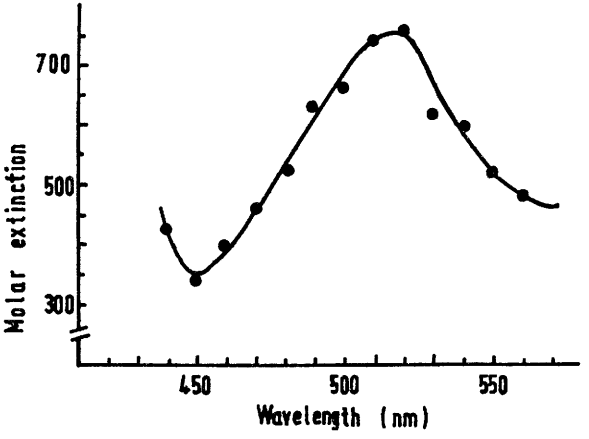


Figure 1 *Visible spectrum of* MnN_3^{2+}. *The experimental points were obtained using a stopped-flow apparatus. From the initial points on the stopped-flow traces for a particular set of concentrations, the absorbance was determined at each wavelength*
(Reproduced by permission from *Inorg. Chem.*, 1968, **8**, 663)

equivalents of Mn^{III} are required for each molecule of hydroxylamine oxidised, the results being interpreted according to the mechanism:

$$Mn^{III} + \overset{+}{N}H_3{\cdot}OH \xrightarrow{k_1} Mn^{II} + NH_2O^{\bullet}_{aq} + 2H^+$$

$$MnOH^{2+} + \overset{+}{N}H_3{\cdot}OH \xrightarrow{k_2} Mn^{II} + NH_2O^{\bullet}_{aq} + H_3O^+$$

$$2H_2O + 5Mn^{III} + NH_2O^{\bullet}_{aq} \xrightarrow{k_3} 5Mn^{II} + NO_3^- + 6H^+$$

with $k_3 \gg k_1, k_2$. The rates for the oxidation of HNO_2 are an order of magnitude higher than for hydroxylamine, suggesting that HNO_2 may be an intermediate in the oxidation of the $NH_2O^{\bullet}_{aq}$ radical to NO_3^-. With hydrazoic acid, an intermediate complex has been identified (MnN_3^{2+}) using a flow device,[106] the visible spectrum being shown in Figure 1. The

[104] H. Diebler, *Z. phys. Chem.* (*Frankfurt*), 1969, **68**, 64.
[105a] G. Davies and K. Kustin, *Inorg. Chem.*, 1969, **8**, 484.
[105b] N. Hlasivcova and J. Novak, *Coll. Czech. Chem. Comm.*, 1969, **34**, 3995.
[106] G. Davies, K. Kustin, and L. J. Kirschenbaum, *Inorg. Chem.*, 1969, **8**, 663.

stability constant of this species (82 ± 20) is about half that for the corresponding mono-fluoro species [107] (1·7 ± 0·2 × 10^2). In the azide study, under the conditions used (large excesses of hydrazoic acid) the mechanism proposed:

$$2MnN_3^{2+} \rightleftharpoons Mn^{2+} + [Mn(N_3)_2]^{2+} \quad (4)$$

$$[Mn(N_3)_2]^{2+} \longrightarrow Mn^{2+} + 3N_2$$

$$[Mn(N_3)_2]^{2+} \longrightarrow MnN_3^{+} + N_3^{+}$$

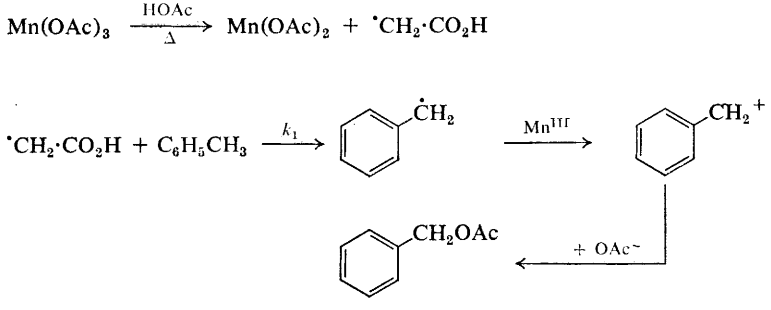
$$HN_3 + N_3^{+} \longrightarrow 3N_2 + H^{+}$$

involves the formation of the bis-azidomanganese(IV) complex from the reaction of two mono-azido species. Reaction (4) suggests that in high azide concentrations the azide group may act as a bridging ligand. It is interesting to note that the mechanism postulated here differs from that previously described under slightly different conditions.[108] The lability of both Mn^{II} and Mn^{III} makes difficult the distinction between outer- and inner-sphere mechanisms for reactions of manganese(III) (see ref. 12, Introduction).

It may be that the rates of some reactions (*e.g.* with H_2O_2, hydroquinone, and HNO_2) are substitution-controlled. Based on comparisons with reactions of the aquated cobaltic ion, however, it appears that the rates of water exchange in Mn^{III} and $Mn(OH)^{2+}$ are $\leqslant 1$—10×10^6 and $\sim 2 \times 10^6$ s^{-1} respectively.

The oxidation of organic compounds by metal salts is becoming increasingly studied, and manganese(III) acetate has been shown to oxidise aromatic hydrocarbons [109] *via* two mechanisms;

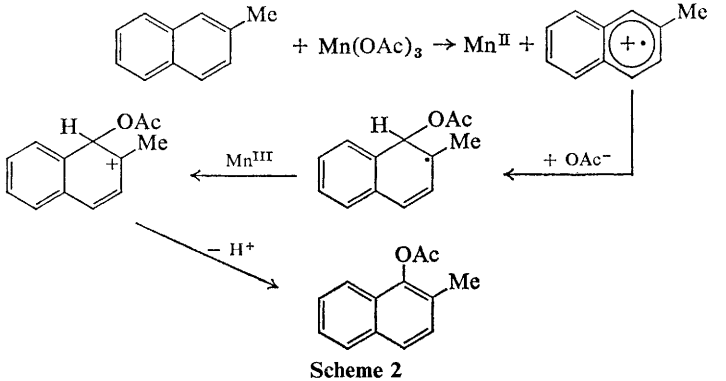
(*a*) a carboxymethyl radical is generated by thermolysis of the manganic acetate, which then interacts with the hydrocarbon, *e.g.* in the oxidation of toluene, as shown in Scheme 1.



Scheme 1

[107] G. Davies and K. Kustin, *Inorg. Chem.*, 1969, **8**, 1197.
[108] C. F. Wells and D. Mays, *J. Chem. Soc.* (*A*), 1968, 1622.
[109] E. I. Heiba, R. M. Dessau, and W. J. Koehl, *J. Amer. Chem. Soc.*, 1969, **91**, 138.

(*b*) if the ionisation potential of the hydrocarbon is $\leqslant 8$ eV, then an electron transfer mechanism becomes important; *e.g.* for 2-methylnaphthalene, as shown in Scheme 2.



Scheme 2

In another study of the oxidation of toluenes to benzyl acetates,[110] potassium bromide has been shown to act as a catalyst. In acetic acid at 70 °C, there is an initial one-electron transfer to yield an intermediate cation radical. Good linear correlations have also been observed between the relative reactivities in the bromide-catalysed reactions and the half-wave oxidation potentials of the hydrocarbons, measured in acetonitrile. Manganese(III) acetylacetonate has been used in the metal-ion-catalysed peroxide oxidation of organic substrates.[111] In the selective synthesis of imides from amides, good yields are observed in peracetic acid. The role of transition metals in catalysing the decomposition of hydroperoxides formed in auto-oxidation reactions has been investigated, and the mechanism of auto-oxidation in manganese(III) acetate–acetic acid mixtures containing hydrocarbons has been reported,[112] an electrophilic intermediate being derived from the acetic acid. Manganese–2,2′-bipyridyl complexes have also been shown to catalyse the oxidation of isopropylbenzene.[113]

2 Cobalt(III)

The nature of cobalt(III) in perchlorate solutions has been the subject of discussion,[114] there being controversy over the extent of dimerisation of the cobaltic species. A recent potentiometric study[115] indicates that if the dimers are present this should be apparent from e.m.f. measurements on

[110] J. R. Gilmore and J. M. Mellor, *Chem. Comm.*, 1970, 507.
[111] A. R. Doumaux, J. E. McKeon, and D. J. Trecker, *J. Amer. Chem. Soc.*, 1969, **91**, 3993.
[112] H. Finkbeiner and J. B. Bush, jun., *Discuss. Faraday Soc.*, 1968, *No.* 46, p. 150.
[113] A. Y. Sichev, I. M. Reibel, and L. P. Podgornaya, *Zhur. fiz. Khim.*, 1969, **43**, 676.
[114] C. F. Wells, *Discuss. Faraday Soc.*, 1968, *No.* 46, p. 194.
[115] B. Warnqvist, *Inorg. Chem.*, 1970, **9**, 680.

the reversible Co^{II}–Co^{III} couple, the Nernst slope being half that for monomeric cobalt(III) at constant cobaltous ion concentrations. If both species are in equilibrium, K_d, the dimerisation constant $\{ = [(Co^{III})_2]/[Co^{III}]^2\}$ will be a constant at constant acidity. At 3 °C, in the

$$2Co^{III} \underset{}{\overset{K_d}{\rightleftharpoons}} (Co^{III})_2$$

range 0·05—3 mol l^{-1}, $K_d \lesssim 10$—20 l mol^{-1} and $E^0(Co^{III}$–$Co^{II}) = 1{\cdot}83 \pm 0{\cdot}01$ V, and at 23 °C, $K_d \leqslant 500$ l mol^{-1} when $[H^+] = 0{\cdot}50$ mol l^{-1} and $\leqslant 20$ l mol^{-1} in 3M $HClO_4$ with the corresponding E^0 value $1{\cdot}86 \pm 0{\cdot}01$ V. The emphasis which has been placed on the existence of dimeric forms even at high hydrogen ion concentrations in some recent studies [*e.g.* cobalt(III) plus bromine [114]] is inconsistent with these findings. At 3 °C, an upper limit of 0·01 mol l^{-1} has been derived for the first hydrolysis constant, K_h, of the cobaltic ion.

$$[(H_2O)_6Co]^{3+} \underset{}{\overset{K_h}{\rightleftharpoons}} [(H_2O)_5Co(OH)]^{2+} + H^+$$

A critical review of some aspects of the chemistry of cobalt(III) in aqueous solution has recently been published (see ref. 11, Introduction). Two studies of the oxidation of hydrazoic acid have been made with differing rate laws.[116, 117] Wells and co-workers,[116] working at high initial ratios of $[HN_3]$: $[Co^{III}]$ using a stopped-flow method indicate a rate proportional to $[Co^{III}][HN_3]^2$ which is independent of acidity in the region 0·5—5·0M-$HClO_4$. Typical conditions used in these experiments were $[Co^{III}]_{tot} \sim 6 \times 10^{-4}$ mol l^{-1}, $[H^+] = 0{\cdot}5$—5·0 mol l^{-1}, and $[HN_3]_{tot} = 2{\cdot}5$—15×10^{-3} mol l^{-1}. Sullivan *et al.*,[117] however, using conditions of $[Co^{III}]_{tot} \sim 7$—12×10^{-4}, $[H^+] = 1{\cdot}04$—5·01, and $[HN_3]_{tot} = 2{\cdot}7$—16×10^{-3} mol l^{-1} at the same ionic strength, found the rate law to be first-order in each reactant with a dependence on acidity:

$$\frac{-\,d[Co^{III}]}{dt} = [HN_3][Co^{III}]\{k_1 + k_2/[H^+]\}$$

this form being identical to that described in an earlier study.[118] Small variations in rate constants in the latter investigations have been observed which are the result of medium effects. The intermediate formed in the oxidation of chloride ion has been studied,[119] the mechanism involving the reaction of both the aquated cobaltic ion and the hydroxo-complex $[CoOH]^{2+}$. In this system, the intramolecular redox reaction is sufficiently slow for the formation of the transient species to be studied. The

[116] C. F. Wells and D. Mays, *J. Chem. Soc.* (*A*), 1969, 2175.
[117] R. C. Thompson and J. C. Sullivan, *Inorg. Chem.*, 1970, **9**, 1590.
[118] R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *Inorg. Chem.*, 1968, **7**, 1876.
[119] A. McAuley, M. N. Malik, and J. Hill, *J. Chem. Soc.* (*A*), 1970, 2461.

mechanism involved may be described as:

$$Co^{3+} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CoCl]^{2+} \quad (5)$$

$$[CoOH]^{2+} + Cl^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(OH)Cl]^{+} \quad (6)$$

$$[(H_2O)_5Co(OH_2)]^{3+} \underset{}{\overset{K_h}{\rightleftharpoons}} [(H_2O)_5CoOH]^{2+} + H^+ \quad (7)$$

$$[(H_2O)_5CoCl]^{2+} \underset{}{\overset{K_3}{\rightleftharpoons}} [(H_2O)_4Co(OH)Cl]^{+} + H^+$$

Providing the protolytic equilibria are sufficiently rapidly established, the first-order rate constant for formation of the complex may be expressed as:

$$\text{Rate} = k_{obs}[Co^{III}]_{tot}$$

where

$$k_{obs} = k_{-1} + \frac{k_{-2}K_3}{[H^+]} + \frac{k_{-1}K_1[Cl^-]}{(1 + K_h/[H^+])} + \frac{k_{-2}K_3K_1[Cl^-]}{\{[H^+](1 + K_h/[H^+])\}} \quad (8)$$

Maintaining a constant hydrogen ion concentration, equation (8) may be expressed as:

$$k_{obs} = k_\alpha + k_\beta[Cl^-]$$

with

$$k_\alpha = k_{-1} + k_{-2}K_3/[H^+]$$

and

$$k_\beta = \frac{K_1}{(1 + K_h/[H^+])}\{k_{-1} + k_{-2}K_3/[H^+]\}$$

From the relationship in equation (9), it may be seen that from plots of

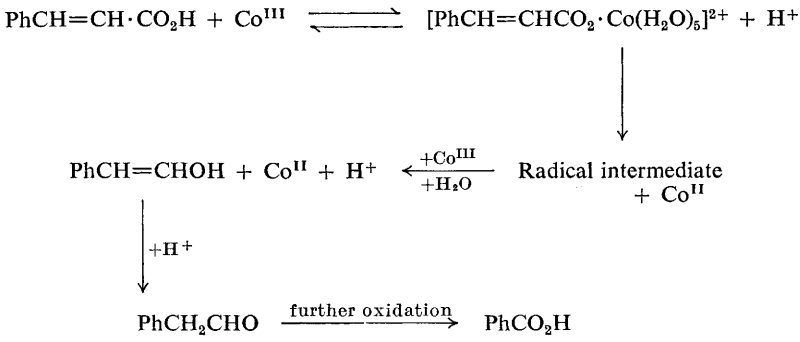
$$\frac{k_\alpha}{k_\beta} = \frac{K_h}{K_1[H^+]} + \frac{1}{K_1} \quad (9)$$

k_α/k_β *versus* $[H^+]^{-1}$ it should be possible to derive values of both the equilibrium constant for the complex (K_1) and the hydrolysis constant (K_h). Previous attempts to determine K_h by application of equation (9) have not been too successful, a probable error arising from complications associated with the subsequent redox reactions which become important at lower acidities (see ref. 11, Introduction). In the chloride investigation, however, an upper limit to K_h of *ca.* 1×10^{-2} l mol^{-1} is derived, in reasonable agreement with recent values.[115] From temperature-dependence studies of K_1, it is possible to evaluate thermodynamic parameters for the complex formation. For the formation of the monochloro-complex $[CoCl]^{2+}$, $\Delta H_1 = 3{\cdot}8 \pm 1{\cdot}5$ kcal mol^{-1} and $\Delta S_1 = 20 \pm 10$ cal deg^{-1} mol^{-1}, the thermodynamic stability of these complexes thus resulting from favourable entropy changes.[119] It would appear that the stopped-flow technique is one of the few methods which are available to evaluate data of this kind when the instability of the oxidant (or complex) precludes the use of conventional

techniques. In the case of the corresponding bromide oxidation,[120, 121] there is no evidence for complex formation, the redox step here being significantly faster. Similar observations have been made in the oxidation of thiourea and some *N*-substituted derivatives [122] and of H_2O_2, HNO_2, and SCN^-.[121] The available data on the rate of reaction of the aquated ion Co^{3+} are still scant, but there would appear to be several reactions at least where the rate-determining step is the loss of a water molecule from the inner co-ordination sphere of the cation. In the case of reactions of $[CoOH]^{2+}$, due to the uncertainty in the value of K_h, comparisons have been made [121] using the composite constant $k_2 K_h$ [see equations (6) and (7)]. The narrow range of values in this case suggests that the common ligand-independent mechanism again involves a water-exchange process, and a comparison of the available data for complexation with $[FeOH]^{2+}$ tends to support the inner-sphere mechanism since, for example, the rate of oxidation of SCN^- by $[CoOH]^{2+}$ is faster than the rates of oxidation of Br^- and HN_3 by about the same factor as is observed in the formation of the corresponding $[FeOH]^{2+}$ complexes. The rate constants for reaction with iodide [121] and hydroquinone [121] are considerably greater than those for the other systems, and it appears that the hydroxide ligand is acting preferentially as a bridge for electron transfer. Whilst in this investigation [121] using quinol as substrate there is no kinetic or spectrophotometric evidence for the existence of complexes, in another study on the same substrate [123] the rapid rise in optical density followed by a slower decay when the reagents are mixed is interpreted as indicative of formation of an intermediate Co^{III}–hydroquinone complex. In this investigation the treatment of the data is similar to that used in the corresponding manganese(III) oxidation.[103] The reaction rate is invariant with acidity and the energy of activation ($= 9{\cdot}7 \pm 0{\cdot}5$ kcal mol^{-1}) is intermediate between those of iron(III) and manganese(III) on the one hand and cerium(IV) ($E_a \sim 0$) on the other. Thermodynamic data for the overall reactions of cobalt(III) with various substrates have been compared with those for other oxidants.[124] The oxidations of hydrazine and hydroxylamine have been investigated [125] in nitrate media, where there appears to be little evidence for ion-pair formation, but in the oxidation of carboxylic acids by cobalt(III) sulphate,[126, 127] the nature of the oxidising species is more uncertain. In the reaction with maleic and fumaric acids in the presence of sulphate ions, a complex is formed [128] and a mechanism involving attack by cobalt(III) on the double bond postulated. The stepwise oxidative degradation of 4-methyl-4-phenylpentanoic acid by cobalt(III)

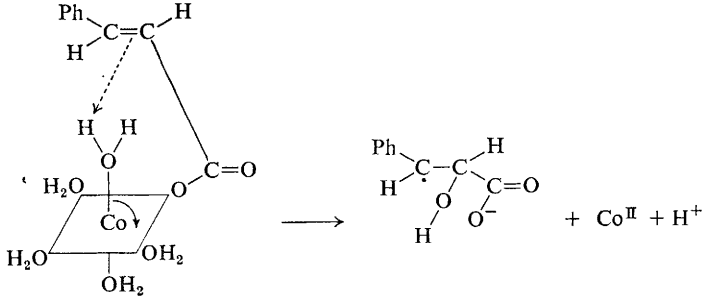
[120] M. N. Malik, J. Hill, and A. McAuley, *J. Chem. Soc.* (*A*), 1970, 643.
[121] G. Davies and K. O. Watkins, *J. Phys. Chem.*, 1970, **74**, 3388.
[122] A. McAuley and U. D. Gomwalk, *J. Chem. Soc.* (*A*), 1969, 977.
[123] C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc.* (*A*), 1969, 2930.
[124] R. C. Thompson, *J. Phys. Chem.*, 1968, **72**, 2642.
[125] K. Jijee and M. Santappa, *Proc. Indian Acad. Sci., Sect. A*, 1969, **69**, 117.
[126] K. Dzhidzhi, A. Meenaski, and M. Santappa, *Kinetika i. Kataliz*, 1969, **10**, 740.
[127] A. Meenaski and M. Santappa, *Current Sci.*, 1969, **38**, 311.
[128] M. A. Beg and F. Ahmed, *Indian J. Chem.*, 1969, **46**, 794.

has been examined [129] and the oxidation of unsaturated acids investigated [130] in 25% aqueous acetonitrile. In this study, the rate law is first-order in both cobalt(III) and reductant, with formation of a 1 : 1 complex, *e.g.* for cinnamic acid, as shown in Scheme 3, the variety of products formed



Scheme 3

depending on the extent of oxidation. The main oxidative route is considered to involve a direct attack on the double bond of the cinnamic acid with transfer of a hydroxy-group from the hydration shell of the cobalt(III) and subsequent labilisation of the co-ordination structure on formation of the cobalt(II):



The large positive entropy of activation involved is consistent with a process of this type. Anhydrous cobalt(III) nitrate has been prepared [131] by the reaction:

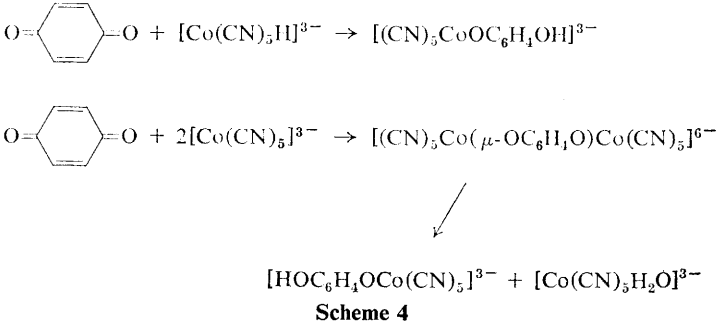
$$CoF_3 + N_2O_5 \longrightarrow Co(NO_3)_3 + 3NO_2F,$$

the pure material being dark green in colour. The absence of any reaction in solvents such as carbon tetrachloride is thought to be consistent with a low-spin (diamagnetic) d^6 ion. In water, however, there is a vigorous

[129] P. R. Sharan, P. Smith, and W. A. Waters, *J. Chem. Soc.* (*B*), 1969, 857.
[130] P. Smith and W. A. Waters, *J. Chem. Soc.* (*B*), 1969, 462.
[131] R. J. Fereday, N. Logan, and D. Sutton, *J. Chem. Soc.* (*A*), 1969, 2699.

reaction on dissolving the complex, yielding a green solution which rapidly evolves oxygen while producing cobalt(II). Freshly prepared solutions oxidise ferrous ion (quantitatively) and iodide, and solvents such as DMF, DMSO, acetone, and alcohols are also oxidised, with reduction of cobalt(III) to the pink cobaltous ion.

Several studies have been made on the redox reactions of other cobalt(III) complex ions. In the reaction of pentacyanocobalt(III) hydride, $[Co(CN)_5H]^{3-}$, with *p*-benzoquinone [132] there are two paths in alkaline solution; (*a*) the (slow) direct reaction of the hydride complex ($k_1 \sim 13$ l mol^{-1} s^{-1}), and (*b*) a fast reaction of $[Co(CN)_5]^{4-}$ formed by deprotonation



Scheme 4

of the hydride ($k \sim 10^9$ l mol^{-1} s^{-1}). The two reaction paths are shown in Scheme 4. A redox addition mechanism is postulated with the formation of a bridged intermediate. Direct hydride transfer between the *p*-benzoquinone and the hydrido-complex *via* a bridge mechanism has been discounted, a seven-co-ordinate activated complex being suggested where the quinone molecule is attached with its π-bonding orbitals to the electron pair of the Co—H bond, forming a three-centre electron-deficient bond. This process then increases the Co—H bond length and decreases the ionisation potential of the corresponding electron pair, making it thus available for the redox process. The low rate of reaction would be in accord with the steric requirements involved. The pentacyanocobaltate(I) species $[Co(CN)_5]^{4-}$ has also been generated in two ways; (*a*) in highly alkaline media in a chemically reversible redox process at a dropping mercury electrode, the species being a sufficiently strong base to extract protons from both proton donors and water,[133] and (*b*) in the pulse radiolysis of aqueous cobalt(II)–cyanide complexes,[134] where the hydrated electrons react with $[Co(CN)_5]^{3-}$ in a second-order reaction:

$$\text{Rate} = k_1[e^-_{aq}][Co(CN)_5^{3-}]$$

($k_1 = 1{\cdot}4 \pm 0{\cdot}1 \times 10^{10}$ l mol^{-1} s^{-1}) to yield the species $[Co(CN)_5]^{4-}$ as a

[132] J. Hanzlick and A. A. Vlcek, *Inorg. Chem.*, 1969, **8**, 669.
[133] J. Hanzlick and A. A. Vlcek, *Chem. Comm.*, 1969, 47.
[134] G. D. Venerable, E. J. Hart, and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 7538.

transient intermediate which decomposes in a first-order manner:

$$[Co(CN)_5]^{3-} + e^-_{aq} \xrightarrow{k_1} [Co(CN)_5]^{4-}$$

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

The rate constant $k_2 = 1{\cdot}0 \times 10^5\ s^{-1}$ and the reaction is six times slower in D_2O. In the radiolysis study with the cobalt(III) complex $[Co(CN)_6]^{3-}$, two initial products are observed which subsequently decompose:

$$[Co(CN)_6]^{3-} + e^-_{aq} \begin{cases} \nearrow I_a \rightarrow [Co(CN)_5]^{3-} + CN^- \\ \searrow I_b \rightarrow [Co(CN)_6]^{3-} + OH^- + \tfrac{1}{2}H_2 \end{cases}$$

Proposals made for the configurations of the intermediates are that I_a is a linkage isomer of $[Co(CN)_5]^{3-}$, *i.e.* $[Co(CN)_4(NC)]^{3-}$ and that I_b corresponds to the hexacyanocobaltate(II) ion $[Co(CN)_6]^{4-}$. An intermediate has also been described in the reaction of cyanide ion with 1,2-diaminocyclohexanetetra-acetatocobaltate(II) ion, [Co cydta]$^{2-}$.[135] As part of a temperature-jump study of the equilibrium:

$$[Co\ cydta]^{2-} + CN^- \rightleftharpoons [Co\ cydta\ CN]^{3-}$$

in the presence of large excesses of cyanide, it was shown that a slower reaction occurs with displacement of the cydta^{4-} group and formation of $[Co(CN)_5]^{3-}$ and its aerially oxidised products:

$$[Co\ cydta\ CN]^{3-} + 2CN^- \xrightarrow{slow} Intermediate$$

$$Intermediate + 2CN^- + H^+ \xrightarrow{fast} [Co(CN)_5]^{3-} + H\ cydta^{3-}$$

$$[Co(CN)_5]^{3-} \xrightarrow{O_2} \{[Co(CN)_5]_2O_2\}^{6-} + [Co(CN)_5H_2O]^{2-}$$

An investigation has been made of the hydrogenation of the pentacyanocobaltate(II) ion.[136] In the presence of alcohol, the reaction:

$$5LiCN + CoCl_2 \longrightarrow Li_3[Co(CN)_5] + 2LiCl$$

takes place, and the green solution of the cobalt(II) complex absorbs hydrogen smoothly at room temperature to produce a pale yellow solution of the hydrido-anion $[Co(CN)_5H]^{3-}$. The rate of hydrogenation is dependent on the presence of water, being second-order in water concentration as well as second-order in cobalt(II) complex:

$$Rate = k_0[Co^{II}]^2[H_2]$$

[135] J. P. Jones and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 1486.
[136] G. Pregaglia, D. Morelli, F. Conti, G. Gregorio, and R. Ugo, *Discuss. Faraday Soc.*, 1968, *No.* 46, p. 110.

where

$$k_0 = k_1 + k_2[H_2O]^2$$

The kinetic data are consistent with a rapid equilibrium of the solvated anion $[Co(CN)_5EtOH]^{3-}$:

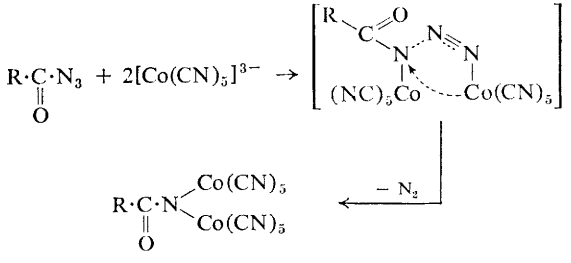
$$2[Co(CN)_5EtOH]^{3-} + 2H_2O \overset{K}{\rightleftharpoons} 2[Co(CN)_5H_2O]^{3-} + 2EtOH$$

$$2[Co(CN)_5EtOH]^{3-} \xrightarrow[(k_1)]{H_2} 2[Co(CN)_5H]^{3-} + 2H_2O$$

It has also been shown [136] that the hydroperoxide ion formed by the interaction:

$$[Co(CN)_5H]^{3-} + O_2 \longrightarrow [Co(CN)_5OOH]^{3-}$$

undergoes first-order decomposition to the corresponding hydroxo-complex $[Co(CN)_5OH]^{3-}$, the rate-determining step being considered as either the homolytic rupture of the O—O bond or of the Co—O bond of the hydroperoxide. In an interesting redox reaction, it has been shown [137] that pentacyanocobaltate(II) [and hexacyanonickelate(I)] reacts with organic azides in water to (quantitatively) liberate nitrogen, forming the corresponding benzamido-bis[pentacyanocobaltate(III)] complex ion, as shown in Scheme 5. The mechanism of the reaction between cobalt(II)



Scheme 5

and the potassium salt of 1-nitroso-2-napthol-3,6-disulphonic acid (Knrs) has been studied, the cobalt(III) complex being produced in two ways depending on the acidity of the solution.[138] In alkaline media, 3 moles of nrs^- react per mole of cobalt(II) in the presence of oxygen, but at pH ~ 4,

$$Co^{II} + 3nrs^- \xrightarrow{O_2} Co^{III}nrs_3$$

four moles of ligand react, and here the ligand itself appears to be an

[137] W. C. Kaska, C. Sutton, and E. Serros, *Chem. Comm.*, 1970, 100.
[138] G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1783.

oxidant which can compete with oxygen, *e.g.*

$$Co^{II} + 2nrs^- \overset{\text{fast}}{\rightleftharpoons} [Co^{II}(nrs)_2]$$

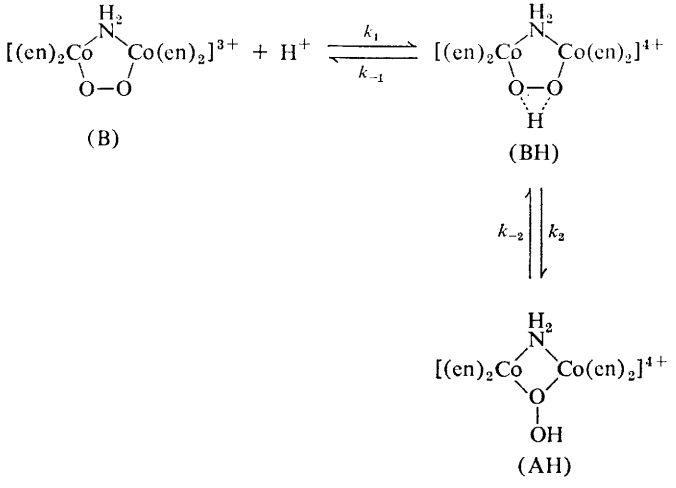
$$[Co^{II}(nrs)_2] + nrs^- \rightleftharpoons [Co^{II}(nrs)_3]^-$$

$$[Co^{II}(nrs)_3]^- \xrightarrow[+O_2]{k_1} [Co^{III}(nrs)_3]$$

$$[Co^{II}(nrs)_3]^- \xrightarrow[k_2]{+nrs^-} [Co^{III}(nrs)_3]$$

The reduction of $[Co(CN)_6]^{3-}$ by hypophosphorous acid has also been investigated,[139] effective cyanide displacement yielding $Co(CN)_2,2H_2O$ as product.

The oxidising properties of bridged dinuclear cobalt(III) complexes have been studied.[140–142] In the reaction of μ-amido-μ-peroxobis(ethylenediamine)cobalt(III) complex with iodide,[142] three forms of the oxidant have



been shown to exist, here designated B, BH, and AH. Reduction of the various forms yields the corresponding μ-amido-μ-hydroxo-complex. The reaction of B is slow, whereas with AH the rate law:

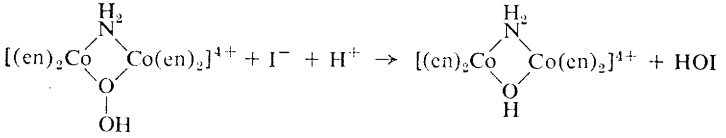
$$\text{Rate} = k_{AH}[AH][I^-]$$

is observed, $k_{AH} = 5{\cdot}81\,\text{mol}^{-1}\,\text{s}^{-1}$ at 2 °C in 0·245M-$NaClO_4$. The mechanism postulated may be written as in Scheme 6. A two-term rate law:

$$\text{Rate} = k_{BH}[BH][I^-]^2 + k_2[BH]$$

[139] P. S. Poskosim, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 933.
[140] T. Asai and T. Hara, *Bull. Chem. Soc. Japan*, 1969, **42**, 3580.
[141] A. G. Sykes and J. A. Weil, 'Progress in Inorganic Chemistry', ed. J. O. Edwards, Wiley,
[142] 1970, vol. 13, pp. 1—106.
R. Davies, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1261.

is given when the other protonated complex reacts, and in this case ion-pairing with one or both iodide anions may precede the redox step. It is of



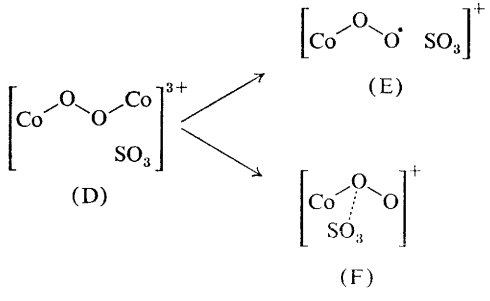
$$HOI + I^- + H^+ \longrightarrow H_2O + I_2$$

Scheme 6

interest that in the reactions with iodide in the case of the superoxide complexes,[141] the rate constants increase in the order $[(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5]^{5+} < [(NH_3)_4Co\cdot\mu(NH_2\cdot O_2)\cdot Co(NH_3)_4]^{4+} < [(en)_2Co\cdot\mu(NH_2\cdot O_2)\cdot Co(en)_2]^{4+}$ and again it may be that there is more extensive ion-pairing in the bis-ethylenediamine complex than in the ammine analogue. In the corresponding reaction with sulphite,[143] the extent of transfer of oxygen atoms from the oxidant to the reductant has been established using ^{18}O tracer studies. In the presence of large excess of sulphite the stoicheiometry is:

$$[(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5]^{5+} + 2SO_3^{2-} \longrightarrow [Co(NH_3)_5SO_4]^+ + Co^{2+} + SO_3^{2-} + 5NH_3$$

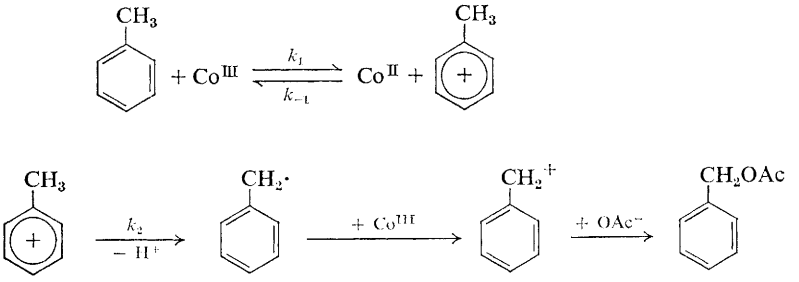
and it has been shown that significant retention of the oxygen atoms from the superoxo bridge occurs in both sulphate fractions, being greater in the case of the complexed species. The mechanism of reaction is believed to involve formation of an intermediate of the type D, which loses Co^{II} on charge transfer to yield either E or F with a rapid attack of the second sulphite group on one or other of these intermediates.



The use of cobaltic acetate as an oxidant in non-aqueous solvents has been studied.[144] The reaction with toluene (and other aromatic hydrocarbons) in acetic acid,[145–147] is considered to involve the formation of

[143] R. Davies, A. K. E. Hagopian, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 623.
[144] M. Pszonicka and W. Skwara, *Chem. analit.*, 1970, **15**, 175.
[145] K. Sakota, Y. Kamiya, and N. Ohta, *Canad. J. Chem.*, 1969, **47**, 387.
[146] E. Heiba, R. M. Dessau, and W. J. Koehl, *J. Amer. Chem. Soc.*, 1969, **91**, 6830.
[147] Y. Ogata and T. Morimoto, *J. Chem. Soc.* (*B*), 1969, 74.

cation radicals which have been examined using an e.s.r. flow device.[148] A mechanism consistent with these findings may be written as in Scheme 7.[146] The relative reactivity of the substituted toluenes follows a Hammett



Scheme 7

σ–ρ relationship with good correlation involving σ^+. The high value ($-$ 2·4) indicates considerable positive charge development in the aromatic hydrocarbon in the transition state. Addition of organic bromides has been shown [147] to catalyse the reaction rate. The reaction of Co^{III} acetate with benzyl hydroperoxide has been investigated at 25 °C in acetic acid.[149] In this system, both the Co^{II} and Co^{III} complexes are involved with possible monomer–dimer equilibrium of the trivalent species, the rate-determining step involving monomeric species one of which is complexed to a hydroperoxide ligand. Complexes with chloride ion have also been characterised in the same medium,[150] the ion $[CoCl_6]^{3-}$ being an unstable species showing an intense peak at 460 nm. The decomposition of this complex is found to be dependent on the chloride ion concentration of the medium, the products being the tetrahedral cobalt(II) chloride together with the products of reaction of chlorine radicals. Catalytic oxidations of cumene and tetralin have also been examined in the presence of cobalt naphthenate.[151]

3 Cerium(IV)

Many rate studies involving cerium(IV) have been made in sulphate media (see ref. 9, Introduction) where there may be competition between the sulphate and any ligand for positions in the primary co-ordination sphere of the ceric ion in any inner-sphere mechanism. Recently, however, investigations have been made in perchlorate solutions where the effect is greatly diminished due to the weak co-ordinating power of the perchlorate anion. The oxidation of H_2O_2 has been reported,[152] stopped-flow traces indicating

[148] R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, 1970, **92**, 412.
[149] E. J. Y. Scott, *J. Phys. Chem.*, 1970, **74**, 1174.
[150] A. W. Chester, E. Heiba, and R. M. Dessau, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 277.
[151] I. M. Reibel, A. F. Sander, and I. B. Khakham, *Zhur. fiz. Khim.*, 1969, **43**, 642, 647.
[152] C. F. Wells and M. Husain, *J. Chem. Soc.* (*A*), 1970, 1013.

the rapid formation of a transient intermediate with an inner-sphere electron transfer. The reaction:

$$2Ce^{IV} + H_2O_2 \longrightarrow 2Ce^{III} + O_2 + 2H^+$$

is known to involve HO_2 radicals as intermediates and the rate of decay of the transient metal complex is independent of initial cerium(IV), hydrogen peroxide, cerium(III), and hydrogen ion concentrations. A mechanism consistent with these observations is:

$$Ce^{IV} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ce^{IV}(HO_2^-)] + H^+$$

$$[CeOH]^{3+} + H_2O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ce^{IV}(HO_2^-)]$$

$$[Ce^{IV}(HO_2^-)] \xrightarrow{k_3} Ce^{III} + HO_2^{\bullet}$$

$$Ce^{IV} + HO_2^{\bullet} \xrightarrow{\text{fast}} Ce^{III} + H^+ + O_2$$

any complexes between H_2O_2 and the metal being considered to be much weaker than those involving the HO_2^- anion. The rate-determining step (k_3) is the decomposition of the metal complex. The value of $k_3 \sim 2{\cdot}4 \times 10^2\ s^{-1}$ in the temperature range 18—45 °C indicates a low activation energy. In the oxidation of H_2O_2 by cerium(IV) species, the reactivity decreases in the order aquocerium(IV) > sulphatocerate(IV) > oxalatocerate(IV). Intermediate complex formation has also been reported in the oxidations of hydrazoic acid [153] and quinol.[154] In the former system, the rate is first-order in cerium(IV) and zero-order in both $[H^+]$ and $[HN_3]$, the overall reaction being written as:

$$2Ce^{IV} + 2HN_3 \longrightarrow 2Ce^{III} + 3N_2 + 2H^+$$

The rate-determining step is again considered to involve the decay of the metal complex of high thermodynamic stability. In contrast to other oxidations of azide by metal ions, the activation energy for the process is again very small. Independence of the rate constant with temperature is also a feature of the oxidation of hydroquinone,[155] where the rate is zero-order in ligand concentration and independent of acidity. Treatment of the data again requires that $[Ce(H_2Q)]^{4+}$ and/or $[Ce(HQ)]^{3+}$ have high formation constants. The rate-determining decay of these species ($k \sim 100\ s^{-1}$) is slightly slower than for the corresponding hydroperoxide complex.[152] The formation of 1 : 1 complexes has also been reported in the reaction with edta in nitrate media,[155] where the reduction pattern differs

[153] C. F. Wells and M. Husain, *J. Chem. Soc.* (*A*), 1969, 2981.
[154] C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc.* (*A*), 1969, 2575.
[155] E. A. Malinina, L. J. Martynenko, N. I. Pechurova, and V. J. Spitsyn, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, **9**, 2075.

from that in sulphate. The oxidation of isopropyl alcohol proceeds more

$$2Ce^{IV} + Me_2CHOH \longrightarrow 2Ce^{III} + Me_2C{=}O + 2H^+$$

slowly,[156] again with intermediate complex formation. In this case, however, the species $Ce^{IV}.(Me_2CHO)^-$ is formed not from the reaction of $[Ce(OH)]^{3+}$ but by proton dissociation of $Ce^{IV}.(Me_2CHOH)$. The reactions (10) and (11) are followed by a fast interaction between the radical and a

$$Ce^{IV}.(Me_2CHOH) \xrightarrow{k_\alpha} Ce^{III} + Me_2\dot{C}OH + H^+ \qquad (10)$$

$$Ce^{IV}.(Me_2CHO)^- \xrightarrow{k_\beta} Ce^{III} + Me_2\dot{C}OH \qquad (11)$$

second cerium(IV) species, the values of k_α and k_β being about 10^5 times lower than for other ligands [152, 154] (Table 1). In this study, the equilibrium constant between the ceric ion and the neutral ligand is evaluated at 10 l mol^{-1} at 25 °C. For reaction (10), the low entropy of activation ($\Delta S^\ddagger \sim 1{\cdot}8$ e.u.) is explained in terms of a concerted transfer of an electron to the cation and of a proton to the bulk solvent. The first process would produce a high entropy in the transition state from the loss of hydration of the metal cation, and for the second process a low entropy would be expected in the activated complex, associated with the increased restriction imposed on the solvent. The value for this reaction thus results from a balance of these two interactions and is comparable with the low $\Delta S^\ddagger$ values derived for outer-sphere oxidations of secondary alcohols by manganese(III).

The ceric ion oxidations of alcohols have been measured in 70% acetonitrile,[157] complex formation being observed in this system and in the case of bicyclo[2,2,1]heptan-2-ol and bicyclo[2,2,2]octan-2-ol,[158] where the intermediate is considered to decompose through oxidative cleavage of the C^1–C^2 bond to give a radical which is then further oxidised by another cerium(IV) species. The formation of 2-methyltetrahydrofuran by oxidation of pentan-1-ol has been described,[159] and in the reactions of glycols with both cerium(IV) and lead(IV), the question of one- and two-electron oxidative cleavages has been discussed.[160] Calorimetric methods have been used to investigate the stoicheiometry of the rapid conversion of oximes to the parent carbonyl compounds in alcohols, acetonitrile, and acetic acid.[161] The mechanism of the oxidation of glucose and cellulose [162] has been examined, and substituent effects on the rate of oxidation of benzyl alcohol

[156] C. F. Wells and M. Husain, *Trans. Faraday Soc.*, 1970, **66**, 679.
[157] L. B. Young and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, 1969, **91**, 5060.
[158] W. S. Trahanovsky, P. J. Flash, and L. M. Smith, *J. Amer. Chem. Soc.*, 1969, **91**, 5068.
[159] W. S. Trahanovsky, M. G. Young, and P. M. Nave, *Tetrahedron Letters*, 1969, 2501.
[160] W. S. Trahanovsky, L. B. Young, and M. H. Bierman, *J. Org. Chem.*, 1969, **34**, 869.
[161] J. W. Bird and D. G. M. Diaper, *Canad. J. Chem.*, 1969, **47**, 145.
[162] C. R. Pottenger and D. C. Johnson, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1970, **8**, 301.

Table 1 *Metal ion–ligand oxidation and reduction*‡

Reductant	k_{25}	I(M)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Manganese(III)					
Hydroquinone	$4{\cdot}8 \times 10^3$	3·90	—	—	102
*Hydroquinone[a]	$3{\cdot}3 \times 10^4$	3·90	—	—	102
$NH_3NH_2^+$	$\leqslant 5{\cdot}2 \times 10^2$	2·3[b]	—	—	101
*$NH_3NH_2^+$ [a]	$10{\cdot}3 \times 10^3$	2·3[b]	—	—	101
$CH_3NH_2NH_2^+$	$\leqslant 80$	2·3[b]	—	—	101
*$CH_3NH_2NH_2^+$ [a]	3×10^3	2·3[b]	—	—	101
$(CH_3)_2NHNH_2^+$	$\leqslant 130$	2·3[b]	—	—	101
*$(CH_3)_2NHNH_2^+$ [a]	4×10^3	2·3[b]	—	—	101
$CH_3NH_2NHCH_3^+$	$\leqslant 20$	2·3[b]	—	—	101
*$CH_3NH_2NHCH_3^+$ [a]	$4{\cdot}3 \times 10^2$	2·3[b]	—	—	101
$(CH_3)_2NHN(CH_3)_2^+$	280	2·3[b]	—	—	101
*$(CH_3)_2NHN(CH_3)_2^+$ [a]	30	2·3[b]	—	—	101
Cobalt(III)					
HN_3	2·3	5·0	—	—	117, 118
*HN_3	32[c, d]	5·0	13·1	5	117, 118
Cl^-	6·0[c]	0·50	25·4	20	119
*Cl^-	6[c, d]	0·50	—	—	119
Br^-	11·2[e]	0·50	21·4	23	120
*Br^-	12[d, e]	0·50	9·4	− 14	120
*Thiourea	52[d]	0·82[g]	15·7	3	122[f]
HNO_2	18	3·0	18·3	9	121
*HNO_2	17·2[d]	3·0	21·7	19	121
ClO_2	$\lesssim 1$	2·1	—	—	121, 124
*ClO_2	59·6[d]	2·1	21·8	23	121, 124
Br^-	$\leqslant 5$	3·0	—	—	121
*Br^-	30·4[d]	3·0	26·1	37	121
SCN^-	86·5	3·0	20·6	20	121

Table 1 (*cont.*)

Reductant	k_{25}	I(M)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
*SCN^-	79·6[d]	3·0	25·6	37	121
Hydroquinone	$2·2 \times 10^3$	3·0	18·2	18	121
*Hydroquinone	$1·28 \times 10^3$ [d]	3·0	18·6	17	121
I^-	8×10^3	3·0	19·4	25	121
*I^-	$2·86 \times 10^3$ [d]	3·0	21·5	30	121
*NH_3OH^+	3·26	2·1	22·5	20	125
*$NH_3NH_2^+$	1·06	2·1[h]	23·8	22	125
H_2O_2	$\leqslant 2$	3·0	—	—	121
*H_2O_2	23·0[d]	3·0	23·5	3	121
Cerium(IV)					
H_2O_2	280[i]	2·0	1	− 49	152
Hydroquinone	100[i]	2·0	1	− 51	154
HN_3	260[i]	2·0	1	− 49	153
$(CH_3)_2CHOH$	$2·2 \times 10^{-3}$ [i]	2·06	21	− 1·8	156
$(CH_3)_2CHO^-$	$1·0 \times 10^{-3}$ [i]	2·06	27·3	17·8	156
Thallium(III)					
1,2-cyclohexanedione	13	2·0	24	27	252
*1,2-cyclohexanedione	93·7	2·0	7·0	− 26	252
Peroxodisulphate					
$[Fe(bipy)_3]^{2+}$	0·4	0·1—0·4	10·0	− 26·7	275
$[Fe(phen)_3]^{2+}$	0·21	0·1—0·4	12·1	− 21·5	275
$[Fe(5\text{-Me-phen})_3]^{2+}$	0·086	0·1—0·4	12·2	− 24·7	275
$[Fe(5\text{-Cl-phen})_3]^{2+}$	0·27	0·1—0·4	17·3	− 7·4	275
$[Fe(5\text{-}NO_2\text{-phen})_3]^{2+}$	1·29	0·1—0·4	9·1	− 27·6	275
$[Fe(4,4'\text{-dimethyl-bipy})_3^{2+}$	5·78	0·1—0·4	7·6	− 29·2	275

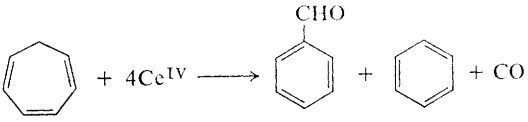
Table 1 (*cont.*)

Reductant	k_{25}	I(M)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Chlorate					
$[Fe(phen)_3]^{2+}$	10^{-5}	1·0	—	—	288
V^{III} [j]	2·0	2·0—3·0	—	—	288
V^{IV} [j]	$5{\cdot}7 \times 10^{-2}$	2·0—3·0	—	—	288
Cr^{II} [j]	39	2·0—3·0	—	—	288, 290
$[Fe(phen)_3]^{2+} + Cl_2$	2·3	1·0	—	—	289
$[Fe(phen)_3]^{2+} + ClO_2^-$	3×10^5 [k, l]	1·0	—	—	288
$[Fe(phen)_3]^{2+} + ClO_2$	1·86 [k]	1·0	—	—	288
Fe edta^{2-} + ClO_2^-	3×10^4	1·0	—	—	291
$[Cu(NH_3)_2]^+ + ClO_2^-$	44	1·0	—	—	291
$Fe^{II} + Br_2^-$	$8{\cdot}2 \times 10^6$ [m]	—	—	—	294
$Mn^{II} + Br_2^-$	$1{\cdot}4 \times 10^6$ [m]	—	—	—	294
$Co^{I} + Br_2^-$	1×10^{10} [m]	—	—	—	294
Vanadium(II) Reductions					
Cl_2	5×10^2	1·0	—	—	318
Br_2	$3{\cdot}0 \times 10^4$	1·0	3·5	− 26	318
I_2	$7{\cdot}5 \times 10^3$	1·0	5·9	− 21	318
I_3^-	$9{\cdot}7 \times 10^2$	1·0	9·1	− 14	318
Ruthenium(II)					
ClO_4^-	$3{\cdot}3 \times 10^{-3}$	1·0	—	—	29, Chapter 1
ClO_4^-	$3{\cdot}2 \times 10^{-3}$ [n]	0·3	19·4	− 5·0	319
ClO_4^- [o]	$2{\cdot}6 \times 10^{-2}$	—	—	—	17, Introduction
ClO_4^- [p]	$3{\cdot}0 \times 10^{-4}$	0·62	—	—	17, Introduction

‡ Second-order rate constants at 25 °C (k_{25}) are in l mol^{-1} s^{-1}: $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ values are kcal mol^{-1} and cal deg^{-1} mol^{-1} respectively. Reactions marked with an asterisk refer to MOH^{n+} as oxidant.

* [a] Oxidant is MOH^{2+}. [b] Ionic strength varied from 2·3—4·1 mol l^{-1}. [c] T = 13 °C, complex formation reaction. [d] Composite rate constant $k_2 K_h$ quoted (s^{-1}),see text, ref. 121. [e] T = 15 °C. [f] See ref. 11, Introduction. [g] Ionic strength varied from 0·8—1·27 mol l^{-1}. [h] Nitrate media. [i] First-order decay of intermediate complex, rate constant in s^{-1}. [j] T = 20 °C, [H$^+$] = 0·5—0·6 mol l^{-1}. [k] T = 35 °C. [l] Calculated value assuming dissociation of $[Fe\ phen_3]^{2+}$ to be rate-determining process. [m] T = 20 °C. [n] Rate-determining step considered as substitution rate for the metal ion. [o] Reductant is $[Ru(NH_3)_5OH_2]^{2+}$. [p] Reductant is $[Ru(NH_3)_6]^{2+}$.

in perchlorate media.[163] In the reaction with cyclohepta-1,3,5-triene,[164] there is strong evidence for a tropilium ion as an intermediate, the ratio of benzaldehyde to benzene produced being 4 : 1 in most solvents used. The kinetics of the oxidation of benzaldehyde to benzoic acid have been



investigated in 85% aqueous acetic acid.[165] The reaction rate is markedly affected by the presence of oxygen, and both 1 : 1 and 2 : 1 benzaldehyde–cerium(IV) complexes are considered to be present. In aqueous acetic acid, it has been found that the ceric ion is involved in a monomer–trimer equilibrium:

$$3M \rightleftharpoons M_3$$

with the intermediate complex being considered to result from reaction of the monomer. The oxidation rate involves terms both first- and second-order in acid concentration, the data being described by the mechanism:

$$H^+ + M \rightleftharpoons Ce^{IV} + HOR$$

$$Ce^{IV} + RCHO \rightleftharpoons \text{Complex(1)} \xrightarrow{+H^+} RCO^{\bullet} + Ce^{III}$$

$$\text{Complex(1)} + RCHO \rightleftharpoons \text{Complex(2)} \xrightarrow{+2H^+} RCO^{\bullet} + Ce^{III} + RCHO$$

$$RCO^{\bullet} + Ce^{IV} \xrightarrow{\text{fast}} RCO_2H + Ce^{III}$$

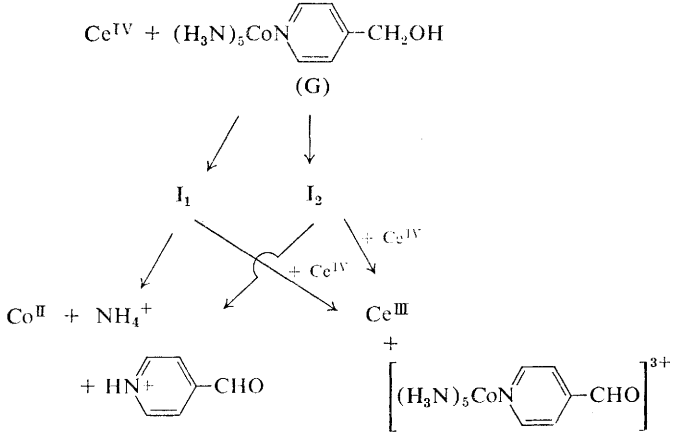
Evidence is found for formation of benzoyl radicals, which are considered to interact in a rapid step with a second mole of oxidant. The rate is strongly accelerated by oxygen and is retarded by nitrate.

Several studies have been carried out in sulphate media. The mechanism of oxidation of 1-naphthylamine and 8-aminonaphthalene-1-sulphonic acid has been described[166] and complex formation invoked in the reactions with benzilic acid[167] and formaldehyde.[168] Hydrochloric acid reduces cerium(IV) at a measurable rate at room temperature[169] and silver(I) acts as a catalyst for the reaction. The activated complex is considered to involve both sulphatocerate and chloride anions. The large overall heats of reaction with α-thiolocarboxylic acids[170] and thioureas[171] have been

[163] T. R. Balasubramanian and I. N. Venkatasubramian, *Indian J. Chem.*, 1970, **8**, 305.
[164] W. S. Trahanovsky, L. B. Young, and M. D. Robbins, *J. Amer. Chem. Soc.*, 1969, **91**, 7084.
[165] K. B. Wiberg and P. C. Ford, *J. Amer. Chem. Soc.*, 1969, **91**, 124.
[166] A. Tockstein, V. Velich, and K. Komers, *Coll. Czech. Chem. Comm.*, 1969, **34**, 3017.
[167] V. K. Grover and Y. K. Gupta, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1403.
[168] R. N. Mehrotra, *Chem. Comm.*, 1969, 1357.
[169] A. A. Alexiev and P. R. Bontchev, *Z. phys. Chem. (Leipzig)*, 1969, **242**, 333.
[170] W. A. Alexander, C. J. Mash, and A. McAuley, *Talanta*, 1969, **16**, 535.
[171] W. A. Alexander, C. J. Mash, and A. McAuley, *Analyst*, 1970, **95**, 657.

measured, and in the latter study it is suggested that in the presence of sulphuric or hydrochloric acids enthalpimetric titration serves as a method of assay of these substrates, since it is possible using this technique to monitor the slower secondary reactions between the cerium(IV) and the oxidised products which might interfere in other methods of evaluation. Among other systems investigated are citric and glyoxylic acids,[172] (±)-, (−)-atrolactic and 2-hydroxybutyric acids,[173] chlorprothiazene,[174] *p*-bromomandelic acid,[175] and the carcinogenic substituted *NN*-dimethyl-4-aminoazobenzene dyes.[176]

Induced electron transfer has been investigated in the action of one-electron oxidants on pyridinemethanolpentammine–cobalt(III) complexes.[177] The direct [and silver(I)- and cobalt(II)-catalysed] oxidations of pentammine-(pyridine-4-methanol)cobalt(III) (G) and the corresponding pyridine-3-methanol complex by cerium(IV) yield aldehydic complexes of cobalt(III)



together with some free aldehyde and cobalt(II), the ratio of the bound to free aldehyde in the products increasing with increasing oxidant concentration. Two intermediates are formed which differ, with one being trappable by external oxidant, the other non-trappable one undergoing an internal oxidation yielding cobalt(II), the partition here being almost identical when Ce^{IV} in perchlorate, or Co^{III} in perchlorate or sulphate is used as the external oxidising agent. The similarity of the rates of oxidation of (G), and the free protonated ligands supports the view that the cobalt(III) centre of the complex does not assist the external oxidant and the

[172] K. K. Sengupta, *Bull. Chem. Soc. Japan*, 1969, **42**, 298.
[173] V. K. Grover and Y. K. Gupta, *Austral. J. Chem.*, 1970, **23**, 757.
[174] S. P. Agrawal and M. I. Blake, *J. Pharm. Pharmacol.*, 1969, **21**, 556.
[175] V. K. Grover, S. K. Mishra, and Y. K. Gupta, *Indian J. Chem.*, 1970, **48**, 247.
[176] M. Matrka, J. Marhold, V. Chmatal, V. Sterba, Z. Sagner, and J. Kroupa, *Coll. Czech. Chem. Comm.*, 1969, **34**, 3952.
[177] J. E. French and H. Taube, *J. Amer. Chem. Soc.*, 1969, **91**, 6951.

conclusion that radical intermediates of finite lifetime are generated in the rate-determining step of the reaction.

4 Chromium(VI)

Studies have been reported on both inorganic and organic substrates under a variety of conditions, and several mechanisms are suggested in the reduction steps from $Cr^{VI} \rightarrow Cr^{III}$, involving Cr^{V} and/or Cr^{IV} as transient species. In the oxidation of iodide,[178] the rate law is:

$$\frac{-\,d[HCrO_4^-]}{dt} = [HCrO_4^-]\{k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]\}$$

the mechanism being presumed to involve the steps:

$$Cr^{IV} + I^- \longrightarrow Cr^{III} + I^\bullet$$

$$^\bullet I + Cr^{VI} \longrightarrow Cr^{V} + HOI$$

The reaction rate is unaffected by manganese(II), chloride, benzaldehyde, and oxygen, and the path involving k_2 may be described as:

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4$$

$$H_2CrO_4 + I^- \rightleftharpoons ICrO_3^- + H_2O$$

$$ICrO_3^- + H^+ + I^- \xrightarrow{\text{slow}} Cr^{IV} + I_2$$

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

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

$$HOI + H^+ + I^- \longrightarrow I_2 + H_2O$$

the rate-determining process involving a two-electron step. A similar two-electron exchange is suggested in the formation of tetrathionate in the reaction of chromium(IV) and thiosulphate.[179] In this system, studied in excess thiosulphate, the equilibrium constant for the fast reaction:

$$HCrO_4^- + HS_2O_3^- \rightleftharpoons H_2O + [CrS_2O_6]^{2-}$$

is considered to be sufficiently large that all the chromium(VI) is present in the form of the complex. The mechanism may then be written:

$$[CrS_2O_6]^{2-} + HS_2O_3^- \xrightarrow{k_2} Cr^{IV} + S_4O_6^{2-}$$

$$[CrS_2O_6]^{2-} + HS_2O_3^- + H^+ \xrightarrow{k_3} Cr^{IV} + S_4O_6^{2-}$$

$$Cr^{IV} + S_2O_3^{2-} \xrightarrow{\text{fast}} Cr^{III} + S_2O_3^-$$

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

[178] D. S. Gaswick and J. H. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 2240.
[179] I. Baldea and G. Niac, *Inorg. Chem.*, 1970, **9**, 110.

the paths involving k_2 and k_3 being rate-determining. In the reaction with hypophosphorus acid,[180] and phenylphosphorous acid,[181] an intermediate complex is involved, the slow step being the reduction of $Cr^{VI} \rightarrow Cr^{IV}$, with the principal phosphorus product being P^{III}. Nitrogen is formed in the corresponding oxidation of hydrazine:[182]

$$4HCrO_4^- + 3N_2H_5^+ \longrightarrow 4[Cr(H_2O)_6]^{3+} + 3N_2$$

In the pH range 1·9—3·0, the rate law may be expressed as:

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

with an internal two-electron redox process yielding Cr^{IV}. In the presence of concentrated sulphuric acid, however,[183] it has been found that chromium(VI) species are unstable and are reduced to Cr^V, with the complex ion $[O_2Cr(OH)(OSO_3H)]$ as a possible reactive intermediate.

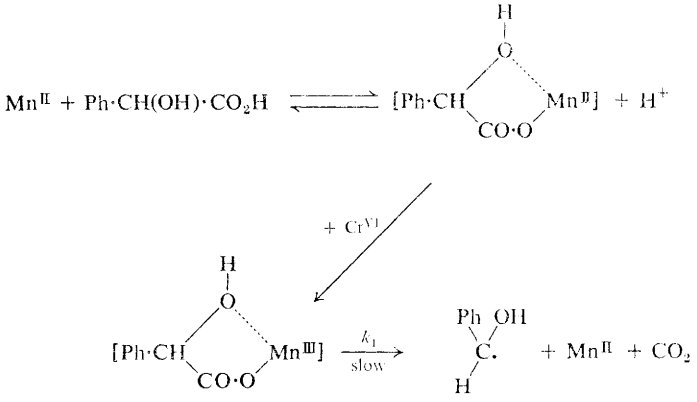
In the reaction with mandelic acid,[184] the effect of mineral acids on the rate has been shown to follow the order $HClO_4 > HNO_3 > H_2SO_4 > H_3PO_4 > HF > HCl > HBr$, linear correlations being observed with H_0. The formation of a Cr^{VI}-mandelic acid complex is followed by the rate-determining breakdown of the species to yield a Cr^{IV} entity. The oxidation has also been shown to be catalysed by manganese(II) if its concentration exceeds that of the chromium(VI) by a factor of 100.[185] Two equilibria are suggested:

$$Mn^{II} + Cr^{VI} \rightleftharpoons Cr^V + Mn^{III}$$

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

with the mechanism of Scheme 8. Further redox reactions involving Cr^V and Cr^{IV} with both the free-radical and the manganese(II)–mandelic acid complex take place. The effect of complexing agents on the Cr^{VI} oxidation of lactic and malic acids has been studied in aqueous acetic acid using 2,2′-bipyridyl and 1,10-phenanthroline.[186] The rate increases with increasing concentrations of complexing ligand, whilst added pyridine has no effect. A much larger influence on the rate is observed, however, when Cr^{III}–2,2′-bipyridyl or –phenanthroline complexes are present, and it may be that the complexed Cr^{III} species take part in the activated complex. Catalysis of these reactions by manganese(II) is also reported.[187] There is no evidence

[180] J. N. Cooper, *J. Phys. Chem.*, 1970, **74**, 955.
[181] K. K. Sengupta, *Bull. Chem. Soc. Japan*, 1970, **43**, 590.
[182] M. T. Beck and D. A. Durham, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1971.
[183] M. Marcantonantos, M. I. Bernardo, and D. Monnier, *Helv. Chim. Acta*, 1969, **52**, 291.
[184] K.-H. Heckner, K.-H. Grupe, and R. Landsberg, *Z. phys. Chem. (Leipzig)*, 1969, **242**, 225.
[185] F. B. Beckwith and W. A. Waters, *J. Chem. Soc. (B)*, 1969, 929.
[186] N. Ventakasubramanian and S. Sundaram, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1761.
[187] S. Sundaram and N. Ventakasubramanian, *Proc. Indian Acad. Sci. Sect. A*, 1969, **69**, 162.



Scheme 8

for intermediate complex formation in the oxidation of glyoxylic acid,[188] and in the reaction with aromatic alcohols studied in 80% acetic acid containing sulphuric acid,[189] second-order rates are observed with the corresponding benzophenones as products. The mechanism of the oxidation of secondary alcohols has been investigated,[190] the evidence strongly suggesting a one-electron cleavage involving a chromium(IV) intermediate:

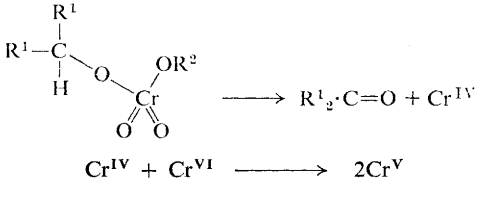
$$Cr^{VI} + R^1{\cdot}CH(OH){\cdot}R^2 \longrightarrow Cr^{IV} + \text{ketone}$$

$$2Cr^{IV} + 2R^1{\cdot}CH(OH){\cdot}R^2 \longrightarrow 2Cr^{III} + 2R^1{\cdot}CHO^{\bullet} + 2R^{2\bullet}$$

$$2Cr^{VI} + 2R^{2}{\cdot} \longrightarrow 2Cr^{V} + 2R^2OH$$

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

the disproportionation of the chromium(V) being seen as the key process. The importance of chromium(V) intermediates is also discussed in the oxidation of isopropyl alcohol,[191] which involves pre-oxidation equilibria with the formation of mono- and di-esters of the type $HO{\cdot}CrO_2{\cdot}OR$ and $RO{\cdot}CrO_2{\cdot}OR$. The oxidation of the organic substrate is effected by the intermediates rather than by the chromium(VI), *e.g.*

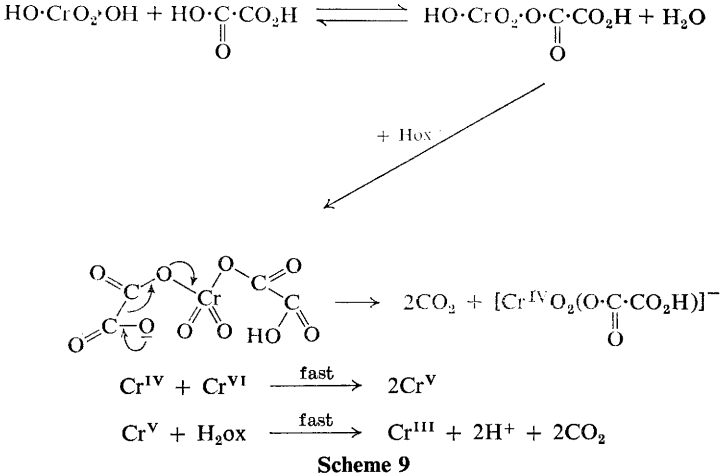


[188] K. K. Sen Gupta and S. D. Bhattacharya, *Z. phys. Chem.* (*Leipzig*), 1969, **240**, 279.
[189] R. Stewart and F. Banoo, *Canad. J. Chem.*, 1969, 47, 3207.
[190] P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, 1970, **92**, 1120.
[191] K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, 1969, **91**, 927, 933.

1·5 Moles of acetone are produced per equivalent of chromium(VI) used, and the decay of the intermediate complexes involving Cr^{V} has been followed using spectrophotometric and e.s.r. techniques. In the reaction with oxalic acid,[192] the rate law:

$$\text{Rate} = k[HCrO_4^-][H_2ox]^2$$

is observed, the chromium(VI)–oxalic acid complex reacting in a slow step with a second bioxalate anion (Scheme 9). In the manganese(II) catalysis



Scheme 9

of the reaction,[192] there may be higher (+ 3 or + 4) oxidation states involved, as previously postulated.[185]

The reduction of the chromium(III) complex $[(H_2O)_5CrN_3]^{2+}$ by nitrous acid has been studied,[193] the rate law for the reaction:

$$[(H_2O)_5CrN_3]^{2+} + HNO_2 \longrightarrow [(H_2O)_6Cr]^{3+} + N_2 + N_2O$$

being:

$$\text{Rate} = k_0[Cr^{III}][HNO_2][H^+]$$

Addition of chloride and bromide accelerates the rate, but there is little evidence of $CrCl^{2+}$ or $CrBr^{2+}$ formed as products. A reaction scheme:

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+$$

$$H_2NO_2^+ + [(H_2O)_5CrN_3]^{2+} \xrightarrow{k_0} [(H_2O)_6Cr]^{3+} + N_2 + N_2O$$

is consistent with the data, there being no evidence for protonation of the co-ordinated azide. No redox reaction takes place, however, within the chromium(III)–iodate complex,[194] which is formed very rapidly due to the rapid exchange of the oxygen atoms of the iodate group.

[192] G. V. Bakore and C. L. Jain, *J. Inorg. Nuclear Chem.*, 1969, **31**, 805, 2527.
[193] R. C. Thompson and E. J. Kauffman, *J. Amer. Chem. Soc.*, 1970, **92**, 1540.
[194] E. E. Mercer and J. A. Hormuth, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2145.

5 Vanadium(v)

The rapid oxidation of quinol[195] has been investigated using a stopped-flow technique, the overall reaction being represented by the equation:

$$2V^{V} + H_2Q \longrightarrow 2V^{IV} + Q + 2H^+$$

where H_2Q = hydroquinone. Oscilloscope traces demonstrated the existence of an intermediate complex (Figure 2) and the reaction is con-

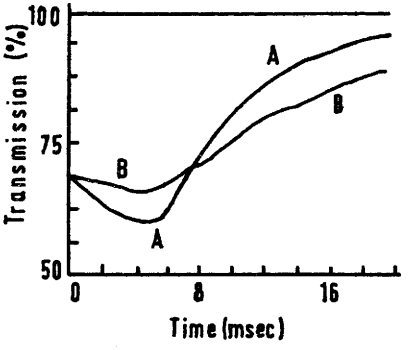


Figure 2 *The formation and decomposition of intermediate* V^{V}–QH_2 *complexes at* μ = 5·00 mol l^{-1}, T = 25 °C. *The initial vanadium*(v) *concentration is* 1·0 × 10^{-3} mol l^{-1} *and that of hydroquinone* 0·02 mol l^{-1}. *Trace A in* 5·00M $HClO_4$, *trace B in* 0·15M $HClO_4$

sidered to take place *via* an inner-sphere mechanism. The rapid increase in absorption is followed by a slower decay in optical density associated with the redox step (rate constant k_0) and an interesting feature of this secondary reaction is that whilst at low acidities plots of k_0 *versus* $[H_2Q]$ are linear, marked curvature is observed at higher acid concentrations. The reaction rate increases with increasing acidity, and a reaction scheme may be written as:

$$\begin{aligned}
VO_2^+ + H^+ &\overset{K_1}{\rightleftharpoons} [VO(OH)]^{2+} \\
VO_2^+ + H_2Q &\overset{\beta_1}{\rightleftharpoons} [VO_2QH_2]^+ \qquad (12) \\
[VO_2QH_2]^+ + H^+ &\overset{K_2}{\rightleftharpoons} [VO(OH)QH_2]^{2+} \\
[VO(OH)]^{2+} + H_2Q &\overset{\beta_2}{\rightleftharpoons} [VO(OH)QH_2]^{2+} \\
[VO_2QH_2]^+ &\xrightarrow{k_\alpha} V^{IV} + {}^{\bullet}QH + H^+ \\
[VO(OH)QH_2]^{2+} &\xrightarrow{k_\beta} V^{IV} + {}^{\bullet}QH \\
V^{V} + {}^{\bullet}QH &\xrightarrow{\text{fast}} V^{IV} + Q + H^+
\end{aligned}$$

[195] C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc.* (*A*), 1970, 1372.

where the reaction of vanadium(v) with the radical is considered to be much faster than either k_α or k_β. Using the above mechanism, the rate law:

$$\frac{-\,d[V]_{tot}}{dt} = \frac{2\beta_1(k_\alpha + k_\beta K_2[H^+][V^V]_{tot}[H_2Q]_{tot})}{1 + K_1[H^+] + \beta_1[H_2Q]_{tot}(1 + K_2[H^+])}$$

may be written, the first-order rate constants $k_\alpha = 3{\cdot}3 \times 10^2$ and $k_\beta = 1{\cdot}6 \times 10^2\ s^{-1}$ respectively being evaluated, the associated activation energies for the redox reactions being low, < 1 kcal mol^{-1}. Due to the non-linearity of the plots of k_0 against $[H_2Q]_{tot}$, it is possible to derive values for the equilibrium constant for reaction (12), β_2 being 5·5 l mol^{-1} at 25 °C. Temperature variation of β_2 yields $\Delta H_{(12)} = 10$ kcal mol^{-1} and $\Delta S_{(12)} = 37$ e.u., the endothermicity of the equilibrium being offset by the large entropy contribution. The kinetics of the reaction with iodide have been investigated in sulphate media [196] in an atmosphere of nitrogen, the species $[VO(OH)]^{2+}$ again being considered reactive. The rate law:

$$\frac{d[I_2]}{dt} = (k_1[H^+] + k_2[H^+]^2)[V^V][I^-]$$

is described by the mechanism:

$$[VO(OH)]^{2+} + I^- \rightleftharpoons [VO(OH)\cdot I]^+$$

$$[VO(OH)I]^+ + H^+ \rightleftharpoons [VO(OH_2)I]^{2+} \xrightarrow{\text{slow}} V^{IV} + H_2O + I^\bullet$$

$$+H^+$$

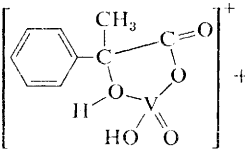
$$[V(OH)(OH_2)I]^{3+} \longrightarrow V^{IV} + I^\bullet + H_2O + H^+$$

$$2I^\bullet \xrightarrow{\text{fast}} I_2 \xrightarrow{+I^-} I_3^-$$

The e.s.r. spectra of oxovanadium ions in redox systems have been reported.[197] The interaction of free-radicals generated using the reactions of cerium(IV) or ferrous ions with hydrogen peroxide with oxovanadium(v), produces a complex which decays in a first-order manner ($k = 6{\cdot}2\ s^{-1}$ at 22 °C) with the formation of vanadium(IV). The oxidation of phenetidines by bromate is catalysed by vanadium(v) [198] and kinetic parameters involved in the interactions of various substrates with vanadium(v) have been correlated with electron configurations.[199] The redox behaviour of oxo-3,5-disulphocatecholatovanadium(v) has been studied [200] and the acidity dependence in the reaction with phenylethyl alcohol reported.[201] In the

[196] G. St. Nikolov and D. Mihailova, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2499.
[197] M. S. Bains, J. C. Arthur, and O. Hinojosa, *J. Amer. Chem. Soc.*, 1969, **91**, 4673.
[198] K. B. Yatsimirskii, A. P. Filippov, and V. M. Zyatkovskii, *Ukrain. khim. Zhur.*, 1969, **35**, 233, 451.
[199] G. St. Nikolov and K. B. Yatsimirskii, *Teor. i eksp. Khim.*, 1969, **5**, 773.
[200] D. Braun-steinle and S. Fallab, *Chimia (Switz.)*, 1969, **23**, 269.
[201] B. Ganapathysunder and N. Ventakasubramian, *Current Sci.*, 1969, **38**, 542.

$$V^{V} + Ph(CH_3)C(OH)CO_2H \rightleftharpoons$$



$$+ H^{+}$$

oxidation of atrolactic acid,[202] complex formation is described, the rate-determining step involving the rupture of the C—C bond with subsequent rapid reaction between the radical formed and the oxidant. A distinction has been made on the basis of overall thermodynamic parameters between systems involving C—H bond rupture as the rate-determining process and those where C—C bond fission is the important step (see ref. 9, Introduction). The data are summarised in Table 2, where it may be seen that C—H fission in the activated complex is accompanied by a fairly large negative entropy of activation (~ -20 e.u.).

Table 2 *Thermodynamic parameters for oxidation of organic substrates by vanadium*(v) *(from ref. 9, Introduction and references therein)*

Substrate	E_a (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1})
Glycollic acid	16·7	− 16
Lactic acid	16·5	− 20
Mandelic acid	14·0	− 20
α-Hydroxyisobutyric acid	21·8	− 0·4
Pinacol	22·8	9·5
Oxalic acid	23·4	6·5
Tartaric acid	22·8	5·9
2-Hydroxy-2methylpropionic acid	22·0	− 1·0

Several redox reactions involving vanadium(IV) have been reported. In the reaction with chlorate,[203] the rate is first-order in each reactant

$$VO^{2+} + ClO_3^- \xrightarrow{k_1} VO_2^+ + ClO_2$$

($k_1 = 6 \times 10^5$ l mol^{-1} s^{-1}), at 21·1 °C, the presence of vanadium(V) causing only a minor reduction (< 5%) in rate. Chloride ions also produce a slight deceleration. The oxidation of methyl cyanide in the presence of chloride has also been investigated.[204] Electron-transfer reactions of vanadium(IV) and some oxyanion oxidants have been investigated in perchloric acid,[205] the mechanism in the case of $HCrO_4^-$ being:

$$Cr^{VI} + VO^{2+} + H_2O \underset{}{\overset{K}{\rightleftharpoons}} Cr^{V} + VO_2^+ + 2H^+$$

$$VO^{2+} + Cr^{V} \xrightarrow{k_1} V^{V} + Cr^{IV}$$

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

[202] J. N. Kar, G. B. Behera, and M. K. Rout, *Indian J. Chem.*, 1969, **46**, 400.
[203] D. R. Rosseinsky and J. Zlotnick, *J. Chem. Soc.* (*A*), 1970, 1200.
[204] C. A. Van Driel and W. L. Groeneveld, *Rec. Trav. chim.*, 1969, **88**, 891.
[205] D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc.* (*A*), 1970, 1196.

the rate-determining step involving $Cr^{V} \rightarrow Cr^{IV}$ being associated with a change in co-ordination number from six to four. In the case of the corresponding permanganate reaction,[205] the stoicheiometry:

$$MnO_4^- + 5VO^{2+} + H_2O \longrightarrow Mn^{II} + 5VO_2^+ + 2H^+$$

holds only at low acid concentrations, and in some experiments at higher acidities in the presence of excess MnO_4^-, the value falls to as low as 2·8 moles of V^{IV} reacting. The catalytic action of manganese(II) in this system is considered to arise from the formation of Mn^{III}, which is known to react faster with vanadium(IV) than does permanganate.

6 Iron(III)

Although iron(III) is known to oxidise both inorganic and organic substrates (see ref. 9, Introduction) under conditions where the oxidant exists in the cationic form, studies are now being made of the oxidising nature of anionic complexes, especially those involving cyanide ligands. Two investigations have been made of the oxidation of ascorbic acid by $[Fe(CN)_6]^{3-}$.[206, 207] Under conditions of high acidity,[206] the rate shows a first-order dependence in both oxidant and substrate, with a proportionality to $[H^+]^{-1}$ which is ascribed to ionisation of the acid. A radical mechanism is postulated (AH_2 = ascorbic acid):

$$AH_2 \rightleftharpoons AH^- + H^+$$

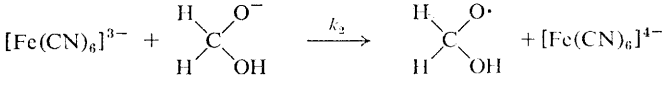
$$[Fe(CN)_6]^{3-} + AH^- \xrightarrow{k_2} AH^{\bullet} + [Fe(CN)_6]^{4-}$$

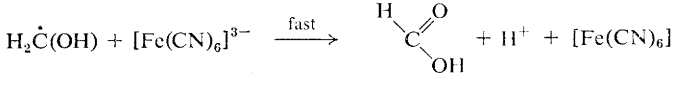
$$AH^{\bullet} + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} A + [Fe(CN)_6]^{4-} + H^+$$

the value of k_2 of 130 l mol^{-1} s^{-1} at 25 °C falling with a decrease in dielectric constant of the medium. Using optically transparent electrodes, however, at pH ~ 2, the same hydrogen-ion dependence is reported, the rate law being:

$$\text{Rate} = \left(k_{AH_2} + k_{AH^{\bullet}} \frac{K_1}{[H^+]}\right) [Fe(CN)_6^{3-}][AH_2]$$

In this study, the rate constant for the interaction of the neutral substrate (k_{AH_2}) has also been evaluated (6·7 ± 0·5 l mol^{-1} s^{-1}), and is considerably lower than that involving the negatively charged ascorbate ion. In the





[206] U. S. Mehrotra, M. C. Agrawal, and S. P. Mushran, *J. Phys. Chem.*, 1969, **73**, 1996.
[207] N. Winograd, H. N. Blount, and T. Kuwana, *J. Phys. Chem.*, 1969, **73**, 3456.

oxidation of formaldehyde [208] there is a very rapid initial reaction followed by a simple process which is first-order in $[Fe(CN)_6^{3-}]$, $[OH^-]$, and formaldehyde, the rate-determining step being followed by a rapid oxidation of the radical produced. The kinetics of the corresponding oxidation of thioglycollic acid are, however, more complex,[209] the reaction:

$$2RSH + 2[Fe(CN)_6]^{3-} \longrightarrow RSSR + 2[Fe(CN)_6]^{4-} + 2H^+$$

decreasing in rate with increasing acidity. The inverse proportionality to the initial concentration of $[Fe(CN)_6]^{3-}$ is described by Scheme 10. The

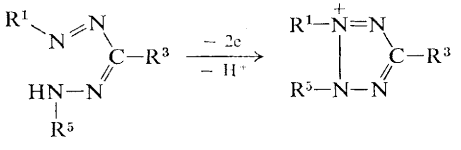
$$RS^{2-} + [Fe(CN)_6]^{3-} \underset{k\beta}{\overset{k\alpha}{\rightleftharpoons}} [Fe(CN)_6]^{4-} + RS^-$$

$$RS^- + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} RS^{\bullet} + [Fe(CN)_6]^{4-}$$

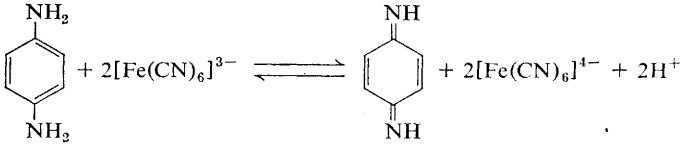
$$2RS^{\bullet} \longrightarrow RSSR$$

Scheme 10

oxidation of methyldithiobiuret has been studied in alkaline media,[210] and the effect of water–methanol mixtures on the rate of reaction of ferricyanide with hydrazine investigated.[211] Formazans contain the characteristic atom chain —N=N—C=N—NH— and exhibit good solubility in ethanol and acetone. They are oxidised to tetrazolium salts



by hexacyanoferrate(III),[212] in 45% ethanol–water mixtures containing ammonia. A dependence on ammonia concentration in the rates is ascribed to the fact that $[Fe(CN)_6]^{3-}$ is considered to oxidise the weakly acidic substrates in the form of the anions (formazan$^-$) and it may be that NH_4^+ acts as a bridge in the redox reaction between the two anionic species. The reaction with *p*-phenylenediamine [213] has been shown to yield the corresponding *p*-benzoquinone di-imine at pH 8·5:



[208] V. N. Singh, M. C. Gangwar, B. B. L. Saxena, and M. P. Singh, *Canad. J. Chem.*, 1969, **47**, 1051.
[209] R. C. Kapoor, O. P. Kachhwaha, and B. P. Sinha, *J. Phys. Chem.*, 1969, **73**, 1627.
[210] G. S. Desmukh and R. K. Nandi, *Current Sci.*, 1969, **38**, 190.
[211] V. K. Jindal, M. C. Agrawal, and S. P. Mushran, *Z. Naturforsch.*, 1970, **25a**, 188.
[212] A. M. A. Verwey and S. Balt, *Inorg. Chim. Acta*, 1969, **3**, 178.
[213] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 207, 213, 818.

the rapidly-established equilibrium being essentially completely in favour of the di-imine. In the presence of excess oxidant, further reaction takes place utilising quantitatively six moles of $[Fe(CN)_6]^{3-}$ to yield a tricyclic condensation product. A redox equilibrium process has also been suggested in the oxidation of arsenic(III) in alkaline media:[214, 215]

$$As^{III} + OH^- \rightleftharpoons [As^{III}—OH]^-$$

$$[As^{III}OH] + [Fe(CN)_6]^{3-} \rightleftharpoons [Fe(CN)_6]^{4-} + As^{IV}$$

$$As^{IV} + [Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} As^{V} + [Fe(CN)_6]^{4-}$$

with the rapid interaction of the arsenic(IV) intermediate with a further equivalent of oxidant. In an interesting study of the catalysis of the reaction

$$2[Fe(CN)_6]^{3-} + 3I^- \longrightarrow 2[Fe(CN)_6]^{4-} + I_3^-$$

by metal surfaces it has been shown [216] that the mechanism does not involve a direct transfer between adjacently adsorbed ions but proceeds by transfer of electrons through the metal (platinum). The kinetics and mechanism of the oxidation of acetone and ethyl methyl ketone by alkaline ferricyanide, catalysed by osmium tetroxide, have been reported,[217] the reaction involving the formation of an activated complex between an enolate anion and the OsO_4 which rapidly decomposes. The reaction is zero-order in hexacyanoferrate(III), the fast reaction involving an oxidation of the reduced osmium species:

$$R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R{\cdot}\overset{\overset{O^-}{|}}{C}{=}CH_2 + H_2O$$

$$R{\cdot}\overset{\overset{O^-}{|}}{C}{=}CH_2 + OsO_4 \xrightarrow{k_2} \left[R{\cdot}\overset{\overset{O}{\|}}{C}{\cdot}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Os}}{=}O\right]$$

$$\downarrow$$

$$R{\cdot}\overset{\overset{O}{\|}}{C}{\cdot}CH_2OH + [OsO_4]^{2-}$$

$$[OsO_4]^{2-} + 2[Fe(CN)_6]^{3-} \xrightarrow{\text{fast}} OsO_4 + 2[Fe(CN)_6]^{4-}$$

[214] B. Krishna and H. S. Singh, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2964.
[215] M. C. Agrawal, V. K. Jindal, and S. P. Mushran, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1257.
[216] M. Spiro and P. W. Griffin, *Chem. Comm.*, 1969, 262.
[217] V. N. Singh, H. S. Singh, and B. B. L. Saxena, *J. Amer. Chem. Soc.*, 1969, **91**, 2643.

The oxidation of methyl ethyl ketone by iron(III)–1,10-phenanthroline complexes has also been investigated [218] and cationic iron(III) complexes have also been shown to oxidise phenylhydrazine and phenylhydrazine sulphonic acids.[219] Studies of the iron(II)–iron(III) couple have been made in acetonitrile, and the oxidation of thiocyanate by the latter investigated;[220] the catalysis of the oxidation of ascorbic acid in the presence of ferric chelates has been examined.[221] Redox processes are also reported in the interaction of haem iron with thiols.[222] Complexes of haemoglobin and myoglobin with H_2S or methanethiol at pH 6 and iron in the trivalent state are stable in the presence of oxygen, the species being typical of low-spin iron(III)–haem complexes, with the iron strongly associated with the thiol ligand. In the reaction of iron(II)–phthalocyanine with HCl in DMSO, the adduct reported may contain iron(IV).[223] Iron(III)– and ruthenium(III)–bipyridyl complexes have also been used to characterise probable structures of amino-polycarboxylate complexes of cobalt(II) in solution, the reactions being outer-sphere with low energies and negative entropies of activation.[224] (See Table 1, Chapter 1.)

7 Manganese(VII)

The mechanism of decomposition of alkaline permanganate solutions to

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + O_2 + 2H_2O$$

yield manganate(VI) is trace-metal-catalysed [225, 226] and if metal ions are present in only very small amounts ($< 10^{-9}$ mol l^{-1}) the reaction is almost immeasurably slow. The reduction does not involve the formation of hydroxyl radicals, but probably proceeds *via* polynuclear hydroxo-complexes, *e.g.* of cobalt(II) and nickel(II), the catalyst being oxidised by MnO_4^- through an electron transfer mechanism. Isotope effects show that the oxygen evolved originates from the water, and it is considered that a peroxo-ligand formed in the inner co-ordination sphere of the metal ion is further oxidised to molecular oxygen with replacement in the primary co-ordination site by hydroxyl ions. The reaction with nitrite [227] is moderately fast ($0{\cdot}5 < t_{\frac{1}{2}} < 20$ s) the rate being described in terms of hydrogen and nitrite concentrations by the expression:

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

[218] V. D. Komissarov and E. T. Denisov, *Zhur. fiz. Khim.*, 1969, **43**, 769.
[219] A. M. A. Verwey and S. Balt, *Rec. Trav. chim.*, 1969, **88**, 1289.
[220] B. Kratochvil and R. Long, *Analyt. Chem.*, 1970, **42**, 43.
[221] Y. Kurimura, K. Murakami, and E. Tsuchida, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1969, **72**, 1698.
[222] E. Bayer, H. A. O. Hill, A. Roder, and R. J. P. Williams, *Chem. Comm.*, 1969, 109.
[223] J. G. Jones and M. V. Twigg, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 245.
[224] R. G. Wilkins and R. E. Yelin, *J. Amer. Chem. Soc.*, 1970, **92**, 1191.
[225] J. Veprek-Siska and V. Ettel, *J. Inorg. Nuclear Chem.*, 1969, **31**, 7891.
[226] J. Veprek-Siska, *Discuss. Faraday Soc.*, 1968, *No.* 46, p. 184.
[227] L. Dozsa and M. T. Beck, *Inorg. Chim. Acta*, 1970, **4**, 219.

The rate is independent of permanganate concentration and the mechanism for the paths corresponding to rate constants k_1 and k_2 may be written as:

$$H^+ + NO_2^- \rightleftharpoons HNO_2$$

$$HNO_2 \xrightarrow{k_1} NO^+ + OH^-$$

$$2HNO_2 \xrightarrow{k_2} N_2O_3 + H_2O$$

$$NO^+ + MnO_4^- \xrightarrow{\text{fast}} NO_2^+ + MnO_3^-$$

$$N_2O_3 + MnO_4^- \xrightarrow{\text{fast}} NO_3^- + MnO_3^- + NO^+$$

with further rapid reactions of the unstable intermediates to yield nitrate and manganese(II) as final products. The interaction of nitrite with other oxidants is compared with that involving MnO_4^-. The oxidation of hydroxylamine complexes of Pt^{II} has been reported,[228] the products being N_2O, N_2, $H_2N_2O_2$, and Pt^{IV} if more than eight moles of MnO_4^- are used. In the presence of smaller quantities of oxidant, however, no oxidation of the metal takes place.

Oxidations of organic substrates have also been reported. In the reaction with benzyl alcohol [229] the reactive species is considered to be $HMnO_4$, the rate-determining step being the cleavage of the C—H bond of the alcohol. The oxidation of secondary and tertiary aromatic alcohols [230] in acid solution proceeds *via* the formation of an ester:

$$Ar_2CHOH + H^+ \xrightarrow{\text{slow}} Ar_2CH^+ + H_2O$$

$$Ar_2CH^+ + MnO_4^- \xrightarrow{\text{fast}} Ar_2CH\cdot O\cdot MnO_3 \xrightarrow{\text{fast}} \text{products}$$

although the rate-determining step in both cases in solutions more acidic than $H_0 = -0{\cdot}50$ was found to be the ionisation of the carbinol to give a carbonium ion. In concentrated aqueous base, tertiary benzylic hydrogen atoms are oxidised [231] to hydroxyl, the process being first-order in each component. The mechanism is considered to involve hydrogen abstraction by the permanganate, with subsequent electron transfer to yield Mn^{VI} in the

$$R_3CH + MnO_4^- \longrightarrow [R_3C\cdot MnO_4\cdot H]$$

complex formed. The oxidations of furfurals in alkaline media and of cyclohexanenitronate [232] have also been investigated, together with the corresponding reactions of 4-thiouracil derivatives.[233]

[228] A. I. Stetsenko and A. A. Grinberg, *Zhur. priklad. Khim.*, 1969, **42**, 1992.
[229] K. K. Banerji and P. Nath, *Bull. Chem. Soc. Japan*, 1969, **42**, 2038.
[230] F. Banoo and R. Stewart, *Canad. J. Chem.*, 1969, **47**, 3199.
[231] J. I. Brauman and A. J. Pandell, *J. Amer. Chem. Soc.*, 1970, **92**, 329.
[232] F. Freeman, J. B. Brant, N. B. Hester, A. A. Kamego, M. L. Kasner, T. C. McLaughlin, and E. W. Paull, *J. Org. Chem.*, 1970, **35**, 982; F. Freeman, A. Yeramyan, and F. Young, *ibid.*, 1969, **34**, 2438.
[233] M. Yano and H. Hayatsu, *Biochim. Biophys. Acta*, 1970, **199**, 303.

8 Silver(II) and Silver(III)

The rapid silver(II) oxidation of peroxide has been investigated, and is of the same order of velocity as that for Mn^{III} but much faster than that for Co^{III} or Fe^{III}.[234] The first-order rate is independent of $[Ag^I]$ and of the initial $[Ag^{II}]$: $[H_2O_2]$ ratio with no variation in the acidity range 1·5—3·7M $HClO_4$. An inner-sphere mechanism is postulated, involving the formation of a complex with a high equilibrium constant:

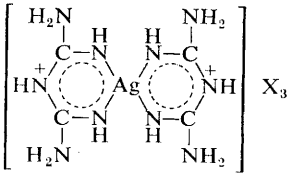
$$Ag^{II} + HO_2^- \rightleftharpoons [AgHO_2]^+$$

$$[AgHO_2]^+ \xrightarrow{k_{obs}} Ag^I + HO_2^{\bullet}$$

$$Ag^{II} + HO_2^{\bullet} \xrightarrow{\text{fast}} Ag^I + H^+ + O_2$$

the secondary interaction of the radical produced with the oxidant being very fast. It is considered that a high degree of sp^3d overlap exists in the intermediate complex, due to the strong tendency of the $t_{2g}^6e_g^3$ arrangement of silver(II) to attain the $t_{2g}^6e_{2g}^4$ configuration and to the higher polarisability of anionic oxygen compared to the oxygen atom in water. The strong tendency for the attainment of the d^{10} configuration by d^9 species (and d^5 by d^4) by covalency in (M^{n+} + anion) complexes may be due either to increased covalency arising from the decreased M^{n+}–HO_2^- distance due to Jahn–Teller effects, or to the extra stability of the half-filled or filled *d*-subshells in solution. The oxidation of alcohols and aldehydes by silver(II)–picolinate complexes has been examined, the reactions being faster in DMSO than in water,[235] and silver(II) complexes are also involved in the oxidative decarboxylation of organic acids.[236]

The oxidation of silver(I) biguanide complexes yields the corresponding cationic silver(III) species (H),[237] where X represents a univalent anion. The



(H)

reactions of the bisbipyridyl and ethylenebiguanide complexes of silver(I) with peroxodisulphate have been examined,[238] with the formation of silver(II) and (III) complexes of the type shown. The Ag^{II}–bipyridyl species is formed in a reaction which is first-order in both reagents, whereas in the

[234] C. F. Wells and D. Mays, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 9.
[235] T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley, and B. Scanlon, *Canad. J. Chem.*, 1969, **47**, 1649.
[236] J. M. Anderson and J. K. Kochi, *J. Org. Chem.*, 1970, **35**, 986.
[237] D. Sen, *J. Chem. Soc.* (*A*), 1969, 1304.
[238] J. D. Miller, *J. Chem. Soc.* (*A*), 1968, 1778.

formation of the Ag^{III} complex, two consecutive steps are involved, the evidence pointing to the interactions of silver with $S_2O_8^{2-}$ as one-electron processes. For ethylenebiguanide (enbig):

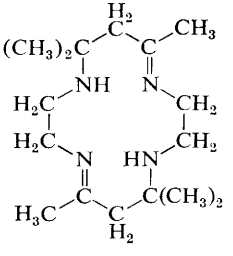
$$[Ag\,enbig]^+ + S_2O_8^{2-} \longrightarrow [Ag\,enbig]^{2+} + A$$

$$[Ag\,enbig]^{2+} + S_2O_8^{2-} \longrightarrow [Ag\,enbig]^{3+} + A$$

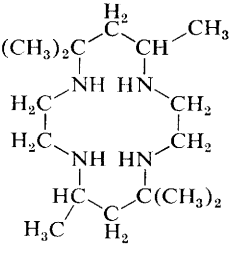
where A represents either $S_2O_8^{3-}$ (or both SO_4^- and SO_4^{2-}) and does not react with the silver complexes but probably oxidises water. This is in marked contrast to the reaction with bipyridyl as ligand, where the rate data suggest that the intermediate (presumably SO_4^-) formed in the initial reaction is a rapid oxidant in a further reaction with another Ag^+ complex ion. Silver(III) may also be used as an oxidative titrant [239] in the determination of sugars, carboxylic acids, and inorganic ions. The oxidant is stabilised as the tellurato-complex, and $[Fe(CN)_6]^{4-}$, H_2O_2, Cr^{III}, and $S_2O_3^{2-}$ require 1, 2, 3, and 8 equivalents in reaction, the products being $[Fe(CN)_6]^{3-}$, $H_2O + O_2$, Cr^{VI}, and SO_4^{2-} respectively.

9 Copper(II)

The redox nature of co-ordination complexes with macrocyclic ligands has been examined using the *trans*-14-diene system.[240] The electrolytic reduction of the copper(II) complex of macrocyclic Schiff bases of the type *trans*-14-diene (or tet-a) yields the highly reactive yellow cuprous complex



trans-14-diene



tet-a

$[Cu(trans\text{-}14\text{-}diene)]^+$, the redox couple being highly reactive due to the unfavourable co-ordination environment of the copper(I). To determine the reducing nature of the lower oxidation species, the reaction with $[Co(NH_3)_5Br]^{2+}$ was used, the one-equivalent reduction indicating a copper(I) and not a copper(0) complex. A copper(I)–copper(II) redox system which is more readily reversible (with atmospheric oxygen as the oxidising agent) involves the iodide species in the presence of imidazole.[241] The

[239] P. K. Jaiswal and K. L. Yadava, *Talanta*, 1970, **17**, 236.
[240] J. M. Palmer, E. Papaconstinantinou, and J. F. Endicott, *Inorg. Chem.*, 1969, **8**, 1516.
[241] D. M. L. Goodgame, M. Goodgame, and G. W. Raymer-Canham, *Nature*, 1969, **222**, 866.

reversibility arises from the presence of two types of ligand, the imidazole, which strongly favours the higher oxidation state, and the iodide, which normally reduces copper(II).

The kinetics and mechanism of the oxidation of carbon monoxide [242] and formaldehyde [243] in aqueous media have been investigated at high temperatures. In the case of carbon monoxide, the reaction is homogeneous and proceeds *via* two paths, one of which is virtually independent of carbon monoxide pressure due to the formation of the stable cuprous carbonyl complex $Cu(CO)^+$. In the second route, a possible mechanism involves the steps:

$$Cu^{II} + CO + H_2O \longrightarrow [Cu{-}C(OH)]^{2+} \xrightarrow{+\,Cu^{II}} CO_2 + 2Cu^{I} + 2H^+$$

the slow process being the attack of the copper(II) ion on the carbon monoxide insertion complex. The reaction with formaldehyde [243] proceeds according to the reaction:

$$2Cu^{II} + HCHO + H_2O \longrightarrow Cu^{I} + {}^{\bullet}OCH_2OH$$

$${}^{\bullet}OCH_2OH + Cu^{II} \xrightarrow{\text{fast}} Cu^{I} + HCHO + H^+$$

Redox potentials of metal ions have been determined in anhydrous DMF and pyridine.[244] The values for the Cu^{II}–Cu^{I} and Fe^{III}–Fe^{II} couples vary greatly from those in water and it is of interest that, while the potential for the reaction $Cu^{II} + e \rightarrow Cu^{I}$ falls from 0·625 V in dimethylformamide (in the presence of 0·5M HCl) to 0·425 V in pyridine under the same conditions, the corresponding values for the iron(III) reduction show an increase from 0·405 V to 0·695 V. The redox nature of these species has been investigated in their reactions with thiols,[244] the products given being the reduced metal ion and disulphides. Cuprous chloride–pyridine catalysts have also been used in the oxidation of *o*-cresol and phenol.[245] Phenols are also oxidised by copper–ammine complexes,[246] these systems providing model systems for investigation of the properties of phenol-oxidising enzymes such as laccase and tyrosinase. The reduction of the 2,2,6,6-tetramethylpiperidine nitroxide radical by copper(II) perchlorate is considered to proceed *via* a complex,[247] and the nature of the intermediate formed in the reduction of copper(II) chloride by acetone has been

[242] J. J. Byerley and E. Peters, *Canad. J. Chem.*, 1969, **47**, 313.
[243] J. J. Byerley and W. K. Teo, *Canad. J. Chem.*, 1969, **47**, 3355.
[244] Z. Hladky and J. Vrestal, *Coll. Czech. Chem. Comm.*, 1969, **34**, 984, 1098.
[245] T. Kobayashi and T. Hara, *J. Chem. Soc. Japan Ind. Chem. Sect.*, 1969, **72**, 2270.
[246] D. G. Hewitt, *Chem. Comm.*, 1970, 227.
[247] C. M. Paleos, N. M. Karayannis, and M. M. Labes, *Chem. Comm.*, 1970, 195.

discussed.[248] The reaction:

$$2CuCl_2 + CH_3 \cdot CO \cdot CH_3 \longrightarrow 2CuCl + ClCH_2 \cdot CO \cdot CH_3 + HCl$$

takes place readily at room temperature, the rate being first-order with respect to chloride. The intense band at 475 nm found in this system is ascribed to a chlorocuprate(II)–acetone species formed in the course of the reaction. On addition of water, the complex breaks down to a copper(II) species.

10 Thallium(III)

The mechanism of the reaction of thallium(III) with hypophosphite

$$Tl^{III} + H_3PO_2 + H_2O \longrightarrow Tl^{I} + H_3PO_3 + 2H^+$$

has been reported,[249] the rate law being described as:

$$\frac{-\,d[Tl^{III}]}{dt} = \frac{k[Tl^{III}][H_3PO_2]}{1 + K_1[H_3PO_2]}$$

with no hydrogen ion effects and (spectrophotometric) evidence for the formation of a complex between Tl^{III} and H_3PO_2. Chloride ion increases the rate. An alternative mechanism could involve reaction *via* two one-

$$Tl^{III} + H_3PO_2 \longrightarrow [Tl(H_3PO_2)]^{3+} \xrightarrow{k_1} Tl^{I} + H_2PO_2^+ + H^+$$

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

electron steps with intermediate formation of Tl^{II} which rapidly reacts with the $H_2PO_2^+$ formed. Complex formation is also demonstrated in the reaction with oxalic acid,[250] the equilibrium constant for the system:

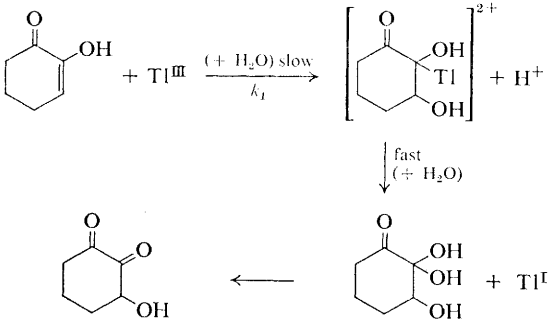
$$Tl^{III} + H_2C_2O_4 \rightleftharpoons [TlC_2O_4]^+ + 2H^+$$

being $8{\cdot}6 \times 10^2$ mol l^{-1} at 25 °C, $I = 3{\cdot}0$ mol l^{-1}, with $\Delta H^\circ = -3{\cdot}4$ kcal mol^{-1}. The subsequent decomposition:

$$[TlC_2O_4]^+ \xrightarrow{k} Tl^+ + 2CO_2$$

is slow ($k = 3 \times 10^{-5}$ s^{-1}, $\Delta H^\ddagger = 28{\cdot}4$ kcal mol^{-1}, $\Delta S^\ddagger = +13$ e.u.). The reduction of Tl^{III} by SCN^- shows a rate law second-order in thallium(III),[251] and the redox step is considered to proceed *via* an activated complex of the form $[Tl{-}SCN{-}Tl]^{5+}$. In the oxidation of cyclohexane-1,2-dione, however,[252] the rate-determining process is the formation of the thallium(III)–enolate complex, which decomposes in a fast step. Both Tl^{III} and $TlOH^{2+}$ are reactive species (Table 1), and traces of chloride catalyse the reaction. Bis-perfluorophenylthallium(III) bromide has been used as an

[248] N. P. Kirpichnikova and R. M. Nalbandyan, *Zhur. fiz. Khim.*, 1969, **43**, 2256.
[249] K. S. Gupta and Y. K. Gupta, *J. Chem. Soc.* (*A*), 1970, 256.
[250] L. B. Monsted, O. Monsted, and G. Nord(Waind), *Trans. Faraday Soc.*, 1970, **66**, 936.
[251] L. Treindl and M. Fico, *Coll. Czech. Chem. Comm.*, 1969, **34**, 2873.
[252] R. Favier and M. Zador, *Canad. J. Chem.*, 1969, **47**, 3539.



oxidant in the formation of perfluorophenyl–metal complexes.[253] With Hg_2Cl_2, for example, $(C_6F_5)_2TlBr$ produces derivatives of the metal in an oxidation state two higher than in the reactant, the Tl^{III} being reduced to Tl^{I} with transfer of the two C_6F_5 groups.

11 Actinides

The neptunium(VII) species has been prepared electrolytically in molar sodium hydroxide.[254] In dilute perchloric acid solutions, the ion oxidises water with rapid disappearance of the characteristic green colour. The reaction proceeds *via* two paths, one of which is first-order, the other second-order in neptunium(VII) with no direct evidence for participation of perchlorate in

$$\frac{-\,d[Np^{VII}]}{dt} = k_1'[Np^{VII}] + k_2'[Np^{VII}]^2$$

either route. In the case of the first mechanism, a proportionality to $[H^+]$ is also observed. Preliminary studies on the oxidations of Ag^{I}, Co^{II}, Ce^{III}, Cr^{III}, and Np^{V} by this reagent indicate that at 25 °C in 1—4M $HClO_4$ (with reactants $\sim 10^{-3}$ molar) all are complete within 10—15 s, and the estimated potential of the Np^{VII}–Np^{VI} couple is + 2·0 V. The formal potential for the Bk^{IV}–Bk^{III} couple has been measured potentiometrically in sulphuric acid (0·5—2·0 mol l^{-1}) [255] the value of 1·36 ± 0·1 V being comparable with that of cerium(IV)–(III) of 1·42 V. The oxidation of thallium(I) by neptunium(VII) has also been reported,[256] the rate:

$$\frac{-\,d[Np^{VII}]}{dt} = k'[Np^{VII}][Tl^{I}]$$

showing an acidity dependence:

$$\ln k' = \ln k + n \ln [H^+]$$

with no evidence for Tl^{II} as a kinetically important intermediate.

[253] R. S. Nyholm and P. Royo, *Chem. Comm.*, 1969, 421.
[254] J. C. Sullivan and A. J. Zeilen, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 927.
[255] J. R. Stokeley, R. D. Baybarz, and W. D. Shuets, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 877.
[256] R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, 1970, **92**, 3028.

In the oxidations of $edta^{2-}$ and oxalic acid by neptunium(VI) in perchloric acid,[257] carbon dioxide is produced. One mole of $edta^{2-}$ reacts with six moles of Np^{VI}, the rate being first-order in both reagents with an inverse hydrogen-ion dependence. On mixing the reactants, a distinct colour change is observed which is ascribed to complex formation, the

$$NpO_2^{2+} + edta^{2-} + H_2O \xrightarrow{\text{slow}} [NpO_2(OH)edta]^- + H^+$$

$$NpO_2^{2+} + edta^{2-} + H_2O \xrightarrow{\text{slow}} [NpO_2(OH)_2edta] + 2H^+$$

fractional dependence on $[H^+]^{-1}$ arising from the extent of reaction of the two Np^{VI} complex ions in the equilibrium. The products are derived in fast subsequent reactions with Np^{VI}. In the reaction with oxalic acid,[257] the rate law:

$$\frac{-\,d[Np^{VI}]}{dt} = \frac{k[Np^{VI}][H_2C_2O_4]_{tot}}{[H^+]}$$

is observed with a one-electron reduction of $Np^{VI} \rightarrow Np^{V}$. As in the case of the edta reaction, complex formation is observed, the reaction:

$$NpO_2^{2+} + H_2C_2O_4 + H_2O \xrightarrow{\text{slow}} [NpO_2(OH)H_2C_2O_4]^+ + H^+$$

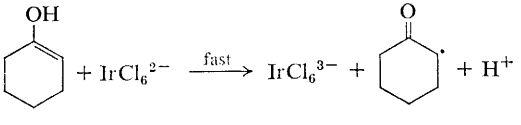
being followed by further fast reactions of the complex with NpO_2^{2+} to yield NpO_2^+.

12 Miscellaneous Reagents

The nature of hexachloroiridate(IV) in solution has been examined.[258] In neutral or weakly acidic media, the reaction $IrCl_6^{2-} \rightarrow Ir^{III}$ may take place, but it occurs spontaneously in solutions of pH 11, with evolution of a gas and a colour change from reddish-brown (Ir^{IV}) to pale yellow-green (Ir^{III}). The equilibrium:

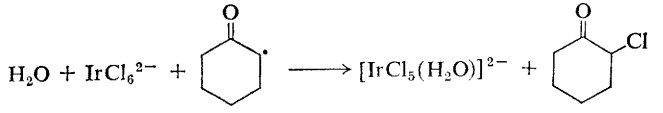
$$2IrCl_6^{2-} + 2OH^- \rightleftharpoons 2IrCl_6^{3-} + \tfrac{1}{2}O_2 + H_2O$$

lies well to the right at 25 °C. The spontaneous reduction is followed by hydroxylation, and there may be re-oxidation to give polymeric hydroxy-complexes of Ir^{IV}. A survey of oxidations of organic substrates by $IrCl_6^{2-}$ has been made,[259] the rate-determining step in the case of mandelic, oxalic, and pyruvic acids being the attack by the hexachloroiridate(IV) species. In the corresponding reaction with cyclohexanone,[260] the one-equivalent oxidation of the enol form proceeds *via* an outer-sphere



[257] N. K. Shastri and E. S. Amis, *Inorg. Chem.*, 1969, **8**, 2484, 2487.
[258] D. A. Fine, *Inorg. Chem.*, 1969, **8**, 1014.
[259] R. Cecil, A. J. Fear, and J. S. Littler, *J. Chem. Soc.* (*B*), 1970, 632.
[260] R. Cecil, J. S. Littler, and G. Easton, *J. Chem. Soc.* (*B*), 1970, 626.

mechanism yielding the 2-oxocyclohexyl radical, which then further reacts with hexachloroiridate(IV) in an inner-sphere (ligand transfer) step to produce 2-chlorocyclohexanone and aquopentachloroiridate(III). The reactions of $[(H_2O)IrCl_5]^{2-}$, $[(H_2O)_2IrCl_4]^-$, and $IrBr_6^{2-}$ are all similar to



that shown above. The effect of activation of hexachloroiridate(III) complexes on the value of the redox potential of the $IrCl_6^{4-}$–$IrCl_6^{3-}$ couple has also been described.[261]

Two studies are reported on the oxidation of iodide by octacyanomolybdate(v) ions.[262, 263] For the reaction:

$$2[Mo(CN)_8]^{3-} + 3I^- \longrightarrow 2[Mo(CN)_8]^{4-} + I_3^-$$

the simple second-order rate law:

$$\frac{-\,d[Mo(CN)_8^{3-}]}{dt} = k_0[Mo(CN)_8^{3-}][I^-]$$

is observed, in contrast to the more complicated expressions found for other transition-metal cyanide complexes. There is, however, some evidence for retardation of the reaction by the product $[Mo(CN)_8]^{4-}$. The mechanism may be written as:

$$[Mo(CN)_8]^{3-} + I^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Mo(CN)_8]^{4-} + I^{\bullet} \qquad (13)$$

$$2I^{\bullet} \xrightarrow{\text{fast}} I_2$$

$$I_2 + I^- \xrightarrow{\text{fast}} I_3^-$$

the reversibility in reaction (13) being suggested from the deviation from linearity of first-order plots. The variation of rate constant with ionic strength (I) may be expressed in the form,[261]

$$\log k_2 = \log k_1 + 1{\cdot}02\, Z_A Z_B \sqrt{I}$$

where $Z_A Z_B = 3{\cdot}06$, suggesting that ion pairs do not play an important role in this reaction. The value of $\Delta S^{\ddagger} = -40$ e.u. for the reaction corresponding to k_2 is in good agreement with the value of -30 e.u. calculated from the equation $\Delta S^{\ddagger} = -10 Z_A Z_B$, which assumes that, among other things, the only contribution to the entropy of activation arises from the electrostatic free-energy term. Specific salt effects may be written in the order[262] $Et_4N^+ \ll Li^+ < (C_2H_4OH)_4N^+ \simeq Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Ba^{2+}$. The oxidation of halide ions by bismuth(v) has

[261] V. I. Kravtsov, *Elektrokhimiya*, 1969, **5**, 327.
[262] M. H. Ford-Smith and J. H. Rawsthorne, *J. Chem. Soc.* (*A*), 1969, 160.
[263] F. Ferranti, *J. Chem. Soc.* (*A*), 1970, 134.

been investigated,[264] with evidence for Bi^{IV} as an intermediate. The rates of the reaction:

$$Bi^{V} + 2X^{-} \longrightarrow Bi^{III} + X_2$$

where $X^- = I^-$, Cl^-, or Br^-, are identical and zero-order with respect to halide ion concentration. The mechanism:

$$Bi^{V} + H_2O \underset{}{\overset{k_1}{\rightleftharpoons}} Bi^{IV} + OH^{\bullet} + H^{+}$$

$$Bi^{IV} + X^{-} \xrightarrow{\text{fast}} Bi^{III} + X^{\bullet}$$

$$OH^{\bullet} + X^{-} \xrightarrow{\text{tast}} OH^{-} + X^{\bullet}$$

$$2X^{\bullet} \xrightarrow{\text{fast}} X_2$$

is proposed, with $k_1 \sim 160\ s^{-1}$ at $T = 25\ °C$, $I = 2{\cdot}0\ mol\ l^{-1}$; and the suggestion is made that the electrode potential for the Bi^{V}–Bi^{IV} couple is $\leqslant 2{\cdot}0$ V.

The one-electron oxidation:

$$2W_2Cl_9^{3-} + X_2 \longrightarrow 2W_2Cl_9^{2-} + 2X^{-}$$

has been studied in dichloromethane[265] where X = Cl, Br, or I, and there is no incorporation of the oxidant into the anion. The structure of the oxidised species is still not completely assigned. Studies of this type are important in that metal–metal bonding is in part responsible for the stability of metal clusters, and such oxidations will result in either partial or complete loss of those electrons which are extensively involved in these metal–metal bonds.

The preparation, spectrum, and stability of indium(I) in aqueous solution have been described,[266] concentrations of $\sim 3 \times 10^{-4}\ mol\ l^{-1}\ In^{I}$ being prepared by anodisation of an indium electrode. Conventional techniques have been used to investigate the reaction:

$$In^{I} + 2H^{+} \longrightarrow In^{III} + H_2$$

The rate law may be expressed as:

$$\frac{-\,d[In^{I}]}{dt} = k_1[In^{I}][H^{+}]$$

with no evidence for a dependence on In^{III}, the mechanism involving the intermediate formation of In^{II}:

$$In^{I} + H^{+} \xrightarrow{k_1} In^{II} + H^{\bullet}$$

$$In^{II} + H^{+} \xrightarrow{\text{fast}} In^{III} + H^{\bullet}$$

$$H^{\bullet} + H^{\bullet} \xrightarrow{\text{fast}} H_2$$

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

[264] M. H. Ford-Smith and J. J. Habeeb, *Chem. Comm.*, 1969, 1445.
[265] R. Saillant and R. A. D. Wentworth, *J. Amer. Chem. Soc.*, 1969, **91**, 2174.
[266] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2419.

The spectrum of In^{II} has also been derived (Figure 3) by the pulse radiolysis of 10^{-2} mol l^{-1} In^{III} solutions in lithium perchlorate. The radiolysis of aqueous solutions of hexammine- and chloropentammine-ruthenium(III) shows the rate constant (k_1) for the reaction:[267]

$$e_{aq}^- + [Ru(NH_3)_6]^{3+} \xrightarrow{k_1} [Ru(NH_3)_6]^{2+}$$

to be $6{\cdot}8 \pm 0{\cdot}1 \times 10^{10}$ l mol^{-1} s^{-1}, and that for the similar reduction of $[Ru(NH_3)_5Cl]^{2+}$ to be $6{\cdot}2 \times 10^{10}$ l mol^{-1} s^{-1}, with aquation of the

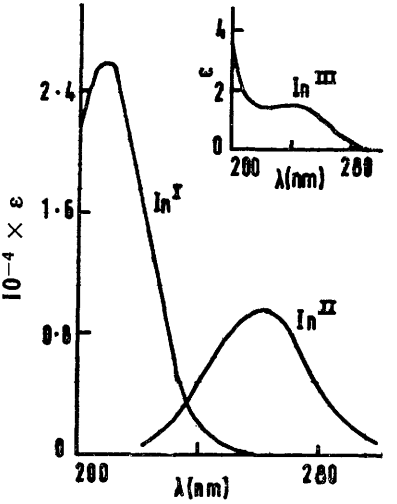


Figure 3 *Spectra of indium*(I), *indium*(II), *and indium*(III) *in aqueous perchlorate media,* μ = 0·7M $LiClO_4$

$[Ru(NH_3)_5Cl]^+$ produced to yield $[Ru(NH_3)_5H_2O]^{2+}$. This aquo ion reduces the pentamminechloro-complex in the reaction:

$$[Ru(NH_3)_5H_2O]^{2+} + [Ru(NH_3)_5Cl]^{2+} \xrightarrow{k_2} [Ru(NH_3)_5H_2O]^{3+} + [Ru(NH_3)_5Cl]^+$$

with $k_2 = 1 \times 10^3$ l mol^{-1} s^{-1}. The oxidation of $[Ru(NH_3)_6]^{3+}$ by hydroxyl radicals yields $[Ru(NH_3)_6]^{4+}$, which is considered to disproportionate according to the reaction:

$$2[Ru(NH_3)_6]^{4+} \xrightarrow{k} [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{5+}$$

where $k = 4{\cdot}5 \times 10^9$ l mol^{-1} s^{-1}, with further slower reactions to give oxy-compounds of the higher oxidation states of ruthenium. Similar reactions are reported for $[Ru(NH_3)_5Cl]^{2+}$. Studies have been made on the nature of ruthenium(IV) and its reduction products in perchlorate solutions,[268] ion-exchange and membrane studies indicating that Ru^{IV} is

[267] J. H. Baxendale, M. A. J. Rodgers, and M. D. Ward, *J. Chem. Soc.* (*A*), 1970, 1246.
[268] R. M. Wallace and R. C. Propst, *J. Amer. Chem. Soc.*, 1969, **91**, 3779.

tetrameric. Coulometry and cyclic voltammetry show that the tetramer may be reduced reversibly by two one-electron processes to yield species with formal oxidation states of 3·75 and 3·5. Ru(3·5) is reduced irreversibly to a transient Ru^{III} species which rapidly converts to a stable polymeric Ru^{III} complex. Correlations between polarographic and spectral parameters have also been described for some di-acidotetramminerhodium(III) complexes,[269] the energy for the process:

$$Rh^{III}(t_{2g}^6) \longrightarrow Rh^{I}(t_{2g}^6\, e_g^2)$$

being decreased by substitution of an ethylenediamine group by heteroligands. Studies on the rhenium(v)–nitrate reaction have been reported,[270] the rapid reaction of $[ReCl_4O(OH_2)]^-$ with NO_3^- in 10M HCl following the equation:

$$Re^V + NO_3^- \xrightarrow{k_1} ReO_4^- + NO_2^-$$

A subsequent slower reaction with NO_2^- has the stoicheiometry:

$$5Re^V + NO_2^- \xrightarrow{k_2} 3ReO_4^- + 2[ReCl_5NO]^{2-}$$

both systems being first-order in each reactant, the second-order rate constants at 25 °C being $k_1 = 2{\cdot}19\ l\,mol^{-1}\,s^{-1}$ and $k_2 = 0{\cdot}64\ l\,mol^{-1}\,s^{-1}$. In the Re^V–NO_3^- reaction, the labile H_2O group *trans* to the multiply-bonded oxygen atom in $[ReCl_4O(H_2O)]^-$ may be replaced in an initial equilibrium step by NO_2^+ followed by a two-electron transfer from Re^V to N^V to yield the Re^{VII} and N^{III} products:

$$[ReCl_4O(OH_2)]^- + NO_2^+ \underset{k_b}{\overset{k_a}{\rightleftharpoons}} [ReCl_4(O)(ONO)] + H_2O$$

$$[ReCl_4(O)(ONO)] \xrightarrow{k_c} ReO_4^- + NO_2^- + [Re^{VII}—N^{III}]$$

The rate-determining step may be either the association of the NO_2^+ into the inner sphere of the Re^V or (more likely) the electron-transfer process. The second reaction with NO_2^- is considered to involve an associative equilibrium step with NO^+. The monomeric product $[ReCl_5NO]^{2-}$ is an octahedral complex, and exchange studies show that one of the chloride ions is exchanged at a rate $\sim 10^2$ times faster than the other four. The technetate ion (TcO_4^{2-}) has been shown[271] to disproportionate rapidly in aqueous alkaline media. In the electrochemical reduction of $Tc^{VII} \rightarrow Tc^{VI}$, if gelatine is present in the solution, the reaction:

$$2TcO_4^{2-} \xrightarrow{k_1} TcO_4^- + TcO_4^{3-}$$

[269] D. R. Crow, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 291.
[270] J. A. Casey and R. K. Murmann, *J. Amer. Chem. Soc.*, 1970, **92**, 78.
[271] G. Kissel and S. W. Feldberg, *J. Phys. Chem.*, 1969, **73**, 3082.

takes place with $k_1 \sim 1{\cdot}5 \times 10^5\ l\ mol^{-1}\ s^{-1}$ at $I = 1{\cdot}0\ mol\ l^{-1}$. The kinetics of the oxidation of ascorbic acid by osmium(VIII) have been studied in the presence of HCl.[272] The reactive organic substrate in the conditions used is the ascorbate anion, (AH^-) the rate-determining step being:

$$H_2OsO_5 + AH^- \longrightarrow A + H_2OsO_4 + OH^-$$

The redox nature of palladium(II) salts has been investigated, methods being described for the study of the rates of oxidation of olefins.[273] The reduction of benzoquinone by π-allylpalladium chloride in aqueous hydrochloric acid solutions has also been reported.[274]

13 Peroxodisulphate

The kinetics of oxidation of six iron(II) complexes containing 2,2′-bipyridyl or 1,10-phenanthroline as ligands have been studied,[275] the mechanism postulated being:

$$[Fe(AA)_3]^{2+} + S_2O_8^{2-} \underset{}{\overset{K}{\rightleftharpoons}} [Fe(AA)_3^{2+}.S_2O_8^{2-}]$$

$$[Fe(AA)_3^{2+}.S_2O_8^{2-}] \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} [Fe(AA)_3]^{3+} + SO_4^{2-} + SO_4^-$$

$$SO_4^- + [Fe(AA)_3]^{2+} \xrightarrow[\text{fast}]{k_2} [Fe(AA)_3]^{2+} + SO_4^{2-}$$

where (AA) represents the chelating species. Evidence for the equilibrium step is given by the decrease in the second-order rate constants with increasing $S_2O_8^{2-}$ concentration. Assuming the equilibrium to be rapidly established, in the presence of a large excess of $S_2O_8^{2-}$:

$$k_{obs} = \frac{k_1 K}{1 + K[S_2O_8^{2-}]}$$

and from plots of $1/k_{obs}$ *versus* $1/[S_2O_8^{2-}]$, both k_1 and K have been evaluated (Table 1). The presence of alcohol is seen to retard the reaction due to interaction with the SO_4^- radical. Linear plots are observed of $\Delta G^{\ddagger}$ against ΔG^{o} (Figure 4), the overall free energy for the redox reaction, but the value for the slope deviates from that predicted by the Marcus theory for a series of chemically related redox systems. The extensive electron delocalisation of the π-system of the ligands may not favour the electron

[272] U. S. Mehrotra and S. P. Mushran, *Canad. J. Chem.*, 1970, **48**, 1148.
[273] M. N. Vargavtik, O. G. Levanda, A. P. Belov, L. M. Zakharova, and I. I. Moiseev, *Kinetika i Kataliz*, 1969, **10**, 1016.
[274] A. P. Belov, I. I. Moiseev, N. G. Satsko, and Y. K. Sirkin, *Izvest. Akad. Nauk, S.S.S.R., Ser khim*, 1969, 2573.
[275] S. Raman and C. H. Brubaker, jun., *J. Inorg. Nuclear Chem.*, 1969, **31**, 1091.

transfer process, and it is difficult to distinguish between an outer- and inner-sphere mechanism. Although the contact between the Fe^{II} nucleus and the $S_2O_8^{2-}$ is not easily established, it is sterically possible to accommodate a peroxodisulphate ion between the ligands. An important factor in determining the reaction rate is the large free-energy of the oxidation step, the high negative entropies of activation being described in terms of formation of the intermediate.

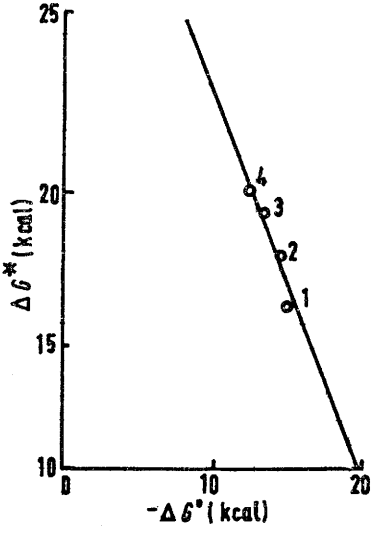


Figure 4 *Correlation between free-energy of activation and the standard free-energy of the redox step for reactions of*: (1) $[Fe(4,4'\text{-dimethyl-bipy})_3]^{2+}$; (2) $[Fe(bipy)_3]^{2+}$; (3) $[Fe(5\text{-Me-phen})_3]^{2+}$; (4) $[Fe(phen)_3]^{2+}$ *with peroxodisulphate*
(Reproduced by permission from *J. Inorg. Nuclear Chem.*, 1969, **31**, 1091)

In the reaction with antimony(III) [276] the rate expression is:

$$\frac{-\,d[Sb^{III}]}{dt} = k[S_2O_8^{2-}][Sb^{III}]$$

with no evidence for variation with hydrogen ion or catalysis by silver(I), a chain mechanism involving the reactions:

$$SO_4^- + Sb^{III} \longrightarrow SO_4^{2-} + Sb^{IV}$$

and:

$$Sb^{IV} + S_2O_8^{2-} \longrightarrow Sb^{V} + SO_4^{2-} + SO_4^-$$

being postulated. The kinetics of the oxidation of cerium(III) induced by

[276] A. P. Bhargava and Y. K. Gupta, *Z. phys. Chem.* (*Leipzig*), 1969, **242**, 327.

cobalt-60 γ-radiation have been reported [277] and a value [278] of $1{\cdot}06 \times 10^{10}$ l mol^{-1} s^{-1} derived for the rate of the reaction:

$$e^- + S_2O_8^{2-} \longrightarrow SO_4^- + SO_4^{2-}$$

Studies on the kinetics and mechanism of the oxidation of ascorbic acid [279] show the rate to be independent of the concentration of organic substrate. A chain mechanism is proposed with reaction between the radical anion of ascorbic acid and the peroxodisulphate ion. Although the influence of neutral salts is negligible and that of acid slight, the presence of allyl acetate strongly inhibits the rate, suggesting the formation of SO_4^- radical ions. In the reaction with lactic acid,[280] a similar rate expression is observed although the description of the mechanism is different.

Metal ions are known to catalyse oxidations involving peroxodisulphate, especially silver(I), and the catalysis of the oxidation of $[Ru(bipy)_3]^{2+}$ has been described in the presence of this ion.[281] The chelated complex is inert to hydrolysis and oxidised only slowly in the absence of metal ions. The mechanism in sulphuric acid (Scheme 11) involves the formation of a weak 1 : 1 complex between Ag^+ and $S_2O_8^{2-}$, with subsequent rapid reactions of

$$Ag^+ + S_2O_8^{2-} \rightleftharpoons AgS_2O_8^-$$

$$[Ru(bipy)_3]^{2+} + AgS_2O_8^- \xrightarrow{k_1} [Ru(bipy)_3]^{3+} + Ag^{II} + 2SO_4^{2-}$$

$$AgS_2O_8^- \xrightarrow{k_2} Ag^{II} + SO_4^- + SO_4^{2-}$$

$$Ag^+ + SO_4^- \xrightarrow{\text{fast}} Ag^{II} + SO_4^{2-}$$

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

Scheme 11

an intermediate postulated as Ag^{II}. In nitrate media, however, the rate-determining step is considered to be the disproportionation of two moles of $AgS_2O_8^-$. In the corresponding reaction with ethyleneglycol,[282] the reaction is first-order with respect to oxidant and silver(I), and zero-order in substrate. A similar dependence is observed in the oxidative decarboxylation of carboxylic acids.[283, 284] Here the catalytic mechanism is explained [283] by the scheme:

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

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

[277] R. W. Matthews, H. A. Mahlman, and T. J. Sworski, *J. Phys. Chem.*, 1970, **74**, 2475.
[278] W. Roebke, M. Renz, and A. Henglein, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 39.
[279] U. S. Mehrotra and S. P. Mushran, *Indian J. Chem.*, 1970, **47**, 41.
[280] K. Kumar and L. K. Saxena, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1053; 1970, **32**, 1050.
[281] J. D. Miller, *J. Chem. Soc.* (*A*), 1969, 2348.
[282] M. M. Khan and S. P. Srivastava, *Indian J. Chem.*, 1969, **46**, 574.
[283] J. M. Anderson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1970, **92**, 1651.
[284] S. P. Srivastava and S. K. Singhal, *Indian J. Chem.*, 1969, **46**, 705.

$$Ag^{II} + RCO_2H \longrightarrow Ag^{I} + RCO_2^{\bullet} + H^+$$
$$RCO_2^{\bullet} \longrightarrow R^{\bullet} + CO_2$$
$$R^{\bullet} + Ag^{II} \longrightarrow Ag^{I} + R_{ox}^{+}$$

where R_{ox}^+ represents an alcohol, alkane, or ester. The silver(II) species is considered directly responsible for the decarboxylation, the absence of any significant difference in the rates involving pivalic, isobutyric, and n-butyric acids militating against simultaneous fission of the alkyl-carbon bond in the decarboxylation step. The co-catalysis with copper(II) has also been investigated, the formation of alkyl radical intermediates being supported by the independence of the reaction rate at relatively low copper(II) concentrations due to the efficient scavenging action by this ion for such intermediate species. In the catalysis of the oxidation of tellurium(IV),[285] a chain mechanism is suggested involving copper(I) formed by reaction of the cupric species with $HO_2^{\bullet}$ radicals. A similar mechanism is also described for the copper-ion-catalysed oxidation of antimony(III).[286] The catalysis of the reactions with malic and lactic acids by mercury(II) probably involves the formation of both Hg^{I} and Hg^{0} in the overall reaction scheme.[287]

The oxidation of vanadium(IV) by peroxodiphosphate has been reported in aqueous acidic solutions,[288] two vanadyl ions being oxidised per $P_2O_8^{4-}$:

$$H_2P_2O_8^{2-} + 2VO^{2+} + 2H_2O \longrightarrow 2H_2PO_4^{-} + 2VO_2^{+} + 2H^+$$

The reaction is first-order in both vanadium(IV) and oxidant, the mechanism being:

$$VO^{2+} + H_2P_2O_8^{2-} \longrightarrow VO_2^{+} + PO_4^{3-} + PO_4^{2-} + 2H^+$$
$$VO^{2+} + PO_4^{2-} + H_2O \xrightarrow{\text{fast}} VO_2^{+} + PO_4^{3-} + 2H^+$$

Although peroxodisulphate often oxidises through an outer-sphere mechanism, it is considered that in the case of peroxodiphosphate, an inner-sphere route is preferred. Also, the fact that $S_2O_8^{2-}$ will not oxidise V^{IV} or Mn^{II}, whereas $H_2P_2O_8^{2-}$ does, is attributed to kinetic rather than thermodynamic differences.

14 Halogens and Oxy-halogeno-species

The oxidation of tris-(1,10-phenanthroline)iron(II) by chlorite, chlorate, and chlorine dioxide has been investigated,[289a] and the mechanism compared with that for the reaction of chlorine.[289b] In the case of ClO_2^- and Cl_2, the reaction rate is controlled by the first dissociation step of the $[Fe(phen)_3]^{2+}$

[285] R. K. Shinghal, M. C. Agrawal, and S. P. Mushran, *Indian J. Chem.*, 1969, **46**, 1025.
[286] A. P. Bhargava, Y. K. Gupta, and K. S. Gupta, *J. Inorg. Nuclear Chem.*, 1969, **31**, 777.
[287] K. Kumar and L. K. Saxena, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2801; *Bull. Chem. Soc. Japan*, 1969, **42**, 3148.
[288] M. Anderson, J. O. Edwards, Sister A. A. Green, and Sister M. D. Wiswell, *Inorg. Chim. Acta*, 1969, **3**, 655.
[289a] B. Z. Shakhashiri and G. Gordon, *J. Amer. Chem. Soc.*, 1969, **91**, 1103.
[289b] B. Z. Shakhashiri and G. Gordon, *Inorg. Chem.* 1968, **7**, 2454.

complex, the product being an iron(III) dimeric species:

$$[Fe(phen)_3]^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(phen)_2]^{2+} + phen$$

$$[Fe(phen)_2]^{2+} + ClO_2^- \xrightarrow{k_3} [(phen)_2Fe{-}O{-}Fe(phen)_2]^{4+}$$

or

$$[Fe(phen)_2(OH)]_2$$

a calculated value of k_3 being $\sim 3 \times 10^5$ l mol^{-1} s^{-1}. The detailed mechanism of the redox step is, however, still uncertain. No detectable reaction takes place between $[Fe(phen)_3]^{2+}$ and ClO_3^- under a variety of conditions, confirming the observation that of all the chlorine oxidants the chlorate ion is the slowest to react with metal ions.[290] In the reaction with ClO_2, the major product in the presence of a large excess of oxidant was $[Fe(phen)_3]^{3+}$, and since the reaction rate exceeds that for the dissociation of $[Fe(phen)_3]^{2+}$, it is concluded that the mechanism involves an outer-sphere route. It is of interest to note that most oxidants of $[Fe(phen)_3]^{2+}$ may be classified into one of two categories depending on whether $[Fe(phen)_3]^{3+}$ is formed as the principal product: Ce^{IV}, Co^{III}, Mn^{III}, Cl_2, and ClO_2 all react rapidly, forming this oxidised complex, whereas ClO_2^- and $P_2O_8^{4-}$ are much slower to react, with formation of dimers. The corresponding reaction with MnO_2 involves the reduction of Mn^{IV} to Mn^{II} in two one-electron steps whereas that with H_2O_2 falls into the second category. Homogeneous oxidation rates for the reaction of chlorite ion with iron(II) and copper(II) complexes have been derived in a polarographic study.[291] The reaction orders for iron(II)–citrate, –tartrate, and –edta complexes and for copper(I)–ammine species are first-order in both chlorite and the reduced reactant. In 1M NH_3–1M NH_4Cl medium, the oxidation rates of the citrate and tartrate complexes are not reproducible (rate constants being 10^3—10^4 l mol^{-1} s^{-1}) due to the presence of polymeric species in slow equilibrium with the monomeric ions. The generation of catalytic current derives from the process:

$$ML_p^{z+} + ne^- \xrightarrow{k_s} ML_p^{(z-n)+}$$

and:

$$2H_2O + \alpha ML_p^{(z-n)+} + ClO_2^- \xrightarrow{k_h} Cl^- + \alpha ML_p^{z+} + 4OH^-$$

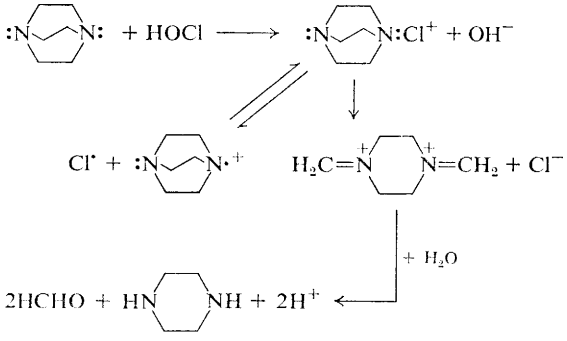
where k_s represents the electrochemical reduction rate constant and k_h the homogeneous rate; $\alpha = 4/n$, with n the number of electrons involved in the electrochemical reduction. For the reaction:

$$[Cu(NH_3)_2]^+ + 2NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + e^-$$

the relatively slow rate of oxidation is attributed to the effect of ligand rearrangement, and it may be that the rate of oxidation of such species

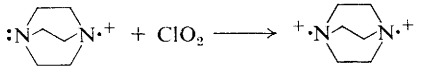
[290] R. C. Thompson and G. Gordon, *Inorg. Chem.*, 1966, **5**, 562.
[291] R. L. Birke and W. L. Marzluff, *J. Amer. Chem. Soc.*, 1969, **91**, 3481.

is governed by their structure. Since in these reactions the overall process involves the rupture of all the oxygen bonds of the oxyanion, the rate-determining step may be either electron transfer from the central metal ion to an orbital on the halogen, or an atom transfer involving an oxygen atom with a two-equivalent exchange. The role of cationic intermediates has also been reported in the oxidation of triethylenediamine by ClO_2 and hypochlorous acid.[292] The reaction mechanism may be written as in Scheme 12,



Scheme 12

with further oxidation of the cyclic diamine to ethylenediamine. The cationic radical has been identified by e.s.r. techniques. The reaction of ClO_2 again involves the cationic radical, which undergoes further oxidation to yield the dipositive species, which with subsequent hydrolysis gives the same products as identified previously.



The kinetics and mechanism of the oxidation of aromatic aldehydes by bromine have been investigated, the rate of production of benzoic acid being little affected by substitution of the aldehyde.[293] Radical bromine ions Br_2^- have also been used as an oxidant.[294] Flash photolysis of 10^{-3} mol l^{-1} sodium bromide solutions may be used to generate the radical anions:

$$Br^- \xrightarrow{h\nu} Br^{\bullet} + e^-$$

$$Br^- + Br^{\bullet} \longrightarrow Br_2^-$$

and in the absence of substrates the second-order decay of the species may be described as:

$$Br_2^- + Br_2^- \longrightarrow Br_3^- + Br^-$$

[292] L. A. Hull, W. P. Giordano, D. H. Rosenblatt, G. T. Davis, C. K. Mann, and S. B. Milliken, *J. Phys. Chem.*, 1969, **73**, 2147.
[293] I. R. L. Barker and R. H. Dahm, *J. Chem. Soc.* (*B*), 1970, 650.
[294] A. T. Thornton and G. S. Laurence, *Chem. Comm.*, 1970, 443.

and:

$$Br_2^- + e^- \longrightarrow 2Br^-$$

If Fe^{2+} or Mn^{2+} and Co^+ are present, however, reactions of the type:

$$M^{x+} + Br_2^- \longrightarrow M^{(x+1)+} + 2Br^-$$

take place, no interaction being observed between Co^{II} and the oxidant. The similarity of the rate constant for the ferrous ion with that for the exchange rate of the hexaquo cation suggests in this instance that the rate-determining step is the substitution of Br_2^- into the inner co-ordination sphere of the metal ion, the formation of the transient $FeBr^{2+}$ confirming this view. A relatively long-lived complex in the reaction of Mn^{II} may be $MnBr^{2+}$. The formation of radical anions of this type has also been examined in the case of I_2^- and $(CNS)_2^-$,[295] use being made of pulse radiolysis to generate the hydroxyl radical, which then oxidises the ions:

$$X^- + OH^\bullet \xrightarrow{k_1} X^\bullet + OH^-$$

with $k_1 \sim 3 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$. The rate constant for the forward rate (k_2) in the equilibrium:

$$I^- + I^\bullet \underset{}{\overset{k_2}{\rightleftharpoons}} I_2^-$$

is $\sim 7 \times 10^9\,mol^{-1}\,s^{-1}$ with the enthalpies of formation of the species (ΔH) having values $-5{\cdot}6$ and $-6{\cdot}4\,kcal\,mol^{-1}$ for I_2^- and $(CNS)_2^-$ respectively. The oxidation of hydrazoic acid by bromate has been studied in perchlorate media.[296] In the presence of excess reductant, N_2 and N_2O are the sole products, the rate law being expressed in the form:

$$\frac{-\,d[BrO_3^-]}{dt} = k_0[BrO_3^-][HN_3][H^+].$$

The reactions were carried out with some allyl alcohol in solution to scavenge the hypobromous acid product, and ^{18}O tracer studies indicate that most but not all of the oxygen of the nitrous oxide product is derived from the solvent. Also, ^{15}N studies may be rationalised by the mechanism:

$$BrO_3^- + H\overset{*}{N}\overset{*}{N}N + H^+ \xrightarrow{\text{slow}} HBrO_2 + \overset{*}{N}N + \overset{*}{N}OH$$

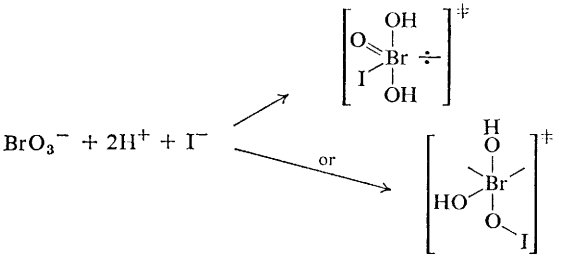
$$HBrO_2 + H\overset{*}{N}\overset{*}{N}N \longrightarrow HOBr + \overset{*}{N}N + \overset{*}{N}OH$$

$$2\overset{*}{N}OH \longrightarrow \overset{*}{N}\overset{*}{N}O + H_2O$$

the isotopic composition of the products being as shown. A mechanism involving $N_3^\bullet$ radicals is discounted, since these have previously been shown to combine rapidly to form nitrogen exclusively. In the reaction

[295] J. H. Baxendale and P. L. T. Bevan, *J. Chem. Soc.* (*A*), 1969, 2240.
[296] R. C. Thompson, *Inorg. Chem.*, 1969, **8**, 1891.

between bromate and iodide ions,[297] however, a slightly different rate law is observed, the transition state being formulated in one of two ways:



This reaction, and that involving iodate as oxidant, is catalysed by carboxylate and phosphate ions. The autocatalytic oxidation of cerium(III) by bromate has also been reported.[298] The reduction of hexahydroxoantimonate(v) by iodide has been studied in acidic media,[299] the mechanism

$$Sb^{V} + 3I^{-} \longrightarrow Sb^{III} + I_3^{-}$$

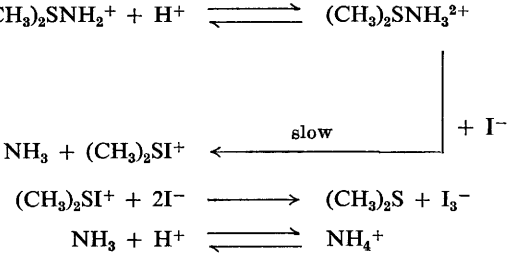
involving protonation in pre-equilibrium steps, the order with respect to reductant being 2. The reaction orders in the corresponding system involving arsenic acid [300] are complex, the mechanism being postulated to involve As^{V} as the reactive intermediate. The kinetics and mechanism of

$$(CH_3)_2SNH_2^{+} + 3I^{-} + 2H^{+} \longrightarrow (CH_3)_2S + NH_4^{+} + I_3^{-}$$

the iodide reduction of *SS*-dimethylsulphiminium perchlorate have been investigated [301] in water and DMSO–water mixtures, the rate law being:

$$\frac{d[I_3^{-}]}{dt} = k_1[(CH_3)_2SNH_2^{+}][I^{-}][H^{+}]$$

The reaction is catalysed by thiourea but not by Br^{-} or Cl^{-}, the mechanism involving a nucleophilic displacement at the sulphur centre:



[297] A. F. M. Barton and G. A. Wright, *J. Chem. Soc.* (*A*), 1968, 1747.
[298] V. A. Vavillin and A. M. Zhabotinskii, *Kinetika i Kataliz*, 1969, **10**, 83.
[299] A. Bahsoun and J. Lefebvre, *Bull. Soc. chim. France*, 1970, 881.
[300] F. Secco, A. Indelli, and P. L. Bonora, *Inorg. Chem.*, 1970, **9**, 337.
[301] J. H. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 4974.

In the oxidation of mandelic acid by metaperiodic acid,[302] a complex is formed which is considered to be the reactive intermediate.

15 Miscellaneous Oxidations

The oxidation of metal thiocyanates by nitric and nitrous acids has been reported,[303, 304] the reaction being autocatalytic in nitrous acid. In ~ 1M-HNO_3, the products are H_2SO_4, HCN, $S(CN)_2$, and HNO_2, the first two species predominating in the early stages of the reaction. The mechanism involves the formation of dinitrogen tetroxide, which oxidises isothiocyanic acid to hypothiocyanous acid, which is then converted to thiocyanogen:

$$H^+ + SCN^- \underset{\text{rapid}}{\rightleftharpoons} HNCS$$

$$H^+ + HNO_2 + NO_3^- \rightleftharpoons N_2O_4 + H_2O$$

$$N_2O_4 + HNCS \longrightarrow HOSCN + N_2O_3$$

$$N_2O_3 + H_2O \underset{\text{rapid}}{\rightleftharpoons} 2HNO_2$$

$$HOSCN + H^+ + SCN^- \rightleftharpoons (SCN)_2 + H_2O$$

$$CN^- + (SCN)_2 \longrightarrow S(CN)_2 + SCN^-$$

$$HOSCN \longrightarrow HO_2SCN \longrightarrow HO_3SCN$$

$$HO_3SCN + H_2O \longrightarrow H_2SO_4 + HCN$$

$$H^+ + HNO_2 + SCN^- \longrightarrow NOSCN + H_2O$$

The transient red colour of the solutions is ascribed to the formation of the nitrosyl thiocyanate. The copper(II)-catalysed reaction of hydroxylamine and peroxonitrite in alkali has been investigated.[305] In the absence of oxygen, the reaction:

$$2NH_2OH + 2ONO_2^- \longrightarrow 2NO_2^- + N_2O + 3H_2O$$

takes place *via* the formation and dimerisation of a nitroxyl ion NO^-. When oxygen is present, however, the hydroxylamine is oxidised to nitrite without apparent loss of peroxonitrite, the mechanism being:

$$ONO_2^- + NH_2OH + OH^- \xrightarrow{Cu^{II}} NO^- + NO_2^- + 2H_2O$$

$$NO^- + O_2 \longrightarrow ONO_2^-$$

Complexes of the type $Ge(OH)_2L$ and $Ge(OH)_2L_2$ have been postulated in the polarographic reduction of germanium(IV) in acidic catechol media [306] where it is considered that the *trans*-effect in the mixed complexes increases

[302] P. S. Verma and K. C. Grover, *Indian J. Chem.*, 1969, **46**, 141.
[303] G. Stedman and P. A. E. Whincup, *J. Chem. Soc.* (*A*), 1969, 1145.
[304] M. N. Hughes, E. D. Phillips, G. Stedman, and A. E. Whincup, *J. Chem. Soc.* (*A*), 1969, 1148.
[305] M. N. Hughes and H. G. Nicklin, *J. Chem. Soc.* (*A*), 1970, 925.
[306] R. G. Canham, D. A. Aikens, N. Winograd, and G. Mazepa, *J. Phys. Chem.*, 1970, **74**, 1082.

the release of the co-ordination sphere on interaction of the germanium at the electrode.

The hexachloroantimonate(v) ion has been shown to act as a one-electron oxidant in electron transfer reactions with organic substrates,[307] complex chlorides of Sb^{III} being produced. The reaction with iodide is fast, and it

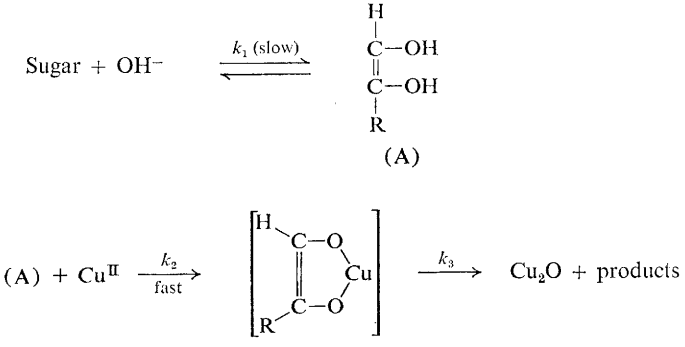
$$SbCl_6^- + 3I^- \xrightarrow{MeOH} Sb^{III} + I_3^-$$

is considered that the redox potential of the Sb^V–Sb^{III} couple differs little from that in water. The oxidation of ferrocene occurs readily:

$$[X^+][SbCl_6^-] + 2Fe(C_5H_5)_2 \longrightarrow [X^+][SbCl_6^{3-}] + 2Fe(C_5H_5)_2^+$$

and when $X^+ = Ph_3C^+$ the products were formed immediately, the system being unaffected by the presence of oxygen, demonstrating that the electron transfer involves the antimony(v) species and not the carbonium ion.

Several studies have been made of the oxidation of sugars by metal ions in alkaline or ammoniacal media. The kinetics of the oxidation of glucose and fructose in ammoniacal silver nitrate have been studied,[308] and in the reaction of *l*-sorbose, *d*-galactose, and xylose with hexacyanoferrate(III) in the presence of NH_3 [309, 310] the reaction is zero-order with respect to the oxidant and first-order in sugar concentration. Studies of the reaction between disaccharides [311] and sugars [312] and copper(II) in alkali again exhibit a rate law zero-order in metal ion. A mechanism consistent with these data may be expressed as:



The reaction of sugar with alkali forms an enediol which rapidly interacts with the metal ion to produce an intermediate complex, the rate of oxidation of the sugars being the rate of enolisation.

[307] G. W. Cowell, A. Ledwith, A. C. White, and H. J. Woods, *J. Chem. Soc.* (*B*), 1970, 227.
[308] A. P. Modi and S. Ghosh, *Indian J. Chem.*, 1969, **46**, 687, 807.
[309] S. C. Tiwari and M. P. Singh, *Z. phys. Chem.* (*Leipzig*), 1969, **242**, 145.
[310] K. C. Gupta and M. P. Singh, *Bull. Chem. Soc. Japan*, 1969, **42**, 599.
[311] S. V. Singh, U. Shanker, and M. P. Singh, *Z. phys. Chem.* (*Leipzig*), 1969, **240**, 400.
[312] S. V. Singh, O. Saxena, and M. P. Singh, *J. Amer. Chem. Soc.*, 1970, **92**, 537.

16 Metal-ion Reductions

In general, the interactions of metal ions in a reduced oxidation state with organic and inorganic substrates have been much less investigated than the corresponding oxidations. Studies have, however, recently been made on chromium(II) reductions, the reaction with quinones being carried out in chloride media [313] and that involving 2-methylhex-3-yne-2,7-diol in the presence of sulphate.[314] Alkylchromium species have been identified as intermediates in the reduction of alkyl halides.[315] Chromium(II) perchlorate and ethylenediamine react rapidly in aqueous DMF, in the absence of air, to form Cr^{II}–en complexes which reduce (quantitatively) primary alkyl chlorides to alkanes and aryl bromides and iodides to arenes:

$$Cr^{II}(ClO_4)_2 + n(en) \longrightarrow Cr^{II}(en)_n^{2+}$$

$$Cr^{II}(en)_n^{2+} + RX + H_2O \xrightarrow{DMF} RH + [Cr^{III}(en)_2OH]^{2+} + [Cr^{III}(en)_2X]^{2+}$$

Marked colour changes occur during the reaction, the dark purple $Cr^{II}(en)_n^{2+}$ species converting to an orange intermediate with a gradual change to the red coloration of the chromic species on evolution of the alkane. The intermediate is identified as an alkyl(ethylenediamine)-chromium(III) species which is hydrolytically unstable, *e.g.* in the reaction of n-butyl bromide:

$$Bu^nX + [Cr^{II}(en)_n]^{2+} \longrightarrow [CH_3CH_2CH_2CH_2Cr^{III}(en)_2]^{2+} + X^-$$

$$[CH_3CH_2CH_2CH_2Cr^{III}(en)_2]^{2+} \xrightarrow{+H_2O} CH_3CH_2CH_2CH_3 + [Cr^{III}(en)_2(OH)]^{2+}$$

The kinetics of formation of the intermediate are first-order in each reactant, the mechanism:

$$RX + [Cr^{II}(en)_2]^{2+} \longrightarrow R^\bullet + [Cr^{III}(en)_2X]^{2+}$$

$$R^\bullet + [Cr^{II}(en)_2]^{2+} \xrightarrow{fast(k_2)} [RCr^{III}(en)_2]^{2+}$$

involving the rate-determining transfer of a halogen atom from the alkyl halide to the chromium(II) complex followed by a rapid interaction of the alkyl radical with a second equivalent of reductant ($k_2 \sim 4 \times 10^7$ l mol^{-1} s^{-1}). Competition methods have been used to evaluate the relative reaction rates of the organic species. For a given halide, the reduction rates for the alkyl group are in the order tertiary > secondary > primary in the ratio 100 : 10 : 1 approximately, and for any alkyl group the iodides are reduced

[313] J. R. Hanson and S. Mehta, *J. Chem. Soc.* (*C*), 1969, 2349.
[314] W. E. Willy and W. E. Thiessen, *J. Org. Chem.*, 1970, **35**, 1235.
[315] J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, 1970, **92**, 137.

faster than the chlorides, the bromides having intermediate reactivity. Chromium(II) solutions have also recently been used as a reducing titrant for organic compounds.[316] Intermediate complexes have also been described from spectral considerations of the reactions of vanadium(II) with maleic and fumaric acids, where the overall stoicheiometry of the reaction is:[317]

$$2V^{II}_{aq} + HO_2C\cdot RC{=}CH\cdot CO_2H \longrightarrow 2V^{III} + HO_2C\cdot CHR\cdot CH_2\cdot CO_2H$$

Vanadium(II) has also been examined in its reducing action on halogens.[318] The reactions with I_3^-, I_2, and Br_2 have been studied using a stopped-flow device, the overall processes being written as:

$$2V^{II} + X_2 \longrightarrow 2V^{III} + 2X^-$$

and:

$$2V^{II} + X_3^- \longrightarrow 2V^{III} + 3X^-$$

The primary mechanistic steps in the bromine reaction may be expressed as:

$$V^{II} + Br_2 \longrightarrow V^{III} + Br^{\bullet} + Br^-$$

$$V^{II} + Br^{\bullet} \xrightarrow{\text{fast}} V^{III} + Br^-$$

with no vanadium(IV) formation. The ruthenium(II)-catalysed reduction

$$8Cr^{II} + ClO_4^- + 8H^+ \xrightarrow{Ru^{II}} CrCl^{2+} + 7Cr^{III} + 4H_2O$$

of perchlorate ion by Cr^{II} has been described (see ref. 29, Chapter 1) the reaction being independent of [chromium(II)]. In this reaction, the rate-determining process is seen as the initial reduction of ClO_4^- by ruthenium(II):

$$Ru^{II} + ClO_4^- \longrightarrow Ru^{IV} + ClO_3^-$$

The nature of the interactions of this type involving ruthenium(II) complexes has been the subject of some discussion. The reduction of perchlorate by $[Ru(NH_3)_5OH_2]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ follows the rate law (see ref. 17, Introduction):

$$\frac{-\,d[Ru^{III}]}{dt} = k_2[Ru^{III}][ClO_4^-]$$

with k_2 values of $2{\cdot}6 \times 10^{-2}$ l mol^{-1} s^{-1} and 3×10^{-4} l mol^{-1} s^{-1} respectively, the hundred-fold increase in rate in the case of the mono-aquo-complex being attributed to its greater lability with the access of the perchlorate ion to a co-ordination site in the complex ion in the activated species. A seven-co-ordinate intermediate has been described in the reaction involving the hexammine. Recently, the kinetics of the Ru^{II}-

$$[Ru(H_2O)_6]^{3+} + X^- \xrightarrow{Ru^{II}} [Ru(H_2O)_5X]^{2+} + H_2O$$

[316] W. Buechler, P. Gisske, and J. Meier, *Analyt. Chim. Acta*, 1970, **49**, 309.
[317] E. Vrachnou-Astra, P. Sakellaridis, and D. Katakis, *J. Amer. Chem. Soc.*, 1970, **92**, 811.
[318] J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, 1969, **8**, 1407.

catalysed formation of the complexes $[Ru(H_2O)_5X]^{2+}$ (where $X^- = Cl^-$, Br^-, or I^-) have been described [319] the rate law being expressed as:

$$\frac{d[RuX^{2+}]}{dt} = k[Ru^{II}][X^-]$$

The mechanism may be written as:

$$Ru^{2+} + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RuX^+$$

$$RuX^+ + Ru^{3+} \xrightarrow{k_3} RuX^{2+} + Ru^{2+}$$

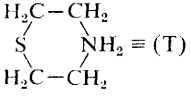
with the electron-transfer reaction (k_3) being substantially faster than the substitution step. The rate constants vary little with ligand X^-, with $k_1 \sim 9 \times 10^{-3}$ l mol^{-1} s^{-1}. The reduction of perchlorate by Ru^{II} conforms to the rate law:

$$\frac{d[Ru^{III}]}{dt} = 2k_4[Ru^{II}][ClO_4^-]$$

$$2Ru^{2+} + ClO_4^- + 2H^+ \longrightarrow 2Ru^{3+} + ClO_3^- + H_2O$$

and a comparison with the activation parameters for k_4 ($\approx 3 \times 10^{-3}$ l mol^{-1} s^{-1}) with those for the substitution reactions above suggests that the redox process is substitution-controlled. The rate of reduction of perchlorate ion by various metal ions decreases in the order [319] $Ru^{II} > Ti^{III} > Mo^{III} > V^{II} > V^{III} > Cr^{II}$, the rate-determining step in all cases except Ru^{II} being the electron transfer. The corresponding values of $10Dq$ for these ions are in the order $Ru^{II} > Ti^{III} > Mo^{III} > V^{III} > Cr^{II} > V^{II}$, and since $10Dq$ is a measure of the polarisability of the *d*-orbitals of the metal ion, the good correlation between $10Dq$ and the reduction rate suggests considerable involvement of the metal ion *d*-orbitals in the mechanism of deformation and reduction of the perchlorate ion.

The kinetics of the reduction of palladium(IV) by 3-thiomorpholine (T) have been examined in perchlorate media,[320] the reaction involving a



$$[PdCl_6]^{2-} + 2T + 2H_2O \longrightarrow [Pd(OH)_2T_2]$$

reduction of the co-ordination number of the palladium from six to four. The system is more complicated than that for the corresponding platinum complex, the mechanism:

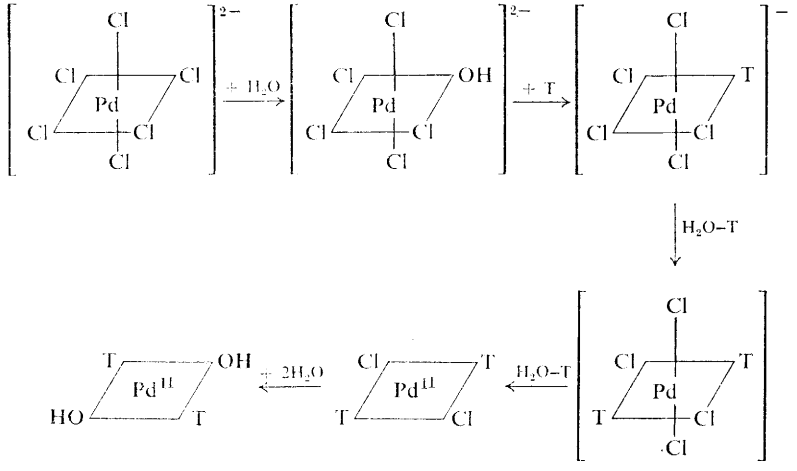
$$[PtCl_6]^{2-} + T + H_2O \xrightarrow{\text{slow}} [PtCl_4]^{2-} + T{=}O + 2H^+ + 2Cl^-$$

$$[PtCl_4]^{2-} + 2T \longrightarrow [PtCl_2T_2] + 2Cl^-$$

being consistent with the observed second-order kinetics. For the palladium species, however, pH *versus* time plots showed a rapid initial

[319] T. W. Kallen and J. E. Earley, *Chem. Comm.*, 1970, 851.
[320] D. De Fillipo, F. Devillanova, and C. Preti, *Inorg. Chim. Acta*, 1969, **3**, 341.

increase followed by a slower decrease. A possible mechanism may be written as in Scheme 13, the hydrolysis of the chloropalladate(IV) being



Scheme 13

followed by displacement of the hydroxo-group to yield the mono-(thiomorpholine) complex. Further hydrolysis and attack by reductant involves the change in oxidation state of the metal ion, the activation energy for the configurational rearrangement being 18·9 kcal mol^{-1}. The redox step is about five times faster for palladium than for the platinum analogue.

The rates of oxidation of cuprous chloride by a range of aromatic sulphonyl chlorides have been derived.[321] The reaction:

$$R \cdot C_6H_4 \cdot SO_2Cl + CuCl \rightleftharpoons R \cdot C_6H_4SO_2^{\bullet} + CuCl_2$$

involves a chlorine transfer mechanism, the reaction rates being measured in acetonitrile by the addition of styrene to the sulphonyl chloride, to yield as product the species $R \cdot C_6H_4SO_2 \cdot CH_2 \cdot CH(Cl) : Ph$. Hammett's equation is obeyed for the reaction (which is governed by the rate-determining process as written) where a wide range of σ values are associated with the aryl substituents. This is the first instance of a relationship of this type having been shown to be valid for a homolytic abstraction of an atom other than hydrogen. The redox transfer mechanism requires the $CuCl_2$ to scavenge the compound radicals since no polymeric products were encountered. The mechanism of the reduction of alkyl halides by metal–ammonia solutions has been reported.[322] Reactions of the type:

$$RX + 2M + NH_3 \longrightarrow RH + MX + MNH_2$$

[321] A. Orochov, M. Asscher, and D. Vofsi, *J. Chem. Soc.* (*B*), 1969, 255.
[322] J. Jacobus and J. F. Eastham, *Chem. Comm.*, 1969, 138.

have been shown to be very fast (at − 33 °C) for both saturated and unsaturated halides with the exception of saturated fluorides. The mechanism of interaction may be written as:

$$M + NH_3 \longrightarrow M^+(NH_3) + e^-(NH_3)$$

$$RX + e^-(NH_3) \longrightarrow RX^-$$

$$RX^- \xrightarrow{A} R\cdot + X^- \xrightarrow{+\,e^-(NH_3)} R^- \xrightarrow{NH_3} RH$$

$$RX^- \xrightarrow[+\,e^-(NH_3)]{B} R^- + X^- \xrightarrow{NH_3} RH$$

involving either (A) a free-radical pathway or (B) a carbanionic route. Neither alkyl fluorides nor polyfluoroalkanes are reduced in the metal–ammonia solutions.

Complexes of titanium(II) have been shown to act as intermediates in the de-oxygenative coupling of allyl and benzyl alcohols to hydrocarbons:[323]

$$ArCH_2OH \text{ or } >C{=}C<_{CH_2OH} \longrightarrow ArCH_2CH_2Ar \text{ or } \left(>C{=}C<_{CH_2}\right)_2$$

The reaction takes place on reduction of chlorides of titanium in oxidation state (III) or (IV) by metallic potassium or alkyl-lithium with subsequent decomposition of the organo-titanium species on warming. Titanium metal alkoxide radical anion systems have also been shown to act as catalysts in the conversion of elemental nitrogen to hydrazine:[324]

$$N_2 + 4e^- + 4H^+ \longrightarrow N_2H_4$$

In this system the intermediates involved may be described by Scheme 14,

$$Ti(OR)_4 \xrightarrow{Na\ np} [Ti(OR)_2]_x \xrightarrow{N_2} [Ti(OR)_2N_2]_x$$

$$[Ti(OR)_2N_2]_x^{4-} \xrightarrow{2Na\ np} [Ti(OR)_2N_2]_x^{6-}$$

(4Na np)

$$[Ti(OR)_2N_2]_x^{4-} \xrightarrow{+\,4H^+} N_2H_4$$

$$[Ti(OR)_2N_2]_x^{6-} \xrightarrow{+\,6H^+} 2NH_3$$

Scheme 14

[323] E. E. Van Tamelen, B. Akermark, and K. B. Sharples, *J. Amer. Chem. Soc.*, 1969, **91**, 1552.

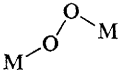
[324] E. E. Van Tamelen, R. B. Fechter, and S. W. Schneller, *J. Amer. Chem. Soc.*, 1969, **91**, 7196.

where ^{-}OR = isopropoxide anion and the reductant Na np is sodium naphthalenide. The lack of appreciable molecular nitrogen liberation during the protonation step is consistent with the absence of di-imide bound nitrogen, since this, on protonation, would generate free di-imide with subsequent rapid disproportionation to elemental nitrogen and hydrazine.

3

Reactions Involving Oxygen and Hydrogen Peroxide

The use of molecular oxygen as a powerful oxidant in solution is hindered by the fact that its reactions at room temperature generally proceed fairly slowly. Recent studies have been made in an attempt to describe the formation of stable and unstable adducts, together with the nature of the bonding involved. It has been suggested [325] that the type of co-ordination of oxygen may be dependent more on electronic properties than on the steric configurations and co-ordination number of the metal ion. Metals



(A)



(B)

in high oxidation states prefer configuration A whereas 'soft' metals favour co-ordination as in B. The nature of the other ligands around the metal ion is important in the oxygenated complex in that they may modify substantially the properties of the species. The role of the metal ion itself in the reversible uptake of oxygen has also been examined using the crystal structures [326] of the addition complexes of bis[bis(diphenylphosphino)-ethane]iridium(I) hexafluorophosphate $\{Ir(O_2)[(C_6H_5)_2P\cdot CH_2CH_2\cdot P(C_6H_5)_2]_2\}(PF_6^-)$ and its rhodium(I) analogue. The iridium species is involved in an irreversible oxygen addition with a strong Ir–O bond and weak O–O linkage; the bond distance between the oxygen atoms, 1·625 Å, is considerably longer than that expected (1·49 Å) for an O–O σ-bond. In the rhodium complex, however, where the oxygenation is reversible, the M–O bond is weaker whilst the O–O distance of 1·418 Å is indicative of a stronger linkage.

1 Cobalt(II) Complexes

The uptake of oxygen by ammoniacal cobalt(II) solutions has been examined.[327] Equilibrium constants for the formation of the μ-peroxo-

[325] R. Ugo, *Discuss. Faraday Soc.*, 1968, *No.* 46, p. 97.
[326] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301.
[327] J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1969, **91**, 1325.

species, from the corresponding pentammine:

$$2Co(NH_3)_5(H_2O)^{2+} + O_2 \rightleftharpoons (NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{4+} + 2H_2O$$

have been derived. The cobalt(II) pentammine complex reacts rapidly with dissolved oxygen in a second-order process,

$$Co(NH_3)_5H_2O^{2+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(NH_3)_5O_2^{2+} + H_2O$$

$$Co(NH_3)_5O_2^{2+} + Co(NH_3)_5H_2O^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{4+} + H_2O$$

the initial equilibrium being followed by fast reaction of a second mole of cobalt(II) complex in a redox step. Reactions were carried out under varying ammonia concentrations (0·2—9·0 mol l^{-1}), and whilst the pentammine species is the kinetically important oxygen carrier, a secondary path involving the hexammine is suggested at higher ammonia concentrations and at higher temperatures. A mechanism similar to that shown above also holds for chelated complexes where the ligands involved are diethylenetriamine (dien), histamine (hist), ethylenediamine, and 2-aminomethylpyridine (amp).[328] In the case of the dien complexes for both the mono- and bi-nuclear adducts, one of each of the two co-ordinated diens has a free $-CH_2CH_2NH_2$ grouping to allow formation of the peroxo-unit. At pH = 10, the increase in rate constant by ~ 15% on changing from a 3-fold to 75-fold excess of ligand over cobalt is explicable in terms of oxygenation of the bis-dien complex and a protonated analogue $Co(dien)_2H^{3+}$. For the histidine species both the bis- and tris-complexes are reactive but the mono form does not contribute to the rate. In processes subsequent to oxidation, it appears that complexes involving bidentate ligands are not involved in the breakdown of the peroxo-bridge since the oxygen may be recovered by acidification up to 30 min after reaction has taken place. A slower reaction, apparently independent of metal, ligand, and hydroxide concentrations, was observed in the reaction of tris-complexes, the change being associated with the formation of a dibridged species:

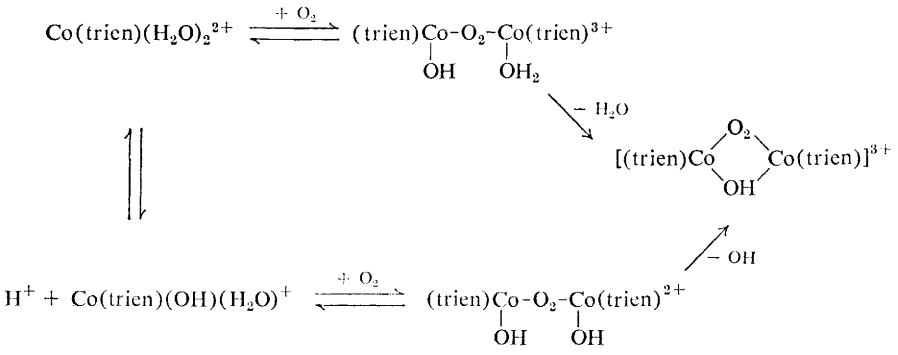
$$CoL_3^{2+} + O_2 \xrightarrow{\text{fast}} [L'L_2Co\cdot O_2'CoL_2\cdot L']^{4+}$$

$$[L_2Co\overset{O_2}{\underset{L}{\diagdown\diagup}}Co\cdot L_2]^{4+} \xleftarrow[-L]{\text{slow}}$$

where L′ is a unidentate form of the ligand. Pre-equilibria and the formation of single- and double-bridged complexes have also been observed [329]

[328] F. Miller, J. Simplicio, and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1969, **91**, 1962.
[329] F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1970, **92**, 2687.

in the cobalt(II)–triethylenetetramine system, [Co^{II}–trien]:



With the exception of $Co(en)_2(H_2O)_2^{2+}$ (Table), the k_1 values for all the lower complexes fall within a factor of 20 of each other, with $\Delta H^{\ddagger} \sim 4$—6 kcal mol^{-1} suggesting a common mode of substitution by O_2. The

Table *Reactions involving molecular oxygen*

Reductant	*k* (25 °C)	*I*	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	*Ref.*
Cobalt(II)[a]		mol l^{-1}	kcal mol^{-1}	e.u.	
$Co(NH_3)_5H_2O^{2+}$	$2{\cdot}5 \times 10^4$	2·0	4·0	− 25	327
$Co(NH_3)_6^{2+}$	$1{\cdot}2 \times 10^3$	2·0			327
$Co(dien)_2^{2+}$	$1{\cdot}2 \times 10^3$	0·20	10	− 12	328
$Co(hist)_2^{2+}$	$6{\cdot}8 \times 10^4$	0·20	8	− 8	328
$Co(amp)_3^{2+}$	47	1·0	17	+ 5	328
$Co(en)_3^{2+}$	10^4	1·0			328
$Co(tetren)(H_2O)^{2+}$	10^5				328
$Co(hist)_2(H_2O)_2^{2+}$	$1{\cdot}8 \times 10^4$	0·20	5	− 23	328
$Co(en)_2(H_2O)_2^{2+}$	$4{\cdot}7 \times 10^5$	1·0	15	+ 19	328
$Co(amp)_2(H_2O)_2^{2+}$	$7{\cdot}2 \times 10^2$	1·0	6	− 25	328
$Co(trien)(H_2O)_2^{2+}$	$2{\cdot}5 \times 10^4$	0·20	7	− 15	329
$Co(trien)(OH)(H_2O)^4$	$2{\cdot}8 \times 10^5$	0·2	8	− 7	329
Iron(II)					
$Fe(Htpp)_2 + O_2$[b]	40	0·2			346
$Fe(cyst) + O_2$[c]	5×10^3	0·1			347
$Fe(cyst)^{2-} + O_2$[c]	2×10^4	0·1			347

[a] Rate of formation of adduct. [b] pH 6—8. [c] cyst = *l*-cysteine.

uptake of oxygen by complexes is not attributable to one factor, however, and it may be that three nitrogen donors are a minimum condition for reaction to occur. The lack of interaction of complexes with carboxyl or heterocyclic ligand systems may be ascribed [328] to the withdrawal of electron density from the metal centre, thus hindering the electron transfer from the cobalt to the oxygen which is apparently required in the formation of peroxo-complex. The minimum requirement of three chelating nitrogen donors in the ligand for activation of the cobaltic complex towards oxygen

has also been demonstrated in a recent study.[330] In the case of dien and *N*-(2-picolyl)ethylenediamine complexes, oxygen adducts are metastable intermediates whereas with *N*-(2-picolyl)oxamide irreversible formation of the cobaltic species is rapid and, except in strongly basic solutions, the O_2 adducts are present only in steady-state concentrations. The mechanism is similar to that postulated for other ammine complexes. In the oxygenation and oxidation of chelates involving amino-acids and dipeptides, proton balance studies on the binuclear products show that both hydroxo and oxygen bridges are present.[331] In the absence of oxygen, however, glycylglycine undergoes a Co^{II}-promoted amide hydrogen ionisation near pH = 10, yielding a 2 : 1 complex of light blue colour. The magnetic moment of 4·1 BM is suggestive of an equilibrium between high- and low-spin states in the octahedral species. The yellow oxygenated complexes are rapidly formed on admission of oxygen. Two possible pathways are considered to exist for the oxidation of the high-spin cobalt(II) complex ($t_{2g}^5e_g^2$) to the low-spin cobalt(III) species (t_{2g}^6). In the first case, the loss of an electron is postulated to yield an unstable Co^{III} complex with two unpaired spins ($t_{2g}^5e_g^1$) which subsequently undergoes spin pairing. The second route involves spin pairing of the cobalt(II) complex ($t_{2g}^6e_g^1$) followed by the loss of the e_g electron. Oxygenation, together with the requirement for a minimum number of nitrogen donor atoms, provides a mechanism for some degree of stabilisation of the low-spin cobalt(II) complex in this pathway. For practical purposes this latter mechanism is considered to be most likely in reactions of this type. The high energy requirements in the first route are shown by the fact that with glycylsarcosine (where no oxygenated complex is formed) no Co^{III} species is produced even on long standing. The products of the irreversible oxidation of dipeptide complexes have also been isolated.[332]

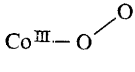
Complexes involving the Schiff bases salen [*NN'*-bis(salicylaldehydo)-ethylenedi-iminato anion] and its bis-acetylacetonato analogue, acacen, have been prepared [333–335] and e.s.r. measurements carried out in solution. Manometric studies [333] confirm that the physical state is important in deciding stoicheiometry. In the presence of dimethylformamide, the equilibrium

$$Co^{II}\,salen + DMF + O_2 \underset{}{\overset{K}{\rightleftharpoons}} Co\,salen\cdot DMF\cdot O_2$$

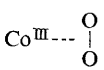
exists with $K \sim 0{\cdot}5\ l\,mol^{-1}$ at 25 °C. For the acacen complex,[334] $K = 130$ at − 10 °C. In solution the monomeric adducts are stable, the reactions

[330] P. Donatsch, K. H. Gerber, A. Zuberbühler, and S. Fallab, *Helv. Chim. Acta*, 1970, **53**, 262.
[331] M. S. Michailidis and R. B. Martin, *J. Amer. Chem. Soc.*, 1969, **91**, 4683. F. Petru and F. Jursik, *Coll. Czech. Chem. Comm.*, 1969, **34**, 3153.
[332] E. D. McKenzie, *J. Chem. Soc.* (*A*), 1969, 1655.
[333] M. Green and D. Mettrick, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 149.
[334] A. L. Crumbliss and F. Basolo, *Science*, 1969, **164**, 1168; *J. Amer. Chem. Soc.*, 1970, **92**, 55.
[335] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

at – 10 °C being rapid and completely reversible. At higher temperatures, however, there is a slower continuous uptake of oxygen over a period of days suggesting a cobalt(II)-catalysed oxidation of the organic ligand. Oxygen adduct formation is found to be a function of the base strength of the ligand in the axial position. If the cobaltous complex is not formally oxidised on interaction with oxygen, the adducts of the type (base)Co^{II}-(acacen)(O_2) would contain a low-spin cobalt(II). Spin Hamiltonian parameters for these complexes are, however, inconsistent with the formulation having an unpaired electron in the $3d_{z^2}$ orbital and it is suggested [336] from e.p.r. studies that in the monomeric adducts the unpaired electron is largely associated with the co-ordinated oxygen, the cobalt being present in the trivalent state, and that the oxygen is reduced to the superoxide ion O_2^-. Supporting evidence for a description of this type is derived from a comparison of the spin Hamiltonian parameters of the μ-superoxo- and μ-amido-μ-superoxo-dicobalt(III) complexes. It is of interest that the findings of the e.p.r. studies at low temperatures suggest that in the monomers structure C is preferred to that of D. Similar observations have



(C)



(D)

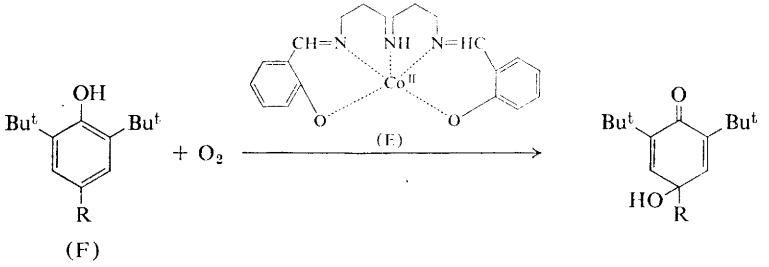
been made in the case of the 1 : 1 adduct between vitamin B_{12r} [cobalt(II) cobalamin] and oxygen.[336, 337] Polarographic studies [338] on the monomeric adducts show a reversible one-electron reduction which is attributed to the process:

$$L \cdot Co\ salen \cdot O_2 + e \longrightarrow [L \cdot Co\ salen \cdot O_2]^-$$

with the product involving either Co^{III}–O_2^{2-} or Co^{II}–O_2^- linkages. Bis(dimethylglyoximato)cobalt(II) complexes react with molecular oxygen to yield [339] diamagnetic μ-superoxo dimeric complexes of the type $B \cdot Co(G_2H_2) \cdot O_2 \cdot Co(G_2H_2) \cdot B^+$, where B is a base (pyridine) and G is the dianion of dimethylglyoxime. In these complexes the unpaired electron is symmetrically delocalised over the Co–O–O–Co system. The monomeric peroxo-radical $py \cdot Co(G_2H_2) \cdot O_2$ is closely similar to that of peroxocobalamin, thus indicating the similarity of the electron environments of the $Co–O_2$ system in both species. Reversible oxygen uptake has been shown to take place when complexes of Schiff's bases are adsorbed on polymer surfaces.[340] Under these conditions, however, no dimerisation is observed

[336] S. A. Cockle, H. A. O. Hill, and R. J. P. Williams, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 131.
[337] J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, 1969, **91**, 2775.
[338] G. Costa, A. Puxeddu, and L. B. Stefani, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 191.
[339] G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, 1970, **92**, 1551.
[340] A. Misono, S. Koda, and Y. Uchida, *Bull. Chem. Soc. Japan*, 1969, **42**, 3470.

at low temperatures, possibly due to the fact that the chelates are fixed on the less mobile polymer chains. Recently it has been shown [341] that di-(3-salicylideneaminopropyl)aminecobalt(II) (E), which forms a 1 : 1 complex with oxygen, acts as a homogeneous catalyst for the oxidation



of phenols by molecular oxygen in organic media. In the autocatalytic autoxidation of 4-alkyl-2,6-di-t-butylphenol (F) there is selective introduction of an oxygen atom in the *para*-position to yield the corresponding *p*-quinol.

2 Iron(II) Complexes

The mechanism of oxygenation of the iron(II) ion in neutral aqueous media has been re-investigated,[342] the observed rate law being:[343]

$$\frac{-\,\mathrm{d}[\mathrm{Fe^{II}}]}{\mathrm{d}t} = k_0[\mathrm{Fe^{II}}][\mathrm{O_2}][\mathrm{OH^-}]^2$$

Previously postulated reaction schemes [344, 345] are discounted and a new one proposed:

$$\mathrm{Fe^{II}} + \mathrm{OH^-} \rightleftharpoons \mathrm{Fe(OH)^+}$$

$$\mathrm{O_2} + \mathrm{OH^-} \rightleftharpoons \mathrm{O_2 \cdot OH^-}$$

$$\mathrm{FeOH^+} + \mathrm{O_2OH^-} \xrightarrow{k_1} \mathrm{Fe(OH)_2^+} + \mathrm{O_2^-}$$

$$\mathrm{O_2^-} + \mathrm{H^+} \overset{k_2}{\rightleftharpoons} \mathrm{HO_2^\bullet}$$

where the equilibria are rapidly established, and the rate-determining step is the interaction of an iron(II) hydroxo-complex with the oxygenated species $\mathrm{O_2 \cdot OH^-}$. The calculated value for $k_1 \sim 10^{10}$ suggests that the reaction is likely to be diffusion controlled since the associated activation energy is low.

[341] T. Matsuura, K. Watanabe, and A. Nishinaga, *Chem. Comm.*, 1970, 163.
[342] K. Goto, H. Tamura, and N. Nagayama, *Inorg. Chem.*, 1970, **9**, 963.
[343] J. E. Schenk and W. J. Weber, *J. Amer. Water Works Assoc.*, 1968, **60**, 199.
[344] J. Weiss, *Naturwiss.*, 1935, **23**, 64.
[345] E. Abel, *Z. Elektrochem.*, 1955, **59**, 903.

In the presence of tripolyphosphate (tpp) in the pH range 2—8 the reaction may be written as:[346]

$$Fe^{II} + Htpp^{4-} \rightleftharpoons Fe^{II}(Htpp^{4-})$$

$$Fe^{II}(Htpp^{4-}) + Htpp^{4-} \rightleftharpoons Fe^{II}(Htpp^{4-})_2$$

$$Fe^{II}(Htpp^{4-}) + O_2 \xrightarrow{k_1} Fe^{III}(Htpp^{4-}) + O_2^-$$

$$Fe^{II}(Htpp^{4-})_2 + O_2 \xrightarrow{k_2} Fe^{III}(Htpp^{4-})_2 + O_2^-$$

$$O_2^- + H^+ \rightleftharpoons HO_2^\bullet$$

with both the 1 : 1 and 1 : 2 complexes reacting. At pH 6—8 in the presence of an excess of ligand, the latter reaction is rate determining. The increase in the rate of oxidation in the presence of iron(II) ions under these conditions may be due to the fact that the oxidation products are stabilised to a greater extent than the corresponding iron(II) species. Mono- and bis-cysteinate complexes of iron(II) have also been invoked as reactive species in the corresponding reaction with cysteine,[347] the reaction scheme being similar to that described previously. Although the product iron(III) complexes undergo an intramolecular redox reaction, this is sufficiently slow not to interfere with the oxidation. In these systems, the redox reaction is considered to take place by the transfer of an electron from the metal ion into an antibonding orbital of the oxygen molecule having π-symmetry. In the presence of nitrogen donor ligands (σ-donors) there is little enhancement of the oxidation reaction. In the cysteine complexes, however, where M–S bonding may involve a degree of π-overlap between the vacant *d*-orbitals of the sulphur atom and the metal ion *d*-electrons, there is the possibility on adduct formation of a three-centre π-system involving the sulphur, metal, and oxygen atoms. Under these conditions, the electron transfer is considered to be greatly facilitated.

The kinetics of the oxidation and catalytic decomposition of the hexacyanoferrate(II) ion[348] has been investigated, the reaction

$$4Fe(CN)_6^{4-} + 4H^+ + O_2 \longrightarrow 4Fe(CN)_6^{3-} + 2H_2O$$

proceeding only in acid solution in the absence of light. The first-order rate constants are proportional to the sum of the concentrations of the species $[HFe(CN)_6^{3-}]$ and $[H_2Fe(CN)_6^{2-}]$, indicating that these protonated species are involved in the oxidation process. The oxidation is considered to proceed *via* an electron transfer from the complex to the proton to yield a hydrogen radical which then produces $HO_2^\bullet$ on interaction with an oxygen molecule.

[346] Y. Kurimura and H. Kuriyama, *Bull. Chem. Soc. Japan*, 1969, **42**, 2239.
[347] A. D. Gilmour and A. McAuley, *J. Chem. Soc.* (*A*), 1970, 1006.
[348] S. Asperger, I. Murati, and D. Pavlovic, *J. Chem. Soc.* (*A*), 1969, 2044.

3 Copper(I) Complexes

The speed of oxygenation of the copper(I) ion, together with the competing disproportionation reaction of the species and the rarity of soluble Cu(I) salts, has made difficult quantitative studies on the kinetics of the interaction of this ion with molecular oxygen. Recently, however, studies have been made in perchloric acid–acetonitrile solutions.[349] An interesting feature of the reaction of monovalent copper with oxygen is that H_2O_2 is not detected in reaction solutions containing chloride ion or imidazole,[350] and in media buffered with phosphate, acetate, citrate, or ammonia, less than stoicheiometric amounts of this product are detected on completion of the oxygen consumption. In the presence of acetonitrile,[349] the rate law:

$$\frac{d[Cu^{II}]}{dt} = \frac{-d[Cu(CH_3CN)_2^+]}{dt} = \frac{k_c[Cu(CH_3CN)_2^+][O_2][H^+]}{[CH_3CN]^2}$$

is observed with $k_c = 6{\cdot}9 \pm 0{\cdot}3 \times 10^7$ l^2 mol^{-2} s^{-1} at 30 °C. The data are interpreted in terms of a bimolecular reaction of the CuO_2^+ complex with a proton in the rate-determining stage of a sequence of steps involving the rapid dissociation of the bisacetonitrile complex:

$$Cu(CH_3CN)_2^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cu^+ + 2CH_3CN$$

$$Cu^+ + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CuO_2^+$$

$$CuO_2^+ + H^+ \xrightarrow{k_4} Cu^{II} + HO_2^\bullet$$

$$Cu^+ + HO_2^\bullet \longrightarrow Cu^{II} + HO_2^-$$

$$H^+ + HO_2^- \rightleftharpoons H_2O_2$$

Under the conditions of study, the reaction with H_2O_2 is slower than that with O_2. Attempts to explain the mechanism on the basis of reactions involving two-electron transfers, *e.g.*

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

appear to be ruled out by the fact that no hydroxy-radicals were detected, whereas they are known to be produced when copper(III) reacts with water. Stopped-flow techniques have also been used to investigate the autoxidation of copper(I)–acetonitrile complexes in the presence of monodentate nitrogen ligands such as imidazole and ammonia.[351] Complexes of the type $CuL_2O_2^+$ and $CuL_3O_2^+$ (where L = base) are considered as intermediates, the latter being more reactive.

Copper(II) ions are known to catalyse the oxidation of iron(II) complexes. In tripolyphosphate solutions,[352] the rate of oxidation of Fe^{II} by O_2[346] is

[349] R. D. Gray, *J. Amer. Chem. Soc.*, 1969, **91**, 56.
[350] A. Zuberbühler, *Helv. Chim. Acta*, 1967, **50**, 466.
[351] A. Zuberbühler, *Chimia* (*Switz.*), 1969, **23**, 416.
[352] Y. Kurimura and K. Murakami, *Bull. Chem. Soc. Japan*, 1969, **42**, 2715.

markedly increased in the presence of copper(II) ions, due to the added reactions:

$$Fe^{II}(Htpp^{4-})_n + Cu^{II} \rightleftharpoons Fe^{III}(Htpp^{4-})_n + Cu(^{I})$$

$$Cu^{I} + O_2 \longrightarrow Cu^{II} + O_2^-$$

The copper(I) species may also be complexed. The effects of copper(II) and sulphate ions on the oxidation of iron(II) sulphate solutions [353] have been studied. At 40 °C, whilst the oxidation to Fe^{III} is quantitative, the reaction appears to be complex, being first-order in oxygen, with higher order dependences in both copper(II) and iron(II) concentrations. In an interesting study [354] it has recently been shown that the poly-*l*-lysine–copper(II) complex catalyses the asymmetrically-selective oxidation of 3,4-dihydroxyphenylalanine (dopa). The initial rate of oxidation of D-dopa is greater than that of L-dopa, the selectivity in the catalysis being attributed to two or more complex copper(II) units acting co-operatively. The assumption is made that the helical structure in the catalyst serves to hold two or more copper(II) complex species in a unique steric configuration which serves as a site for the selective binding of D-dopa.

4 Miscellaneous Complexes

The uranyl-ion-catalysed oxidation of ascorbic acid has been shown to proceed *via* a path first-order with respect to substrate, catalyst, molecular oxygen, and hydrogen (or deuterium) ion concentrations.[355] In the presence of any excess of oxygen, the rate law may be expressed in the form

$$\frac{-\,d[A]}{dt} = k[A_0][UO_2^{2+}][H^+][O_2]$$

where $[A_0]$ represents the total concentration of unreacted ascorbic acid. The mechanism may be described as

$$H_2A \rightleftharpoons HA^- + H^+$$

$$HA^- + UO_2^{2+} \rightleftharpoons UO_2HA^+ \overset{+H^+}{\rightleftharpoons} UO_2 \cdot H_2A^{2+}$$

$$UO_2 \cdot H_2A^{2+} + H^+ \rightleftharpoons UO_2 \cdot H_3A^{3+}$$

$$UO_2 \cdot H_3A^{3+} + O_2 \rightleftharpoons UO_2 \cdot H_3A \cdot O_2^{3+}$$

$$UO_2 \cdot H_3A \cdot O_2^{3+} \xrightarrow{k} UO_2 \cdot H_3A(O_2^{\bullet})^{3+}$$

$$UO_2 \cdot H_3A(O_2^{\bullet})^{3+} \xrightarrow{\text{fast}} UO_2^{2+} + H_2O_2 + H^+ + A$$

The triprotonated species, $UO_2 \cdot H_3A \cdot O_2^{3+}$ is considered to involve two protons on the oxo-oxygens of the uranyl ion with the other on one of the ascorbate oxygen donor atoms. The rate-determining process is the

[353] A. N. Dokuchaeva, L. Liepina, and B. Macejevskis, *Latvijcis P.S.R. Zinatnu Akad. Vestis Khim Ser.*, 1969, 164, 167 (*Chem. Abs.*, 1969, **70**, 109,509u).
[354] M. Hatano, T. Nozawa, and M. Yoneyama, *Bull. Chem. Soc. Japan*, 1970, **43**, 295.
[355] M. M. Taqui Khan and A. E. Martell, *J. Amer. Chem. Soc.*, 1969, **91**, 4668.

electron transfer within this complex with a subsequent rapid redox reaction to yield the final products. This secondary step may involve the formation of an intermediate of the type $UO_2 \cdot H_3A(O_2^{2-})^{3+}$ with this peroxo-species decomposing as shown. The fact that uranyl ion is less reactive than vanadyl ion by a factor of $\sim 10^3$ in catalysing this reaction is due to the presence of two oxo-oxygens of the uranyl ion interfering with the formation of the oxygenated complex by hindering the attack of the oxygen molecule at the rear of the metal ion complex, whereas this route remains a possibility in the VO^{2+} system.

Preliminary results of the reaction between vanadium(III)–tetrasulphophthalocyanine complex with oxygen have been reported;[356] these data were compared with those obtained for the corresponding reaction of the hexa-aquo complex ion. The oxidation of methyl ethyl ketone by oxygen in the presence of Mn^{II}–phenanthroline complexes has been studied;[357] Mn^{III} complexes were detected as intermediates in the reaction and the enolic form of the ketone hydroperoxide decomposed in a free-radical mechanism. In the oxidation of 1,3,5-trimethylcyclohexane,[358] transition-metal [Cu^{II}, Co^{II}, Ni^{II}, and Fe^{II}] laurates act as catalysts and whereas in the absence of these complexes there is pronounced hydroperoxide formation, this falls to a low stationary concentration in the presence of these species, the assumption being made that a metal–hydroperoxide complex is the initiator in the radical reaction. In the case of nickel, the presence of such hydroperoxides is considered to stabilise the $Ni^{II}O_2$ complex. Ruthenium(I) chloride complexes in dimethylacetamide are active hydrogenation catalysts for olefinic substrates but in the presence of oxygen, the metal ion is oxidised to ruthenium(III),[358] the reaction proceeding stoicheiometrically. Rhodium(I) carbonyl halides have also been shown[359] to catalyse the oxidation of carbon monoxide to carbon dioxide under acidic conditions:

$$H^+ + Rh^I(CO)_2 + O_2 \longrightarrow Rh^{III}CO + CO_2 + H_2O$$

the rhodium(I) species being regenerated in a cyclic process by further reaction of the oxidised ruthenium product with carbon monoxide.

5 Metal Complex–Peroxide Systems

Although previous mention has been made[152] of the oxidation of hydrogen peroxide by transition-metal ions, several studies[360] have been involved with the metal-ion-catalysed decomposition

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

[356] D. J. Halko and J. H. Swinehart, 158th Meeting of the American Chemical Society, New York, 1969, Inorganic Paper 183.
[357] V. D. Komissarov and E. Denisov, *Kinetika i Kataliz*, 1969, **10**, 513.
[358] B. Jadrnicek and K. Vesely, *Coll. Czech. Chem. Comm.*, 1970, **35**, 358.
[359] B. Hui and B. R. James, *Chem. Comm.*, 1969, 198.
[360] J. A. Stanko, G. Petrov, and C. K. Thomas, 158th Meeting of the American Chemical Society, New York, 1969, Inorganic Paper 184.

It has been shown [361] that copper(II) complexes are catalytically active if the co-ordination sphere of the metal ion is not saturated by the complexing ligand, the formation of ternary metal-ion–peroxo-ligand complexes being postulated in the reaction scheme. Such ternary species are known to be important in the discriminating behaviour of metal ions and ligands with regard to their biological significance.[362] In the case of copper(II)–bipyridyl complexes [361, 363] the rate law

$$\frac{-\,\mathrm{d}[H_2O_2]}{\mathrm{d}t} = \frac{k[\mathrm{Cu(bipy)}][H_2O_2]^2}{[H^+]}$$

is observed, together with evidence that only the 1 : 1 metal complexes are active. The mechanism consistent with these findings is postulated as:

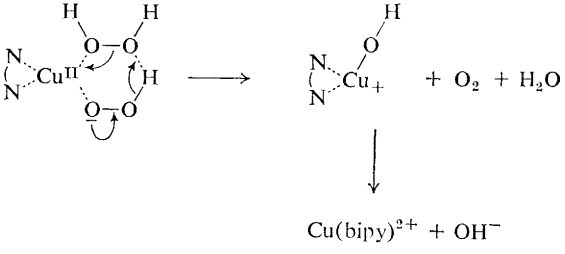
$$H_2O_2 \underset{}{\overset{K_1}{\rightleftharpoons}} HOO^- + H^+$$

$$[\mathrm{Cu(bipy)}]^{2+} + HOO^- \overset{K_2}{\rightleftharpoons} [\mathrm{Cu(bipy)OOH}]^+$$

$$[\mathrm{Cu(bipy)(OOH)}]^+ + H_2O_2 \overset{K_3}{\rightleftharpoons} [\mathrm{Cu(bipy)(OOH)(H_2O_2)}]^+$$

$$[\mathrm{Cu(bipy)(OOH)(H_2O_2)}]^+ \xrightarrow{k} [\mathrm{Cu(bipy)}]^{2+} + O_2 + H_2O + OH^-$$

the values of K_2 and K_3 being small. The rate-determining process is considered to occur *via* a pathway of the type:



Similar intermediates are invoked in the catalysis of the reaction between hydrogen peroxide and hydrazine or hydroxylamine,[364]

$$H_2O_2 + H_2N{\cdot}NH_2 \longrightarrow N_2 + 4H_2O$$

where possible changes in the oxidation state of the metal ion, between Cu^I and Cu^{II}, may occur. The decrease in reactivity of the complex on saturation of the co-ordination sites has also been described in similar reactions with copper(II)–diphenylamine complexes.[365] In the case of cobalt(III) complexes of the tetramine type, the catalytic activity depends

[361] H. Sigel, C. Flierl, and R. Griesser, *J. Amer. Chem. Soc.*, 1969, **91**, 1061,
[362] H. Sigel and D. B. McCormick, *Accounts Chem. Res.*, 1970, **3**, 201.
[363] R. Griesser, B. Prijs, and H. Sigel, *J. Amer. Chem. Soc.*, 1969, **91**, 7758.
[364] H. Erlenmeyer, C. Flierl, and H. Sigel, *J. Amer. Chem. Soc.*, 1969, **91**, 1065.
[365] D. Craciunescu and A. Fruma, *Rev. Roumaine Chim.*, 1969, **14**, 653.

on the composition and structure of both the neutral ligand and the corresponding acido-species, the reactivity falling in the sequence py > NH_3 > trien > phen > dien > en > bipy.[366] In the bis-1,10-phenanthroline complex, however, there is evidence for the formation of ternary complexes similar to those described earlier. In the reactions of divalent metal acetylacetonate complexes[367] the reactivity is in the order Co > Mn > Ni, and it is of interest to note that whereas in going from *N*-bonded to *O*-bonded donor ligands the catalytic activity of Fe^{II} and Cu^{II} complexes decreases, the opposite effect is noted for cobalt. The use of the oxidation of tiron by H_2O_2 in the presence of cobalt(II) has recently been suggested as a catalymetric method of determination of this ion.[368]

Chloride ions have been shown to increase the rate of reaction of Fe^{II} with hydrogen peroxide.[369] The purple species formed in alkaline solutions of Fe^{III}, edta, and hydrogen peroxide has been shown to be $Fe^{III}(edta)O_2^{3-}$ using potentiometric, magnetic, and spectrophotometric techniques; this species is a catalyst for the peroxide decomposition.[370] The rate of decomposition is slow at pH < 8 but at pH = 10·5 the reaction proceeds quantitatively to give oxygen and water. The complex has also been shown to act as an intermediate in the oxidation of glycols and other polyhydroxy organic substrates. After a short induction period, the rate of the decomposition reaction is markedly increased in the presence of ethylene glycol and both glycollate ion and oxygen are released.

Although the radicals formed in the reactions of H_2O_2 with Fe^{II}, Fe^{III}, and Ce^{IV} have been identified, it has been shown that on addition of other metal ions[371] to these redox systems, similar e.s.r. spectra are recorded but the intensity of the signal is dependent on the concentration of the metal ion present. In the presence of ZrO^{2+}, Hf^{4+}, Th^{4+}, and UO_2^{2+}, it would appear that these transition-metal ions in their highest oxidation states form complexes with the free-radical species generated. Relative rate constants have been measured for reactions of hydroxy-radicals formed in the Fe^{II} and Ti^{III} redox systems.[372] Although in the case of titanium(III) the $TiOO^{3+}$ radical is formed, it is suggested that the $FeOH^+$ ions react with peroxide to produce the ferryl ion as an intermediate

$$Fe^{II} + H_2O \rightleftharpoons FeOH^+ + H^+$$

$$FeOH^+ + H_2O_2 \longrightarrow FeO^{2+} + H_2O + HO^-$$

$$FeO^{2+} + H_2O_2 \longrightarrow HO_2^{\bullet} + OH^- + Fe^{III}$$

with subsequent further reaction of any organic substrates present. If the

[366] G. A. Shagisultanova and N. P. Glukhova, *Zhur. fiz. Khim.*, 1969, **43**, 2082.
[367] A. Ya. Sychev, *Zhur. neorg. Khim.*, 1969, **14**, 971.
[368] R. Kucharkowski, *Z. analyt. Chem.*, 1970, **249**, 22.
[369] C. F. Wells, *J. Chem. Soc.* (*A*), 1969, 2740.
[370] C. Walling. M. Kurz, and H. J. Schugar, *Inorg. Chem.*, 1970, **9**, 931.
[371] M. S. Bains, J. C. Arthur, and O. Hinojosa, *Inorg. Chem.*, 1970, **9**, 1570.
[372] W. A. Armstrong, *Canad. J. Chem.*, 1969, **47**, 3737.

Fe^{II} is complexed with edta, however, formation of the iron(II) hydrospecies is suppressed and hydroxy-radicals are formed at higher pH's.

The oxidations of hydrogen peroxide and hydroxylamine by pentacyanocobaltate(II) have been examined.[373] The reactions conform to the stoicheiometry

$$2Co(CN)_5^{3-} + H_2O_2 \longrightarrow 2Co(CN)_5OH^{3-}$$

and exhibit second-order kinetics, first-order with respect to each component. The mechanism may be represented as:

$$Co(CN)_5^{3-} + H_2O_2 \xrightarrow{k_1} Co(CN)_5OH^{3-} + HO^{\bullet}$$

$$Co(CN)_5^{3-} + HO^{\bullet} \xrightarrow{\text{fast}} Co(CN)_5OH^{3-}$$

the entropy of activation (− 31 e.u.) accompanying the process being negative. Addition of iodide to the solutions has no effect on the overall reaction rate but the stoicheiometry is altered, being of the form:

$$2Co(CN)_5^{3-} + H_2O_2 + I^- \longrightarrow Co(CN)_5I^{3-} + Co(CN)_5OH^{3-} + OH^-$$

the iodide reacts with the hydroxy-radicals formed in the rate-determining process to yield hydroxide ion and iodine atoms which subsequently interact rapidly with the pentacyanocobaltate(II). The oxidation of ferrocyanide ions and the reduction of ferricyanide has been examined.[374] In strongly acidic solutions, the oxidation reaction is first-order with respect to H_2O_2 and 0·5 in $[Fe(CN)_6]^{4-}$. The reaction rate reaches a maximum at pH = 4, but at these hydrogen ion concentrations the system is no longer stoicheiometric with more than two moles of the iron(II) complex being oxidised per mole of peroxide. At high pH (> 11) no further oxidation takes place but the reduction is rapid and the overall reaction is second-order. In the reaction of chromium(II) cyanide complexes[375] the stoicheiometry is,

$$2\Delta H_2O_2 = \Delta Cr^{II}$$

and the mechanism is represented as

$$Cr(CN)_5H_2O^{3-} + CN^- \underset{}{\overset{K_1}{\rightleftharpoons}} Cr(CN)_6^{4-} + H_2O$$

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$

$$Cr(CN)_6^{4-} + H_2O_2 \xrightarrow{k_0} Cr(CN)_6^{3-} + OH^{\bullet} + HO^-$$

$$Cr(CN)_5H_2O^{3-} + H_2O_2 \xrightarrow{k_1} Cr(CN)_5OH^{3-} + HO^{\bullet} + H_2O$$

$$Cr(CN)_5H_2O^{3-} + HO_2^- \underset{}{\overset{K_c}{\rightleftharpoons}} [Complex]^{3-} + CN^-$$

$$[Complex]^{3-} \xrightarrow{k_2} \text{products}$$

$$Cr^{II} + HO^{\bullet} \xrightarrow{\text{fast}} Cr^{III} + HO^-$$

[373] P. B. Chock, R. B. K. Dewar, J. Halpern, and L. Y. Wong, *J. Amer. Chem. Soc.*, 1969, **91**, 82.

[374] J. Sobkowski, *Roczniki Chem.*, 1969, **43**, 1729 (*Chem. Abs.*, 1970, **72**, 59,650b).

[375] G. Davies, N. Sutin, and K. O. Watkins, *J. Amer. Chem. Soc.*, 1970, **92**, 1892.

The rate constants evaluated for k_0, k_1, and k_2 are 329, 3570 l mol^{-1} s^{-1}, and 21·3 s^{-1} respectively, the association constant for the ternary complex being 29·5 at 25 °C. The reaction involving the hexacyano-species is considered to be outer-sphere and evidently both $Cr(CN)_6^{4-}$ and $Cr(CN)_5(H_2O)^{3-}$ react more readily with the neutral hydrogen peroxide than with HO_2^-. A comparison has been made between these reactions and the corresponding pentacyanocobaltate(II) systems. In $Co(CN)_5^{3-}$ there is a low-spin square-pyramidal d^7 complex with the donor electron in the d_{z^2} orbital, whereas in $Cr(CN)_6^{4-}$ the donor electron in the low spin octahedral d^4 species is in a t_{2g} orbital. In the cobalt(II) complex, there is little tendency to co-ordinate a sixth ligand, since there is a considerable loss of crystal field stabilisation energy in changing from the square-pyramidal to the octahedral configuration. In the case of $Cr(CN)_5H_2O^{3-}$, however, it is considered that the reaction is inner-sphere, the initial equilibrium constant on interaction with H_2O_2 being $\sim$ 20 l mol^{-1}.[375] It is of interest to note that in the reaction of $Cr(CN)_6^{4-}$ with oxygen, a good yield of $Cr(CN)_6^{3-}$ is produced, whereas dimeric products are obtained from reaction of aqueous and ammoniacal solutions of chromium(II) ion with O_2.

Part II

SUBSTITUTION AND RELATED REACTIONS

1
Non-metallic Elements

In this chapter, substitution, addition–dissociation, and intramolecular reactions of compounds of the non-metals will be covered. Simple compounds of the Group III and Group IV metals are also included; complexes of these elements are mentioned in the appropriate sections of Chapters 6 and 8. Elements are discussed in Periodic Table order.

1 Substitution and Association–Dissociation Processes

Group III.—*Boron.* It has only recently been conclusively shown that the stoicheiometry of the boric acid–tartaric acid complex is 1 : 1. Kinetic results from *T*-jump experiments indicate attack by an alcohol-oxygen lone-pair at the electron-deficient boron.[1] Other references to reaction mechanisms of three-co-ordinate boron compounds deal with hydrolysis and methanolysis of boron halides,[2] with disproportionation of boranes,[3] and with S_H2 radical reactions of alkylboranes.[4]

Hydrogen exchange between bridge and terminal positions in μ-dimethylaminodiborane has been studied in the pure liquid and in solution in methylcyclohexane and in ethers, by ^{11}B n.m.r. spectroscopy over a range of temperatures. The activation parameters (Table 1) show marked

Table 1 *Activation parameters for bridge ⇌ terminal hydrogen exchange in μ-dimethylaminodiborane*

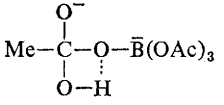
Solvent	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
Pure liquid	17·1	+ 1
Methylcyclohexane	16·8	0
Tetrahydrofuran	6·1	− 26
1,2-Dimethoxyethane	6	− 29

catalysis in ether solutions, ascribed to nucleophilic attack by the ether-oxygen at boron.[5]

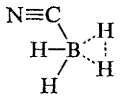
There have been many reports on hydrolysis of tetrahedral boron compounds. Catalytic effects of a variety of cations on hydrolysis of

[1] K. Kustin and R. Pizer, *J. Amer. Chem. Soc.*, 1969, **91**, 317.
[2] J. R. Blackborow, *J. Chem. Soc.* (*C*), 1969, 739.
[3] D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, 1969, **8**, 594.
[4] *E.g.*, A. G. Davies, S. C. W. Hook, and B. P. Roberts, *J. Organometallic Chem.*, 1970, **22**, C37.
[5] R. E. Schirmer, J. H. Noggle, and D. F. Gaines, *J. Amer. Chem. Soc.*, 1969, **91**, 6240.

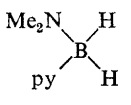
tetrafluoroborate have been described.[6] Kinetics of hydrolysis of the tetra-acetatoborate anion have been studied under acidic, neutral, and alkaline conditions. In acid solution, there is acid catalysis which is, as expected, greater for this anion than for tetrafluoroborate. Alkaline hydrolysis proceeds by two parallel routes, a unimolecular dissociative route and rate-determining attack by hydroxide, which takes place at acetate-carbon rather than at boron to give the transition state (1).[7] The predominant reaction of the Lewis adducts $Me_3N.BH_2X$ over a range of pH values and a range of aqueous dioxan mixed solvents is hydrolysis of the B—X bond. This seems (from the evidence of plots of logarithms of rate constants *vs.* solvent *Y* values, from the lack of dependence of rate on hydroxide concentration in basic solution, and from isotope effects) to be a dissociative process rather than one of bimolecular attack by water or hydroxide. It is possible to draw parallels between this behaviour and that at cobalt(III) centres.[8] Comparison of hydrolysis and exchange rates



(1)



(2)



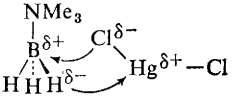
(3)

for the anion $[BH_3CN]^-$ indicates a common intermediate (2).[9] Cations $[R^1R^2BH_2]^+$ are known to hydrolyse fairly readily when R^1 and R^2 are secondary amines, but it has now been shown that rates of hydrolysis are very much lower if R^1 and R^2 contain tertiary nitrogens. The explanation seems to be that for, *e.g.* $R^1 = Me_2NH$ and $R^2 =$ py, reaction can readily proceed through a neutral intermediate (3), which has been characterised. This pathway cannot operate for tertiary amines since it requires proton loss from nitrogen to form such an intermediate.[10] Relative rates of alkaline hydrolysis of borane cations of bases, $[Me_3N \cdot BH_2 \cdot O(base)]^+$, for nitrogen, phosphorus, and sulphur bases have been estimated. Relative rates of boron–oxygen bond breaking do not parallel the estimated bond strengths.[11]

Chlorination of $Me_3N.BH_3$ to $Me_3N.BH_2Cl$, $Me_3N.BHCl_2$, and $Me_3N.BCl_3$ has been investigated by product analysis and stoicheiometry for a variety of chlorinating agents. For compounds such as SO_2Cl_2 and $SbCl_5$, whence it is easy to generate chlorine atoms, the mechanism is of the free-radical chain type, but for compounds like HCl and $HgCl_2$ the mechanism suggested is polar hydride transfer, involving a four-centred transition state [*e.g.* (4)].[12] The mechanism of decomposition of adducts of

[6] H. R. Clark and M. M. Jones, *J. Amer. Chem. Soc.*, 1970, **92**, 816.
[7] I. G. Ryss and V. N. Plakhotnik, *Russ. J. Inorg. Chem.*, 1969, **13**, 1060.
[8] J. R. Lowe, S. S. Uppal, C. Weidig, and H. C. Kelly, *Inorg. Chem.*, 1970, **9**, 1423.
[9] M. M. Kreevoy and J. E. C. Hutchins, *J. Amer. Chem. Soc.*, 1969, **91**, 4329.
[10] V. R. Miller and G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, 1970, **92**, 1558.
[11] N. E. Miller, *Inorg. Chem.*, 1969, **8**, 1693.
[12] J. W. Wiggins and G. E. Ryschkewitsch, *Inorg. Chim. Acta*, 1970, **4**, 33.

the type amine.BCl_3 has been studied.[13] The mechanism of hydrogen elimination from $Me_2NH.BH_3$ is not intramolecular as recently suggested, but probably bimolecular.[14] N.m.r. spectra over a range of temperatures indicate slow intermolecular exchange between boron trifluoride adducts of trimethyl phosphate or of hexamethylphosphoramide, and fast exchange in the case of other R_3PO adducts.[15]



(4)

An SCF–MO treatment of addition reactions of ammonia or amines to boron trifluoride has satisfactorily rationalised their very low activation enthalpies.[16] Exchange reactions of amine–boron and phosphine–boron adducts have been studied over a wide range of temperatures and in a variety of solvents.[17]

Gallium, Indium, and Thallium. Most references to these elements concern organo-non-metallic compounds outside the scope of this Report. However, in connection with the references to Lewis adducts in the preceding section on boron, one might here mention related studies on exchange reactions of a trimethylgallium adduct[18] and intermolecular exchange of trimethylsilyl groups in tris(trimethylsilyl)thallium.[19] The mechanism of trimethylgallium exchange with $Me_3Ga.PMe_3$ is unimolecular and dissociative, like that of trimethylamine exchange with $Me_3B.NMe_3$, but unlike the bimolecular exchange of amines with trimethylgallium or trimethylindium adducts.[18] The rate law for trimethylsilyl exchange with $(Me_3Si)_3Tl$ indicates a second-order reaction; rates are markedly influenced by addition of trimethylamine or trimethylthallium. These observations are most readily accommodated by an intermolecular mechanism with the existence of relatively stable adducts as intermediates.[19]

The result which is of inorganic interest, which emerges from extensive kinetic studies of gallium-trichloride-catalysed chloride exchange for several organic chlorides is the demonstration of the importance of adducts of the type $CH_3Cl.GaCl_3$ and $[(CH_3Cl)_2GaCl_2]^+$ in many cases.[20]

[13] J. R. Blackborow and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1969, 816.
[14] G. E. Ryschkewitsch and J. W. Wiggins, *Inorg. Chem.*, 1970, **9**, 314.
[15] V. Gutmann and J. Imhof, *Inorg. Chim. Acta*, 1970, **4**, 171.
[16] P. G. Perkins and J. J. Stewart, *Inorg. Chim. Acta*, 1970, **4**, 40.
[17] A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.*, 1969, **91**, 2911; G. E. Ryschkewitsch and A. H. Cowley, *ibid.*, 1970, **92**, 745.
[18] K. L. Henold, J. B. de Roos, and J. P. Oliver, *Inorg. Chem.*, 1969, **8**, 2035.
[19] A. G. Lee and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1969, 1055.
[20] F. P. de Haan and H. C. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 4844; F. P. de Haan, H. C. Brown, and J. C. Hill, *ibid.*, p. 4850; F. P. de Haan, H. C. Brown, D. C. Conway, and M. G. Gibby, *ibid.*, p. 4854; F. P. de Haan, M. G. Gibby, and D. R. Aebersold, *ibid.*, p. 4860.

The existence of dimeric and polymeric species in aqueous solutions of indium(III) and thallium(III) has an effect on kinetics of systems which include these reactants. A *T*-jump study of indium(III) perchlorate solution has yielded a value for the rate constant for dimerisation of $[InOH]^{2+}$. Due to ion-pairing complications, it has not proved possible to determine unequivocally, by comparison of rate constants of this and of the indium(III)–sulphate system, whether the rate-determining step in dimerisation of $[InOH]^{2+}$ is loss of a solvating water molecule from the indium.[21] The situation is entirely similar for gallium(III) in perchlorate solution.[22]

Group IV.—*Carbon.* A review of solvent effects on rates of bimolecular reactions [23] concentrates on examples from organic chemistry, but a short discussion on examples drawn from platinum(II) chemistry illustrates the general applicability of the ideas in this review not only to square-planar complexes but to bimolecular reaction of inorganic substrates in general.

Another piece of organic chemistry which may interest inorganic kineticists is the recent discussion of the question of connection or smooth transition between the S_N1 and S_N2 mechanisms of substitution at saturated carbon.[24] Such a discussion is not in itself novel,[25] but the idea that some sort of ion-pairing forms the link between the two formal extremes of dissociative and associative behaviour does seem to be a new contribution to this field, though the importance of ion-pairs as intermediates in reactions of inorganic complexes is not unfamiliar. However, it has been pointed out that the kinetic results which form the basis for this ion-pairing scheme can equally well be interpreted in terms of parallel unimolecular and bimolecular processes.[26]

Much of the chemistry of the remaining elements of this Group is really organic. Cases in which groups containing these elements are considered merely as substituents in an organic system (a common situation for silicon derivatives,[27] in which reactivity is controlled entirely by the organic part of a molecule, as in the study of germanium–germanium bond breaking by bromine,[28] and even Sommer's elegant studies on substitution at asymmetric silicon centres [29]) will be omitted. We shall mention only a few references which seem both to concentrate on the central Group IV atom and which seem fairly closely related to purely inorganic chemistry.

[21] E. M. Eyring and J. D. Owen, *J. Phys. Chem.*, 1970, **74**, 1825.
[22] J. D. Owen and E. M. Eyring, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2217.
[23] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.
[24] *E.g.*, *Nature*, 1969, **222**, 11; R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 362, 6031; R. A. Sneen and H. M. Robbins, *ibid.*, p. 3100.
[25] See, *e.g.* C. K. Ingold, 'Structure and Mechanism in Organic Chemistry', 1st edn., Cornell, 1953, chap. 7.
[26] B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen, *Chem. Comm.*, 1970, 1032.
[27] See, *e.g.*, A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometallic Chem.*, 1969, **20**, 49; H. Alt and H. Bock, *Tetrahedron*, 1969, **25**, 4825; M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **23**, 85.
[28] P. Mazerolles, M. Lesbre, and M. Joanny, *J. Organometallic Chem.*, 1969, **16**, 227.
[29] L. H. Sommer and D. L. Bauman, *J. Amer. Chem. Soc.*, 1969, **91**, 7076, and refs. therein.

Silicon and Germanium. Following logically from the previous references to the importance of ion-pairs in organic substitution mechanisms, are the studies of ion-pairing in chloride exchange at silicon and germanium. For chloride exchange between triphenylsilicon chloride and tetrabutylammonium chloride in benzene solution, the order in tetrabutylammonium chloride is 1·6, which suggests that ion-pairs are an important feature of the mechanism.*[30] This result contrasts with the same reaction in acetone–dioxan, where the exchange reaction involves only free chloride ions. This difference in behaviour seems reasonable in view of the relative solvating abilities of the two solvents. In fact, in acetone–dioxan the situation is more complicated, for ion-pairing does seem to be important for some substrates, for instance 2-phenylethyl- and benzyl-derivatives. These exchange studies and earlier studies of racemisation strongly suggest an associative character for chloride exchange in these solvents, as in nitromethane and in pure acetone, in contrast to racemisation and exchange in chloroform solution, which processes have been suggested to be dissociative. There have been relatively few direct comparative studies of reactivity of analogous silicon and germanium compounds. In the present case, direct comparison is difficult to carry out in view of the number of variables, but there does seem to be a general trend towards lower values of activation enthalpies and more negative values of activation entropies for germanium compounds than for their silicon analogues.[32]

Whereas ion-pair formation is important in determining reactivities in chloride exchange reactions, in solvolysis reactions it is solvent structure which can be particularly significant. There is already considerable evidence for participation of solvent oligomers in alcoholysis of trialkylsilicon and trialkylgermanium chlorides. In the reaction of triphenylsilicon chloride with isopropyl alcohol in carbon tetrachloride solution, the order in isopropyl alcohol is about 2·4, which is evidence for participation of solvent oligomers in this particular case. Moreover, the presence of a hydrochloric-acid-catalysed pathway suggests that not only alcohol $\cdots$ alcohol species but also alcohol $\cdots$ HCl species are significant components of the reaction mechanism.[33] The effects of solvents, and of added lithium cations, on the stereochemistry of substitution at germanium have been studied.[34]

The majority of the above systems involve a bimolecular substitution mechanism. Evidence for the transient existence of R_3Si^+ as an intermediate, and hence for a dissociative mechanism of substitution at silicon, has been sought but not obtained.[35] Another variant on simple S_N2 substitution at

[30] M. W. Grant and R. H. Prince, *Nature*, 1969, **222**, 1163.
[31] P. Beronius, U. Isacsson, and A.-M. Nilsson, *Acta Chem. Scand.*, 1970, **24**, 189.
[32] M. W. Grant and R. H. Prince, *J. Chem. Soc.* (*A*), 1969, 1138.
[33] A. D. Allen and S. J. Lavery, *Canad. J. Chem.*, 1969, **47**, 1263.
[34] A. Jean and M. Lequan, *Tetrahedron Letters*, 1970, 1517.
[35] F. Carré, R. Corriu, and B. Henner, *J. Organometallic Chem.*, 1970, **22**, 589.

* As a cautionary footnote, one should mention the demonstration of kinetic inactivity of bromide ion-pairs in a slightly different bromide exchange system.[31]

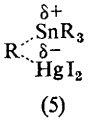
silicon is the four-centre transition state proposed on the basis of observations of rate, activation parameter, and isotope effects for reaction of trichlorosilane with aromatic sulphoxides.[36]

Tin. Full interpretation of solvent effects on reaction rates depends on knowledge of solvation of initial states and of transition states. In principle, thermochemical parameters for the former can be obtained by direct measurement, while the difference between initial-state and transition-state solvation is reflected in the kinetic parameters for the reaction. Unimolecular solvolysis of t-butyl chloride in aqueous alcohols has been treated in these terms, and a similar approach is now being used for a series of bimolecular reactions, particularly of tetra-alkyltin compounds reacting with mercury(II) halides. Solvent effects have been separated into initial-state and transition-state contributions for enthalpies, entropies, and free energies. For reaction of tetraethyltin with mercury(II) chloride, it appears that (as for solvolysis of t-butyl chloride) solvent effects are of comparable importance in the initial and transition states.[37] This situation may be contrasted with that in the Menschutkin reaction of trimethylamine with methyl iodide, where the effect on the rate of adding water to the non-aqueous solvent can be ascribed almost entirely to its effect on the free energies of the reactants. The small influence of solvent on the transition state suggests only a small charge separation therein.[38] Another study of the Menschutkin reaction has investigated the role of the solvent by correlation of rates with dielectric constants over a wide range of solvents.[39] A similar reaction is that of methyl iodide with ammonia or with methylamines, for which the effects of solvent on reactivity have been studied in benzene and in aqueous solutions.[40]

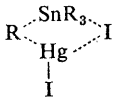
Reactions of tetra-alkyltin compounds with mercury(II) iodide in 96% methanol,[41] as with mercury(II) chloride,[37, 42] are bimolecular. The variation of rate constant with alkyl group suggests an open S_E2 transition state (5). Further evidence for this mechanism is provided by the variation of rate constant with solvent Y values for the particular case of the tetraethyltin compound reacting with mercury(II) chloride in a range of aqueous methanol mixtures.[43] Solvent effects in this last series of reactions have been separated into initial state and transition state contributions by the determination of heats of solution and of transfer of the reactants.[44] The effect of added lithium perchlorate on reaction rates for tetra-alkyltin compounds with mercury(II) iodide again indicates bimolecular electrophilic

[36] T. H. Chan and A. Melnyk, *J. Amer. Chem. Soc.*, 1970, **92**, 3718.
[37] M. H. Abraham, F. Behbahany, M. J. Hogarth, R. J. Irving, and G. F. Johnston, *Chem. Comm.*, 1969, 117; M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *ibid.*, 1969, p. 930.
[38] M. H. Abraham, *Chem. Comm.*, 1969, 1307.
[39] H. Hartmann and A. P. Schmidt, *Z. phys. Chem.* (*Frankfurt*), 1969, **66**, 183.
[40] M. H. Abraham, *Chem. Comm.*, 1970, 293.
[41] M. H. Abraham and T. R. Spalding, *J. Chem. Soc.* (*A*), 1969, 399.
[42] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 193.
[43] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 188.
[44] M. H. Abraham, R. J. Irving, and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 199.

substitution with an open (5) rather than a four-centred or cyclic (6) transition state.[45] The importance of polarity in tin–carbon bond cleavage has been probed by reacting tetra-alkyltin compounds with iodine monobromide.[46]

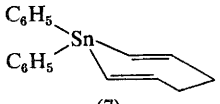


(5)



(6)

Photochemical or radical reactions of tetra-alkyltin and analogous compounds have also been studied. Examples include the foregoing reaction of tetra-alkyltins with iodine monobromide under photochemical conditions [46] and photolysis of the thermally stable compound 1,1-diphenyl-1-stannacyclohepta-2,6-diene (7).[47] Reactions of tetra-alkyltin compounds



(7)

with *N*-bromosuccinimide proceed by a bimolecular homolytic mechanism or S_H2 (*cf.* boron).[48]

Turning from the commonly studied tetrahedral compounds of tin to octahedral complexes, the kinetics of substitution at $SnCl_4py_2$ in nitrobenzene have been investigated.[49] The activation parameters are reported to an astonishing precision; the mechanism for solvolysis, as for chloride exchange, is said to be dissociative despite the very different rates reported for the two reactions.

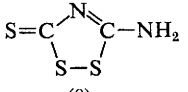
Group V.—*Nitrogen.* The rather disconnected collection of references to nitrogen compounds will be dealt with in order of co-ordination number, starting with one-co-ordinate nitrogen in nitric oxide and proceeding to four-co-ordinate tetrahedral compounds.

Preliminary work on the exchange of oxygen between nitric oxide and water has been described.[50] An earlier study of the decomposition of peroxonitrite in alkaline solution has now been complemented by a report of the rate–pH profile under acidic conditions, whence a pK_a of 6·6 for peroxonitrous acid has been estimated.[51] Peroxonitrite appears again

[45] M. H. Abraham and T. R. Spalding, *J. Chem. Soc.* (*A*), 1969, 784.
[46] G. Redl, B. Altner, D. Anker, and M. Minot, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 861.
[47] T. Sato and I. Moritani, *Tetrahedron Letters*, 1969, 3181.
[48] A. G. Davies, B. P. Roberts, and J. M. Smith, *Chem. Comm.*, 1970, 557.
[49] S. S. Sandhu and J. C. Bhatia, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2445.
[50] F. T. Bonner, *Inorg. Chem.*, 1970, **9**, 190.
[51] W. G. Keith and R. E. Powell, *J. Chem. Soc.* (*A*), 1969, 90.

amongst the products of photolysis of nitrates in alkaline solution. There seems to be little evidence for transient formation of nitrate radicals and solvated electrons in this system, but photolysis of azide solutions does involve generation of azide radicals and solvated electrons.[52] Reaction of sodium hyponitrite with dinitrogen tetroxide is much faster in nitromethane than in liquid dinitrogen tetroxide, carbon tetrachloride, or chloroform. The higher dielectric constant of nitromethane favours ionisation of the N_2O_4 to give NO^+, which can attack at the hyponitrite-oxygen. Products observed from the (heterogeneous) reaction of N_2O_4 with hyponitrite suspended in acetonitrile support this *O*-nitrosation mechanism.[53]

The kinetics of the conversion of isocyanate to ammonia indicate parallel acid-catalysed hydrolysis of HNCO and spontaneous hydrolysis of HNCO and of NCO^-. Marked catalysis by dinegative anions is attributed to a reaction path involving their carbamoyl derivatives.[54] Despite two investigations,[55] some details of the mechanism of hydrolysis of (iso)thiocyanic acid and of thiocyanates are still not clear. Lack of a kinetic isotope effect precludes protonation in transition-state formation. Nucleophilic attack of water at carbon in H_2NCS^+, which would seem a plausible mechanism, is not an acceptable hypothesis since rates do not conform to the patterns predicted by the Bunnett or Zucker–Hammett theories. The appearance of carbonyl sulphide amongst the products suggests thiocarbamic acid as a possible unstable intermediate. Products, stoicheiometry,[56] and kinetics [57] of the reaction of thiocyanate with nitrous acid and with nitric acid indicate that dinitrogen tetroxide, hypothiocyanous acid (HOSCN), and thiocyanogen are important intermediates. Rates and activation parameters have been reported for the conversion of thiocyanate to 5-amino-1,2,4-dithiazole-3-thione (8). The first step in the



(8)

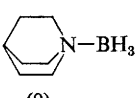
mechanism is reaction of thiocyanic acid with thiocyanate anion to generate cyanodithiocarbamate.[58]

Further studies of the kinetics of proton exchange between ammonia and water are concerned with catalysis by hydroxide and with the importance

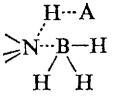
[52] F. Barat, B. Hickel, and J. Sutton, *Chem. Comm.*, 1969, 125; F. Barat, L. Gilles, B. Hickel, and J. Sutton, *J. Chem. Soc.* (*A*), 1970, 1982.
[53] M. N. Hughes and H. G. Nicklin, *Chem. Comm.*, 1969, 80.
[54] G. D. Vogels, L. Uffink, and C. van der Drift, *Rec. Trav. chim.*, 1970, **89**, 500.
[55] T. I. Crowell and M. G. Hankins, *J. Phys. Chem.*, 1969, **73**, 1380; T. D. B. Morgan, E. D. Phillips, and G. Stedman, *J. Chem. Soc.* (*A*), 1969, 2318.
[56] G. Stedman and P. A. E. Whincup, *J. Chem. Soc.* (*A*), 1969, 1145.
[57] M. N. Hughes, E. D. Phillips, G. Stedman, and P. A. E. Whincup, *J. Chem. Soc.* (*A*), 1969, 1148.
[58] W. H. Hall and I. R. Wilson, *Austral. J. Chem.*, 1969, **22**, 513.

of the structure of the solvent.[59] Kinetics of reaction of hydrazines with iodine[60] and with methyl iodide[61] have been interpreted. Tetramethylhydrazine reacts with iodine in non-polar solvents to give a 'charge transfer' complex $N_2Me_4.I_2$; in polar solvents actual transfer of charge to give $N_2Me_4^+.I_2^-$ is favoured by ionic solvation and results in a one-electron-transfer mechanism for the consequent redox reaction. Earlier results pertaining to the reaction of hydrazine with nitrous acid have been reinterpreted, particularly with respect to the pH-dependence of the observed rates.[62] While these reactions proceed mainly by bimolecular mechanisms, the reaction of tetrafluorohydrazine with 2-methylpropane proceeds *via* homolytic fission of the tetrafluorohydrazine to $\cdot NF_2$ radicals. Both rates and activation parameters for this reaction have been determined.[63] Mechanisms of reaction of tetrafluorohydrazine with oxygen, water, hydrogen peroxide, lithium hydride, and butyl-lithium have been proposed on the basis of qualitative evidence.[64] Products and stoicheiometry provide the basis for discussion of possible mechanisms of reaction of monochloramine and of *N*-chlorodimethylamine with arsines.[65]

The majority of reactions of Lewis adducts of the type $X_3B.NR_3$ are either dissociative or involve attack at electron-deficient boron; they have already been mentioned in the section on boron. Hydrolysis of the borane adducts of triethylamine and of quinuclidine (9), studied in aqueous



(9)



(10)

dioxan, proceeds by attack at the nitrogen. The general form of the transition state is shown in formula (10); some interaction between A and the boron, to give a four-centre transition state, is possible. Rates and activation parameters are reported. It is the similarity of the kinetic parameters for the two sterically very different adducts which provides some of the strongest evidence in favour of the proposed mechanism. Rearside attack at the nitrogen would manifestly be much easier for the triethylamine than for the quinuclidine adduct.[66]

[59] M. Alei and A. E. Florin, *J. Phys. Chem.*, 1969, **73**, 857.
[60] D. Romans, W. N. Bruning, and C. Michejda, *J. Amer. Chem. Soc.*, 1969, **91**, 3859.
[61] R. A. Hasty, *J. Phys. Chem.*, 1969, **73**, 317; R. A. Hasty and S. L. Sutter, *ibid.*, p. 3154.
[62] V. S. Koltunov and V. I. Marchenko, *Kinetika i Kataliz*, 1969, **10**, 939 (*Chem. Abs.*, 1969, **71**, 129,262g).
[63] A. V. Pankratov, L. A. Akhanshchikova, and Yu. A. Adamova, *Russ. J. Inorg. Chem.*, 1968, **13**, 1513.
[64] A. V. Pankratov, L. A. Akhanshchikova, Yu. A. Adamova, O. N. Shalaeva, and V. V. Antipova, *Russ. J. Inorg. Chem.*, 1969, **13**, 1516.
[65] L. K. Krannich and H. H. Sisler, *Inorg. Chem.*, 1969, **8**, 1032.
[66] H. C. Kelly and J. A. Underwood, *Inorg. Chem.*, 1969, **8**, 1202.

Phosphorus. Reactions of three-co-ordinate phosphorus(III) compounds generally involve associative mechanisms, as in exchange at $(Me_2As)_2P(CF_3)$,[67] in the reaction of phosphines with hydroxide,[68] and of trialkyl phosphites with hypochlorite.[69] In the last case, the phosphorus appears to be five-co-ordinate in the transition state. The reaction sequence for trialkyl phosphites plus phosphorus trifluoride includes a Michaelis–Arbuzov rearrangement.[70] The first stereochemical study of reactions of phosphorus(III) compounds with radicals demonstrates retention of configuration; this result is consistent with more than one possible mode of reaction.[71] Further examples of reactions of phosphorus(III) compounds appear later, when analogous derivatives of phosphorus(III) and phosphorus(V) are compared.

Reactions of three-co-ordinate phosphorus(V) include hydrogen exchange in hypophosphites[72] and condensation of phosphite with chromate.[73] This latter is not a redox reaction, in contrast to such apparently similar systems as chromate plus thiosulphate, which is an *sp*-oxoanion analogue of the classical inner-sphere redox mechanism of transition-metal complex chemistry.[74] Several associative mechanisms are feasible for reactions of phosphites with thionyl chloride. The phosphorus lone-pair can approach either the sulphur, the oxygen, or perhaps even one of the chlorines, which are rendered slightly positive by electron withdrawal to other sites in the thionyl chloride molecule.[75]

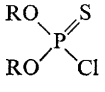
The vast majority of references to kinetic and mechanistic studies of phosphorus compounds concern tetrahedral species of the element in oxidation state five: phosphate anions, neutral oxophosphorus compounds $R_3P{=}O$, and organophosphorus cations. The last two classes are fully discussed in another Specialist Periodical Report devoted to organophosphorus chemistry,[76] but several references will be briefly mentioned here to set the developing picture of mechanisms of substitution at phosphorus(V) into the general context of mechanisms of inorganic reactions.

Products and kinetics of hydrolysis of polyphosphates have been reported for several systems.[77] Transition-metal cations can have an accelerating or

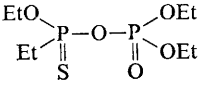
[67] A. H. Cowley and D. S. Dierdorf, *J. Amer. Chem. Soc.*, 1969, **91**, 6609.
[68] S. M. Bloom, S. A. Buckler, R. F. Lambert, and E. V. Merry, *Chem. Comm.*, 1970, 870.
[69] J. H. Finley and D. B. Denney, *J. Amer. Chem. Soc.*, 1970, **92**, 362.
[70] D. H. Brown, K. D. Crosbie, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1969, 872.
[71] W. G. Bentrude, J. H. Hargis, and P. E. Ruser, *Chem. Comm.*, 1969, 296.
[72] G. C. Roper, T. E. Haas, and H. D. Gillman, *Inorg. Chem.*, 1970, **9**, 1049.
[73] S. A. Frennesson, J. K. Beattie, and G. P. Haight, *Acta Chem. Scand.*, 1969, **23**, 3277.
[74] I. Baldea and G. Niac, *Inorg. Chem.*, 1970, **9**, 110.
[75] A. Zwierzak, *Tetrahedron*, 1969, **25**, 5177.
[76] 'Organophosphorus Chemistry,' (Specialist Periodical Report), ed. S. Trippett, The Chemical Society, London, 1970.
[77] D. L. Miller, G. J. Krol, and U. P. Strauss, *J. Amer. Chem. Soc.*, 1969, **91**, 6882; W. Wieker and E. Thilo, *Rev. Chim. minérale*, 1969, **6**, 89 (*Chem. Abs.*, 1970, **72**, 36,312d); J. B. Gill and S. A. Riaz, *J. Chem. Soc.* (*A*), 1969, 183; S. I. Vol'fkovitch, A. S. Cherepanova, and I. A. Grishina, *Zhur. priklad. Khim.*, 1970, **43**, 3 (*Chem. Abs.*, 1970, **72**, 104,437a).

inhibiting effect on phosphate hydrolysis; this has recently been fully documented for 2-, 3-, and 4-pyridylmethylphosphates. The catalytic effects are ascribed in all cases to interaction at the phosphate rather than at the pyridyl-nitrogen part of the substrate.[78]

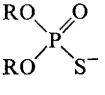
Electrophilic substitution at four-co-ordinate oxophosphorus(v) in the reaction of the benzyl ester of diphenylphosphinyl formate with iodide in acetone takes place by a dissociative mechanism through $(C_6H_5)_2P{=}O^-$.[79] Nucleophilic substitution at this type of phosphorus centre is considerably more widely studied. Kinetics of chloride exchange at thiophosphoryl compounds (11; R = Me, Et, or Pr^n) are consistent with a bimolecular reaction involving a five-co-ordinated transition state. Exchange at this, as at other thiophosphoryl centres, is slower than at equivalent (oxo)phosphoryl centres, due to polarity differences between $\rangle P{-}S$ and $\rangle P{-}O$.[80] The demonstration of Walden inversion, with full inversion of configuration, in hydroxide attack at thiophosphoryl compounds of the type (12), suggests that the trigonal-bipyramidal product of nucleophilic attack is a transition state rather than an intermediate, for some racemisation of the latter would be expected to lead to less than complete inversion in the overall reaction.[81] Attack of cyanogen bromide at dialkylphosphorothioic anions (13) also occurs by bimolecular nucleophilic attack at phosphorus.[82]



(11)

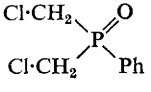


(12)



(13)

Again, kinetic results indicate rate-determining bimolecular attack of water in transition-state formation in hydrolysis of di(2,4-dinitrophenyl)phosphate in acid or neutral solution.[83] The variation of rates of hydrolysis of phenyl bischloromethylphosphinate (14) with solvent composition in aqueous sulphuric acid suggests the participation of two water molecules in the transition state, which would thus contain six-co-ordinated phosphorus.[84]



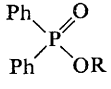
(14)

[78] Y. Murakami and M. Takagi, *Bull. Chem. Soc. Japan*, 1969, **42**, 3478.
[79] S. Warren and M. R. Williams, *Chem. Comm.*, 1969, 180.
[80] M. Mikolajczyk, J. Michalski, A. Halpern, and R. Sochaxcka, *Monatsh.*, 1969, **100**, 1266.
[81] J. Michalski, M. Mikolajczyk, B. Mlotkowska, and J. Omelanczuk, *Tetrahedron*, 1969, **25**, 1743.
[82] R. R. Engel, *Canad. J. Chem.*, 1969, **47**, 1258.
[83] C. A. Bunton and S. J. Farber, *J. Org. Chem.*, 1969, **34**, 767.
[84] V. E. Bel'skii and M. V. Efremova, *Russ. J. Phys. Chem.*, 1968, **42**, 1553.

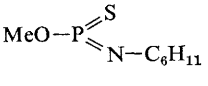
Thermal decomposition of alkyl diphenylphosphinates (15) has also been investigated.[85]

In the foregoing examples of nucleophilic substitution at phosphorus(v), an associative mechanism appears to operate. In contrast, both solvent effects and product stereochemistry in solvolysis of methyl *N*-cyclohexylphosphoramidothioic chloride can be interpreted much more readily in terms of a dissociative mechanism of reaction *via* the three-co-ordinated transition state (16).[86] Stereochemical studies of reactions of cyclic phosphorus(v) esters also suggest a dissociative mechanism.[87]

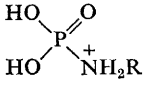
Results from various sources on the hydrolysis of orthophosphoramidates have been collated to discover what factors control whether reaction proceeds by an associative or a dissociative mechanism. Compounds which have a protonated nitrogen atom adjacent to the phosphorus, as in (17), react by a dissociative mechanism, but compounds in which the nitrogen next to the phosphorus is not protonated, and hence is not positively charged (18), react by an associative or S_N2 mechanism.[88]



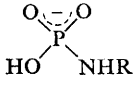
(15)



(16)



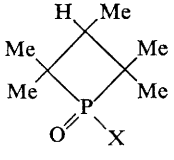
(17)



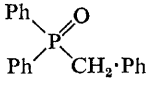
(18)

There is a similar difference in mechanism between closely related groups of compounds in hydrolysis of phosphate esters. Monoester hydrolysis proceeds by an initial dissociative step, but hydrolysis of anions of diesters takes place by bimolecular nucleophilic attack of solvent at phosphorus.[89] Further studies of mechanisms of reaction of phosphate esters have been described.[90]

The stereochemical course of reactions at tetrahedral phosphorus(v) and interpretation in terms of preferred configurations and pseudorotation in a trigonal-bipyramidal transition state continue to generate much interest. It has, however, been suggested that, at least in some cases [for instance, acid hydrolysis of the cyclic compound (19)], the mechanism is



(19)



(20)

[85] K. D. Berlin, J. G. Morgan, M. E. Peterson, and W. C. Pivonka, *J. Org. Chem.*, 1969, **34**, 1266.

[86] A. F. Gerrard and N. K. Hamer, *J. Chem. Soc.* (*B*), 1969, 369.

[87] W. Wadsworth and H. Horton, *J. Amer. Chem. Soc.*, 1970, **92**, 3785.

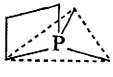
[88] C. J. Peacock, *Z. Naturforsch.*, 1969, **24b**, 391.

[89] A. J. Kirby and M. Younas, *J. Chem. Soc.* (*B*), 1970, 510.

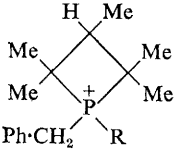
[90] A. J. Kirby and M. Younas, *J. Chem. Soc.* (*B*), 1970, 1165, 1187; S. A. Kahn and A. J. Kirby *ibid.*, p. 1172; S. A. Khan, A. J. Kirby, M. Wakselman, D. P. Horning, and J. M. Lawlor, *ibid.*, p. 1182.

simple S_N2 with no five-co-ordinate intermediate of sufficient lifetime to permit pseudorotation.[91] The lack of ^{18}O exchange in base hydrolysis of (20) might similarly be explained in terms of a simple S_N2 mechanism.[92]

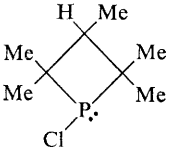
The effects on pseudorotation in postulated five-co-ordinate intermediates of inclusion of the phosphorus in a ring system are being intensively studied. In general, acyclic phosphonium salts undergo nucleophilic substitution with inversion of configuration, whereas cyclic compounds containing small rings, which show a marked preference to have apical–equatorial positioning of the ring in the transition state (21), are substituted with retention of configuration.[93] However, the picture is not entirely clear-cut, for alkaline hydrolysis of some phosphetanium salts, *e.g.* (22; R = Me or Ph), results in partial inversion.[94] For the analogous phosphorus(III) compound (23), which could be considered as (22) with an



(21)

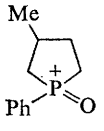


(22)

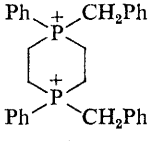


(23)

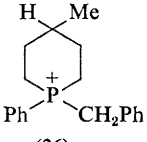
electron pair replacing the alkyl group, nucleophilic substitution proceeds with predominant inversion.[95] The rôle of ring strain and the ease of approach of the nucleophile to the phosphorus(III) in this type of compound have been assessed.[96] The stereochemical constraint in the transition state is less for a five-membered ring, as shown in substitution in the phospholan system based on (24),[97] while pseudorotation in transition states from (25)[98] and (26)[99] is unimpeded by any conformational preference of



(24)



(25)



(26)

[91] P. Haake, R. D. Cook, T. Koizumi, P. S. Ossip, W. Schwarz, and D. A. Tyssee, *J. Amer. Chem. Soc.*, 1970, **92**, 3828.

[92] P. Haake and G. W. Allen, *Tetrahedron Letters*, 1970, 3113.

[93] *E.g.*, W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465; S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200.

[94] J. R. Corfield, J. R. Shutt, and S. Trippett, *Chem. Comm.*, 1969, 789; S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *ibid.*, p. 769.

[95] D. J. H. Smith and S. Trippett, *Chem. Comm.*, 1969, 855.

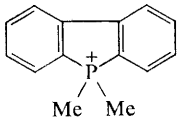
[96] R. Greenhalgh, J. E. Newbery, R. Woodcock, and R. F. Hudson, *Chem. Comm.*, 1969, 22.

[97] W. Egan, G. Chauvière, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Comm.*, 1970, 733.

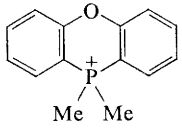
[98] G. E. Driver and M. J. Gallagher, *Chem. Comm.*, 1970, 150.

[99] K. L. Marsi and R. T. Clark, *J. Amer. Chem. Soc.*, 1970, **92**, 3791.

the six-membered ring. Another study of five- and six-membered ring compounds incorporating tetrahedral phosphorus(v) concerns 9-phosphoniafluorene compounds, *e.g.* the iodide of (27), and phenoxaphosphonium compounds, *e.g.* the iodide of (28). Discussion of mechanism is here complicated by the occurrence of ring fission and expansion.[100] There has been a report of acyclic phosphorus(v) compounds which behave as if the mechanism includes an intermediate, in which the phosphorus(v) becomes incorporated into a ring system, which pseudorotates according to the usual rules.[101]



(27)



(28)

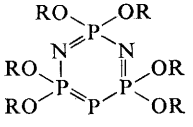
Apart from stereochemical requirements of small rings, the other important factor in determining the stereochemical course of a reaction is the sheer bulk of the substituents on the relatively small phosphorus atom. One t-butyl group has only a small effect on rates of alkaline hydrolysis of phosphonium salts, but two t-butyl groups on the same phosphorus result in a large retardation of rate.[102] This observation parallels an earlier one on rates of hydrolysis for analogous phosphorus esters, and subsequent studies on nucleophilic substitution at t-butyl derivatives of phosphorus(III).[103] The retarding effect of the two t-butyl groups in, say, hydroxide attack at the phosphonium salt can easily be understood if a hydroxide ion attacks opposite a bulky t-butyl group. Then the presence of one t-butyl group has only a directing effect, but the substitution of the second t-butyl will hinder the approach of hydroxide from the direction opposite the first, and thus have a marked retarding influence. Now hydroxide attack at that face of the tetrahedron which is opposite the t-butyl group is not the expected route, but the exceptional nature of substitution in compounds containing one t-butyl group is confirmed by the observation that (−)-benzyl-t-butylmethylphenylphosphonium iodide reacts with hydroxide with retention of configuration, and not, as expected, with inversion.[102] But, as with the effects of small rings on the stereochemical course of reactions at tetrahedral phosphorus(v), the situation is not entirely simple, for the exceptional effect of one t-butyl group is only observed for poor leaving-groups, such as phenyl in the case just cited; for good leaving-groups, the normal stereochemical course of inversion applies.[104]

[100] D. W. Allen and I. T. Millar, *J. Chem. Soc.* (*B*), 1969, 263; *J. Chem. Soc.* (*C*), 1969, 252.
[101] D. C. Gay and N. K. Hamer, *J. Chem. Soc.* (*B*), 1970, 1132.
[102] N. J. De'Ath and S. Trippett, *Chem. Comm.*, 1969, 172.
[103] A. P. Stewart and S. Trippett, *J. Chem. Soc.* (*C*), 1970, 1263.
[104] R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *Chem. Comm.*, 1969, 1010.

There is yet one other cause of control of stereochemistry in nucleophilic substitution at tetrahedral phosphorus(v). Just as small rings control stereochemistry by their marked preference for an apical–equatorial conformation in the five-co-ordinate phosphetan transition state, so strongly electronegative groups control it by their preference for axial positions in trigonal-bipyramidal structures. This effect is illustrated in the study of hydroxide attack on dialkoxyphosphonium salts, where the presence of three electronegative groups (two alkoxy- and one hydroxy-group) in the trigonal-bipyramidal transition state means that at least one such group must be in an unfavourable (equatorial) position.[105]

Very relevant to this section, in which stereochemical observations are so important in determining mechanisms, one should report the sad story of the misinterpretation inadvertently caused by the *X*-ray crystallographer who, in picking the best crystal from a product, selected one consisting of a minor impurity rather than of the major product.[106]

The remaining references to substitution at tetrahedral phosphorus(v) deal with cyclophosphazenes (29). Base-catalysed decomposition appears to be a bimolecular process, controlled by electronic rather than steric factors,[107] and involves phosphorus–nitrogen bond breaking at an early stage in the reaction sequence.[108]



(29)

Mechanisms of reactions of five- and six-co-ordinate compounds, *e.g.* PF_5 and PF_6^-, will be discussed with the exactly analogous arsenic and antimony compounds in the following section on those elements.

Arsenic and Antimony. Three studies of reaction mechanisms for tetrahedral antimony(v) compounds are reported. These are of the reaction of trimethylantimony sulphide (Me_3SbS) with alkyl halides, where a four-centre transition state seems possible,[109] the reaction of R_4Sb^+ cations with alkoxide ions,[110] and the ageing of antimonic acid in aqueous solution.[111]

Both thermal and photochemical decomposition of pentaphenylantimony have been investigated. Whereas the products of the photochemical reaction are numerous, though all derived from phenyl radicals, the

[105] K. E. DeBruin and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 7393.
[106] S. E. Cremer, *Chem. Comm.*, 1970, 616.
[107] H. R. Allcock and E. J. Walsh, *Chem. Comm.*, 1970, 580.
[108] H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, 1969, **91**, 3102.
[109] J. Otera and R. Okawara, *J. Organometallic Chem.*, 1969, **16**, 335.
[110] W. E. McEwen, G. H. Briles, and B. E. Giddings, *J. Amer. Chem. Soc.*, 1969, **91**, 7079.
[111] S. Cahuzac and J. Lefebvre, *Bull. Soc. chim. France*, 1969, 771.

products of thermal reaction are triphenylantimony and biphenyl. Moreover, the latter is produced in an intramolecular step, for no free phenyl radicals could be detected.[112]

Five- and six-co-ordinate compounds, of phosphorus as well as of arsenic and antimony, are linked by a qualitative study of fluorine exchange in a wide variety of systems. Whether this exchange was slow or fast was determined for eighteen combinations of compounds by ^{19}F n.m.r. spectroscopy. Fluorine exchange is fast when fluorine bridges between compounds can be formed, as in well-known cases involving, *e.g.*, Sb—F—Sb bridges and in newly established cases such as P—F—Sb and As—F—As.[113]

The main interest in reaction kinetics for octahedral compounds of the Group V elements centres on the hexafluoro-complexes and closely related series of complexes. For PF_6^-, as for other MF_6^- species, acid catalysis is significant. Rates are greater, activation enthalpies lower, in acid than in neutral solution. The rate law implies association of one proton with each PF_6^- anion; Raman evidence suggests that the reactive species is an ion-pair H^+,PF_6^- rather than simply the neutral molecule HPF_6.[114] AsF_6^- is considerably more resistant to hydrolysis than is PF_6^-. AsF_6^- is not hydrolysed in alkaline solution, but it is hydrolysed in concentrated sulphuric acid. Correlation of rates with the acidity function H_- indicates that, as for PF_6^-, there is fast pre-equilibrium with a proton to give $HAsF_6$ (here assumed to be the simple molecule), followed by slow and reversible attack by water to give $HAsF_5(OH)$.[115] The ion $AsF_5(OH)^-$ hydrolyses over a wide pH range. Observed first-order rate constants can be accommodated in a three-term rate law whose terms correspond to an S_N1ca path predominant in strong acid, an S_N1 path, and an S_N1cb path predominant in alkaline solution. The last term is assigned as an S_N1cb rather than an S_N2 mechanism from the value of the determined activation entropy. It is interesting to compare $AsF_5(OH)^-$, hydrolysed in basic solution, with AsF_6^-, which has no irremovable proton for an S_N1cb reaction path and is totally unreactive in alkaline solution.[116]

Hydrolysis of $SbCl_6^-$ is not acid-catalysed. The difference between MCl_6^- and MF_6^- in these Group V complexes exactly parallels that of octahedral transition-metal complexes, *e.g.* *cis*-$[Co\,en_2F_2]^+$ and *cis*-$[Co\,en_2Cl_2]^+$. But rates of hydrolysis of $SbCl_6^-$ in alkaline solution are a function of hydroxide ion concentration. Presumably there is associative attack by hydroxide ion since $SbCl_6^-$ has no acidic protons to permit an S_N1cb mechanism. The kinetic pattern here is complicated by the presence of the buffers used, for these can and do complex with the antimony.[117]

[112] Kei-wei Shen, W. E. McEwen, and A. P. Wolf, *J. Amer. Chem. Soc.*, 1969, **91**, 1283.
[113] S. Brownstein, *Canad. J. Chem.*, 1969, **47**, 605.
[114] A. E. Gebala and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1969, **31**, 771.
[115] W. L. Lockhart, M. M. Jones, and D. O. Johnston, *J. Inorg. Nuclear Chem.*, 1969, **31**, 407.
[116] A. E. Gebala, W. L. Johnson, and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3495.
[117] S. B. Willis and H. M. Neumann, *J. Amer. Chem. Soc.*, 1969, **91**, 2924.

Hydrolysis of complexes of the type MF_6^- is catalysed not only by acid but also by a series of metal ions.[118] Kinetic data have been obtained for catalysis of hydrolysis of PF_6^-, AsF_6^-, $AsF_5(OH)^-$, and also of BF_4^-, by beryllium(II), aluminium(III), zirconium(IV), and thorium(IV).[6] Again this may be seen as an extension of studies on cation catalysis of hydrolysis of transition-metal complexes, *e.g.* the numerous studies of mercury(II)-catalysed aquations of cobalt(III)-ammine-halide complexes, or the recent study of metal ion catalysis of chloro(ethylenediaminetriacetato)-cobaltate(III).[119]

Chloride exchange between $[SbCl_4(OR)_2]^-$ and $SbCl_3$ is found to occur by the same mechanism as established earlier for chloride exchange between $[SbCl_5(OR)]^-$ and $SbCl_3$. Differences in rates between R = Me and R = Et can be explained in terms of relative bond strengths.[120]

Hydrogen (deuterium) exchange in the acid systems HF–SbF_5, FSO_3H–SbF_5, and H_2SO_4–SbF_5 has been studied semiquantitatively. The suggested mechanism involves such species as H_3^+ and D_3^+, and the mixed cations H_2D^+ and HD_2^+, at least as transition states if not real intermediates, and provides another illustration of the similarity between gas-phase and super-acid chemistry.[121]

Group VI.—*Sulphur: general.* The reactivity of elemental sulphur, in the forms S_6, S_7, S_8, and S_{12}, has been probed by a study of its reaction with *o*-tolyldiphenylphosphine to give the sulphide $S{=}PPh_2(o\text{-tolyl})$. These reactions, conducted in solution in carbon disulphide, are second-order. Rates and activation parameters were determined; the highest activation enthalpy was for S_8.[122]

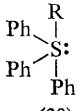
The primary salt effect on rates of electron spin exchange in solutions of Fremy's salt is consistent with bimolecular reaction species with a charge product ($z_A z_B$) of + 4, which supports a mechanism involving collision between two $[(SO_3)_2NO]^{2-}$ anions ($z_A = z_B = -2$).[123]

Two-co-ordinate sulphur. Opinions seem divided as to whether nucleophilic attack at two-co-ordinate sulphur,[124–127] which is an associative process, has a synchronous [125] or an addition–elimination [126] mechanism. For reaction of diaryl sulphides with aromatic hydrocarbons, formation of a sulphonium cation and then of a four-co-ordinate sulphur intermediate has been proposed.[128] The rôle of the 3*d* orbitals on sulphur in nucleophilic substitutions has been discussed.[124]

[118] H. R. Clark and M. M. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 4302.
[119] S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1969, 1164.
[120] L. Colditz, R. Dlaske, and G. Heller, *Z. Chem.*, 1969, **9**, 348.
[121] G. A. Olah, J. Schen, and R. D. Schlosberg, *J. Amer. Chem. Soc.*, 1970, **92**, 3831.
[122] F. Fehér and D. Kurz, *Z. Naturforsch.*, 1969, **24b**, 1089.
[123] M. Alibhai, A. Hudson, and H. A. Hussain, *J. Chem. Soc.* (*A*), 1969, 678.
[124] A. I. Shatenstein and H. A. Gvozdeva, *Tetrahedron*, 1969, **25**, 2749; E. Ciuffarin and G. Guaraldi, *J. Org. Chem.*, 1970, **35**, 2006.
[125] L. Senatore, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, 1970, **92**, 3035.
[126] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, 1970, **92**, 2731.
[127] J. Michalski and A. Skrowronska, *J. Chem. Soc.* (*C*), 1970, 703.
[128] Chung Hwa Han and W. E. McEwen, *Tetrahedron Letters*, 1970, 2629.

Nucleophilic attack at trithionate ($S_3O_6^{2-}$), studied in aqueous methanol using nucleophiles EtS^-, PhS^-, PPh_3, or CN^-, follows a second-order rate law and involves bimolecular attack of the incoming nucleophile at the two-co-ordinate central sulphur atom. The order of reactivity towards different nucleophiles can be discussed in terms of the concept of hard and soft acids and bases, with the central sulphur atom regarded as a soft acid centre.[129] In these trithionate reactions, sulphur–sulphur bond breaking occurs subsequent to the rate-determining step; a more direct study of sulphur–sulphur bond breaking can be found in organosulphur chemistry.[130] Heterolytic fission of sulphur–sulphur bonds in symmetrical disulphides has been demonstrated. Activation entropies and rate variations with solvent composition are both consistent with significant solvent assistance to formation of a charge-separated transition state.[131] Formation of sulphur–sulphur bonds in disulphides involves bimolecular attack of one sulphide at the sulphur of the other, generating a sulphonium ion intermediate.[132]

Three-co-ordinate sulphur. The most inorganic example has been the study of the kinetics and mechanism of hydrolysis of dithionites.[133] Kinetics of attack of iodide and of thiourea at the *SS*-dimethylsulphinium cation ($Me_2S{\cdot}NH_2^+$) in water and in aqueous dimethyl sulphoxide indicate pre-equilibrium protonation followed by a rate-determining associative process. The overall activation entropy is negative.[134] Nucleophilic substitution, by vinyl-lithium, at the triphenylsulphonium cation (Ph_3S^+) is also associative. Indeed the species (30) is an intermediate rather than a transition state.[135] Comparison of the stereochemical courses of reactions at tetrahedral phosphorus and at three-co-ordinate sulphur, which is



(30)

effectively tetrahedral due to the presence of the lone-pair, suggests that there is no pseudorotation in transition states for associative substitution at the sulphur compounds.[136]

Grignard synthesis of optically active sulphoxides has now been fully

[129] R. D. Ritter and J. H. Krueger, *J. Amer. Chem. Soc.*, 1970, **92**, 2316.
[130] F. Pietra and D. Vitali, *J. Chem. Soc.* (*B*), 1970, 623.
[131] A. M. Kiwan and H. M. N. H. Irving, *Chem. Comm.*, 1970, 928.
[132] M. Oki and K. Kobayashi, *Bull. Chem. Soc. Japan*, 1970, **43**, 1229.
[133] W. J. Lem and M. Wayman, *Canad. J. Chem.*, 1970, **48**, 776; M. Wayman and W. J. Lem, *ibid.*, p. 782; L. Burlamacchi, G. Guarini, and E. Tiezzi, *Trans. Faraday Soc.*, 1969, **65**, 496.
[134] J. H Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 4974.
[135] B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, 1969, **91**, 2175.
[136] R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 5644.

proved to proceed with inversion of configuration at the sulphur.[137] However, the conversion of methionine sulphoxide to the sulphimine has been reported as the first example of nucleophilic substitution at sulphoxide-sulphur to proceed with retention of configuration.[138] Nucleophilic substitution at sulphur(IV) in sulphoxides and at four-co-ordinate sulphur(VI) in sulphones has been compared. The mechanisms are the same, but there is a marked difference in activation energies.[139]

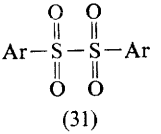
Four-co-ordinate sulphur. The rate of decomposition of peroxodisulphate in aqueous dimethyl sulphoxide increases as the solvent becomes less aqueous. This trend is attributed to decreasing solvation of the initial state as the proportion of dimethyl sulphoxide increases.[140] Kinetic parameters are reported for silver(I)-catalysed decomposition of peroxodisulphate[140, 141] and of peroxomonosulphate[141] in aqueous solution. The activation energy for dissociation of peroxodisulphuryl difluoride into $\cdot SO_3F$ radicals has been determined by e.s.r. and by ^{19}F n.m.r. spectroscopy.[142] The first determination of the stereochemical course of nucleophilic substitution at tetrahedral sulphur(VI), for reaction of (−)-menthyl-phenylmethane sulphonate with *p*-tolyl magnesium bromide, has been reported.[143]

The very precise kinetic work in which the variation of activation enthalpy with temperature has been determined, to give $\Delta C_p^{\ddagger}$ and thence, in conjunction with kinetic solvent isotope effects, detailed information about solvation changes in going from the initial to the transition state, has been extended from carbon to nucleophilic substitution at tetrahedral sulphur(VI) in sulphonyl chlorides, $R \cdot SO_2Cl$.[144] The empirical Grunwald–Winstein method of elucidating solvolysis mechanisms from the solvent variation of rates[145] has been applied to solvolysis of dimethylsulphamoyl chloride ($Me_2N \cdot SO_2Cl$) in aqueous acetone. An associative mechanism is indicated by this treatment of the rate data; it is supported by the large negative activation entropies determined.[146] This study has been extended to other nucleophiles, including substituted pyridines[147] and acetate,[148] where again the variation of rates with solvent composition suggests an associative mechanism for these substitutions at tetrahedral sulphur(VI).

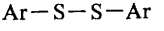
[137] H. Hope, U. de la Camp, G. D. Homer, A. W. Messing, and L. H. Sommer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 612.
[138] B. W. Christensen and A. Kjaer, *Chem. Comm.*, 1969, 934.
[139] J. L. Kice and G. J. Kasperek, *J. Amer. Chem. Soc.*, 1969, **91**, 5510.
[140] T. Rahkonen and E. Tommila, *Acta Chem. Scand.*, 1969, **23**, 2573.
[141] R. Schulze-Rettmer, B. Buchheim, and W. Schlenter, *Ber. Kernforschungsanlage Juelich* 1969, *Juel*-591-*DE* (*Chem. Abs.*, 1970, **72**, 6549u).
[142] R. A. Stewart, *J. Chem. Phys.*, 1969, **51**, 3406.
[143] M. A. Sabol and K. K. Andersen, *J. Amer. Chem. Soc.*, 1969, **91**, 3603.
[144] R. E. Robertson, B. Rossail, S. E. Sugamori, and L. Treindl, *Canad. J. Chem.*, 1969, **47**, 4199.
[145] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29; and refs. therein.
[146] O. Rogne, *J. Chem. Soc.* (*B*), 1969, 663.
[147] O. Rogne, *J. Chem. Soc.* (*B*), 1970, 727.
[148] O. Rogne, *J. Chem. Soc.* (*B*), 1970, 1056.

Further kinetic information on hydrolysis of sulphonyl chlorides ($R \cdot SO_2Cl$) is contained in a paper which correlates kinetic data for hydrolysis of these and other halides, for example of phosphonic and phosphinic acids, with i.r. and n.q.r. spectroscopic data.[149] Hydrolysis of the adduct $Me_2EtN.SO_3$ has been studied over a wide pH range.[150] The rate-law determined in basic solution indicates S_N2 attack by hydroxide at the sulphur atom, as earlier proposed for the parent adduct $Et_3N.SO_3$.

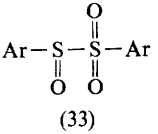
Thermal decomposition of aryl disulphones (31) in diglyme or bromobenzene occurs by sulphur–sulphur homolysis, as does decomposition of aryl disulphides (32), mentioned earlier in this section.[131] Rates and activation parameters are reported for decomposition of the disulphones. The reaction follows simple first-order kinetics, but the product distribution is complicated. The present work forms part of a systematic study of sulphur–sulphur bond fission for molecules containing pairs of sulphur atoms variously in oxidation states of two, four, and six, the oxidation state being fixed by the presence of the appropriate number of oxygen atoms. The completed study will include the symmetrical compounds, ranging from the disulphides (32) to the sulphones (31), as well as unsymmetrical compounds such as (33). The least stable member of the group appears to be the disulphinyl series (34), for no such compound has yet been isolated. Reactivities in this group of compounds depend both on the sulphur–sulphur bond strengths and on the stabilities of the radicals resulting from homolysis.[151] The first reported example of general-base catalysis at sulphonyl-sulphur has been observed for substitution at disulphones (31).[152]



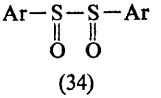
(31)



(32)



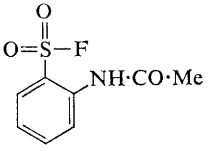
(33)



(34)

Sulphur–fluorine bonds are generally inert to hydrolysis, not only in sulphur hexafluoride but also in sulphonyl fluorides. Exceptions to this general pattern occur when neighbouring-group participation is possible, as in the relatively fast hydrolysis, with concomitant acetyl loss, of the arylsulphonyl fluoride (35).[153] All the foregoing examples have concerned

[149] A. A. Neimysheva and I. L. Knunyants, *Doklady Akad. Nauk S.S.S.R.*, 1968, **181**, 697.
[150] I. G. Ryss, L. P. Bogdanova, S. L. Idel's, and T. N. Kotlyar, *Russ. J. Inorg. Chem.*, 1969, **14**, 1577.
[151] J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, 1970, **35**, 114.
[152] J. L. Kice and G. J. Kasperek, *J. Amer. Chem. Soc.*, 1970, **92**, 3393.
[153] M. E. Aberlin and C. A. Bunton, *J. Org. Chem.*, 1970, **35**, 1825.



(35)

tetrahedral sulphur(VI). One example of a kinetic study pertaining to an alternative four-co-ordinate stereochemistry, the eccentrically shaped sulphur(IV) tetrafluoride, arises as a by-product from pulse radiolysis studies. Kinetics of hydrolysis in acidic, neutral, and basic solution show both acid and base catalysis. It is suggested that H_3O^+ can attack at the lone-pair on the sulphur, while both H_2O and OH^- attack at the sulphur in the normal S_N2 manner.[154]

Group VII.—A qualitative study of oxygen exchange with perbromate indicates a slow rate of exchange. Thus perbromate fits into its expected place in reactivity trends for oxygen exchange with halogen oxoanions.[155] No exchange of oxygen between chlorine dioxide and water could be detected.[156] There are a few remarks on rates and mechanism of hydrolysis of Ipy.ICl_2 in a paper primarily devoted to charge-transfer phenomena.[157]

Group 0.—Studies of mechanisms of reactions of compounds of the noble gases appear to have been restricted, in the period covered by this report, to an ^{18}F tracer and ^{19}F n.m.r. investigation of fluorine exchange between $XeOF_4$ and XeO_2F_2.[158]

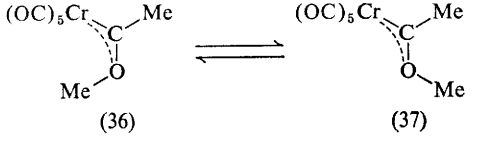
2 Intramolecular Processes

Introduction.—This section covers the intramolecular processes inversion, isomerisation, pseudorotation, and internal rotation for compounds of the non-transition elements. Much of this ground is organic chemistry; we shall concentrate on compounds wherein the main rôle, *e.g.* the pivot for inversion, is taken by an element other than carbon. Examples of kinetic studies of internal rotation cover a continuum from (*a*) purely organic examples of restricted rotation about carbon–carbon bonds, through (*b*) a variety of carbon–non-carbon rotations to (*c*) purely inorganic examples. In general, (*a*) and (*b*) will not be discussed in this review, except in special cases, for instance where a nearby inorganic moiety has a profound effect on restricted rotation, or where there is some interpretative doubt over the assignment of observed rates to inversion at X or to hindered rotation about a carbon–X bond. References will be dealt with in Periodic Table order, after initial mention of some references of general applicability.

[154] K.-D. Asmus, W. Grünbein, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1970, **92**, 2625.
[155] E. H. Appelman, *Inorg. Chem.*, 1969, **8**, 223.
[156] R. K. Murmann and R. C. Thompson, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1404.
[157] B. Jones, G. J. Moody, and J. D. R. Thomas, *Inorg. Chem.*, 1970, **9**, 114.
[158] H. D. Frame, J. L. Huston, and I. Sheft, *Inorg. Chem.*, 1969, **8**, 1549.

There have been many discussions of a general nature on classification and representation of intramolecular processes in simple compounds AB_n. Intramolecular isomerisation in octahedral compounds has been discussed in relation to recent published examples.[159] Both matrix[160] and topological[161] representations of trigonal and rhombic twists, and representations of digonal twists[162] have been surveyed for octahedral systems. Similarly, intramolecular processes in trigonal bipyramidal systems have been described in topological terms for simple AB_5 compounds[163] containing up to five different ligands (B)[164] or chelate rings,[163] and in terms of matrices.[165] This last is an extension of an earlier treatment of octahedral systems, as in a further non-topological discussion of trigonal bipyramidal compounds.[166]

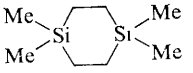
Group IV.—*Carbon.* The effect of nearby inorganic moieties on kinetic characteristics of hindered rotation about a carbon to *sp*-element bond is illustrated by variable temperature n.m.r. studies of hindered rotation about carbon–oxygen in (36) ⇌ (37),[167] and about carbon–nitrogen in *NN*-dimethyl[$^2H_3$]acetamide in various environments.[168] For the latter compound the barrier is 21·0 kcal mol^{-1} in aqueous solution, but only 19·0 kcal mol^{-1} when the compound is complexed by silver(I). Barriers to rotation about the phenanthroline-carbon to methyl-carbon bonds in methyl-substituted 1,10-phenanthroline complexes of chromium(III) can be estimated from n.m.r. spectra. The interest here is that these barriers are solvent sensitive; their variation with solvent may prove a useful probe in examining solvation and its effect on reactivity of this type of complex.[169]



(36) (37)

Silicon. The barrier to inversion at the two silicon atoms in chair ⇌ chair interconversion of 1,1,4,4-tetramethyl-1,4-disilacyclohexane (38) is low, less than 6 kcal mol^{-1}. This is much lower than in the organic analogue; the difference arises from the molecular geometry, specifically from the

[159] J. E. Brady, *Inorg. Chem.*, 1969, **8**, 1208.
[160] M. Gielen, G. Mayence, and J. Topart, *J. Organometallic Chem.*, 1969, **18**, 1.
[161] M. Gielen and J. Topart, *J. Organometallic Chem.*, 1969, **18**, 7.
[162] M. Gielen, *Bull. Soc. chim. belges*, 1969, **78**, 351.
[163] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1969, **91**, 4115; and refs. therein.
[164] M. Gielen and J. Nasielski, *Bull. Soc. chim. belges*, 1969, **78**, 339.
[165] M. Gielen, M. de Clerq, and J. Nasielski, *J. Organometallic Chem.*, 1969, **18**, 217.
[166] M. Gielen, C. Depasse-Delit, and J. Nasielski, *Bull. Soc. chim. belges*, 1969, **78**, 357.
[167] C. G. Kreiter and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 761.
[168] P. A. Temussi, T. Tancredi, and F. Quadrifoglio, *J. Phys. Chem.*, 1969, **73**, 4227.
[169] G. N. La Mar and G. R. van Hecke, *J. Chem. Phys.*, 1969, **50**, 537; 1970, **52**, 5676.



(38)

greater length of silicon–carbon bonds.[170] The effect of substituting silicon for carbon on the internal motion of cyclopentane has been described, and compared with the effects of oxygen and sulphur substitution.[171] The appropriate data are collected in Table 2.

Table 2 *Barriers to internal motion in cyclopentane and its derivatives* $\boxed{\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Y}}$

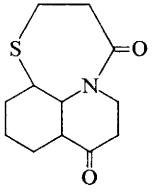
Y	*Barrier* (kcal mol^{-1})
CH_2	0
O	0·16
S	2·8
Si	3·89

Tin. Inversion at tin is generally fast. The one example in the literature (1900) of resolution of a tin compound has been reinvestigated and found to be incorrect.[172] Fast pseudorotation in a trigonal-bipyramidal transition state permits ready isomerisation and inversion at tin in reactions of methylneophylphenyltin chloride.[173]

Group V.—*Nitrogen.* In many organonitrogen compounds there are several possible modes of intramolecular rearrangement, any of which could be responsible for changes in n.m.r. spectra with temperature. A good example of this is provided by thiazepinoquinoline (39), where the possibilities include inversion at nitrogen, ring inversion, or restricted rotation about the nitrogen to carbonyl–carbon bond in the large and flexible sulphur-containing ring.[174] Other cases of rotation or inversion have been discussed.[175–178] The intramolecular process observed in n.m.r. measurements on protonated guanidines is rotation – indeed there are up to four rotational barriers – but in the parent non-protonated bases the observed process is inversion. The barrier to inversion is, perhaps surprisingly, insensitive to solvent.[176] In the case of *N*-(α-methylbenzylidene)-aniline the observed process is again inversion, for it is stopped, or at least enormously slowed down, by complexing with aluminium trimethyl.[177]

[170] R. W. Murray and M. L. Kaplan, *Tetrahedron*, 1969, **25**, 1651.
[171] J. Laane, *J. Chem. Phys.*, 1969, **50**, 1946.
[172] G. Redl, *J. Organometallic Chem.*, 1970, **22**, 139.
[173] G. J. D. Peddle and G. Redl, *J. Amer. Chem. Soc.*, 1970, **92**, 365.
[174] J. L. Huppatz and G. F. Katekar, *Tetrahedron Letters*, 1970, 1751.
[175] H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.
[176] H. Kessler and D. Leibfritz, *Tetrahedron Letters*, 1970, 1423.
[177] E. A. Jeffery, A. Meisters, and T. Mole, *Tetrahedron*, 1969, **25**, 741.

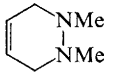
Inversion is again the observed process with alkyldifluoramines.[178] The best way to avoid hindered rotation is to incorporate the nitrogen into an alicyclic ring. Ring inversion is then avoided by incorporating a bridge. This procedure is neatly illustrated by (40).[179]



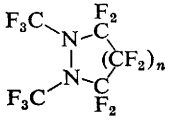
(39)



(40)

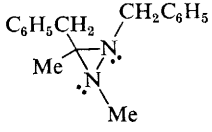


(41)

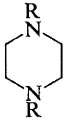


$n = 0, 1, 2$

(42)



(43)



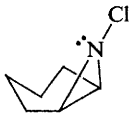
(44)

The question of distinguishing between hindered rotation about a nitrogen–nitrogen bond and inversion at nitrogen crops up again in kinetic studies of substituted hydrazines,[180] where recourse to cyclic compounds, *e.g.* (41)[181] and (42),[182] again eliminates restricted rotation. An extreme case of a substituted hydrazine is the diaziridine (43), where inversion is so slow that invertomers have been separated.[183] While on the subject of heterocyclic compounds containing two ring nitrogens, the reports of inversion kinetics for (44), R = alkyl[184] or CF_3,[182] may be mentioned. Whereas ring strain generally seems to be the dominant factor in inversion of cyclic compounds containing one nitrogen per ring, it seems that steric factors assume greater importance in rings containing two nitrogens.

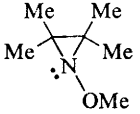
The same question of distinguishing between inversion and restricted rotation is also relevant to a variety of heteronuclear cases, for instance nitrogen–oxygen,[185] nitrogen–sulphur,[186] nitrogen–boron,[187] nitrogen–

[178] S. K. Brauman and M. E. Hill, *J. Chem. Soc.* (*B*), 1969, 1091.
[179] J. M. Lehn and J. Wagner, *Chem. Comm.*, 1970, 415.
[180] J. R. Fletcher and I. O. Sutherland, *Chem. Comm.*, 1969, 706; M. J. S. Dewar and W. B. Jennings, *J. Amer. Chem. Soc.*, 1969, **91**, 3655; *Tetrahedron Letters*, 1970, 339.
[181] J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 6371.
[182] P. Ogden, *Chem. Comm.*, 1969, 1084.
[183] A. Mannschreck and W. Seitz, *Angew. Chem. Internat. Edn.*, 1969, **8**, 212.
[184] J. J. Delpuech, Y. Martinet, and B. Petit, *J. Amer. Chem. Soc.*, 1969, **91**, 2158.
[185] M. Raban and G. W. J. Kenney, *Tetrahedron Letters*, 1969, 1295.
[186] M. Raban, G. W. J. Kenney, and F. B. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 6677.
[187] K. N. Scott and W. S. Brey, *Inorg. Chem.*, 1969, **8**, 1703.

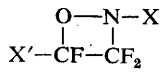
phosphorus,[188] and phosphorus–phosphorus.[189] Methods of disentangling contributions from rotation and inversion by careful selection of substituents are illustrated in, for instance, the nitrogen–phosphorus case.[188] Even after considering the possibility of rotation and of inversion contributing to the variation of n.m.r. spectra with temperature there is a further complication, *i.e.* misinterpretation of features due to coupling.[190]



(45)



(46)



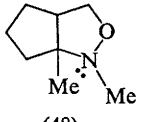
X = H, F, Cl, CF_2·CFCl·OEt

X′ = F, Cl

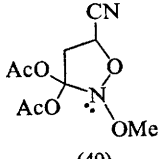
(47)

Since the separation of the cyclic 7-chloro-7-azabicyclo[4,1,0]heptane (45) into its isomers[191] there has been much interest in slow inversion at nitrogen in heterocyclic compounds. Slow inversion in a diaziridine (43) has already been mentioned.[183] *N*-Methoxyaziridines, *e.g.* (46), also invert slowly,[192] as do oxazetidines (47),[193] the isoxazolidine (48),[194] and the oxazolidine (49).[195] Solvent effects on inversion rates were investigated for the compound (48).[194] *X*-Ray experiments have confirmed the existence of two isomers of the compound (49).[196] Further examples of studies of intramolecular processes in oxygen–nitrogen ring compounds include those of the three-membered ring series (50).[197]

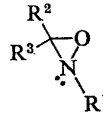
Slow inversion has also been observed for the two aza-norbornadiene



(48)



(49)



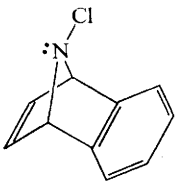
R^1 = Me, Bu^t

R^2 = Ph, CH_2Ph

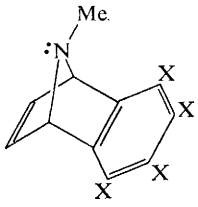
R^3 = Me, Ph

(50)

[188] H. Goldwhite and D. G. Rowsell, *Chem. Comm.*, 1969, 713.
[189] J. B. Lambert, G. F. Jackson, and D. C. Mueller, *J. Amer. Chem. Soc.*, 1970, **92**, 3093.
[190] See, *e.g.*, A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 1085.
[191] D. Felix and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1968, **7**, 224.
[192] S. J. Brois, *J. Amer. Chem. Soc.*, 1970, **92**, 1079.
[193] J. D. Readio and R. A. Falk, *J. Org. Chem.*, 1970, **35**, 927; J. D. Readio, *ibid.*, p. 1607.
[194] M. Raban, F. B. Jones, E. H. Carlson, E. Banucci, and N. A. Le Bel, *J. Org. Chem.*, 1970, **35**, 1496.
[195] K. Müller and A. Eschenmoser, *Helv. Chim. Acta*, 1969, **52**, 1823.
[196] M. Dobler, J. D. Dunitz, and D. M. Hawley, *Helv. Chim. Acta*, 1969, **52**, 1831.
[197] A. Mannschreck, J. Linss, and W. Seitz, *Annalen*, 1969, **727**, 224; F. Montanari, I. Moretti, and G. Torre, *Chem. Comm.*, 1969, 1086.

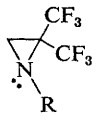


(51)



X = F, Cl

(52)



(53)

derivatives (51)[198] and (52).[199] The dependence of inversion rate on the extracyclic atom or group bonded to the nitrogen in aziridines has been investigated for the series (53), for R = methyl, phenyl, or halogen. Direct comparison is somewhat difficult due to the variation in solvents used, but for R = Br or F the barrier to inversion is, as for R = Cl, very high. For R = phenyl, the barrier is surprisingly low.[200] A discussion of factors which control rates of inversion at nitrogen in heterocyclic compounds appears in a paper on the preparation of diastereoisomers.[201]

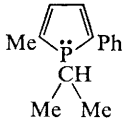
Barriers to inversion at nitrogen have been calculated by an SCF–MO method for a variety of pyramidal compounds, and the agreement with experimentally determined values is encouraging.[202] An *ab initio* SCF–LCAO–MO approach to inversion at nitrogen in silylamine has indicated a small π-bonding contribution between silicon and nitrogen in both the initial and transition states.[203]

A review of pyramidal inversion concentrates on nitrogen and phosphorus compounds.[204]

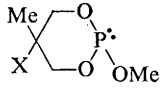
Phosphorus. Pyramidal inversion at a series of acyclic phosphines has been described and compared with inversion at a series of analogous sulphoxides.[205] Satisfactory agreement between calculated and observed energy barriers for inversion at phosphorus(III) has been reported.[206] The facile thermal racemisation of allylmethylphenylphosphine could occur either by inversion at phosphorus or by an intramolecular allyl rearrangement. The demonstration that this allyl compound racemises more slowly than the approximately isosteric n-propyl compound contraindicates racemisation by an allylic rearrangement. Labelling experiments also support a mechanism of racemisation by inversion at phosphorus in the

[198] V. Rautenstrauch, *Chem. Comm.*, 1969, 1122.
[199] G. W. Gribble, N. R. Easton, and J. T. Eaton, *Tetrahedron Letters*, 1970, 1075.
[200] R. G. Kostyanovsky, I. I. Tchervin, A. A. Fomichov, and Z. E. Samojlova, *Tetrahedron Letters*, 1969, 4021.
[201] D. R. Boyd, R. Spratt, and D. M. Jerwa, *J. Chem. Soc.* (*C*), 1969, 2650.
[202] M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, 1969, **91**, 3654.
[203] J. M. Lehn and B. Munsch, *Chem. Comm.*, 1970, 994.
[204] A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, 1970, **9**, 400.
[205] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 3090.
[206] J. M. Lehn and B. Munsch, *Chem. Comm.*, 1969, 1327.

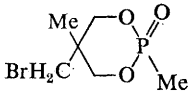
allyl compound.[207] Inversion at acyclic phosphorus(III) is usually, as here, easy, but at cyclic phosphorus(III) it is difficult. However, if the phosphorus(III) is incorporated in an aromatic ring, as in (54), inversion is again easy, probably because the planar transition state is stabilised by delocalisation of the phosphorus lone-pair over the aromatic system, which is not possible in the ground state.[208]



(54)



(55)



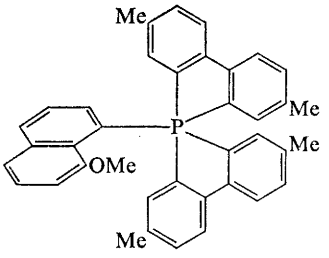
(56)

Inversion at phosphorus(III) in cyclic phosphites [*e.g.* (55)] and at phosphorus(V) in cyclic phosphates is generally very slow. However, in the case of *cis*- or *trans*-5-bromomethyl-2,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan (56), ^{1}H n.m.r. measurements on a deuteriochloroform solution indicate that inversion at phosphorus is occurring. The comparison of analogous phosphorus(III) and phosphorus(V) centres here suggests that the lone-pair on the former is more sterically demanding than a small group on the latter.[209] Further examples of inversion in cyclic phosphonates have been reported.[210] Kinetics of inversion and isomerisation at an acyclic phosphorus(V) centre have been reported for the system based on allylmethylphenylphosphine sulphide.[211]

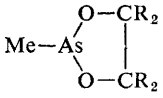
The nature of the barriers to intramolecular rearrangement and of the transition states has been considered for a wide variety of trigonal-bipyramidal molecules, including phosphorus(V) compounds such as PF_5, PF_2Cl_3, other neutral molecules such as $SbMe_5$ and $NbCl_5$, and even transition-metal complex ions such as $CuCl_5^{3-}$ and $Ni(CN)_5^{3-}$.[212]

The study of pseudorotation in five-co-ordinate phosphorus(V) compounds is undertaken not only out of intrinsic interest but also for its relevance to rearrangements in transition states for nucleophilic substitution at tetrahedral phosphorus(V) compounds (*cf.* pp. 118—120). Pseudorotation in the stable compound $Me_2N{\cdot}PF_4$ takes place *via* a square-pyramidal transition state. The variation of line widths with temperature for various lines in the n.m.r. spectrum permits a distinction to be drawn between possible processes involving simultaneous interchange of two pairs of fluorine atoms, as required for the Berry mechanism for pseudorotation, or of only one pair.[213] Inversion or pseudorotation in

[207] R. D. Baechler, W. B. Farnham, and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 5686.
[208] W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 1442.
[209] R. S. Edmundson, *Tetrahedron Letters*, 1969, 1905.
[210] R. S. Edmundson and E. W. Mitchell, *J. Chem. Soc.* (*C*), 1970, 752.
[211] W. B. Farnham, A. W. Herriott, and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 6878.
[212] R. R. Holmes, R. M. Dieters, and J. A. Golen, *Inorg. Chem.*, 1969, **8**, 2612.
[213] G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, 1969, **91**, 5384.



(57)



(58)

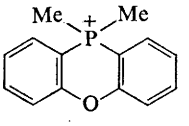
the phosphorane (57) is slow, *i.e.* the barrier is about 23·5 kcal. mol^{-1} at 160 °C, which is hardly surprising in view of the geometry of the groups around the phosphorus.[214] A detailed study of pseudorotation in cyclic alkyloxyphosphoranes shows two barriers to molecular rearrangement. The lower temperature barrier is to placing alkyl (aryl) groups apical, the higher temperature barrier is due either to putting the five-membered ring equatorial–equatorial or to ring opening and closing.[215]

Variation of coupling constants with temperature in n.m.r. spectra of $PF_2 \cdot S \cdot PF_2$ has been interpreted in terms of rotation about phosphorus–sulphur bonds, though other interpretations seem not inconsistent with the experimental observations.[216]

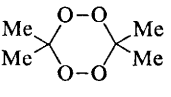
Arsenic. The barrier to inversion at pyramidal arsenic(III) in dioxarsolans (58) and dithiarsolans is greater than 25 kcal mol^{-1}. An earlier report of rapid inversion at arsenic in a compound of this type seems to have been based on an accidental coincidence of lines in ^1H n.m.r. spectra.[217] The study of pseudorotation at five-co-ordinate phosphorus(v) is being extended to arsenic(v).[218] Pseudorotation of a different sort, that corresponding to the intramolecular motion of cyclopentane, has been qualitatively investigated for $(MeAs)_5$ in deuteriobenzene solution.[219]

Group VI.—*Oxygen.* Linking Groups V and VI is the tricyclic phosphonium salt (59), in which the barrier to inversion of the hetero-ring is small.[220] Barriers to inversion have been determined for two-oxygen ring systems in 1,3-dioxans,[221] and for a four-oxygen ring system in 3,3,6,6-tetramethyl-1,2,4,5-tetroxan (60).[222] $\Delta G^{\ddagger}$ values are reported for the dioxans, and the full range of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for the tetroxan. Non-bonding electron pair repulsions are important in determining rates of

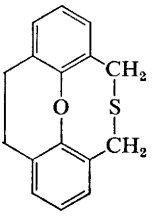
[214] D. Hellwinkel and H. J. Wilfinger, *Tetrahedron Letters*, 1969, 3423.
[215] D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1970, **92**, 634; D. Gorenstein, *ibid.*, p. 644.
[216] R. A. Newmark, A. D. Norman, and R. W. Rudolph, *Chem. Comm.*, 1969, 893.
[217] J. P. Casey and K. Mislow, *Chem. Comm.*, 1970, 999.
[218] H. Goldwhite, *Chem. Comm.*, 1970, 651.
[219] C. L. Watkins, L. K. Krannich, and H. H. Sisler, *Inorg. Chem.*, 1969, **8**, 385.
[220] D. W. Allen and I. T. Millar, *J. Chem. Soc.* (*C*), 1969, 252.
[221] G. Eccleston and E. Wyn-Jones, *Chem. Comm.*, 1969, 1511; E. Coene and M. Anteunis, *Bull. Soc. chim. belges*, 1970, **79**, 37.
[222] K. Wulz, H. A. Brune, and W. Hetz, *Tetrahedron*, 1970, **26**, 3.



(59)



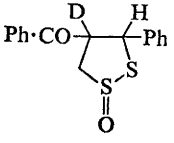
(60)



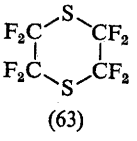
(61)

inversion. A large constraint is required to slow inversion at ether-oxygen atoms to the n.m.r. frequency range. This seems to have been achieved for (61), but in this compound some sort of motion of the sulphur–oxygen ring may be combined with inversion at the oxygen.[223]

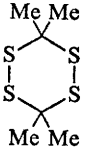
Sulphur. In acyclic compounds containing sulphur–sulphur bonds inversion at the sulphur is relatively easy, but in the cyclic compound (62) there is no evidence for inversion at sulphur.[224] The first n.m.r. kinetic study of ring inversion for a 1,4-dithian has been of the perfluoro-compound



(62)



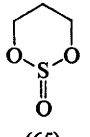
(63)



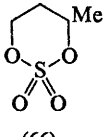
(64)

(63);[225] 1,2- and 1,3-dithians have been investigated previously. Kinetic parameters for inversion in the sulphur analogue (64) of the tetroxan (60) mentioned above have been determined.[226]

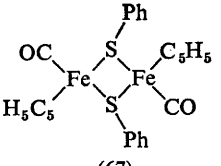
Inversion in the cyclic sulphite (65)[227] and the cyclic sulphate (66)[228] has been studied by ultrasonic techniques. Isomerisation of the cyclic iron–sulphur derivative (67) appears, from kinetic evidence, to take place by an intramolecular inversion process.[229]



(65)



(66)



(67)

[223] A. J. Gordon and J. P. Gallagher, *Tetrahedron Letters*, 1970, 2541.
[224] F. Wudl, R. Gruber, and A. Padura, *Tetrahedron Letters*, 1969, 2133.
[225] J. E. Anderson, D. R. Davis, and J. D. Roberts, *J. Org. Chem.*, 1970, **35**, 1195.
[226] B. Magnusson, B. Rodmar, and S. Rodmar, *Arkiv Kemi*, 1969, **31**, 65; C. H. Bushweller, J. Golini, G. U. Rao, and J. W. O'Neil, *Chem. Comm.*, 1970, 51; *J. Amer. Chem. Soc.*, 1970, **92**, 3055.
[227] G. Eccleston, R. A. Pethrick, E. Wyn-Jones, P. C. Hamblin, and R. F. M. White, *Trans. Faraday Soc.*, 1970, **66**, 310.
[228] R. A. Pethrick, E. Wyn-Jones, P. C. Hamblin, and R. F. M. White, *J. Chem. Soc. (A)*, 1969, 2552.
[229] M. Dekker, G. R. Knox, and C. G. Robertson, *J. Organometallic Chem.*, 1969, **18**, 161.

2
Solvent Exchange

Solvent exchange is merely a special case of substitution. However, this topic will be treated separately, as a more convenient arrangement of material can be thus achieved. Solvent exchange involving unmixed solvates in pure solvents will be discussed first, followed by mixed ligand complexes in pure solvents, then solvent exchange in mixed solvents. Proton exchange between bulk and co-ordinated solvents is covered in the final section.

Single-ligand Solvates in Pure Solvents.—*Water Exchange.* Kinetic data for water exchange with aquo-cations are collected in Table 1. The determination of the kinetic parameters for water exchange at vanadium(II) [1] has an important bearing on discussions of mechanisms of reductions effected by this cation, for the lack of knowledge of these water exchange rates and the lability of vanadium(III) had combined to make assignment of an inner- or outer-sphere mechanism difficult in most cases. Water exchange at the d^1 ion titanium(III) shows several of the characteristics of an associative reaction. Formation of a bond between cation and the incoming water during formation of the transition-state seems much more plausible here than at cobalt(II) or nickel(II), where there are so many more *d*-electrons to discourage direct nucleophilic attack.[2] A ^{17}O n.m.r. study has set lower limits to water exchange rates at several lanthanide cations; these limits correlate with ionic radii.[3] Rates and activation parameters for water exchange at magnesium(II) have also been determined by ^{17}O n.m.r. spectroscopy. Bulk and co-ordinated ^{17}O resonances were separated by the addition of manganese(II) to broaden greatly the bulk ^{17}O signal.[4] The water exchange rate at the aquated uranyl(VI) cation UO_2^{2+} has been estimated from results obtained in a kinetic study of its dimerisation.[5] Techniques for separating (from each other) contributions arising from proton exchange, whole water molecule exchange, and proton spin relaxation effects to n.m.r. spectra have been discussed with special reference to exchange at chromium(III).[6]

[1] M. N. Olsen, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, 1969, **51**, 289.
[2] A. Chmelnik and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4238.
[3] J. Reuben and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4918.
[4] J. Neely and R. Connick, *J. Amer. Chem. Soc.*, 1970, **92**, 3476.
[5] V. Frei and H. Wendt, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 593.
[6] B. F. Melton and V. L. Pollak, *J. Phys. Chem.*, 1969, **73**, 3669.

Table 1 *Kinetic parameters for water exchange at aquo-cations*

Cation	*Method*	k (s^{-1}) [temperature (°C)]	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	*Ref.*
Magnesium(II)	^{17}O n.m.r.	$5{\cdot}3 \times 10^5$ [25]	10·2	+ 2	4
Vanadium(II)	^{17}O n.m.r.	90 [25]	16·4	+ 5·5	1
Titanium(III)	^{17}O n.m.r.	7×10^4 [25]	6·2	− 15	2
Uranyl(VI)	*T*-jump	$\sim 10^5$ [3]	—	—	5

Alcohol Exchange. Kinetic parameters for solvent exchange at cations in solution in alcohols [2, 7–10] are collected in Table 2. In all cases, the kinetic parameters can be assigned to exchange of whole molecules, since either ^{17}O resonances were monitored, or methyl- or methylene-protons were observed to show the same behaviour as hydroxyl-protons. The assignment of mechanism by the favourite method (from activation entropies) leads to the conclusion that ethanol exchange at magnesium(II) approximates to S_N1(lim), but that ethanol exchange at iron(III) is associative in mechanism. Exchange rates for methanol and for ethanol at iron(III) seem anomalously high compared with rates of water or dimethyl sulphoxide exchange and with analogous rates for nickel(II); some rationalisation in steric terms is possible.[10]

Table 2 *Kinetic parameters for solvent exchange at cations in alcohols; rate constants at* 25·0 °C

Cation	*Solvent*	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	*Ref.*
Magnesium(II)	MeOH	$4{\cdot}7 \times 10^3$	16·7	+ 14	11
	EtOH	$2{\cdot}8 \times 10^6$	17·7	+ 30	9
Titanium(III)	MeOH	$1{\cdot}3 \times 10^5$	3·3	− 24	2
Manganese(II)	MeOH	$3{\cdot}7 \times 10^5$	6·2	− 12	7
Iron(II)	MeOH	$5{\cdot}0 \times 10^4$	12·0	+ 3	7
Iron(III)	MeOH	$5{\cdot}1 \times 10^3$	10·1	− 8	7
	EtOH	$2{\cdot}0 \times 10^4$	6·2	− 18	10
Nickel(II)	EtOH	$1{\cdot}1 \times 10^4$	10·8	− 4	10
Copper(II)	MeOH	10^8	10	+ 13	7
Zinc(II)	MeOH	—	14	+ 15	8

Other Solvents. Two recent determinations [12, 13] of rates and activation parameters for dimethyl sulphoxide exchange at nickel(II) give tolerably consistent results, but there is a disturbing lack of agreement between these

[7] F. W. Breivogel, *J. Chem. Phys.*, 1969, **51**, 445.
[8] S. A. Al-Baldawi and T. E. Gough, *Canad. J. Chem.*, 1969, **47**, 1417.
[9] T. D. Alger, *J. Amer. Chem. Soc.*, 1969, **91**, 2220.
[10] F. W. Breivogel, *J. Phys. Chem.*, 1969, **73**, 4203.
[11] S. Nakamura and S. Meiboom, *J. Amer. Chem. Soc.*, 1967, **89**, 1765.
[12] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 2579.
[13] L. S. Frankel, *Chem. Comm.*, 1969, 1254.

and earlier determinations,[14] which themselves show considerable disagreement. The reported activation enthalpies range from 8 to 13·0 kcal mol^{-1}; the activation entropies range from − 16 to + 3 e.u. All determinations have been made from n.m.r. line-broadening experiments. There appears to be no correlation between activation enthalpies for solvent exchange at nickel(II) with solvent *Dq* values.[12]

Rates and activation parameters have been reported for solvent exchange at gallium(III)[15] and at iron(III)[10] in dimethylformamide. These activation enthalpies and entropies, and earlier ones for dimethylformamide exchange and for water exchange at aluminium(III) and at beryllium(II), are collected in Table 3. Intercomparison of activation entropies suggests a more associative mechanism of solvent exchange at gallium(III) than at aluminium(III) or beryllium(II); the range of activation parameters is much less wide in dimethylformamide than in aqueous solution.

Table 3 *Activation parameters for solvent exchange in dimethylformamide and in aqueous solution*

	$\Delta H^{\ddagger}$ (kcal mol^{-1})		$\Delta S^{\ddagger}$ (e.u.)	
Cation	*DMF*	*Water*	*DMF*	*Water*
Beryllium(II)	14·6	—	+ 2·6	—
Aluminium(III)	17·7	27	+ 4·7	+ 28
Gallium(III)	14·6	6·3	− 8·3	− 22
Iron(III)	12·5	—	− 10	—

Rates and activation parameters for solvent exchange at manganese(II) in liquid ammonia are very similar to those for water exchange. In both cases, a low activation enthalpy is found, which is explained in terms of the absence of crystal field stabilisation energy, and hence activation energy, for this d^5 ion.[16] Rates of solvent exchange for manganese(II), iron(II), and copper(II) in trimethyl phosphate or in dimethyl methylphosphonate could be only roughly estimated since relaxation due to the paramagnetic cation played a comparable part to chemical exchange in determining linewidths in these systems.[17] ^{1}H n.m.r. spectra are not controlled by chemical exchange at all for solutions of cobalt(II) or nickel(II) in TMPA, so one can only estimate limits to solvent exchange rates.[12]

Acetonitrile exchange at manganese(II) has a rate constant of 1·2 × 10^7 s^{-1} at 25·0 °C; the activation enthalpy is 7·25 kcal mol^{-1} and the activation entropy − 1·8 e.u. These values were obtained from variable-temperature studies of the ^{14}N nuclear relaxation times. Logarithms of

[14] S. Blackstaffe and R. A. Dwek, *Mol. Phys.*, 1968, **15**, 279; S. Thomas and W. J. Reynolds, *J. Chem. Phys.*, 1967, **46**, 4164; N. A. Matwiyoff, personal communication to authors of ref. 12.
[15] W. G. Movius and N. A. Matwiyoff, *Inorg. Chem.*, 1969, **8**, 925.
[16] M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1969, **91**, 6318.
[17] L. S. Frankel, *Inorg. Chem.*, 1969, **8**, 1784.

rate constants for acetonitrile exchange correlate with those for water exchange at manganese(II), cobalt(II), and nickel(II), which is consistent with a dissociative rate-determining step in acetonitrile exchange at manganese(II).[18]

Mixed-ligand Complexes in Pure Solvents.—*Vanadyl*(IV). One of the most popular cations in this category is vanadium(IV), for which kinetic results[19–21] are collected in Table 4. The line-widths of ^{1}H n.m.r. spectra are not controlled by chemical exchange in dimethyl sulphoxide, trimethyl phosphate, or trimethyl phosphite, so one can only set limits to rates of solvent exchange in these cases.[21] In $[VO(MeOH)_5]^{2+}$ in methanol, both proton and methanol exchange is observed, but $[VO\,acac_2(MeOH)]$ exchanges only protons and not whole solvent molecules with solvent methanol. There is no proton exchange at all in trifluoroacetic acid solutions of $[VO\,acac_2]$. Solvent exchange at vanadyl(IV) has been described as primarily dissociative in mechanism, though the activation entropies for dimethylformamide and for acetonitrile exchange (Table 4) suggest some associative character for exchange of these solvents. However, both here and at several other places in this section, one should bear in mind that solvent structure as well as the associative or dissociative character of the mechanism as seen by the cation may have a significant effect on activation entropies.

Table 4 *Kinetic parameters for solvent exchange at vanadyl*(IV); *rate constants at* 25·0 °C

Solvent	$10^3\,k$ (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	*Ref.*
H_2O (neutral)[a]	0·50	13·7	− 0·6	22
H_2O (neutral)[b]	7·7	12	0	19
D_2O (neutral)	3·3	14	+ 2·4	19
MeOH	0·57	9·5	− 14	20
MeCN	2·85	7·1	− 20	21
DMF	0·58	7·3	− 16	23

[a] Rate constant calculated on the assumption of five water molecules per vanadium exchanging.
[b] Assumption that four water molecules are exchanging.

Nickel(II). The other popular centre for studies of solvent exchange in mixed ligand complexes is nickel(II). Kinetic results are collected in Table 5. The main interest lies in correlating rates of water exchange with the number and nature of the other substituents. For the ligands chloride,[24]

[18] W. L. Purcell and R. S. Marianelli, *Inorg. Chem.*, 1970, **9**, 1724.
[19] J. Reuben and D. Fiat, *J. Amer. Chem. Soc.*, 1969, **91**, 4652.
[20] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 1824.
[21] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 65.
[22] K. Wüthrich and R. E. Connick, *Inorg. Chem.*, 1967, **6**, 583.
[23] N. S. Angerman and R. B. Jordan, *J. Chem. Phys.*, 1968, **48**, 3983.
[24] S. F. Lincoln, F. Aprile, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1968, **7**, 929.

thiocyanate,[25] ammonia,[26] and ethylenediamine[27] there is a good linear correlation between logarithms of rates of water exchange and the number of water molecule ligands. This rather arbitrary correlation has not been explained in detail; it does not include water exchange rates for 2,2′-bipyridyl[28] and for 2,2′,6′,2″-terpyridyl[29] complexes, where the presence of these ligands has very little effect on the exchange rates, though not on the activation parameters, for the remaining water molecules. There is no doubt that it is the exchange of complete water molecules that is being monitored in all these cases since the results derive from ^{17}O n.m.r. spectroscopy, and moreover there is confirmatory evidence in some cases from ligand substitution studies.[30]

Table 5 *Kinetic parameters for water exchange at mixed ligand complexes of nickel*(II). *Rate constants are values for one water molecule, at* 25·0 °C

Complex	$10^{-5}\,k$ (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	*Ref.*
$[Ni(OH_2)_6]^{2+}$, 1 < pH < 7	0·27—0·44	10·8—12·3	− 5—+ 4	26—28, 31
$[NiCl(OH_2)_5]^{+}$, in 7M-LiCl	1·4	8	—	24, 27
$[Ni(NH_3)(OH_2)_5]^{2+}$	2·5	10·6	+ 1·8	26
$[Ni\ en(OH_2)_4]^{2+}$	4·4	10·0	+ 10	27
$[Ni(NH_3)_2(OH_2)_4]^{2+}$	6·1	7·8	− 6·0	26
$[Ni(NH_3)_3(OH_2)_3]^{2+}$	25	10·2	+ 5·0	26
$[Ni(NCS)_3(OH_2)_3]^{-}$	11	6	− 11	25, 26
$[Ni\ en_2(OH_2)_2]^{2+}$	54	9·1	+ 2·6	27
$[Ni(OH_2)_6]^{2+}$ pH = 3	0·32	12·1	+ 2·6	28
$[Ni\ bipy(OH_2)_4]^{2+}$ pH = 3	0·49	12·6	+ 5·1	28
$[Ni\ terpy(OH_2)_3]^{2+}$ pH = 3	0·52	10·7	− 1·0	29
$[Ni\ bipy_2(OH_2)_2]^{2+}$ pH = 3	0·66	13·7	+ 9·2	28

The activation enthalpy for methanol exchange with $[NiCl(MeOH)_5]^{+}$ is somewhat lower than that with $[Ni(MeOH)_6]^{2+}$. This behaviour parallels that observed earlier for the analogous cobalt(II) complexes.[32] The activation energy for methanol exchange at $[NiCl(MeOH)_5]^{+}$ is 15·8 kcal mol^{-1}, which is much more than that for water exchange at $[NiCl(OH_2)_5]^{+}$, which has a value of 8 kcal mol^{-1}.

Solvent Exchange in Mixed Solvents.—Systems in which mixed ligand complexes exchange with mixed solvents or solutions are inherently complicated and difficult to analyse to find precise kinetic data. Thus in

[25] R. B. Jordan, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1966, **5**, 1906.
[26] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1970, **92**, 798.
[27] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1969, **91**, 5001.
[28] M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1970, **92**, 2321.
[29] D. Rablen and G. Gordon, *Inorg. Chem.*, 1969, **8**, 395.
[30] J. P. Jones, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 1875.
[31] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; R. E. Connick and D. E. Fiat, *J. Chem. Phys.*, 1966, **44**, 4103.
[32] Z. Luz, *J. Chem. Phys.*, 1969, **51**, 1206.

aqueous ammoniacal solutions of cobalt(II) there is exchange involving several cationic complexes, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5(OH_2)]^{3+}$, and $[Co(NH_3)_4(OH_2)_2]^{3+}$. In fact, rates and activation energies for ammonia exchange, at least for the first two complexes, seem to be similar in magnitude.[33] For cobalt(II) in hydrochloric acid there are tetrahedral and octahedral species to be characterised prior to estimation of exchange rates.[34] Dimethyl sulphoxide exchange at aluminium(III) in aqueous dimethyl sulphoxide takes place by different mechanisms depending on the composition of the solvent.[35] The solvation number of aluminium(III) in acetonitrile solution of aluminium chloride is 1·5, determined from peak areas of n.m.r. spectra indicating the presence of mixed acetonitrile–chloride complexes. Rates and activation parameters for acetonitrile exchange have been determined.[36]

Considerable simplification in mixed-solvent work can be achieved by working in a mixture of a co-ordinating and a non-co-ordinating solvent. In DMSO, and in DMSO–nitromethane and DMSO–methylene chloride mixtures, both cobalt(II) and nickel(II) exist as $[M(DMSO)_6]^{2+}$, so it is possible to study the effects of mixed solvents on the kinetics of DMSO exchange at a constant complex species and thereby use the particular properties of mixed solvents in elucidating the reaction mechanism. In particular, composition variation in DMSO–methylene chloride mixtures has a large effect on solvent dielectric constant and thus on the concentration of any ion-pairs. The observation that rates of DMSO exchange are almost independent of solvent composition shows, rather surprisingly, that ion-pairs do not contribute significantly to the reaction mechanism in this case. The independence of rates on solvent composition, *i.e.* on fluidity, ligand (DMSO) concentration, and solvating power as well as on dielectric constant, is more readily interpreted in terms of a dissociative mechanism.[13]

Proton Exchange.—In some of the cases cited above, ^1H n.m.r. spectra have shown that protons exchange between bulk solvent and the co-ordination sphere both as such and as components of complete solvent molecules. The mechanism of proton transfer, as opposed to water exchange, from $[Al(OH_2)_6]^{3+}$ has been shown from ^1H n.m.r. kinetic studies and deuterium isotope experiments to be a bimolecular process. Proton transfer to $[Al(OH)(OH_2)_5]^{2+}$ is significant.[37] A ^{27}Al n.m.r. study of the same system at varying pH is consistent with bimolecular exchange. The variation of line-width with temperature is ascribed to changes in $Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H_3O^+$ equilibrium rather than to kinetic effects.[38] But ^{27}Al

[33] R. Murray, S. F. Lincoln, H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 1969, **8**, 554.
[34] A. H. Zeltmann, N. A. Matwiyoff, and L. O. Morgan, *J. Phys. Chem.*, 1969, **73**, 2689.
[35] S. Thomas and W. L. Reynolds, *Inorg. Chem.*, 1970, **9**, 78.
[36] J. F. O'Brien and M. Alei, *J. Phys. Chem.*, 1970, **74**, 743.
[37] Dodd-Wing Fong and E. Grunwald, *J. Amer. Chem. Soc.*, 1969, **91**, 2413; A. Takahashi, *J. Phys. Soc. Japan*, 1970, **28**, 207.
[38] J. W. Akitt, N. N. Greenwood, and G. D. Lester, *J. Chem. Soc.* (*A*), 1969, 803.

n.m.r. also indicates the presence of solvated aluminium(III) dimers in acid solution, and indicates that these may also be involved in proton exchange. The demonstration of the presence of these dimers is also interesting in the light it may throw on frequent experimental observations of solvation numbers slightly less than 6 for aluminium(III) cations.[39] This aluminium(III) system has also been studied by pH-stat techniques; the kinetic results are very much at variance with those from the ^{1}H and ^{27}Al n.m.r. investigations.[40]

Rates of proton exchange between bulk and co-ordinated water have also been determined for chromium(III), where, as for aluminium(III), a bimolecular mechanism is indicated,[41] and for beryllium(II).[42]

[39] J. W. Akitt, N. N. Greenwood, and G. D. Lester, *Chem. Comm.*, 1969, 988.
[40] H. Ohashi and T. Morozumi, *Denki Kagaku Oyobi Butsuri Kagaku*, 1969, **37**, 510 (*Chem. Abs.*, 1970, **72**, 36,299e).
[41] L. D. Rich, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, 1969, **73**, 713.
[42] G. Schwarzenbach and H. Wenger, *Helv. Chim. Acta*, 1969, **52**, 644.

3

Metals: Four-, Five-, and Eight-co-ordinate

1 Tetrahedral Complexes

Kinetic studies of substitution in tetrahedral complexes of metals in low oxidation states, for instance nickel tetracarbonyl or tetrakistrialkylphosphitenickel(0), are dealt with in the organometallic Chapter. Here we shall deal with reactions of oxoanions, isomerisation of tetrahedral complexes to square-planar forms and *vice versa*, and with the addition of ligands to tetrahedral to give octahedral complexes.

Aquation of dichromate exhibits general-acid catalysis, which may operate by protonation of the bridging oxygen atom.[1] The mechanism of aquation of the peroxoanion $[Cr(O_2)_4]^{3-}$ has been investigated by kinetic and tracer experiments. The tracer results, and the observed effects of added inhibitors on reaction rates, show that the rate law for aquation is deceptively simple.[2] Base hydrolysis of $[Mo_7O_{24}]^{6-}$ to $[MoO_4]^{2-}$ takes place by successive bimolecular attacks by hydroxide at the molybdenum atoms.[3]

Several n.m.r. investigations have indicated that equilibrium between tetrahedral and square-planar forms of such nickel(II) complexes as exist in both stereochemistries involves forward and reverse reactions which are fast on the n.m.r. time-scale. Now reports have appeared of a number of compounds where rates of stereochemical interconversion can be estimated by n.m.r. techniques. The rate of interconversion of $(Ph_2MeP)_2NiBr_2$ is less than that of the iodide, which suggests the barrier cannot be entirely steric in origin.[4] This preliminary work has been extended to include other Ph_2RP ligands, and also chlorides. The rate law for interconversion in the presence of excess ligand contains two terms, which fact suggests parallel associative and dissociation mechanisms under these conditions.[5] Rates and activation parameters are reported for the similar compound $[PhMe(p\text{-anisyl})P]_2NiBr_2$; kinetic results could not be obtained for the chloride since too little of the tetrahedral species was present in the equi-

[1] R. Baharad, B. Perlmutter-Hayman, and M. A. Wolff, *J. Phys. Chem.*, 1969, **73**, 4391.
[2] S. B. Brown, J. O. Edwards, I. J. Herman, P. Jones, J. R. Mills, and J. E. Earley, *Inorg. Chim. Acta*, 1969, **3**, 351.
[3] P. Lagrange and J.-P. Schwing, *Bull. Soc. chim. France*, 1970, 1340.
[4] G. N. La Mar and E. O. Sherman, *Chem. Comm.*, 1969, 809.
[5] G. N. La Mar and E. O. Sherman, *J. Amer. Chem. Soc.*, 1970, **92**, 2691.

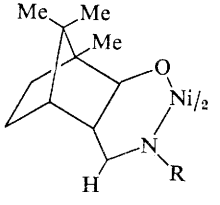
librium mixture.[6] Again, this preliminary report has been followed by the presentation of kinetic results for an extended range (in fact for twenty-six) of these complexes. Rates have been determined for all the compounds and activation parameters for four of them.[7] Rates and activation parameters for tetrahedral to square-planar conversions are collected in Table 1.

Table 1 *Kinetic parameters for tetrahedral → square-planar interconversion for nickel(II) complexes*, NiL_2X_2

L	X	*Solvent*	$10^5 k^a$ (s^{-1})	$\Delta H^‡$ (kcal mol^{-1})	$\Delta S^‡$ (e.u.)	*Ref.*
PMePh(*p*-C_6H_4OMe)	Br	$CHCl_3$	9	16	22	3
$PMePh_2$	Br	$CHCl_3$	8·5	11	6	4
PMe(*p*-$C_6H_4Cl)_2$	Br	$CHCl_3$	3·8	11	4	4
PMe(*p*-$C_6H_4OMe)_2$	Br	$CHCl_3$	1·4	13	9	4
PMe(*p*-$C_6H_4OMe)_2$	Cl	$CHCl_3$	16	10	5	4
$PMePh_2$	Cl	CD_2Cl_2	2·6	—	—	2
	Br	CD_2Cl_2	0·45	9·3	− 6	2
	I[b]	CD_2Cl_2	29	8·5	− 1	2
$PEtPh_2$	Cl	CD_2Cl_2	9·2	9·0	− 1	2
	Br	CD_2Cl_2	1·6	9·0	− 5	2
PPr^nPh_2	Cl	CD_2Cl_2	6·6	9·4	− 1	2
	Br	CD_2Cl_2	1·3	9·8	− 2	2
PBu^nPh_2	Cl	CD_2Cl_2	7·5	9·1	− 1	2
	Br	CD_2Cl_2	1·4	9·2	− 4	2

[a] Extrapolated rate constant at 25° C. [b] Kinetic parameters for other iodides are approximate or limits: see ref. 2.

The interconversion of Δ and Λ forms of tetrahedral nickel(II) complexes is usually very fast. In an attempt to slow such interconversion sufficiently for kinetic observations to be feasible, the bis-complex of ligand (1), with



(1)

R = 1-adamantyl, was synthesised. In fact, the steric hindrance is so great that the rate of interconversion is too slow to be monitored by n.m.r. spectroscopy, so kinetic information of Δ ⇌ Λ interconversion in tetrahedral nickel(II) complexes remains unavailable.[8] Any intramolecular rearrangement of $Co(CO)(NO)(PMe_2Ph)_2$ is also thought to be slow on the n.m.r. time-scale, up to its decomposition temperature of around 100 °C.[9]

[6] L. H. Pignolet and W. de W. Horrocks, *J. Amer. Chem. Soc.*, 1969, **91**, 3976.
[7] L. H. Pignolet, W. de W. Horrocks, and R. H. Holm, *J. Amer. Chem. Soc.*, 1970, **92**, 1855.
[8] G. W. Everett and C. R. Powers, *Inorg. Chem.*, 1970, **9**, 521.
[9] R. J. Mawby, G. Wright, and D. Ewing, *J. Organometallic Chem.*, 1970, **23**, 545.

The tetrahedral–octahedral equilibrium:

$$Co\,py_2Cl_2 + 2py \rightleftharpoons Co\,py_4Cl_2$$

consists of two component equilibria:

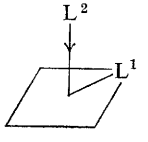
$$Co\,py_2Cl_2 + py \rightleftharpoons Co\,py_3Cl_2 \quad \text{SLOW}$$

$$Co\,py_3Cl_2 + py \rightleftharpoons Co\,py_4Cl_2 \quad \text{FAST}$$

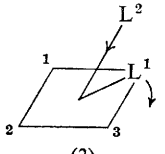
which have been studied, in pyridine and in nitromethane solution, by *T*-jump techniques. The dependence of rate on pyridine concentration rules out the intuitively obvious mechanism involving tetrahedral ⇌ square-planar equilibrium followed by addition of pyridine to the square-planar form.[10] Kinetics of pyridine exchange at $Co\,py_4Cl_2$ (detailed in Part II, Chapter 4, Section 7) are consistent with the above mechanism.[11]

2 Square-planar Complexes

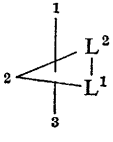
Platinum(II).—Fairly precise information about the direction of entry of an incoming ligand in substitution at a square-planar complex is provided by a study of steric effects in amine substitution at *trans*-$[PtX_2(PR_3)(NHR_2)]$. Substitution rates are particularly sensitive to steric crowding involving the leaving group, which suggests that the incoming amine (L^2 in the simplified diagrams below) does not approach along a line perpendicular to the centre of the square defining the complex [see (2)], but at an angle which is



(2)



(3)



(4)

acute with respect to the leaving group L^1 [see (3)]. This leaving group must move down below the original square-planar unit to give the trigonal-bipyramidal transition state (4), in which pseudorotation is a possibility (*cf.* the section on isomerisation below, and that on phosphorus in Chapter 5). The observation that the rates of replacement of ethylamine by methylamine and *vice versa* are very similar supports this mechanistic picture.[12]

Another approach to the study of the nature of transition states is to determine volumes of activation. A good system to study proves to be bromide substitution at *trans*-$[PtCl_2(PEt_3)_2]$, because electrostriction effects in interchanging bromide and chloride should be small. For the

[10] R. D. Farina and J. H. Swinehart, *J. Amer. Chem. Soc.*, 1969, **91**, 568.
[11] G. D. Howard and R. S. Marianelli, *Inorg. Chem.*, 1970, **9**, 1738.
[12] A. L. Odell and H. A. Raethel, *Chem. Comm.*, 1969, 87.

bromide-concentration-dependent path and for the solvolysis path, in both methanol and aqueous methanol (mole fraction 0·4 methanol), activation volumes lie between -27 and -28 ml mol^{-1}. Hence in all cases, bond formation is the dominant feature of transition-state formation, and from the large values for the activation volumes it is suggested that two platinum to bromine or platinum to solvent bonds are nearly fully formed in the transition state, while both platinum to chlorine bonds remain intact.[13]

Information on reaction mechanisms is often obtained from studies of the variation of rate constants with solvent composition; platinum(II) chemistry has recently afforded several examples of this. Nucleophilic substitution at *trans*-$[PtCl_2(NH_3)_2]$ by water and by ammonia appears to proceed by different mechanisms. For both reagents, logarithms of rate constants correlate with the usual function $D - 1/2D + 1$ of dielectric constant (D) over a range of aqueous methanol, aqueous ethanol, and aqueous acetone solvents. The slopes of the two correlation graphs are very different. This is ascribed to the operation of an associative mechanism for substitution by ammonia (the rate law does have a term in ammonia concentration), but of a dissociative mechanism for aquation.[14, 15] This latter is said to be a non-limiting S_N1 mechanism, but for aquation of *cis*-$[PtCl_2(NH_3)_2]$ and for $[PtCl_2\,en]$, a limiting S_N1 mechanism is proposed.[14, 16] There is some conflict here, both in the case of *trans*-$[PtCl_2(NH_3)_2]$ with the activation volume results discussed in the previous paragraph and, especially for *cis*-$[PtCl_2(NH_3)_2]$ and $[PtCl_2\,en]$, with the usual aversion from the idea of three-co-ordinate platinum(II), even in a transition state. Aquation of *cis*- and of *trans*-$[Pt(NO_2)_2L_2]$, where L = NH_3, PEt_3, SEt_2, py, or thiourea, or L_2 = bipy, also appears to be unimolecular, a conclusion drawn from consideration of the dependence of rate constants on acidity in a range of aqueous sulphuric acid mixtures,[17] which dependence conforms to that expected from the treatments of Bunnett[18] or Zucker and Hammett.[19]

The general rate law for substitution by a ligand L at platinum(II), as at other d^8 complexes, is

$$\text{rate} = k_1[Pt^{II}] + k_2[Pt^{II}][L]$$

Usually the k_1 term corresponds to solvent-assisted dissociation, the k_2 term to direct nucleophilic attack by L, and both paths make comparable contributions to the overall mechanism of substitution. There are, however, exceptions to this general picture. Thus, if the solvent is non-co-

[13] T. Taylor and L. R. Hathaway, *Inorg. Chem.*, 1969, **8**, 2135.
[14] V. D. Panasyuk and N. F. Malashok, *Russ, J. Inorg. Chem.*, 1968, **13**, 1405.
[15] V. D. Panasyuk and N. F. Malashok, *Russ. J. Inorg. Chem.*, 1969, **14**, 661; *Dopovidi Akad. Nauk Ukrain. R.S.R., Ser. B*, 1969, **31**, 39 (*Chem. Abs.*, 1969, **71**, 33787*f*).
[16] V. D. Panasyuk and N. F. Malashok, *Russ. J. Inorg. Chem.*, 1969, **14**, 525.
[17] P. J. Staples and A. Thompson, *J. Chem. Soc.* (*A*), 1969, 1058.
[18] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4978.
[19] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

ordinating, the k_1 path is simple rather than solvent-assisted dissociation; this case is discussed later in the palladium(II) section. The rate law for reaction of $[PtCl_4]^{2-}$ with ethylene has no k_1 term, which is explained by proposing that this path is prevented by extensive association of the metal with ethylene.[20] In substitutions catalysed by $[(allyl)Et_3As]^+$, the first term in the rate law contains the concentration of catalyst; the dissociative path is now arsonium-salt-catalysed rather than solvent-assisted.[21] A further study of catalysis of substitution at platinum(II) concerns the effects of cations on substitution by thiocyanate at the $[Pt(NO_2)_4]^{2-}$ anion.[22] By far the largest group of exceptions to the above two-term rate law are the so-called pseudo-octahedral complexes, for which k_2 approximates to zero, which are discussed in the following paragraphs.

Pseudo-octahedral Behaviour. This is exhibited by those square-planar complexes which have sufficiently bulky ligands to deter the approach of the incoming mucleophile. Recently, a balance between steric hindrance by the bulky ligands and the nucleophilicity of the incoming ligand has been demonstrated, for whereas in most substitutions complexes of Et_4dien show pseudo-octahedral behaviour, when the nucleophile is as powerful as thiosulphate, direct bimolecular attack again becomes significant, and the kinetic behaviour reverts to the normal two-term form. The balance between ligand bulk and nucleophilicity of the incoming substituent is better investigated by using complexes containing mesitylene,[23] or even phenyl or *o*-tolyl,[24] ligands, which are less sterically demanding than Et_4dien. Substitution of *trans*-$[PtCl(mesitylene)(PEt_3)_2]$ by a large number of ligands (for example azide, chloride, thiocyanate, or thiophenoxide) follows the pseudo-octahedral rate law, but substitution by cyanide or selenocyanate follows the two-term rate law. Moreover, the balance between the two patterns of behaviour depends on the solvent. For this same mesitylene complex in DMSO, the two-term rate law applies not only to the good nucleophiles thiourea and selenocyanate, but also to thiocyanate and iodide, which follow pseudo-octahedral behaviour in methanol. Obviously the solvent (k_1) term will be much more important in methanol and may dwarf the k_2 term, while in DMSO the k_1 term will be very much less and may only be comparable in magnitude to the k_2 term.

Thus, amongst the factors determining pseudo-octahedral behaviour are the bulk of the ligands on platinum(II), the nucleophilicity of the incoming ligand, and the nature of the solvent. The next factor for consideration is the bulk of the incoming ligand. The effect of this has been illustrated by the gradual change from normal square-planar behaviour for substitu-

[20] M. Green and C. J. Wilson, *Discuss. Faraday Soc.*, 1969, No. 47, p. 111.
[21] G. Dolcetti, R. Pietropaolo, and U. Belluco, *Inorg. Chem.*, 1970, **9**, 553.
[22] A. Giacomelli, A. Indelli, and U. Belluco, *Inorg. Chem.*, 1969, **8**, 519.
[23] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1969, **8**, 2207.
[24] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1970, **9**, 1525.

tion at $[PtCl_4]^{2-}$ by pyridine, through rate laws with decreasingly important k_2 terms for substitution by picolines, to pseudo-octahedral behaviour for substitution by lutidines. These ligands have similar basicities, so these kinetic effects may be ascribed to the varying steric requirements of the incoming ligands.[25] Reaction of $[PtCl_4]^{2-}$,[26] and of $[PdCl_4]^{2-}$,[27] with 1,10-phenanthroline is slow in aqueous solution; again the bulk of the incoming ligand discourages bimolecular attack at the platinum or palladium. The reaction with $[PtCl_4]^{2-}$ is faster in aqueous ethanol, where the mechanism consists of rate-determining solvolysis followed by reaction with the 1,10-phenanthroline.[28] Similar steric effects and a similar mechanism are likely in the reaction of $[PdCl_4]^{2-}$ with diazacyclopropellanes, though information relating to the mechanism is minimal.[29]

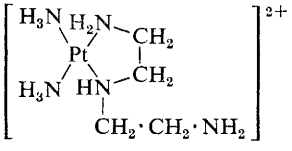
There is yet one other factor which can affect the form of the rate law, and that is the nature of the outgoing ligand. The case reported again relates to palladium(II) rather than to platinum(II), in fast substitution at [Pd dien X]$^+$. Thiocyanate substitution conforms to the pseudo-octahedral pattern, but substitution by selenocyanate follows a two-term rate law. This is claimed to be a unique example of mechanistic control by an outgoing group.[30]

Most work on pseudo-octahedral behaviour is confined to the determination of rate constants and rate laws, but activation enthalpies and entropies for thiocyanate exchange at alkyl-substituted ethylenediamine complexes of the type $[Pt(LL)_2(SCN)_2]$ have been evaluated.[31]

Trans *Effect*. This is one of the basic features of kinetics of reactions of platinum(II), as of other square-planar complexes. A recent study has concerned the lability of ligands *trans* to ethylene, which has been estimated by n.m.r. methods.[32] Both the *trans* effect and the much less investigated *cis* effect of phosphorus and nitrogen bases have been estimated from kinetics of chloride and bromide exchange in a range of platinum(II) complexes.[33] Another kinetic study of the *cis* effect has been concerned with nucleophilic displacement of chloride from *trans*-$[PtCl_2(X\text{-}py)_2]$ by iodide, bromide, thiocyanate, pyridine, and thiourea.[34] The *cis* effect has also been investigated by n.q.r. techniques.[35] The general conclusion from these and earlier studies is that the *cis* effect is primarily a function of ligand basicity, in platinum(II) as in gold(III) complexes.

[25] Yu. N. Kukushkin and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, 1969, **14**, 664.
[26] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 1969, **8**, 524; J. H. Cawley, and J. V. Rund, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1406.
[27] J. V. Rund, *Inorg. Chem.*, 1970, **9**, 1211.
[28] J. V. Rund and F. A. Palocsay, *Inorg. Chem.*, 1969, **8**, 2242.
[29] M. Korat, G. Schmuckler, and D. Ginsburg, *J. Chem. Soc.* (*A*), 1970, 1784.
[30] J. L. Burmeister and J. C. Lim, *Chem. Comm.*, 1969, 1154.
[31] W. Robb and R. J. Mureinik, *Inorg. Chim. Acta*, 1969, **3**, 575; R. J. Mureinik and W. Robb, *ibid.*, p. 580.
[32] T. A. Weil, P. J. Schmidt, and M. Orchin, *Inorg. Chem.*, 1969, **8**, 2138.
[33] G. Carturan and D. S. Martin, *Inorg. Chem.*, 1970, **9**, 258.
[34] L. Cattalini, G. Marangoni, and A. Cassol, *Inorg. Chim. Acta*, 1969, **3**, 74.
[35] C. W. Fryer and J. A. S. Smith, *J. Organometallic Chem.*, 1969, **18**, P35.

Miscellaneous Substitutions. After the foregoing discussions of general principles involved in substitution of platinum(II) and other square-planar complexes it remains to chronicle the remaining kinetic studies of specific systems. $[PtCl_4]^{2-}$ reacts with dien, dienH^+, dienH_2^{2+} according to the pH of the system; the rate-determining step is formation of the first platinum–nitrogen bond.[36] In reaction of $[PtCl_4]^{2-}$ with aliphatic amines and amino-alcohols, the length and degree of branching of the hydrocarbon chain are claimed to have but little influence on reaction rates.[37] Biacetyl-sensitised aquation of $[PtCl_4]^{2-}$ has been described.[38] Studies of sensitised hydrolysis are frequent in organic, but rare in inorganic, chemistry [though see also chromium(III)[39]]. Rates of reaction of the series $[PtCl_{4-n}(NH_3)_n]^{(2-n)-}$ with ammonia have been determined and rationalised in terms of *cis* and *trans* effects.[40] Reaction of *cis*-$[PtCl_2(NH_3)_2]$ with diethylenetriamine produces the cation (5), which is a model for possible intermediates con-



(5)

taining two-thirds-bonded dien in other substitution reactions involving this ligand.[41] Rates and activation parameters have been reported for reaction of $[PtCl_4]^{2-}$, $[PtBr_4]^{2-}$, $[PtCl_3(NH_3)]^-$, and $[PtCl_3py]^-$ with pyridine, ammonia, and mono- and bi-dentate amines.[42] Further studies of platinum(II)–halide–amine systems include those of replacement of chloride or bromide in $[PtX(NO_2)L_2]$ by nitrite,[43] aquation of $[PtCl(acetoxime)_3]^+$,[44] and substitution in $[PtX_2(NH_2OH)_2]$.[45]

Reactions in $[PtCl_4]^{2-}$–ethylene–$[SnCl_3]^-$ systems are dominated by the large π-acceptor and *trans* effect properties of the $[SnCl_3]^-$ ligand.[46] This is also true for analogous systems containing other alkenes.[47] A preliminary

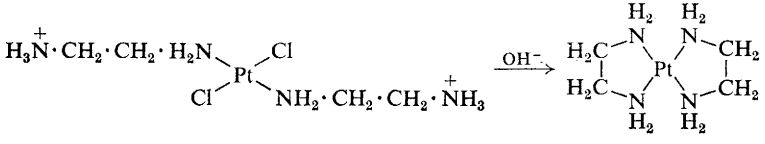
[36] E. D. Smith, J. A. McCann, and J. E. Teggins, *Inorg. Chem.*, 1969, **8**, 1872.
[37] Yu. N. Kukushkin and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, 1968, **13**, 1620.
[38] V. S. Sastri and C. H. Langford, *J. Amer. Chem. Soc.*, 1969, **91**, 7533.
[39] A. W. Adamson, J. E. Martin, and F. D. Camessei, *J. Amer. Chem. Soc.*, 1969, **91**, 7530.
[40] C. B. Colvin, R. G. Gunther, L. D. Hunter, J. A. McLean, M. A. Tucker, and D. S. Martin, *Inorg. Chim. Acta*, 1968, **2**, 487.
[41] J. E. Teggins, J. A. McCann, and E. D. Smith, *Inorg. Chem.*, 1970, **9**, 1294.
[42] Yu. N. Kukushkin and V. B. Ukraintsev, *Russ. J. Inorg. Chem.*, 1968, **13**, 1485.
[43] A. V. Babaeva and R. I. Rudyi, *Russ. J. Inorg. Chem.*, 1969, **14**, 1111.
[44] A. I. Stetsenko, S. G. Strelin, and M. I. Gel'fman, *Russ. J. Inorg. Chem.*, 1969, **14**, 1281.
[45] B. I. Peshchevitskii and R. L. Shchekochikhina, *Russ. J. Inorg. Chem.*, 1969, **14**, 1480.
[46] R. Pietropaolo, M. Graziani, and U. Belluco, *Inorg. Chem.*, 1969, **8**, 1506.
[47] R. Pietropaolo, G. Dolcetti, M. Giustiniani, and U. Belluco, *Inorg. Chem.*, 1970, **9**, 549.

report on pyridine exchange at *trans*-$[PtCl_2(olefin)(X\text{-}py)]$ suggested that the incoming pyridine might attack first at the remote end of the olefin rather than directly at the platinum.[48] The full description of this work has now been published, in which the effects of solvent, temperature, nature of the olefin and of the substituted pyridine are reported.[49] To complement an earlier study of Zeise's salt, $[PtCl_3(C_2H_4)]^-$, reacting with 2,2′-bipyridyl, kinetic parameters have been determined for reaction of an acetylenic analogue $[PtCl_3L]^-$, where L = 2,5-dimethylhex-3-yne-2,5-diol. Differences in behaviour are as anticipated from the known properties of olefins and acetylenes, and from the presence of the hydroxy-groups in the acetylenic ligand. A suggested intermediate containing the cation $[PtClL\ bipy]^+$ was isolated and characterised as its chloride.[50] Mechanisms of reactions involving alkene and alkyne complexes of platinum have been reviewed.[51]

Kinetic parameters for displacement of Group VI ligands have been determined for *cis*- and *trans*-$[PtX_2(SEt_2)_2]$ reacting with ammonia,[52] and for the similar selenium compound *trans*-$[PtI_2(SeEt_2)_2]$ with pyridine, piperidine, and 3,4-lutidine.[53] Displacement by Group VI ligands is much more difficult, *e.g.* the behaviour of hydroxide ion. But hydroxide attack at platinum(II) goes photochemically readily enough, for example at $[PtBr\ dien]^+$.[54] There is also a possibility of hydroxide attack at platinum(II) in hydrolysis of *trans*-$[Pt(Cl)(CO)(PR_3)_2]^+$ cations.[55]

Irradiation of $[Pt(N_3)\ dien]^+$ at its charge-transfer maximum produces azide radicals, and presumably transient platinum(III).[56] Similarly, pulse radiolysis experiments on $[PtCl_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ generate transient platinum(I) and platinum(III) species, whose kinetic properties were investigated.[57]

The following chelate ring-closure reaction is an example of intramolecular substitution in a square-planar complex:



[48] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, 1968, **90**, 4175.
[49] P. D. Kaplan, P. Schmidt, A. Brause, and M. Orchin, *J. Amer. Chem. Soc.*, 1969, **91**, 85.
[50] J. Hubert and T. Theophanides, *Inorg. Chim. Acta*, 1969, **3**, 391.
[51] U. Belluco, B. Crociani, R. Pietropaolo, and P. Uguagliati, *Inorg. Chim. Acta Rev.*, 1969 **3** 19.
[52] V. A. Valyaeva and S. P. Derendyaev, *Russ. J. Inorg. Chem.*, 1968, **13**, 1569, 1699.
[53] M. Nicolini, M. Giustiniani, and A. Palazzi, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2899.
[54] C. Bartocci, F. Scandola, and V. Balzani, *J. Amer. Chem. Soc.*, 1969, **91**, 6948.
[55] H. C. Clark and W. J. Jacobs, *Inorg. Chem.*, 1970, **9**, 1229.
[56] C. Bartocci and F. Scandola, *Chem. Comm.*, 1970, 531.
[57] A. S. Ghosh-Mazumdar and E. J. Hart, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 165.

The kinetic interest lies in relating rate constants for this type of process to equilibrium constants, with a view to finding out how much the greater stability of chelates is reflected in rates of formation.[58]

Isomerisation. It has long been assumed that thermal isomerisation of planar complexes involves consecutive displacement steps. Now experiments on tri-n-butylphosphine-catalysed isomerisation of *cis*-$[PtCl_2(PBu^n_3)_2]$ in cyclohexane solution seem to contradict this view. The three important pieces of evidence are the large catalytic activity of the added phosphine — the rate law is first-order in added phosphine; the observed reduction in rate on adding polar solvents to the cyclohexane; and the activation entropy. A mechanism more in keeping with this evidence is formation of, and subsequent pseudorotation in, a five-co-ordinate intermediate.[59] The *trans*- to *cis*- isomerisation of $[PtCl_2(CO)(NH_2R)]$ cannot go by reversible loss of NH_2R since the reaction proceeds at temperatures well above the boiling points of such ligands. In this case, isomerisation through a tetrahedral configuration is suggested.[60] The displacement mechanism is favoured for *cis* ⇌ *trans* isomerisation of PtX_2L_2, where L = ammonia or substituted pyridine, though (as in the first system mentioned in this paragraph) there is marked catalysis by added ligand.[61]

Inversion at nitrogen co-ordinated to platinum(II) is discussed with analogous examples from platinum(IV) and cobalt(III) chemistry at the end of the chapter on octahedral complexes.

Palladium(II).—Exchange of acac with $Pd(acac)_2$ follows the two-term rate law normal for square-planar d^8 complexes:

$$\text{rate} = k_1[Pd(acac)_2] + k_2[Pd(acac)_2][acac]$$

The novel feature in this investigation is the use of non-polar solvents, in several of which the value of k_1 is the same. The first term in the rate law is said to correspond not to solvent-assisted dissociation, as in the usual polar solvents, but rather to simple dissociation.[62] While the determination of rates and the deduction of rate laws for substitution at palladium(II) is fairly common, determination of activation parameters is rare. These are, however, reported for aquation of *trans*-$[PdCl_2(NH_3)_2]$ and of *trans*-$[PdCl(NO_2)(NH_3)_2]$.[63]

Palladium(II) complexes containing sulphur-bonding ligands have been widely studied. The relative ease of displacement of the dithioethers $C_6H_5{\cdot}S{\cdot}(CH_2)_n{\cdot}S{\cdot}C_6H_5$ (n = 2 or 3) from palladium(II), and from platinum(II), by amines reflects the greater difficulty of palladium–nitrogen

[58] M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.
[59] P. Haake and R. M. Pfeiffer, *Chem. Comm.*, 1969, 1330.
[60] R. Ellis, T. A. Weil, and M. Orchin, *J. Amer. Chem. Soc.*, 1970 **92**, 1078.
[61] L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, 1969, **91**, 312.
[62] K. Saito and M. Takahashi, *Bull. Chem. Soc. Japan*, 1969, **42**, 3462.
[63] V. D. Panasyuk and T. I. Denisova, *Russ. J. Inorg. Chem.*, 1970, **15**, 377.

bond making in transition-state formation.[64] The rate-determining step in displacement of $C_6H_5 \cdot S \cdot (CH_2)_2 \cdot S \cdot C_6H_5$ from palladium(II) by pyridine or one of its substituted derivatives is bimolecular displacement of one sulphur atom to open the chelate ring. If the incoming pyridine has two *ortho*-substituents, then displacement of the second sulphur atom becomes the rate-limiting step.[65] The reverse process, formation of palladium–sulphur bonds, is illustrated by the reaction of $[PdCl_4]^{2-}$ with 3-thiamorpholine (T). The initial, very fast reaction to give $PdCl_2T_2$ is followed by slow reaction of this mixed complex with $[PdCl_4]^{2-}$ to give $[PdCl_3T]^-$.[66] Both the formation and the dissociation of palladium–sulphur bonds have been investigated for sulphinato–palladium(II) complexes.[67]

In the aquation of $[Pd\ dien(NH_3)]^{2+}$, or in its reaction with chloride, there is a rapid preliminary reaction in which equilibrium is established between complexes containing dien co-ordinated through three and two atoms respectively.[68] In the parallel reactions of $[Pd\ en_2]^{2+}$, there is a similar pre-equilibrium established between species containing en co-ordinated by both nitrogen atoms and en co-ordinated by only one nitrogen atom.[69] The recent, almost simultaneous, publication of two different mechanisms derived from consistent sets of results for the reaction of $[Pd(NH_3)_4]^{2+}$ with hydrochloric acid demonstrates the possibility of ambiguity of interpretation of isosbestic points when these appear in studies of consecutive reactions.[70]

A study of acid–base behaviour and of absorption spectra of $[Pd(OH_2)_4]^{2+}$ and of palladium(II)–amine complexes has produced some semiquantitative kinetic observations.[71]

Reaction of olefin complexes of palladium(II) with n-butylamine takes place through an intermediate containing both olefin and amine co-ordinated to the metal.[72] This proposed mechanism contrasts with the reaction of ethylamine with a platinum(II)–olefin complex, where stereochemical evidence suggests that the amine attacks the olefin directly and is not co-ordinated to the platinum at any stage of the reaction.[73]

Pseudo-octahedral behaviour of palladium(II) complexes has already been discussed in the previous section on platinum(II).

Nickel(II).—A number of variables were studied for substitution at square-planar bis-dithiolatonickel(II) complexes. These variables included the reactivity of the incoming nucleophile, leaving-group effects, the *trans* effect, and the denticity of the incoming group. The rate law here is simple

[64] G. Marangoni, S. Degetto, and E. Colon, *Gazzetta*, 1969, **99**, 816.
[65] L. Cattalini, M. Martelli, and G. Marangoni, *Inorg. Chim. Acta*, 1968, **2**, 405.
[66] D. de Filippo and C. Preti, *Inorg. Chim. Acta*, 1969, **3**, 287.
[67] C. W. Dudley and C. Oldham, *Inorg. Chim. Acta*, 1969, **3**, 3.
[68] J. S. Coe and J. R. Lyons, *J. Chem. Soc.* (*A*), 1969, 2669.
[69] J. S. Coe, J. R. Lyons, and M. D. Hussain, *J. Chem. Soc.* (*A*), 1970, 90.
[70] R. A. Reinhardt and J. S. Coe, *Inorg. Chim. Acta*, 1969, **3**, 438.
[71] L. Rasmussen and C. K. Jørgensen, *Inorg. Chim. Acta*, 1969, **4**, 543, 547.
[72] H. Hirai, H. Sawai, and S. Makishima, *Bull. Chem. Soc. Japan*, 1970, **43**, 1148.
[73] A. Panunzi, A. De Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, 1970, **92**, 3488.

second-order, not the two-term form normally encountered for substitution at platinum(II) or palladium(II) complexes, and there is evidence for five-co-ordinate intermediates. This is consistent with the greater stability of five-co-ordination at nickel(II), as in, for instance, $[Ni(CN)_5]^{3-}$. However, the two-term rate law has been observed for other square-planar nickel(II) complexes, for example for the reaction of *trans*-$[NiCl(o\text{-tolyl})(PEt_3)_2]$ with pyridine.[74] Reaction of $[Ni(CN)_4]^{2-}$ with triethylenetetramine is also second-order; kinetics of this and the reverse reaction have been studied.[75] The relaxation observed in aqueous solutions of the nickel(II) complex of 2,3,2-tet is attributed to a square-planar $\rightleftharpoons$ octahedral equilibrium.[76]

Gold(III).—Kinetics of substitution have been described for three gold(III) systems, $[AuCl_4]^-$ plus ethylenediamine,[77] $[AuCl_4]^-$ plus diethylenetriamine,[78] and $[AuBr_4]^-$ plus formic and oxalic acids.[79]

Cobalt(I).—The main interest here is in cobaloximes and similar cobalt(I) chelate complexes as models for reduced forms of vitamin B_{12}. Kinetic studies of alkylation at cobalt(I), as in the recent study of reaction of alkyl halides with, for example, cobaloximes and vitamin B_{12s}, indicate an S_N2 mechanism, with cobalt(I) acting as a very strong nucleophile.[80] The S_N2 mechanism has now been confirmed stereochemically by establishing that these reactions proceed with inversion of configuration at carbon.[81] Reaction of vinyl halides with these cobalt(I) complexes also proceeds by an associative nucleophilic substitution mechanism, rather than *via* acetylenic intermediates.[82]

3 Five-co-ordinate Complexes

Cobalt.—Pentacyanocobaltate(II) reacts with iodine cyanide in aqueous solution according to the equation:

$$2[Co(CN)_5]^{3-} + ICN \longrightarrow [Co(CN)_5I]^{3-} + [Co(CN)_6]^{3-}$$

This is an example of oxidative addition at a five-co-ordinate complex to compare with the more common examples of oxidative addition at square-planar d^8 complexes (see Chapter 12). Hydrogen peroxide and hydroxylamine react similarly with pentacyanocobaltate(II). These reactions are all second-order and proceed by radical mechanisms.[83] The course of

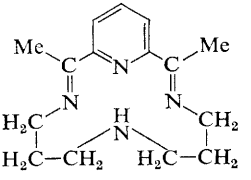
[74] R. G. Pearson and D. A. Sweigart, *Inorg. Chem.*, 1970, **9**, 1167.
[75] G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 1125.
[76] R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4326.
[77] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 1969, **3**, 29.
[78] W. J. Louw and W. Robb, *Inorg. Chim. Acta*, 1969, **3**, 303.
[79] V. P. Kazakov and M. V. Konovalova, *Russ. J. Inorg. Chem.*, 1968, **13**, 1226.
[80] G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, 1969, **91**, 3341.
[81] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1970, **92**, 1414.
[82] K. Nguyen van Duong and A. Gaudemer, *J. Organometallic Chem.*, 1970, **22**, 473.
[83] P. B. Chock, R. B. K. Dewar, J. Halpern, and Lai-Yoong Wong, *J. Amer. Chem. Soc.*, 1969, **91**, 82.

reaction with alkyl and benzyl halides is similar, starting with

$$[Co(CN)_5]^{3-} + RX \longrightarrow [Co(CN)_5X]^{3-} + R^{\bullet}$$

and often yielding simply $[Co(CN)_5R]^{3-}$ as the other final product. In comparison with sodium, or methyl radicals, pentacyanocobaltate(II) is a relatively slow and more selective halogen abstractor.[84] Cations often have a large effect on rates of reactions involving $[Co(CN)_5]^{3-}$; the tendency of $[Co(CN)_5]^{3-}$ to associate with ions of sub-group B elements with the formation of metal–metal bonds is illustrated by the characterisation of $[(NC)_5 \cdot Co \cdot Tl \cdot Co(CN)_5]^{5-}$.[85]

Photochemical dealkylation of alkylcobaloximes and alkylcobalamins is associated with charge transfer between the alkyl group and cobalt; cobalt(II) and alkyl radicals are the initial products.[86] A similar situation exists for the vitamin B_{12} model (6).[87] In both cases, there are close parallels



(6)

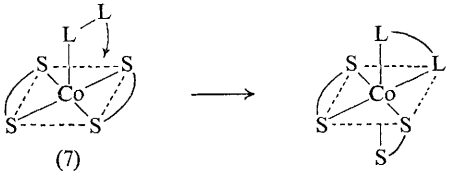
to the behaviour of classical cobalt(III) complexes of the $[CoCl(NH_3)_5]^{2+}$ family, whose photochemistry is discussed in Part II, Chapter 4, Section 2.

Dimethylglyoxime (DMG) complexes of cobalt(II), $Co(DMG)_2L$, react in some ways like pentacyanocobaltate(II). Thus the complexes $Co(DG)_2L$, where DG = dimethylglyoxime, diphenylglyoxime, or one of their substituted derivatives, react with benzyl bromide or 1-bromoethylbenzene by a radical mechanism involving rate-determining halogen abstraction by the cobalt(II) complex. There is a marked contrast between the behaviour of these and of analogous cobalt(I) complexes, which react with alkyl halides by an S_N2 mechanism.[80, 81] The six-co-ordinate complexes $Co(DG)_2L_2$ react very similarly to the five-co-ordinate $Co(DG)_2L$ series, for the former are fully dissociated in solution (benzene or acetone) to the latter and free L.[88]

Substitution at $[Co(mnt)_2(PPh_3)]^-$ by the bidentate ligands ethylenediamine, 2,2′-bipyridyl, 1,10-phenanthroline, and maleonitriledithiolate, and by the monodentate ligand triphenyl phosphite, takes place by two parallel paths. In the first, equilibrium loss of triphenylphosphine is followed by attack of the incoming ligand at the square-planar intermediate

[84] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 582.
[85] E. C. C. Crouch and J. M. Pratt, *Chem. Comm.*, 1969, 1243.
[86] G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *J. Amer. Chem. Soc.*, 1970, **92**, 2997.
[87] E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, **91**, 3201.
[88] P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 77.

thus produced. For the bidentate incoming ligands, it is thought that the slowest step in the reaction sequence is the closing of the chelate ring [(7) → (8)], since one end of one maleonitriledithiolate ligand has to be



(7) (8)

displaced to permit formation of the third chelate ring. The second path involves direct attack of one end of the incoming ligand at the vacant sixth co-ordination position at cobalt, again with slow chelate ring formation as the triphenylphosphine leaves and the maleonitriledithiolate moves around the cobalt.[89]

Platinum.—Intramolecular rearrangement and ligand exchange have been studied for methyldiphosphine adducts of platinum(II) dithiolates.[90]

4 Eight-co-ordinate Complexes

Molybdenum.—There have been several suggestions as to the detailed mechanism of photoaquation of $[Mo(CN)_8]^{4-}$. The most recent investigation [91] has proved that hydroxide ions are released in the primary photoaquation step, and that this step is inhibited by added cyanide. Thus, it supports the hypothesis that this photoaquation step is

$$[Mo(CN)_8]^{4-} + 2H_2O \rightleftharpoons [Mo(CN)_7(OH_2)]^{3-} + HCN + OH^-$$

[89] D. A. Sweigart and D. G. De Wit, *Inorg. Chem.*, 1970, **9**, 1582.
[90] J. P. Fackler, J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, 1969, **91**, 1217.
[91] V. Balzani, M. M. Manfrin, and L. Moggi, *Inorg. Chem.*, 1969, **8**, 47.

4
Metals: Octahedral Complexes

1 Aquation: Introduction and General Approaches

This section starts with a few general references illustrating the main approaches to determination of reaction mechanisms in this area of co-ordination chemistry. Then aquation of individual complexes is discussed, with the first section devoted to the large number of references to cobalt(III) complexes and the remainder containing references to complexes of the other cations, arranged in order of number of *d* electrons. As usual the vast majority of references deal with cobalt(III) and chromium(III) complexes, though there is a fair amount of work on rhodium(III), iridium(III), and iron(II). It is disappointing that after the initial interest a few years ago in d^3 complexes other than chromium(III), there has been no further activity in this field, despite the ready accessibility of vanadium(II) and molybdenum(III) by electrolysis or chemical reduction. It is also disappointing that little further work has been carried out with complexes with few *d* electrons, for d^2, d^1, and especially d^0 complexes should be relatively susceptible to associative nucleophilic attack. However, the 1968 study of bimolecular chloride exchange at titanium(IV) (d^0) has been followed only by studies of formation of monothiocyanatotitanium(III) (d^1) (see later), and of solvent exchange at titanium(III) (see Part II Chapter 2).

The four general approaches to mechanism determination to be mentioned here are the use of linear free energy plots and plots of activation enthalpies against activation entropies, the determination of volumes of activation, the search for transient intermediates, and the study of solvent variation on rates. The last topic is covered in Part II Chapter 6, the other three here.

Several years ago Langford plotted logarithms of rate constants for aquation of a series of cobalt(III) complexes against the logarithms of equilibrium quotients (constants) for the respective aquation reactions. The resulting linear free energy plot indicated that the mechanism of aquation was dissociative, and that the leaving ligands were all but detached from the cobalt atom in the transition state.* All but one of Langford's

[1] R. A. Marcus, *J. Amer. Chem. Soc.*, 1969, **91**, 7224.

* The use of linear free energy plots to estimate the position of the transition state along the reaction co-ordinate has been discussed in theoretical and organic terms.[1]

aquation reactions involved a leaving group of charge − 1; now that two results are available for leaving groups of charge − 2, *viz.* sulphate and oxalate, it is possible to show that these fit into the original linear free energy graph satisfactorily. These two points define a second line, non-coincident with the line for leaving groups of charge − 1, but parallel to it.[2] Two further complexes, $[Co(N_3)(NH_3)_5]^{2+}$ (ref. 3) and $[Co(NO_3)(NH_3)_5]^{2+}$,[4] have recently been shown to fit the linear free energy plot for uni-negative leaving groups. The latter case is the more interesting in that aquation could involve cobalt–oxygen or oxygen–nitrogen bond breaking [cf. nitritochromium(III), Section 8.3]; the present result strongly suggests that it is the cobalt to oxygen bond which breaks. Another example of the usefulness of these linear free energy plots is mentioned in the cobalt(III) base hydrolysis section, where they provide confirmatory evidence for an S_N1cb mechanism.[4] Also in cobalt(III) base hydrolysis is mentioned an example of an activation enthalpy *vs.* activation entropy plot; another example of this is discussed with reference to aquation of *trans*-$[CoCl_2\,en_2]^+$ in mixed aqueous solvents.[5]

The second general approach is to obtain activation volumes, which reflect solvation and electrostriction effects in transition state formation. In the aquation of $[CoX(NH_3)_5]^{n+}$, activation volumes are equal to overall molar volume changes for complete aquation to $[Co(OH_2)(NH_3)_5]^{3+}$ plus the anion, as shown in Table 1. This suggests, in agreement with the linear free energy plot discussion above, that the leaving group is fully solvated in the transition state and therefore almost completely free from the cobalt, and that the incoming water molecule is not fully bonded to the cobalt.[6] In other words the mechanism approximates to the purely dissociative I_d or S_N1(lim). An independent determination of the activation volume for acid aquation of $[CoCl(NH_3)_5]^{2+}$, listed in Table 1, has also been interpreted in terms of a primarily dissociative mechanism, though here the authors seem reluctant to rule out all traces of metal–incoming water interaction in the transition state. The very similar activation volume for acid aquation of $[Cr(NCS)(NH_3)_5]^{2+}$, again in Table 1, suggests a close similarity of mechanism for this chromium(III) complex.[7]

The third general approach is to seek evidence for transient intermediates, for example by trapping $[Co(NH_3)_5]^{3+}$ to gain evidence for a dissociative mechanism for aquation of $[CoX(NH_3)_5]^{n+}$. Indeed, there is some evidence for the generation of $[Co(NH_3)_5]^{3+}$ in aquation, particularly in nitrous acid assisted aquation of $[Co(N_3)(NH_3)_5]^{2+}$. It therefore seemed reasonable to start the search for a comparable five-co-ordinate chromium(III) intermediate with the analogous reaction, nitrous acid

[2] A. Haim, *Inorg. Chem.*, 1970, **9**, 426.
[3] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, 1969, **8**, 1604.
[4] W. E. Jones, R. B. Jordan, and T. W. Swaddle, *Inorg. Chem.*, 1969, **8**, 2504.
[5] G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1206.
[6] W. E. Jones and T. W. Swaddle, *Chem. Comm.*, 1969, 998.
[7] D. L. Gay and R. Nalepa, *Canad. J. Chem.*, 1970, **48**, 910.

Table 1 *Activation volumes* ($\Delta V^{\ddagger}$) *and volumes of reaction* (ΔV) *for aquation of cobalt*(III) *and chromium*(III) *complexes*

Complex	$\Delta V^{\ddagger}$ (ml mol^{-1})	ΔV (ml mol^{-1})	*Ref.*
$[CoCl(NH_3)_5]^{2+}$	− 7·5		7
$[CoCl(NH_3)_5]^{2+}$	− 9·7	− 10·4	6
$[CoBr(NH_3)_5]^{2+}$	− 8·6	− 9·6	6
$[Co(NO_3)(NH_3)_5]^{2+}$	− 5·9	− 6·0	6
$[Co(SO_4)(NH_3)_5]^{+}$	− 16·9	− 15·2	6
$[Cr(NCS)(NH_3)_5]^{2+}$	− 8·6		7

assisted aquation of $[Cr(N_3)(OH_2)_5]^{2+}$. In aqueous solution, no convincing evidence for the transient existence of $[Cr(OH_2)_5]^{3+}$ was obtained,[8] though this could mean either that $[Cr(OH_2)_5]^{3+}$ was not formed, or that it was formed but showed only low discrimination towards nucleophiles. Similar experiments on $[CrX(OH_2)_5]^{2+}$, where X = azide or halide, in a series of aqueous methanol solvents did, however, give positive evidence for reaction through a $[Cr(OH_2)_5]^{3+}$ intermediate.[9] In connection with these transient five-co-ordinate intermediates might be mentioned some stable five-co-ordinate compounds of iridium(I) which have been suggested as models for the transition states of dissociative reactions of octahedral complexes.[10]

The fourth general approach, the study of solvent effects on reactivity, is amply illustrated in Part II Chapter 6.

Stereochemical changes taking place in the course of substitution reactions of octahedral complexes have been reviewed.[11] An improved method for estimating crystal field activation energies has been described.[12]

2 Aquation: Cobalt(III) Complexes

A large number of the results available for simple aquation of octahedral cobalt(III) complexes in aqueous solution can be discussed in two groups, the first consisting of studies where attention is concentrated on the leaving groups themselves, and the second where the main concern is the effect of other ligands present on the ease of loss of some common leaving group, often chloride.

Unidentate Leaving Groups.—The demonstration that aquation of $[Co(NO_3)(NH_3)_5]^{2+}$ involves cobalt–oxygen rather than oxygen–nitrogen bond breaking has already been mentioned.[4] The kinetics of aquation of $[CoF(NH_3)_5]^{2+}$ in acid solution have been reinvestigated since the originally determined activation parameters did not compare in the expected manner with those for related $[MXL_5]^{n+}$ complexes. Improved analysis methods,

[8] R. C. Thompson and E. J. Kaufmann, *J. Amer. Chem. Soc.*, 1970, **92**, 1540.
[9] S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, 1970, **92**, 1215.
[10] D. M. Blake and M. Kubota, *J. Amer. Chem. Soc.*, 1970, **92**, 2578.
[11] R. D. Archer, *Co-ordination Chem. Rev.*, 1969, **4**, 243.
[12] A. L. Companion, *J. Phys. Chem.*, 1969, **73**, 739.

the use of a wider temperature range, and corrections for parallel cobalt–nitrogen bond breaking and consequent ammonia loss permit the determination of more accurate activation parameters for the acid-independent aquation of this complex. Difficulties in determining the equilibrium quotient for this aquation preclude an investigation of how closely this complex conforms to Langford's linear free energy plot.[13]

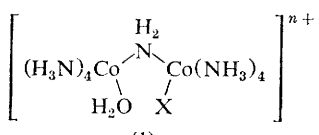
The possibility of determining the likely structure, trigonal bipyramidal or square pyramidal, of the five-co-ordinate transition state for dissociative aquation of cobalt(III)–chloride–ammine complexes has been discussed by Tobe.[14] The stereochemical course and kinetics of aquation of *trans*-$[CoCl_2(NH_3)_4]^+$ have been reinvestigated [15] to ascertain the transition state geometry by Tobe's criteria. While these criteria seem to be satisfactory in complexes containing simple ligands, there is some doubt of their validity when their use is extended to complexes containing polydentate macrocyclic ligands, as discussed in the relevant section later.

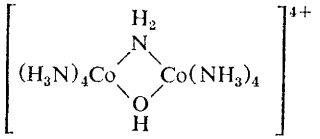
Multidentate Leaving Groups.—Rates of aquation of $[Co(CO_3)(LL)_2]^+$, where LL = en, pn, tn, or $(NH_3)_2$, are strongly acid-dependent, whereas those of the unidentate carbonate complex $[Co(CO_3)(NH_3)_5]^+$ are not. The mechanism of aquation of the chelate complex is thought to involve rate-determining chelate ring opening assisted by water or protonated water molecules.[16]

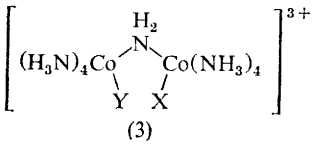
The kinetics of aquation and of anation of $[Co(oxalate)_2(OH_2)_2]^-$ provide information germane to the mechanism of aquation of the anion $[Co(oxalate)_3]^{3-}$. The information on the bis-oxalate complex shows that aquation of the tris-oxalate complex involves rate-determining loss of the first oxalate ligand and that this step is reversible.[17] Information relevant to the mechanism of aquation of $[Co(oxalate)en_2]^+$ comes from oxygen-exchange experiments. Perhaps the most interesting point is that for the cobalt complex, as for the rhodium complex, only half the oxalate-oxygen atoms exchange, whereas for analogous chromium(III) complexes all the oxalate-oxygens exchange with solvent-oxygen.[18]

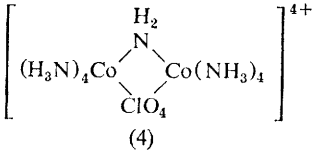
Bridged Dicobalt Complexes.—There is evidence for intramolecular substitution in amido-bridged binuclear cobalt(III) complexes of formula (1) (X = Cl, Br; $n = 4$). The reaction (1) → (2) occurs much more rapidly than would be expected from knowledge of reactivities of analogous $[CoX(NH_3)_5]^{n-}$ complexes. The simplest explanation of this is that the favourable geometry of the binuclear complex constrains the potentially bridging oxygen atom to be close to the cobalt(III) centre from which X^-

[13] T. W. Swaddle and W. E. Jones, *Canad. J. Chem.*, 1970, **48**, 1054.
[14] M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 1260.
[15] R. G. Linck, *Inorg. Chem.*, 1969, **8**, 1016.
[16] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 1969, **91**, 3207; V. S. Sastri and G. M. Harris, *ibid.*, 1970, **92**, 2943.
[17] J. Aggett and R. I. C. Armishaw, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1989.
[18] C. Andrade, R. B. Jordan, and H. Taube, *Inorg. Chem.*, 1970, **9**, 711.


(1)


(2)


(3)


(4)

is being lost.* A term in the rate law which contains the reciprocal of the hydrogen ion concentration indicates that complexes of the formula (3) (X = Cl, Br; Y = OH) are also involved. A limiting S_N1 mechanism seems unlikely, unless reaction of (1), with X = OH_2, n = 5, to give (2) is particularly rapid, since there is no evidence for the formation of a bis-aquo intermediate. On the other hand, although the potentially bridging water or hydroxide ligands are close enough to the other cobalt(III) centre to favour rapid reaction, they are not particularly suitably positioned to form an S_N2(lim) transition state. It seems, therefore, that an intermediate mechanism with just sufficient associative character to explain the exclusive formation of the hydroxo-bridged species is indicated.[20] The nature of the acid is important in aquation of this type of complex, as is shown by both kinetic and spectroscopic studies of solutions of (2) and of its ethylenediamine analogue in strong perchloric acid. Perchlorato-complexes of the formulae (1) with X = ClO_4 and (4) are present.[21] Other substitution reactions of dicobalt(III) complexes whose kinetics have been studied include the interconversion of (1) and (2) where X = NO_3,[22] the reaction of (2) with thiocyanate,[23] and the conversion of (2) to (1) with X = Cl.[24] Complexes of formula (3), with X = Y = Cl and X = Y = NCS have been identified.[23] Aquation of $[CoX(NH_3)_5]^{n+}$ where X is a radical intermediate, appears to occur in the reaction of $[(H_3N)_5Co \cdot O_2 \cdot Co(NH_3)_5]^{5+}$ with sulphite unless the sulphite is in large excess.[25] Reduction of (2) by chromium(II) or vanadium(II) is accompanied by some replacement of ammonia ligands by water.[26] Aquation of (1) with X = Cl in aqueous–

[19] See, *e.g.*, B. L. Vallee and R. J. P. Williams, *Proc. Nat. Acad. Sci.*, 1968, **59**, 498.
[20] M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 937.
[21] R. S. Taylor and A. G. Sykes, *Chem. Comm.*, 1969, 1137.
[22] M. B. Stevenson, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1058.
[23] S. W. Foong, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1064.
[24] A. G. Sykes and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 1424.
[25] R. Davies, A. K. E. Hagopian, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 623.
[26] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 1991.

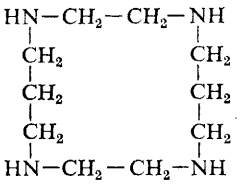
* This example of rate enhancement by favourable geometry making the initial state bear some resemblance to the transition state is a particular case of a type of situation often encountered in biochemical systems.[19]

organic mixtures is mentioned in the subsequent section on solvent variation.

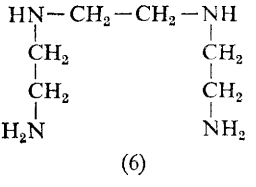
Effects of Non-leaving Ligands.—The effects of non-reacting ligands on the lability of leaving ligands at cobalt(III) have been much studied, especially for chloride as the leaving group. In this paragraph we deal with complexes of the formula $[CoCl\,L\,en_2]^{n+}$. When L = SO_4^{2-}, aquation is rapid; sulphate has a large labilising effect.[27] At elevated temperatures, the complex where L = aniline loses both aniline and chloride on aquation,[28] but at room temperature only chloride is lost. However, for this complex and the related complexes with L = *m*- or *p*-toluidine, the rate of aquation in acid solution varies with pH. This unusual behaviour is explained by the persistence of an S_N1cb mechanism for aquation even in weak acid, since these aromatic amines when complexed to cobalt(III) have considerably lower pK_a values than ammonia similarly complexed.[29] For analogous benzylamine complexes there is no S_N1cb contribution to the aquation mechanism since benzylamine is much more basic than aniline.[30, 31] Rate constants for aquation of another series of $[CoCl\,L\,en_2]^{2+}$ complexes, this time with L = pyridine or 3- or 4-methylpyridine, are all very similar, which is hardly surprising in view of the similar inductive and steric effects of the ligands L.[32] Activation parameters are also practically identical for these three complexes, so the similarity of rates is not due to $\Delta H^{\ddagger} - \Delta S^{\ddagger}$ compensation. In these complexes, as in the aniline and toluidine complexes mentioned above, the rate of aquation in acid solution depends on pH, down to pH ~ 4; there can hardly be S_N1cb aquation as there are no acidic protons on the pyridine ligands to permit conjugate base formation.[33] Aquation of $[CoCl(cycloalkylamine)en_2]^{2+}$ is relatively fast, which is explained by steric acceleration in an S_N1 mechanism.[34]

Quadridentate Ligands. The effect of extent of chelation on aquation rates has been studied for the compounds *trans*-$[Co(NO_2)_2(LLLL)]^+$, where LLLL = $(NH_3)_4$, $(en)_2$, $(pn)_2$, or cyclam (5), and *cis*-$[Co(NO_2)_2(LLLL)]^+$, where LLLL = $(NH_3)_4$, $(en)_2$, or trien (6). Rates of aquation increase as the number and size of chelate rings decrease, which is consistent with a dissociative mechanism.[35] Rates of aquation are also sensitive to steric crowding around the leaving group. This is well illustrated by the 10^5-fold difference in aquation rates of $[Co(CO_3)(LLLL)]^+$ when LLLL = $(en)_2$ or tet-b (7),[36] and by rate variations in the series

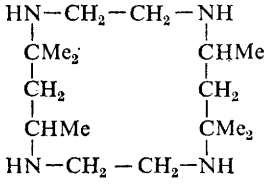
[27] S. C. Chan and P. Y. Leung, *J. Chem. Soc.* (*A*), 1969, 2650.
[28] S. C. Chan and O. W. Lau, *Austral. J. Chem.*, 1969, **22**, 1851.
[29] R. K. Nanda and R. N. Nanda, *Inorg. Chem.*, 1969, **8**, 104.
[30] R. K. Nanda and R. N. Nanda, *Inorg. Chim. Acta*, 1969, **3**, 508; S. C. Chan and O. W. Lau, *Austral. J. Chem.*, 1969, **22**, 1869.
[31] J. Zsakó, C. Várhelyi, and L. Banici, *Studia Univ. Babes-Bolyai, Ser. Chim.*, 1968, **13**, 21 (*Chem. Abs.*, 1969, **71**, 6911k).
[32] S. C. Chan and C. L. Lee, *J. Chem. Soc.* (*A*), 1969, 2649.
[33] J. Zsakó, C. Várhelyi, and D. Dobocan, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1459.
[34] S. C. Chan and T. L. Cheung, *Austral. J. Chem.*, 1970, **23**, 707.
[35] P. D. Grosse and P. J. Staples, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1443.
[36] J. A. Kernohan and J. F. Endicott, *J. Amer. Chem. Soc.*, 1969, **91**, 6977.



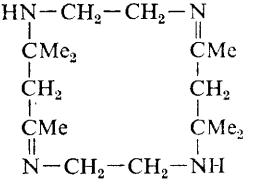
(5)



(6)



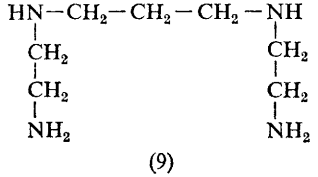
(7)



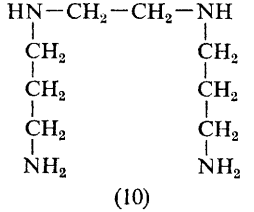
(8)

trans-$[CoX_2(LLLL)]^+$, where LLLL = *trans*-14-diene (8) or tet-a or tet-b, which are stereoisomers of (7).[37]

In comparisons between cyclam and analogous $(en)_2$ complexes there are two structural differences to influence rates, both the cyclic nature of cyclam and the fact that all its nitrogens are secondary. As a link between cyclam and $(en)_2$, the ligands (9), variously called tet and 2,3,2-tet, and (10), called 3,2,3-tet, are useful since they are acyclic yet contain secondary as well as primary nitrogens. Kinetics and steric courses of aquation of *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$,[38] and of *trans*-$[CoCl_2(3,2,3\text{-tet})]^+$,[39] have been reported. Transition state geometry for aquation of these two complexes seems to approximate to square pyramidal. Both here and in aquation of the *trans*-14-diene, tet-a, and tet-b complexes mentioned above,[37] there is some difficulty in extending Tobe's activation entropy rules [14] to complexes of these macrocyclic polydentate ligands. Another example of aquation of complexes of this type of ligand is afforded by photodecomposition of the cobalt(III) complexes $[CoXR(L)]^+$, where L = (11); these are vitamin B_{12} models.[40] An investigation of kinetics and stereochemistry of aquation

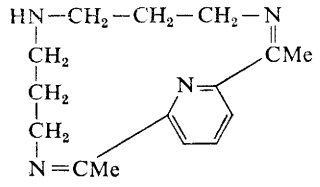


(9)

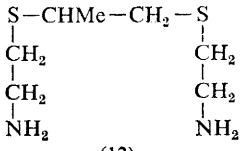


(10)

[37] J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504.
[38] R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, 1969, **8**, 1589.
[39] M. D. Alexander and H. G. Hamilton, *Inorg. Chem.*, 1969, **8**, 2131.
[40] E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, **92**, 3201.



(11)



(12)

of similar complexes of nitrogen- and sulphur-containing ligands has started with establishing retention of geometry and of absolute configuration in acid and in base hydrolysis of $[CoCl_2\,epe]^+$, where epe is the ligand (12).[41]

Miscellaneous. Aquation of *cis*-$[CoCl_2\,phen_2]^+$ also appears to proceed by a dissociative mechanism. The lower lability of the chloride in this complex than in *cis*-$[CoCl_2\,en_2]^+$ is most readily explained by the different electron-releasing and -withdrawing properties of phen and en, which are obvious from their relative pK_a values.[42] Aquation of this and analogous bipy, and chromium(III) compounds has been briefly mentioned.[43]

The *trans*-labilising effect of sulphite ligands is illustrated by the rates and activation parameters for aquation of the complexes $[CoX(SO_3)(DMG)]^{2-}$ and $[CoX(SO_3H)(DMG)]^-$. Variation of rates with composition of mixed solvents indicates an associative mechanism for these aquations.[44]

Rates and activation parameters have been compared, and found to be very similar for aquation of $[Co(NCSe)_2(LL)_2]^{n+}$, for LL = nioxime where E_a = 32·5 kcal mol^{-1} and log A = 15·5, and for LL = dimethylglyoxime where E_a = 33·0 kcal mol^{-1} and log A = 16·1.[45]

Solvent Variation.—Logarithms of rate constants for aquation correlate with logarithms of equilibrium quotients in the Langford free energy plot for $[CoCl(NH_3)_5]^{2+}$ in a series of aqueous ethanol solvent mixtures. At first sight the plot indicates that there is very little cobalt(III)–chloride bond stretching in the transition state, but consideration of the presence and effect of ion-pairs modifies this conclusion to the expected picture of dissociative interchange with considerable cobalt(III)–chloride bond stretching and very little cobalt(III)–water interaction in the transition state.[46] An isokinetic, or activation enthalpy against activation entropy, plot for *trans*-$[CoCl_2\,en_2]^+$ in a variety of mixed aqueous solvents gives

[41] J. H. Worrell, T. E. MacDermott, and D. H. Busch, *J. Amer. Chem. Soc.*, 1970, **92**, 3317.
[42] D. M. Palade and M. K. Boreiko, *Russ. J. Inorg. Chem.*, 1969, **13**, 1556.
[43] J. Josephson and C. E. Schäffer, *Chem. Comm.*, 1970, 61.
[44] G. P. Syrtsova and Nguen Zui Lyong, *Russ. J. Inorg. Chem.*, 1970, **15**, 243; G. P. Syrtsova, L. N. Korletyanu, and Nguen Zui Lyong, *ibid.*, p. 245.
[45] C. Várhelyi, Z. Finta, and J. Szakó, *Z. anorg. Chem.*, 1970, **374**, 326.
[46] G. R. H. Jones, R. C. Edmondson, and J. H. Taylor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1752.

a good straight line. This is interpreted in terms of a common dissociative mechanism throughout the range of solvents studied; earlier there had been a suggestion that an associative mechanism might be favoured in some less aqueous solvents.[5]

Correlation of rates with dielectric constants has often been used as a method for determining whether aquations are primarily associative or dissociative in character. The mechanisms of aquation of *cis*- and *trans*-$[CoBr(NCS)en_2]^+$ and of $[Cl(NH_3)_4Co\cdot NH_2\cdot Co(NH_3)_4(OH_2)]^{5+}$ (ref. 47), and of *cis*- and *trans*-$[CoCl(N_3)en_2]^+$ (ref. 48), have been investigated by this method.

The differing effects of hydrogen ion or of base concentration on thiocyanate substitution rates into *trans*-$[CoCl_2en_2]^+$ and into *trans*-$[CoCl(NO_2)en_2]^+$ in methanol or ethanol support an earlier hypothesis that the mechanisms are not identical for these two complexes, but that there is considerable solvent assistance in the case of the chloronitro-compound.[49] However, one should recall an earlier study in mixed aqueous alcoholic solvents which indicated no difference in substitution mechanisms for these two complexes.[50] Chloride and thiocyanate substitution at *cis*-$[CoCl_2 diars]^+$ in methanol both involve formation of the same intermediate.[51] Solvolysis of optical and geometrical isomers of $[CoCl_2en_2]^+$ in an optically active solvent, propane-1,2-diol, results in stereospecific substitution.[52]

Solvolysis of cobalt(III)–toluato complexes in acetic acid in the presence of sodium acetate is a non-aqueous analogue of base hydrolysis, and is discussed in that section.

Dimethylglyoxime Complexes. Bis-dimethylglyoximatocobalt complexes, $[CoX_2(DMG)_2]^-$, form another group of complexes whose solvolysis in mixed aqueous solvents is a subject of current research. Kinetic results for solvolysis in aqueous dimethylformamide[53–55] are listed, with earlier results for aqueous solution,[56] in Table 2. There is one surprising feature in the activation enthalpy trends, which is the behaviour of the bromide complex, whose activation enthalpy of solvolysis decreases as the proportion of dimethylformamide increases, whereas for the chloride and iodide complexes the activation enthalpy trend is the opposite. Kinetic results for

[47] V. D. Panasyuk and A. V. Arkharov, *Russ. J. Inorg. Chem.*, 1968, **13**, 1279; V. D. Panasyuk and E. R. Falendysh, *Russ. J. Inorg. Chem.*, 1969, **14**, 1456; *Dopovidi Akad. Nauk Ukr. R.S.R., Ser. B*, 1969, **31**, 536 (*Chem. Abs.*, 1969, **71**, 64,689e).
[48] V. D. Panasyuk and A. V. Arkharov, *Russ. J. Inorg. Chem.*, 1970, **15**, 356.
[49] S. Ašperger, M. Flögel, and I. Murati, *J. Chem. Soc.* (*A*), 1969, 569.
[50] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.
[51] A. Peloso and G. Dolcetti, *J. Chem. Soc.* (*A*), 1969, 1506.
[52] A. A. Smith and R. A. Haines, *J. Amer. Chem. Soc.*, 1969, **91**, 6280.
[53] C. Várhelyi, Z. Finta, and J. Zsakó, *Rev. Roumaine Chim.*, 1969, **14**, 1133 (*Chem. Abs.*, 1970, **72**, 59,680m).
[54] J. Zsakó, C. Várhelyi, and Z. Finta, *Studia Univ. Babes-Bolyai, Ser. Chim.*, 1969, **14**, 51 (*Chem. Abs.*, 1970, **72**, 59,684r).
[55] Z. Finta, J. Zsakó, and C. Várhelyi, *Z. phys. Chem.* (*Leipzig*), 1969, **242**, 200.

Table 2 *Kinetic results for solvolysis of* $H[CoX_2(DMG)_2]$ *in mixed aqueous–dimethylformamide solutions*

X	*Solvent*	$10^4 k_1$/s			E_a/kcal mol^{-1}	log *A*	*Ref.*
		25·0 °C	40·0 °C	50·0 °C			
Cl	Water	2·70			23·9	14	56
	Water	2·98	21·4	71·6	24·1	14·1	53
	10% DMF	2·40	19·0		26·0	15·4	53
Br	Water	1·44			24·5		56
	Water	1·50	11·5	36·2	24·4	14·1	54
	10% DMF		10·5	30·1	21·2	11·8	54
	25% DMF		6·8	18·6	20·1	10·9	54
I	Water		0·84	3·22	25·9	14·0	55
	10% DMF			2·70	26·2	14·2	55
	25% DMF			1·21	27·8	14·9	55
	50% DMF			0·40	28·8	15·1	55

Table 3 *Kinetic results for solvolysis fo* $[CoX(OH_2)(DMG)_2]$ *in mixed aqueous–dimethylformamide solutions*

X	*Solvent*	$10^4 k_1$/s			E_a/kcal mol^{-1}	log *A*	*Ref.*
		25·0 °C	40·0 °C	50·0 °C			
Cl	Water	0·99			25·5	14·8	56—58
	Water	1·0	8·0		25·2	14·5	53
	10% DMF	0·7	5·5		25·6	14·7	53
Br	Water	0·62			27·6	16·0	57—58
	Water		3·5	40·1	27·8	16·0	54
	10% DMF		3·5	12·5	24·9	14·0	54
	25% DMF		3·5	9·5	20·2	10·6	54
I	Water			1·5	27·2	14·6	55
	10% DMF			1·25	27·4	14·6	55

solvolysis of the neutral species $[CoX(OH_2)(DMG)_2]$ are collected together, again from recent [53–55] and earlier [56–58] sources, in Table 3.

Aquation of $[CoCl(PR_3)(DMG)_2]$ has been studied in aqueous methanol, with the object of assessing the *trans*-effect of a series of ligands PR_3. There is a fair correlation of logarithms of rate constants with ligand pK_a values; the correlation is good if ligands containing bulky R groups, *viz.* $C_6H_5^-$, $C_6H_{11}^-$, are not included.[59] Compounds $[CoRL(DMG)_2]^{n-}$, where R = Me, Et, or i-Pr, and L = NCS^-, N_3^-, CN^-, NH_3, or py, form good models for biochemical systems as the ligands L are greatly labilised by the

[56] A. Ya. Sychev and A. V. Ablov, *Russ. J. Inorg. Chem.*, 1961, **6**, 1163.
[57] A. V. Ablov and A. Ya. Sychev, *Russ. J. Inorg. Chem.*, 1959, **4**, 1143.
[58] A. Ya. Sychev, A. V. Ablov, and V. A. Zarinskii, *Russ. J. Inorg. Chem.*, 1961, **6**, 421.
[59] G. Costa, G. Tauzher, and A. Puxeddu, *Inorg. Chim. Acta*, 1969, **3**, 41.

strong *trans*-effect of the alkyl groups R, both in the model and in the biochemical cases. Kinetics of aquation, and of formation, of the DMG complexes are reported.[60] A preliminary report on ligand exchange in $[CoMeL(DMG)_2]$ presents an order of relative reactivities for L = a variety of ligands, including acetonitrile, dimethyl sulphide, dimethyl sulphoxide, and phosphorus bases.[61]

Acid Catalysis.—This is a common feature of aquation kinetics for complexes containing ligands that are the anions of weak acids, for instance nitrite or azide. Rates of aquation of $[Co(NO_2)_4(NH_3)_2]^-$ depend on pH and on the nature of the added acid. The pH-dependence arises from protonation of one or two of the nitrito-ligands; the dependence on the nature of acid suggests a significant participation by ion-pairs, most likely for the diprotonated derivative which has unit positive charge.[62] The effect of chelation is illustrated by studies of the acid-dependence of aquation rates of complexes *cis*- and *trans*-$[Co(NO_2)_2(LLLL)]^+$, where LLLL ranges from $(NH_3)_4$, through $(en)_2$, to quadridentate ligands such as the acyclic triethylenetetramine [trien, (6)] and cyclic ligands cyclam (5) and tet-a (7).[35, 63] In some cases the limiting rate corresponding to complete protonation is attained under moderately acid conditions; the cyclic ligands seem to facilitate nitrito-ligand protonation. The expected acid catalysis has not been found for aquation of the uncharged complex *trans*-$[Co(acac)_2(NO_2)(OH_2)]$.[64]

Aquation of *trans*-$[CoCl(N_3)en_2]^+$, which results in loss of azide, is acid catalysed, but the limiting rate depends on the acid used. A study of rates as functions of added acid and added salts indicates that this limiting rate behaviour can be ascribed to the formation of ion-pairs of varying lability.[65] Relevant to acid catalysis of aquation of azides is the characterisation of the perchlorate of the proposed protonated form in aquation, $[Co(N_3H)(NH_3)_5]^{3+}$.[66] Complexes of HPO_4^{2-} can be considered as equivalent to protonated forms of PO_4^{3-} complexes; kinetic parameters for aquation of $[Co(PO_4)(NH_3)_5]$ and of $[Co(PO_4H)(NH_3)_5]^+$ have been obtained.[67]

Aquation of $[Co(NCO)(NH_3)_5]^{2+}$ is also acid catalysed, indeed rates are proportional to hydrogen ion concentration. The products are $[Co(NH_3)_6]^{3+}$ and carbon dioxide, so here the mechanism involves not cobalt–nitrogen but rather intraligand nitrogen–carbon bond fission.[68]

[60] A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1970, **92**, 2593.
[61] L. M. Ludwick and T. L. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 5188.
[62] M. N. Malik and A. McAuley, *J. Chem. Soc.* (*A*), 1969, 917.
[63] B. E. Crossland and P. J. Staples, *J. Chem. Soc.* (*A*), 1970, 1305.
[64] R. J. Kline and R. A. Velapoldi, *Inorg. Chem.*, 1970, **9**, 1312.
[65] P. J. Staples, *J. Chem. Soc.* (*A*), 1970, 811.
[66] F. Monacelli, G. Mattagno, D. Gattegno, and M. Maltese, *Inorg. Chem.*, 1970, **9**, 686.
[67] S. F. Lincoln, J. Jayne, and J. P. Hunt, *Inorg. Chem.*, 1969, **8**, 2267.
[68] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1970, **9**, 1567.

Metal Ion Catalysis.—While hydrogen ions are the most commonly studied catalysts for aquation of octahedral complexes, there are many examples of kinetic studies involving other catalysts, particularly mercury(II). A recent example is the aquation of *cis*-$[CoCl\,L\,en_2]^+$, where L = one of a series of aliphatic primary amines, $R \cdot NH_2$. Here the rates increase and activation enthalpies decrease, as the size of R increases, which observations are consistent with

$$Co^{III}{-}Cl + Hg^{II} \rightleftharpoons Co^{III}{-}Cl{-}Hg^{II} \xrightarrow{\text{slow}} Co^{III} + Cl{-}Hg^{II}$$

rather than rate-determining bimolecular attack by mercury(II).[69] Mercury(II)-catalysed aquation of $[CoX(NH_3)_5]^{2+}$, X = Cl or Br, is further promoted by the presence of the micellar catalysts polysulphonic acids.[70] The mercury(II)-catalysed aquation of β_2-[CoCl(glyOEt)trien]$^{2+}$ proceeds with complete retention of configuration.[71]

Silver(I) is another catalyst for aquation. Unfortunately, a kinetic study of its catalytic effect on aquation of $[CoI(NH_3)_5]^{2+}$ is complicated by heterogeneous catalysis by the silver iodide produced.[72] Indeed this topic of heterogeneous catalysis of aquation of cobalt(III) complexes has recently been reviewed and extended by studies of the kinetic effects of a range of diverse solids, *e.g.* mercury(II) sulphide, silver bromide, and platinum metal.[73]

The catalytic effect of a range of trivalent cations, some simple, *e.g.* La^{3+}, Sc^{3+}, In^{3+}, others complex, *e.g.* $[Co(NH_3)_6]^{3+}$, has been investigated for the complex chloro(ethylenediaminetriacetatoacetate)cobaltate(III), $CoClY^-$. The reaction is displacement of chloride to give CoY^-, containing hexadentate Y, rather than simple aquation. Of the wide range of metal ions investigated, thallium(III), whose effect is comparable with that of mercury(II), is by far the most effective catalyst. Rates and activation parameters are reported; rate constants can be correlated with a function incorporating stability constants of the catalyst with both chloride and carboxylate groups.[74]

A slightly different aspect of catalysis of aquation of complexes is that of aquation of, for instance, azides by nitrous acid. This has already been mentioned in connection with the generation of intermediates of the type $[Co(NH_3)_5]^{3+}$ in the first section of this chapter. A similar system is nitrous acid catalysed aquation of pyridiomethyl- or benzyl-pentacyanocobaltate(III), where aquation proceeds by S_E2 attack at the ligand.[75]

[69] S. C. Chan and S. F. Chan, *J. Chem. Soc.* (*A*), 1969, 202.
[70] H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, 1969, **91**, 563.
[71] D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 11.
[72] G. C. Lalor and D. S. Rustad, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3219.
[73] M. D. Archer and M. Spiro, *J. Chem. Soc.* (*A*), 1970, 68, 73, 78, 82.
[74] S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1969, 1164.
[75] E. H. Bartlett and M. D. Johnson, *J. Chem. Soc.* (*A*), 1970, 523.

Electron Transfer; Photochemistry.—It has been suggested [76] that electron transfer can bring about base hydrolysis of cobalt(III) complexes. Recent examples include the aquation of sulphite complexes, where detection of dithionate as one of the products is good evidence for an electron transfer mechanism,[77] and of the dicobalt μ-superoxo complex $[(H_3N)_5Co \cdot O_2 \cdot Co(NH_3)_5]^{5+}$ in the presence of sulphite.[25]

The remaining references are all concerned with photoaquation. It was earlier reported that in the photoaquation of $[CoCl(NH_3)_5]^{2+}$, which involves an electron transfer step, five ammonia molecules were released per cation. This indicated that electron transfer took place only from chloride to the cobalt. However, recent g.l.c. and mass spectrometry studies show some nitrogen and nitrous oxide amongst the products of photoaquation, so there must also be some electron transfer from ammonia ligands to cobalt(III).[78] Electron transfer from ethylenediamine to cobalt(III) is similarly indicated by the products of photoaquation of *cis*-$[CoX_2en_2]^+$ irradiated at charge-transfer frequencies.[79] Photoaquation of $[Co(N_3)(NH_3)_5]^{2+}$ has also been reinvestigated and found to be more complicated than previously thought. The detection of $[Co(N_3)(OH_2)(NH_3)_4]^{2+}$ among the products rules out the theory of azide to cobalt(III) electron transfer as the sole mechanism of photoaquation. However, there is evidence that photoaquation of *cis*- and of *trans*-$[Co(N_3)_2(NH_3)_4]^+$ may involve electron transfer to cobalt(III) only from the azide ligands.[80] There is some relevant ancillary information on the photochemistry of the azide ion itself.[81] $[Co(N_3)(NH_3)_5]^{2+}$ photoaquates with loss of ammonia or of azide, and similarly *trans*-$[CoCl(NCS)en_2]^+$ photoaquates with loss of thiocyanate or of chloride, in contrast to thermal aquation where only chloride is lost.[82] There are again two routes for photolysis of $[Co(O_2C \cdot CH_3)(NH_3)_5]^{2+}$, *via* acetate to cobalt(III) electron transfer or *via* $\pi \rightarrow \pi^*$ excitation in the acetate-carbonyl group. Symmetry differences preclude interconversion between these.[83] Similar to the carbonyl excitation in the last example is the excitation of a ligand band in *trans*-4-stilbenecarboxylatopenta-amminocobalt(III), which results in intramolecular energy transfer and decomposition of the complex by an electron transfer mechanism.[84] Photochemical aquation of macrocyclic tetradentate nitrogen ligand (11) complexes of cobalt(III) has also been investigated. In this last case there is a good correlation between rate constants for photodecomposition and spectroscopic characteristics of the $3a_1 \leftarrow 2a_1$

[76] R. D. Gillard, *J. Chem. Soc.* (*A*), 1967, 917.
[77] R. S. Murray, D. R. Stranks, and J. K. Yandell, *Chem. Comm.*, 1969, 604.
[78] R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *Chem. Comm.*, 1969, 195.
[79] G. A. Shagisultanova and R. M. Orisheva, *Russ. J. Inorg. Chem.*, 1969, **13**, 951.
[80] J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, 1970, **74**, 1021.
[81] I. Burak, D. Shapira, and A. Treinin, *J. Phys. Chem.*, 1970, **74**, 568.
[82] A. Vogler and A. W. Adamson, *J. Phys. Chem.*, 1970, **74**, 67.
[83] E. R. Kantrowitz, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1970, **92**, 1776.
[84] A. W. Adamson, A. Vogler, and I. Lantzke, *J. Phys. Chem.*, 1969, **73**, 4183.

band. Thus it seems that it is this transition which is responsible for photoaquation here, as in simpler complexes such as the $[CoX(NH_3)_5]^{2+}$ cations.[40]

Photochemical aquation is an efficient pathway for aquation of $[Co(oxalate)_3]^{3-}$, but not for $[Co(NH_3)_6]^{3+}$. Rates of photochemical aquation of the intermediate mixed complexes $[Co(C_2O_4H)(NH_3)_5]^{2+}$, $[Co(C_2O_4)(NH_3)_4]^{+}$, and $[Co(C_2O_4)_2(NH_3)_2]^{-}$ are, as expected, intermediate between the two extremes. The most efficient frequencies for photoaquation are those around the charge-transfer band, indicating ligand to cobalt(III) electron transfer as the decomposition mechanism again.[85] U.v. irradiation of $Co(acac)_3$, which involves irradiation at ligand-to-metal charge-transfer or intraligand excitation bands, leads to ready electron transfer to the metal giving dissociation of the complex accompanied by oxidation and fragmentation of the ligands.[86]

Photochemical and thermal substitution reactions of $[Co(CN)_6]^{3-}$ have been compared. The comparison permits conclusions to be drawn concerning the role of solvation and of ion-pair formation in determining the rates and course of these reactions.[87] Charge-transfer also takes place during radiolysis of cobalt–cyanide solutions. The previously postulated species $[Co^{I}(CN)_5]^{4-}$ has been detected in solutions prepared from $[Co^{II}(CN)_5]^{3-}$, while the attempt to prepare the elusive species $[Co^{II}(CN)_6]^{4-}$ from $[Co^{III}(CN)_6]^{3-}$ may have been successful.[88]

Solid State Reactions.—There are three reports of kinetic and mechanistic studies on substitution in the solid state which may have some interest or relevance to cobalt(III) complex substitution mechanisms in solution. $[Co(NH_3)_6](N_3)_3$ decomposes to give cobalt nitride. The initial step, as in several solution mechanisms cited above, seems to be azide to cobalt electron transfer; there is no evidence for nitrene intermediates.[89] Decomposition of $[Co(NH_3)_6]Cl_3$, which gives cobalt(II) amongst the products, does not proceed *via* formation of $[CoCl(NH_3)_5]Cl_2$, but for some nitrites, *e.g. cis-* and *trans*-$[Co\,en_2(NH_3)_2](NO_2)_3$, nitrite does enter the first co-ordination sphere of the cobalt in the course of reaction.[90] Lastly, the mechanism of thermal and of photochemical decomposition of $[Co(NH_3)_5(OH_2)]X_3$ is said to be similar to the mechanism of reaction in solution, despite the ultimate formation of tetrahedral cobalt(II) complexes in the solid state reactions.[91]

3 Aquation: Chromium(III) Complexes

Unidentate Leaving Groups.—Rate constants and activation parameters

[85] Hla Way and N. Filipescu, *Inorg. Chem.*, 1969, **8**, 1609.
[86] N. Filipescu and Hla Way, *Inorg. Chem.*, 1969, **8**, 1863.
[87] A. W. Adamson, A. Chiang, and E. Zinato, *J. Amer. Chem. Soc.*, 1969, **91**, 5467.
[88] G. D. Venerable, E. J. Hart, and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 7538.
[89] T. B. Joyner, *J. Phys. Chem.*, 1970, **74**, 1552, 1558, 1563.
[90] A. V. Ablov and T. A. Mal'kova, *Russ. J. Inorg. Chem.*, 1969, **14**, 1594.
[91] S. T. Spees and P. Z. Petrak, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1229.

for aquation of the newly-characterised complex $[Cr(O_2C\cdot CF_3)(NH_3)_5]^{2+}$ have been determined. There is no acid catalysis of aquation here, whereas there is for the analogous acetate complex. This difference in behaviour arises from the much greater acid strength of trifluoroacetic than of acetic acid.[92]

Much effort has been devoted to obtaining kinetic parameters for successive steps in aquation sequences. Thus the aquation of $[Cr(CN)_6]^{3-}$ to $[Cr(OH_2)_6]^{3+}$ involves six successive replacements of cyanide ligands by water. Rates and activation parameters have been reported for the last two stages of this reaction sequence, *viz.* *cis*-$[Cr(CN)_2(OH_2)_4]^+$ to $[Cr(CN)(OH_2)_5]^{2+}$ (ref. 93) and of the latter to $[Cr(OH_2)_6]^{3+}$.[94] The analogous reaction sequence starting from $[Cr(CN)_5(NO)]^{3-}$ involves five stages, for all of which kinetic data are now available thanks to the investigation of the steps from $[Cr(CN)_5(NO)]^{3-}$ to $[Cr(CN)_2(NO)(OH_2)_3]^0$.[95] In both the $[Cr(CN)_6]^{3-}$ and $[Cr(CN)_5(NO)]^{3-}$ sequences the zero-charged intermediate complexes $[Cr(CN)_3(OH_2)_3]^0$ and $[Cr(CN)_2(NO)(OH_2)_3]^0$ are particularly unreactive.

Similar examples are afforded by chromium(III)–halide–ammine complexes. Kinetic parameters have been determined for the aquation of $[CrBr_2(NH_3)(OH_2)en]^+$ to $[Cr(OH_2)_4en]^{3+}$; as the kinetics of aquation of the latter are already known, the complete kinetic picture of aquation of the former is now established.[96] Kinetic results have been reported for several other multi-ligand complexes of this type, including $[CrBr_2(NH_3)_2(OH_2)_2]^+$,[97] *cis*- and *trans*-$[CrCl_2(NH_3)(OH_2)_3]^+$, $[CrCl(NH_3)(OH_2)_4]^{2+}$,[98] and $[CrCl_2(NH_3)_3(OH_2)]^+$, which last is an intermediate in the aquation of $[Cr(O_2)_2(NH_3)_3]$ in hydrochloric acid.[99]

Aquation of the nitrito-complexes $[Cr(ONO)(NH_3)_5]^{2+}$ (ref. 100) and $[Cr(ONO)(OH_2)_5]^{2+}$ (ref. 101) is unexpectedly fast. In these cases, aquation takes place without chromium–oxygen bond breaking. Moreover, the aquation of $[CrX(OH_2)_5]^{2+}$, X = Cl or Br, is specifically catalysed by nitrous acid. This is explained by ready formation of $[CrX(ONO)(OH_2)_4]^+$ as an intermediate, by direct attack of nitrous acid on co-ordinated water again without chromium–oxygen bond fission. The suggestion is supported by the observation that aquation of $[CrBr(NH_3)_5]^{2+}$ is not accelerated by nitrous acid.[102]

[92] R. Davies, G. B. Evans, and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 2025.
[93] D. K. Wakefield and W. B. Schaap, *Inorg. Chem.*, 1969, **8**, 811.
[94] D. K. Wakefield and W. B. Schaap, *Inorg. Chem.*, 1969, **8**, 512; J. P. Birk and J. H. Espenson, *Inorg. Chem.*, 1968, **7**, 991.
[95] D. I. Bustin, J. E. Earley, and A. A. Vlček, *Inorg. Chem.*, 1969, **8**, 2062.
[96] T. J. Williams and C. S. Garner, *Inorg. Chem.*, 1969, **8**, 1639.
[97] D. A. House, *Austral. J. Chem.*, 1969, **22**, 647.
[98] T. J. Williams and C. S. Garner, *Inorg. Chem.*, 1970, **9**, 52.
[99] S. H. Caldwell and D. A. House, *Inorg. Chem.*, 1969, **8**, 151.
[100] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1969, 219.
[101] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1969, 1977.
[102] T. C. Matts and P. Moore, *Chem. Comm.*, 1969, 29.

A recent kinetic study [103] confirms the conclusion drawn earlier from product characterisation,[104] that aquation of 4-pyridiomethylpenta-aquochromium(III) involves homolysis to hexa-aquochromium(II) and the $^{+}NH \cdot C_5H_4 \cdot \dot{C}H_2$ radical. There is, however, no evidence for a similar homolytic, or electron transfer [cf. cobalt(III), previous section] mechanism operating in aquation of azide or of iodide complexes.

Correlation of kinetic results with $d \rightarrow d$ spectroscopic data has been attempted for a series of chromium(III) complexes. Spectroscopic data have been expressed in terms of the 'two-dimensional spectrochemical series', for this should give separated σ- and π-contributions and thus facilitate comparison with the kinetic results which for chromium(III) are assumed, as a first approximation, to be a function only of chromium–ligand bond strength.[105]

Multidentate Leaving Groups.—Intermediates $[Cr(dien\ H)(OH_2)_4]^{4+}$, containing bidentate dien, and $[Cr(dien\ H_2)(OH_2)_5]^{5+}$, containing unidentate dien, have been characterised in the aquation of both isomers (1,2,3- and 1,2,6- or *fac*- and *mer*-) of $[Cr(dien)(OH_2)_3]^{3+}$. Rate laws, rate constants, and activation parameters are reported for each individual step in the reaction sequences.[106] Rate laws and kinetic parameters have also been reported for the chromium(III) complexes of iminodiacetate and methyliminodiacetate.[107]

It was previously thought that the first step in aquation of $[Cr(malonate)_3]^{3-}$ was much faster than the subsequent aquation of the *cis*-$[Cr(malonate)_2(OH_2)_2]^{-}$ formed. Further studies have shown that the kinetic pattern is more complicated and that results need to be analysed in terms of consecutive first-order reactions.[108] The complex *cis*-$[Cr(oxalate)_2(OH_2)_2]^{-}$ disproportionates very slowly to give $[Cr(oxalate)(OH_2)_4]^{+}$ and $[Cr(oxalate)_3]^{3-}$.[109]

Bridged Dichromium Complexes.—Aquation and cleavage of the hydroxo-bridged complexes $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ (rhodo), $[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]^{5+}$ (aquoerythro), and $[(NH_3)_5Cr(OH)Cr(NH_3)_4Cl]^{4+}$ (chloroerythro) have been described. There is no acid catalysis, but there is chloride catalysis of aquation of the aquoerythro complex. This suggests reaction of the complex with chloride previous to cleavage. The observed products from the chloroerythro complex show that it is the chromium–oxygen bond from the $Cr(NH_3)_4Cl$ side rather than the $Cr(NH_3)_5$ side that undergoes fission. The stereochemistry of the products was used to establish the stereochemistry of the

[103] A. R. Schmidt and T. W. Swaddle, *J. Chem. Soc.* (*A*), 1970, 1927.
[104] R. G. Coombes and M. D. Johnson, *J. Chem. Soc.* (*A*), 1966, 177.
[105] W. W. Fee and J. N. MacB. Harrowfield, *Austral. J. Chem.*, 1970, **23**, 1049.
[106] D. K. Lin and C. S. Garner, *J. Amer. Chem. Soc.*, 1969, **91**, 6637.
[107] J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, 1969, **8**, 2298.
[108] C. Furlani and E. Mantovani, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1213.
[109] K. L. Stevenson, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 945.

starting bridged complexes; the assumption of no stereochemical change in the aquation and cleavage is reasonable in the light of the known stereochemical behaviour of mononuclear chromium(III) complexes.[110]

Effects of Non-leaving Ligands.—A preliminary study of aquation of *cis*- and of *trans*-$[CrX_2\,cyclam]^+$, where cyclam is the cyclic tetradentate ligand (5), indicates complete retention of configuration. The attraction of studying this system rather than, for instance, *trans*-$[CrCl_2\,en_2]^+$, is that whereas in aquation of the latter there is evidence for parallel loss of ethylenediamine and of chloride, there is no loss of cyclam from chromium during aquation of $[CrCl_2\,cyclam]^+$.[111]

Solvent Variation.—A particularly detailed picture of the mechanism of aquation of $[Cr(NCS)_6]^{3-}$ has emerged from a kinetic and n.m.r. study of this reaction in aqueous acetonitrile. The advantages of this system are, firstly that acetonitrile solvates the complex preferentially, so that the concentration of water in the solvation shell is small and controllable, and secondly that the composition of the solvation shell can be monitored by n.m.r. relaxation techniques.[112] The dependence of solvolysis rate on solvent in a range of pure solvents indicates a dissociative mechanism; the study of rates as a function of solvent composition in aqueous acetonitrile provides the details of the mechanism of dissociative interchange. Thermal aquation rates decrease linearly as the mole fraction of water decreases, but photoaquation rates are almost independent of solvent composition. In thermal aquation, the five-co-ordinate transition state has a very short lifetime, so that if a water molecule is immediately available adjacent to the site vacated by the thiocyanate aquation proceeds, but if there is only acetonitrile in the vicinity, the five-co-ordinate transition state recombines with the thiocyanate, giving no net reaction. Hence the observed variation of thermal aquation rate with solvent composition, specifically with the water : acetonitrile ratio in the solvation shell of the complex. The photoexcited state is thought to have a rather longer lifetime, long enough for rapid water exchange between the solvation shell and bulk solvent to provide a water to combine with the photoexcited state before it decays.[113] Rates and activation parameters for aquation of the closely related complex $[Cr(NCS)_4\,en]^-$ in aqueous methanol mixtures have been determined, but unfortunately there is no information available on solvation shell composition in this case. Results are consistent with solvent-assisted dissociation in which the amount of solvent assistance is small.[114]

Other studies in mixed aqueous solutions include the formation as well as the dissociation of $[Cr(OH_2)_5(DMSO)]^{3+}$, part of an extensive kinetic

[110] D. W. Hoppenjans and J. P. Hunt, *Inorg. Chem.*, 1969, **8**, 505.
[111] J. L. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, 1970, **4**, 109.
[112] L. S. Frankel, *J. Phys. Chem.*, 1969, **73**, 3897; 1970, **74**, 1645; L. S. Frankel, C. H. Langford, and T. R. Stengle, *J. Phys. Chem.*, 1970, **74**, 1376.
[113] S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, 1969, **91**, 2236.
[114] G. Thomas and V. Holbe, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1749.

and thermodynamic investigation of chromium(III) in aqueous DMSO,[115] and the search for $[Cr(OH_2)_5]^{3+}$ in substitution reactions of $[CrX(OH_2)_5]^{2+}$, X = halide or azide, in aqueous methanol, already mentioned in the first section of this chapter.[9]

Acid Catalysis.—An earlier study of acid catalysis of the aquation of *cis*-$[Cr(malonate)_2(OH_2)_2]$ has been extended to cover the range 0·5 to 2·0N perchloric acid.[116]

Other Catalysts.—The presence of an intermediate chromium(III)–oxalate–copper(II) complex in the copper(II)-catalysed aquation of $[Cr(oxalate)_3]^{3-}$ has been demonstrated by solvent extraction techniques.[117] Mercury(II) is also an effective aquation catalyst, as exemplified in the aquation of *cis*- and of *trans*-$[CrCl_2(OH_2)_4]^+$.[118] These aquations were investigated in an attempt to find parallels with formally analogous redox systems, such as the chromium(II)-catalysed aquation of chromium(III) complexes.[119]

Thallium(III), indium(III), gallium(III), and mercury(II) all promote aquation of pyridiomethylpentacyanocobaltate(III). Thallium(III) chloride and mercury(II) chloride in the presence of excess chloride, displace $[Co(CN)_5]^{2-}$ by an S_E2 mechanism. Gallium(III) chloride, indium(III) chloride, and mercury(II) chloride in the absence of added chloride, react initially by interaction with the cyanide ligands.[120] Whilst mercury(II) is a well-known catalyst for aquation, mercury(I) has been much less investigated. It is an effective catalyst for S_E2 aquation of pyridiomethylpenta-aquochromium(III).[121] Nitrous acid also catalyses aquation of pyridiomethylpenta-aquochromium(III), again by an S_E2 mechanism, in which the effective reagents are $H_2NO_2^+$ and, in the presence of Cl^-, NOCl.[75] Nitrous acid catalysis of aquation of $[CrX(OH_2)_5]^{2+}$ has already been mentioned.[102] Aquation of $[CrX(NH_3)_5]^{2+}$ is promoted by benzenehexacarboxylate; kinetic and potentiometric experiments indicate the formation of 1 : 1, 1 : 2, and 1 : 3 ion-pairs.[122]

Oxygen exchange between $[Cr(NH_3)_5(OH_2)]^{3+}$ and solvent water is catalysed by carbon dioxide. The rate law and appropriate rate constants have been determined. The mechanism involves oxygen-atom scrambling through formation of an intermediate carbonate complex.[123]

Photochemistry.—In the photoaquation of $[Cr\ en_3]^{3+}$, irradiation being at $d \rightarrow d$ or charge-transfer frequencies, only the first stage producing the

[115] L. P. Scott, T. J. Weeks, D. E. Bracken, and E. L. King, *J. Amer. Chem. Soc.*, 1969, **91**, 5219.
[116] J. C. Chang, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1402.
[117] J. Aggett, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3319.
[118] J. P. Birk, *Inorg. Chem.*, 1970, **9**, 735.
[119] *E.g.* D. H. Huchital, *Inorg. Chem.*, 1970, **9**, 486.
[120] E. H. Bartlett and M. D. Johnson, *J. Chem. Soc.* (*A*), 1970, 517.
[121] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1970, 460.
[122] K. Cummins and T. P. Jones, *Chem. Comm.*, 1970, 638.
[123] J. E. Earley and W. Alexander, *J. Amer. Chem. Soc.*, 1970, **92**, 2294.

monodentate en complex $[Cr\,en_2(en\,H)(OH_2)]^{4+}$ is photocatalysed. The second stage of the aquation, to $[Cr\,en_2(OH_2)_2]^{3+}$ is a purely thermal reaction.[124] In thermal aquation of $[Cr(NCS)(NH_3)_5]^{2+}$, the thiocyanate group is replaced, but in photoaquation, ammonia is lost to give *trans*-$[Cr(NCS)(NH_3)_4(OH_2)]^{2+}$.[125] Photoaquation of $[CrBr(NH_3)_5]^{2+}$ at $d \rightarrow d$ frequencies produces mainly *cis*-$[CrBr(NH_3)_4(OH_2)]^{2+}$, but at charge-transfer frequencies bromide and ammonia loss are equally important.[126] Photoaquation of $[Cr(NCS)_6]^{3-}$ in aqueous acetonitrile [113] is discussed and related to thermal aquation in the solvent variation section; photoaquation of $[Cr(CN)_6]^{3-}$ in aqueous solution has been qualitatively described.[127] A little kinetic information on photoracemisation of $[Cr(oxalate)_3]^{3-}$ by circularly-polarised light is available.[128] Aquation of chromium(III)–ammine–thiocyanate complexes can be photosensitised by a variety of organic agents, such as biacetyl [cf. platinum(II), Part II Chapter 3, ref. 38] and acridine, and by the $[Cr(urea)_6]^{3+}$ cation.[129]

Solid State Reactions.—Kinetic and mechanistic studies of substitutions in the solid state, which are of some relevance to mechanisms of substitution in solution, include those of $[Cr(NH_3)_5(OH_2)]X_3$, where there seems to be some associative character to the mechanism for X = Br^-, SO_3^{2-} or SO_4^{2-};[130] of $[Cr(NH_3)_6]Cl_3$, $[CrCl(NH_3)_5]Cl_2$, and *cis*-$[CrCl_2(NH_3)_4]Cl$, for which rates and activation parameters were determined;[131] of $[Cr\,en_3](NCS)_3$;[132] and of the racemisation of $K_3[Cr(oxalate)_3]$.[133]

4 Aquation: Other Complexes

d^1: **Titanium**(III).—Apart from the solvent exchange study mentioned in Part II Chapter 2, the only report on titanium(III) concerns a *T*-jump determination of the kinetics of formation and of dissociation of the monothiocyanato complex.[134]

d^1: **Vanadium**(IV).—Aquation of the dimeric cation $[VO(OH)]_2^{2+}$ has been studied by stopped-flow techniques.[135]

d^2: **Vanadium**(III).—Rates and activation parameters for acid aquation of monoazidovanadium(III) have been reported.[136]

[124] W. Geis and H. L. Schläfer, *Z. phys. Chem.* (*Frankfurt*), 1969, **65**, 107.
[125] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1969, **91**, 1076.
[126] P. Riccieri and H. L. Schläfer, *Inorg. Chem.*, 1970, **9**, 727.
[127] H. F. Wasgestian, *Z. phys. Chem.* (*Frankfurt*), 1969, **67**, 39.
[128] B. Norden, *Acta Chem. Scand.*, 1970, **24**, 349.
[129] A. W. Adamson, J. E. Martin, and F. D. Camessei, *J. Amer. Chem. Soc.*, 1969, **91**, 7530.
[130] R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, *Bull. Chem. Soc. Japan*, 1969, **42**, 1881.
[131] N. Tanaka and K. Nagase, *Bull. Chem. Soc. Japan*, 1969, **42**, 2854.
[132] D. A. House and J. C. Bailar, *J. Amer. Chem. Soc.*, 1969, **91**, 67.
[133] D. M. Chowdhury and G. M. Harris, *J. Phys. Chem.*, 1969, **73**, 3366.
[134] H. Diebler, *Z. phys. Chem.* (*Frankfurt*), 1969, **68**, 64.
[135] B. Lutz and H. Wendt, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 372.
[136] J. H. Espenson and J. R. Pladziewicz, *Inorg. Chem.*, 1970, **9**, 1380.

d^4: **Manganese**(III).—A *T*-jump study of the manganese(III)–fluoride system was complicated by side reactions, but has nevertheless allowed a limit to the rate of loss of a water ligand from manganese(III) to be estimated.[134]

d^5: **Iron**(III).—Aquation of $[Fe(CN)_6]^{3-}$ is catalysed by acid. In fact the aquation rate at pH = 7 is zero, so only $[Fe(CN)_5(CNH)]^{2-}$ aquates. There is also redox catalysis by $[Fe(CN)_6]^{4-}$.[137] The rate law for aquation and dissociation of the dimeric cation $[(FeOH)_2]^{4+}$ has been determined.[135] Aquation of $[Fe(bipy)_3]^{3+}$ gives the binuclear complex $[Fe_2(bipy)_4O(OH_2)_2]^{4+}$. The kinetics of this process, studied by chronopotentiometry and cyclic voltammetry, indicate a bimolecular process with seven-co-ordinate iron in the transition state.[138]

d^5: **Ruthenium**(III).—Ruthenium(III) complexes $[RuX(NH_3)_5]^{2+}$, where X = halide or azide, react even in the dark by parallel aquation and redox paths. The latter at least must involve intramolecular electron transfer. For X = chloride, the direct aquation path predominates, but for X = azide, the redox path is more significant, yielding molecular nitrogen complexes of ruthenium(II).[139] The rate constant for aquation of the dinuclear molecular nitrogen complex $[(H_3N)_5RuN_2Ru(NH_3)_5]^{5+}$ has been determined at 25·0 °C.[140]

d^5: **Osmium**(III).—The rate of aquation of $[Os(NH_3)_5(N_2)]^{3+}$ at 25·0 °C has been reported.[140]

d^6: **Rhodium**(III).—Ethylene acts catalytically on the aquation of '$RhCl_3.3H_2O$' to $[RhCl_2(OH_2)_4]^+$. The kinetics are consistent with the generation of a small quantity of a chlororhodium(I) species, which presumably catalyses aquations by a redox mechanism akin to that observed for chromium(II)-catalysed aquation of chromium(III) complexes, and for platinum(II)-catalysed substitution at platinum(IV).[141] Carbon monoxide acts similarly in catalysing the formation of $[RhCl_2(OH_2)_4]^+$ *en route* to the $[RhCl_2(CO)]^-$ anion.[142] Halogen replacement in *trans*-$[RhX_2py_4]^+$ is inhibited by oxygen (the reaction is very fast in degassed solutions) and is catalysed by primary and secondary alcohols. Again, catalysis by rhodium(I) is suggested. There is no evidence for comparable catalysis in substitution at $[RhX_2en_2]^+$; $[RhX_2py_4]^+$ is more readily reducible than $[RhX_2en_2]^+$.[143] Rhodium(I) catalysis seems also to be inoperative in the analogous $[RhX_2phen_2]^+$ series.[144]

[137] J. Duplessis-Legros, *Compt. rend.*, 1970, **270** *C*, 1768.
[138] D. L. Ehman and D. T. Sawyer, *Inorg. Chem.*, 1969, **8**, 900.
[139] T. Eliadas, R. O. Harris, and P. Reinsalu, *Canad. J. Chem.*, 1969, **47**, 3823.
[140] C. M. Elson, J. Gulens, I. J. Itzkovitch, and J. A. Page, *Chem. Comm.*, 1970, 875.
[141] B. R. James, M. Kastner, and G. L. Rempel, *Canad. J. Chem.*, 1969, **47**, 349.
[142] B. R. James and G. L. Rempel, *J. Chem. Soc.* (*A*), 1969, 78.
[143] R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *Chem. Comm.*, 1969, 974.
[144] G. C. Kulasingam, W. R. McWhinnie, and J. D. Miller, *J. Chem. Soc.* (*A*), 1969, 521.

Aquation of $[Rh(N_3)(NH_3)_5]^{2+}$ is, like that of $[Co(N_3)(NH_3)_5]^{2+}$, acid catalysed. From the pH-rate profile the pK_a of the co-ordinated azide in the rhodium compound has been estimated as $-2{\cdot}2$.[145]

***d*⁶: Iridium(III).**—Kinetic studies of substitution at iridium(III) are relatively infrequent, both because of the paucity of preparative information and of the great patience demanded in following the kinetics of reactions with such excessively long half-lives. However, interest in kinetics of reactions of iridium(III) complexes is increasing, helped by the appearance of improved synthetic methods, as for example for the $[IrX_2\,en_2]^+$ series.[146] Ligand substitution at a series of *trans*-$[IrX_2\,en_2]^+$ complexes takes place without stereochemical change. Rates of substitution are independent of the concentration and nature of the incoming ligand and of ionic strength, and there is no acid catalysis.[147] Presumably the mechanism includes an aquo-intermediate:

$$[IrX_2\,en_2]^+ \underset{\text{slow}}{\overset{OH_2}{\rightleftharpoons}} [IrX(OH_2)en_2]^{2+} \xrightarrow{Y^-,\text{fast}} [IrXY\,en_2]^+$$

Kinetics of aquation of such complexes as *trans*-$[IrX_2\,en_2]^+$ are not directly accessible since the equilibrium shown above lies well over to the left—compare the equilibrium positions for analogous rhodium complexes (intermediate) and cobalt complexes (equilibrium far to the right)—so one can only draw indirect conclusions about aquation from ligand replacement or exchange reactions. Rates and activation parameters can be determined for aquation of $[IrCl_6]^{3-}$ and $[IrCl_5(OH_2)]^{2-}$; the activation entropies suggest a dissociative mechanism.[148] Rates and activation parameters for aquation of $[IrCl_6]^{3-}$ in the presence of cations are reported to vary greatly with the nature and concentration of added salts. Activation energies are, for instance, 25·3 kcal mol^{-1} in 0·1M-LiCl, 21·9 kcal mol^{-1} in 1·0M-LiCl, and as low as 14·6 kcal mol^{-1} in 3·0M-LiCl. This very large effect of added salts is ascribed to the orientating effect of the cations on water adjacent to the $[IrCl_6]^{3-}$ anion.[149] Aquation of *trans*-$[IrCl_4\,py_2]^-$ proceeds with retention of configuration; the mechanism of aquation of the *cis*-isomer is complicated.[150]

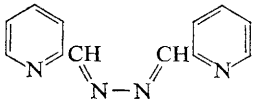
***d*⁶: Iron(II).**—Aquation rates of $[Fe(CN)_5(SO_3)]^{5-}$ vary with pH due to equilibrium with $[Fe(CN)_5(SO_3H)]^{4-}$. Comparison of the reactivities of the protonated and unprotonated forms suggests an important degree of associative character in the mechanism, which is not inconsistent with the strong π-electron-withdrawing properties of the cyanide ligands, which make the iron relatively positive and thus more susceptible to nucleophilic

[145] C. S. Davis and G. C. Lalor, *J. Chem. Soc.* (*A*), 1970, 445.
[146] R. A. Bauer and F. Basolo, *Inorg. Chem.*, 1969, **8**, 2231.
[147] R. A. Bauer and F. Basolo, *Inorg. Chem.*, 1969, **8**, 2237.
[148] A. J. P. Domingos, A. M. T. S. Domingos, and J. M. Peixoto Cabral, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2563.
[149] V. I. Kravtsov, E. G. Tsventarnyi, G. P. Tsayun, and V. A. Yusupova, *Russ. J. Inorg. Chem.*, 1970, **15**, 42.
[150] J. B. Tirsell and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2871.

attack.[151] Photoaquation of $[Fe(CN)_5(OH_2)]^{3-}$ and of the dicyano-bridged complex $[(NC)_5Fe(CN)_2Fe(CN)_5]^{8-}$ produces $Fe^{2+}(aq)$ *via* an intermediate $[Fe(CN)_4]^{2-}$ which can be trapped by nitrosobenzene.[152]

Rates of substitution in $[Fe(CN)_2(bipy)_2]$ in aqueous ethanol correlate with Grunwald–Winstein solvent Y values.[153] The attraction of this mixed complex is that it, like the organic substrates treated by Grunwald and Winstein, is uncharged. Aquation rates of $[Fe(LL)_3]^{2+}$, where LL = phen or a substituted derivative, have been determined in 40% ethanol–water and 92% formic acid–water mixtures. These mixed solvents have the same Y values, in other words have closely similar solvating properties, but the nucleophilicity of water is very much greater in the aqueous alcohol than in the formic acid. The variation of the ratio of aquation rates in the two solvent mixtures suggests a much greater degree of associative character in the aquation mechanism of the 5-nitro complex than of the 4,7-dimethyl complex, a conclusion which is consistent with the relative electron-releasing and -withdrawing properties of the substituents.[154]

A more complicated reaction involving iron(II) complexes is the conversion of $[Fe_2(PAA)_3]^{4+}$ to $[Fe(PAA)_2]^{2+}$, where PAA = 2-pyridinaldazine (13), in aqueous solution. This is a three-step process, involving aquation and recombination.[155]



(13)

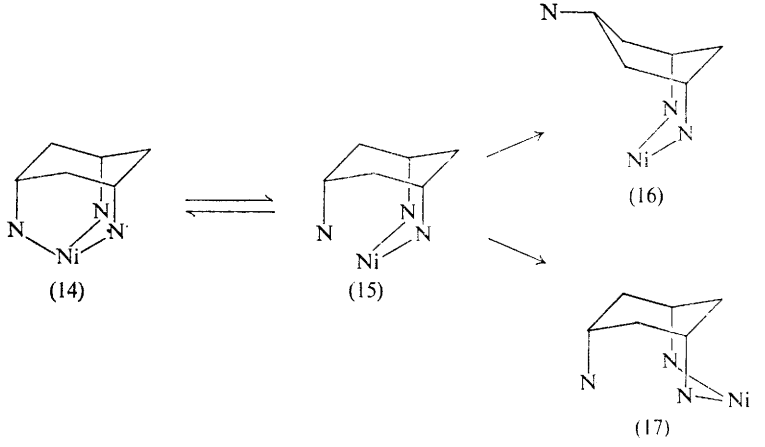
Some substituted tris-1,10-phenanthroline complexes of iron(II) react with peroxodisulphate by a mechanism involving parallel rate-determining oxidation and aquation. In the latter pathway dissociative loss of one ligand is followed by rapid oxidation of the intermediates produced.[156]

d^6: Ruthenium(II).—There is a section on reaction mechanisms in a review of ruthenium(II)–ammine complexes.[157] The activation energy for aquation of molecular nitrogen complexes of ruthenium(II) is *ca.* 23 kcal mol^{-1}. This fairly high value is said to be consistent with strong ruthenium–nitrogen bonding, including a significant π-contribution.[158] Preliminary kinetic observations are reported for aquation of mononuclear and dinuclear

[151] E. J. Baran and A. Müller, *Z. anorg. Chem.*, 1969, **368**, 144.
[152] G. Emschwiller, *Compt. rend.*, 1970, **270** *C*, 1362.
[153] J. Burgess, *Chem. Comm.*, 1969, 1422.
[154] J. Burgess, *J. Chem. Soc.* (*A*), 1969, 1899.
[155] W. J. Stratton, M. F. Rettig, and R. F. Drury, *Inorg. Chim. Acta*, 1969, **3**, 97.
[156] J. Burgess and R. H. Prince, *J. Chem. Soc.* (*A*), 1970, 2111.
[157] P. C. Ford, *Co-ordination Chem. Rev.*, 1970, **5**, 75.
[158] A. K. Shilova and A. E. Shilov, *Kinetika i Kataliz*, 1969, **10**, 267 (*Chem. Abs.*, 1969, **71**, 25 095.)

ruthenium(II)–trien–N_2 complexes.[159] Irradiation of solutions of $[Ru(NH_3)_5L]^{2+}$, where L = pyridine, acetonitrile, ammonia, or water, results in aquation or oxidation depending on the wavelength of the radiation.[160]

d^8: **Nickel(II).**—The mono-(*cis,cis*-1,3,5-triaminocyclohexane)nickel(II) cation is exceptionally inert to aquation. It has a half-life of *ca.* 7 min at 25 °C, which contrasts greatly with the rapid aquation of simple garland tridentate amines, *e.g.* $[Ni(dien)]^{2+}$. The reason for the great inertness of the triaminocyclohexane complex lies in the conformational characteristics of the cyclohexane skeleton. For if one nickel–nitrogen bond is broken [(14) → (15)] the nitrogen atom remains close to the nickel, and can very readily reform the nickel–nitrogen bond, unless the complex inverts, which it can do in two ways, (15) to (16) or (15) to (17). The former inversion of



the cyclohexane will have a barrier of *ca.* 10 kcal mol^{-1}; the latter, which involves inversion at two nitrogen atoms, will also have a large energy barrier. Thus (15) returning to (14) is easier than (15) → (16) or (15) → (17), resulting in a low overall rate of aquation of the complex.[161] A similar but less extreme example is aquation of the 2,6-dicarboxypiperidineacetic acid complex of nickel(II). This ligand is a cyclic analogue of nitriloacetic acid (nta); in the complex the ring holds the acetate groups close to the nickel. In fact, rates of aquation of the cyclic and acyclic compounds are similar, for the forced proximity of acetates to metal in the cyclic compound is balanced by the unfavourable ring strain.[162]

An n.m.r. relaxation study of fluoride complexes of the transition metals gives the expected result that nickel(II) complexes are less labile than those

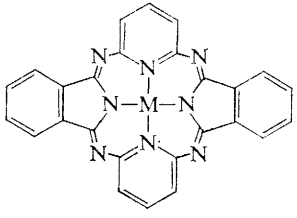
[159] R. O. Harris and B. A. Wright, *Canad. J. Chem.*, 1970, **48**, 1815.
[160] P. C. Ford, D. H. Stuermer, and D. P. McDonald, *J. Amer. Chem. Soc.*, 1969, **91**, 6209.
[161] R. F. Childers and R. A. D. Wentworth, *Inorg. Chem.*, 1969, **8**, 2218.
[162] T. J. Bydalak, T. M. Stokich, and D. M. Coleman, *Inorg. Chem.*, 1970, **9**, 29.

of manganese(II), iron(II), and cobalt(II). There is acid catalysis of aquation of NiF^+.[163]

Rates and activation parameters have been determined for acid aquation of $[Ni_4(OH)_4]^{4+}$, which exists under certain conditions in aqueous alkaline solutions of nickel(II). The activation enthalpy is comparable with that for hydroxo-bridge breaking in $[Cr_2(OH)_2]^{4+}$; the activation entropy is consistent with breakdown of a polymeric structure.[164]

d^9 and d^{10} Cations.—Rates of aquation have been reported for two complexes of the edta family of ligands, for magnesium(II)–cyclohexanediaminetetra-acetate[165] and for cadmium(II)–nitrilotriacetate.[166]

Stereochemistry is important in controlling the reactivity of copper(II) complexes of tet-a, tet-b, and *trans*-14-diene [formulae (7), (7), (8)]. Strongly acidic conditions are required for aquation of complexes of these fairly inflexible ligands.[167] A more widely ranging study led to the determination of kinetic parameters for aquation of zinc(II), cadmium(II), copper(II), nickel(II), and cobalt(II) complexes of some bi-, tri-, and quadridentate macrocyclic ligands, *e.g.* bis-pyridylisoindole (18).[168]



(18)

Actinides.—Dissociation of $[UO_2(OH)]_2^{2+}$ has been studied by stopped-flow techniques. The reaction mechanism differs somewhat from that for dissociation of analogous iron(III) and vanadium(IV) dimers since the uranium(VI) dimer has a very stable conjugate acid and conjugate diacid.[169]

5 Base Hydrolysis

Cobalt(III) Complexes.—Several different approaches have produced evidence confirming the dissociative nature of base hydrolysis of cobalt(III)–ammine–halide complexes. In the first of these, activation enthalpies ($\Delta H^{\ddagger}$) and enthalpy changes for complete reaction (ΔH^0) were compared. From measured values of ΔH^0 and previously reported values of $\Delta H^{\ddagger}$, values for the transition enthalpy (ΔH_T), which is the enthalpy difference between the

[163] M Eisenstadt, *J. Chem. Phys.*, 1969, **51**, 4421.
[164] G. B. Kolski, N. N. Kildahl, and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 1211.
[165] T. Meites and L. Meites, *J. Amer. Chem. Soc.*, 1970, **92**, 37.
[166] C. V. d'Alkaine and J. Koryta, *Coll. Czech. Chem. Comm.*, 1969, **34**, 2138.
[167] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 2151.
[168] R. P. Smirnov and B. D. Berezin, *Russ. J. Phys. Chem.*, 1969, **43**, 1398.
[169] V. Frei and H. Wendt, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 593.

transition state and the products (see the Figure), were calculated. For S_N1cb or S_N1ip mechanism of base hydrolysis of $[CoX(NH_3)_5]^{2+}$, ΔH_T should be independent of X, for the relevant reactions are:

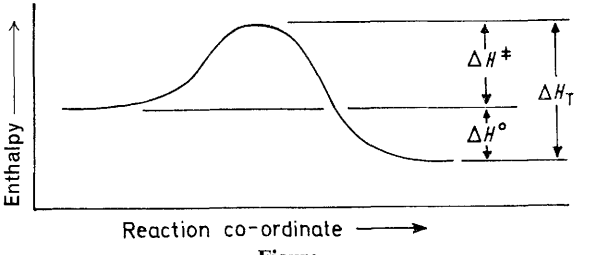
$$S_N1cb: \quad [Co(NH_2)(NH_3)_4]^{2+} + OH_2 \longrightarrow [Co(OH)(NH_3)_5]^{2+}$$

$$S_N1ip: \quad [Co(NH_3)_5]^{3+}, OH^- \longrightarrow [Co(OH)(NH_3)_5]^{2+}$$

But for an S_N2 reaction, ΔH_T will vary with X since the heat of solvation of X^- is involved:

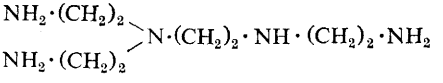
$$S_N2: \quad [CoX(OH)(NH_3)_5]^{+} \longrightarrow [Co(OH)(NH_3)_5]^{2+} + X^-$$

ΔH_T is found to be constant for $X^- = Cl^-$, Br^-, I^-, hence it may be taken that the mechanism is dissociative, S_N1cb or S_N1ip, in character.[170]



Figure

Comparison of base hydrolysis, racemisation, and proton exchange rates for $[CoX(trenen)]^{n+}$, where X = Cl^-, N_3^-, or OH_2, and trenen is the quinquedentate ligand (19) indicates an S_N1cb mechanism for base hydrolysis.[171] The demonstration of linear free energy plots ($\Delta G^{\ddagger}$ *vs.* ΔG^0) of



(19)

unit slope for both base and acid hydrolysis of $[Co(NO_3)(NH_3)_5]^{2+}$ indicates a dissociative process in both basic and acidic media.[4] The mechanism of base hydrolysis of $[CoX(NH_3)_5]^{2+}$ can also be probed by experiments designed to demonstrate competition between nucleophiles for the proposed S_N1 intermediate $[Co(NH_2)(NH_3)_4]^{2+}$. The most recent experiments in this area have involved the use of azide and thiocyanate as the ligands to compete with water and hydroxide. The choice was suggested by the relatively high resistance of $[Co(N_3)(NH_3)_5]^{2+}$ and $[Co(NCS)(NH_3)_5]^{2+}$ to hydrolysis. The transitory existence of $[Co(NH_2)(NH_3)_4]^{2+}$ is supported by the observed products; this intermediate shows low discrimination, for

[170] D. A. House and H. K. J. Powell, *Chem. Comm.*, 1969, 382.
[171] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1969, **8**, 1595.

it attacks thiocyanate at either nitrogen or sulphur.[172] Kinetic results for base hydrolysis of $[Co(NH_3)_6]^{3+}$ do not distinguish between the S_N1cb and S_N1ip mechanisms for reaction. The proposed reaction sequence combines features of both into a four-stage mechanism which includes conjugate base formation from an ion-pair.[173] The choice between S_N1cb and S_N1ip mechanisms is unambiguously in favour of the former for base hydrolysis of *trans*-$[CoX(DMG)_2(NH_3)]$, because ion-pair formation is ruled out by the electrical neutrality of the complex.[174] Rates of base hydrolysis vary only slightly with the nature of the cycloalkylamine (L) in $[CoCl\,L\,en_2]^{2+}$. This is thought to be due to a balance between the equilibrium constant for ion-pair formation and the actual dissociation rate constant.[34]

On the assumption that the mechanism of base hydrolysis is S_N1cb, and that the $-NH_2$ ligand is equatorial in the transition state, it is possible to elucidate fine details of the mechanism by applying the principle of microscopic reversibility. Observed product distributions from experiments using ^{15}N-labelled substrates provide relevant information.[175]

When activation energies for base hydrolysis of $[Co(NH_3)_5X]^{2+}$ are plotted against the energies of the respective first ligand field bands two linear plots are obtained, one for X = Cl, Br, or I, the other for X = N_3, NCS, or NO_2. This difference in behaviour is thought to correspond to some difference in mechanism. Facile electron transfer in one series seems unlikely since the argument is concerned with $d \rightarrow d$ rather than charge-transfer transitions.[5]

Individual steps in chelate ring opening can be followed kinetically during base hydrolysis of $[Co\,en_2CO_3]^+$, in contrast to acid aquation where only one stage can be monitored kinetically. Thus, while the intermediate formation of a unidentate carbonate complex in acid aquation is a postulate, its formation in alkaline solution is kinetically proven.[176] Further discussion on mechanisms of reactions of carbonato complexes will be found in the kinetic section of a general review on the chemistry of these complexes.[177]

Further kinetic results have been obtained in an attempt to resolve differences of opinion on the mechanism of base hydrolysis of *trans*-$[CoCl(OH)en_2]^+$.[178] The effect of ionic strength variation and of possible ion-pair formation in base hydrolysis of $[CoX(NH_3)_5]^{2+}$ has been discussed,[179] while the comparative effects of steric factors and of ion-pair

[172] D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 655.
[173] J. H. Takemoto and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1970, **32**, 175.
[174] S. C. Chan and P. Y. Leung, *Austral. J. Chem.*, 1969, **22**, 2569.
[175] F. R. Nordmeyer, *Inorg. Chem.*, 1969, **8**, 2780.
[176] D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc.*, 1969, **91**, 6626.
[177] K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 1970, **70**, 171.
[178] M. E. Farago, B. Page, and M. L. Tobe, *Inorg. Chem.*, 1969, **8**, 388.
[179] M. B. Davies and G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 799, 2189; M. R. Wendt and C. B. Monk *J. Chem. Soc.* (*A*) 1969, 1624.

formation in base hydrolysis of *cis*-$[CoCl(RNH_2)en_2]^{2+}$ have been the subject of some dispute.[180] Unfortunately the two sets of rate data were obtained at different temperatures; no activation parameters are available.

Rates and activation parameters have been determined for base hydrolysis of $[Co(PO_4)(NH_3)_5]$, $[Co(HPO_4)(NH_3)_5]^+$, and $[Co(H_2PO_4)(NH_3)_5]^{2+}$.[181] Rates of base hydrolysis have also been reported for $[CoXL\,en_2]^{n+}$, where L = aniline,[28] benzylamine,[30] alkylpyridines,[32] and sulphate.[27] Both kinetic and stereochemical data are available for the base hydrolysis of β_2-$[CoCl(glyOEt)trien]^{2+}$.[71]

A non-aqueous analogue of the above examples of base hydrolysis in aqueous solution is solvolysis in acetic acid–acetate solutions. This reaction has been studied for *trans*-$[Co(O_2C\cdot R)_2\,en_2]^+$, where R = *o*-tolyl or *p*-tolyl, whose rates of solvolysis are found to decrease with increasing concentration of added acetate. This behaviour is in direct contrast to that of the aqueous system. In acetic acid the S_N1cb mechanism appears not to operate, and the mechanism must be solvent-assisted dissociation, with ion-pairs less reactive than the free cation.[182]

Other Complexes.—The rate law for base hydrolysis of $[Cr(O_2C\cdot CF_3)(NH_3)_5]^{2+}$ includes terms in the first and second powers of the hydroxide ion concentration. The first term refers to normal base hydrolysis, be it S_N1cb, S_N1ip, or S_N2. The second term, observed also for other $[M(carboxylato)(NH_3)_5]^{2+}$ complexes, can be interpreted by attack of one hydroxide ion at the acyl-carbon and removal of a proton thence by the second hydroxide ion.[92] Activation entropies for acid and for base hydrolysis of $[CrCl(RNH_2)_5]^{2+}$, with R = H, Me, Et, Pr^n, or Bu^n, are remarkably similar, which suggests a dissociative mechanism for base as for acid hydrolysis.[183]

Rates have been determined by stopped-flow spectrophotometry and by polarography for the following reactions in the pentacyanonitrosyliron system:

$$[Fe(CN)_5(NO)]^{2-} \underset{}{\overset{OH^-}{\rightleftharpoons}} [Fe(CN)_5(NO_2H)]^{3-} \overset{OH^-}{\rightleftharpoons} [Fe(CN)_5(NO_2)]^{4-}$$

The equilibrium constant for the right-hand equilibrium was estimated from the forward and reverse rate constants.[184] The reactivity of the co-ordinated nitrosyl group in this and related complexes has been reviewed.[185]

[180] R. W. Hay and P. L. Cropp, *J. Chem. Soc.* (*A*), 1969, 42; S. C. Chan and F. Leh, *J. Chem. Soc.* (*A*), 1966, 126, 129, 134.
[181] S. F. Lincoln, J. Jayne, and J. P. Hunt, *Inorg. Chem.*, 1969, **8**, 2267.
[182] A. W. Chester, *Chem. Comm.*, 1969, 865; *Inorg. Chem.*, 1970, **9**, 1743.
[183] M. Parris and W. J. Wallace, *Canad. J. Chem.*, 1969, **47**, 2257.
[184] J. Mašek and J. Dempir, *Inorg. Chim. Acta*, 1968, **2**, 443; J. Mašek and H. Wendt, *ibid.*, 1969, **3**, 455; J. Mašek, M. G. Bapat, B. Ćosivić, and J. Dempir, *Coll. Czech. Chem. Comm.*, 1969, **34**, 485.
[185] J. Mašek, *Inorg. Chim. Acta Rev.*, 1969, **3**, 99.

The rate law for base hydrolysis of several bisethylenediamine and penta-ammine complexes of ruthenium(III) has a term in hydroxide ion concentration, but this is thought to arise from pre-equilibrium ion-pair formation in a dissociative process rather than from S_N2 hydroxide attack. The rate and activation enthalpy trends for chloride–bromide–iodide triads are in the order usual for dissociative rather than associative processes. The stereochemical course of the reactions is consistent with an S_N1cb or an S_N2 mechanism.[186] Base hydrolysis of *trans*-$[Pt(CN)_4Br_2]^{2-}$ obeys a rate law with a first-order term in hydroxide ion concentration, but again this is ascribed to pre-equilibrium ion-pair formation rather than S_N2 hydroxide attack. This time the evidence cited is the positive value for the activation entropy, which indicates a dissociative process. Obviously an S_N1cb mechanism cannot operate here since there are no protons in the complex.[187]

Activation enthalpies correlate linearly with activation entropies for base hydrolysis of $[RhX(NH_3)_5]^{2+}$ for X = Cl, Br, or I, but not for X = azide.[5] So here, as for base hydrolysis of $[CoX(NH_3)_5]^{2+}$ discussed earlier, the mechanism of base hydrolysis may be different for azide and halide ligands. But the situation is confused by such series as the $[CoX(trenen)]^{2+}$ complexes also mentioned previously,[171] where the mechanism of base hydrolysis seems to be S_N1cb for X = azide as for X = chloride. Kinetic parameters for base hydrolysis of $[IrI(NH_3)_5]^{2+}$ suggest an S_N1cb mechanism.[188]

6 Formation

This topic can be conveniently, if rather arbitrarily, divided into two parts, *viz.* formation of complexes of inert cations and formation of complexes of labile cations. The latter aspect ranges from the simplest examples through to biochemical systems; this whole range is covered in a unified discussion in Part III of this Report. Formation reactions at kinetically inert centres will be discussed in this present section, in which references will be grouped according to the nature of the cation. Two general and comprehensive reviews of the formation of complexes have appeared;[189] the formation of complexes of *sp* elements has also been reviewed.[190]

d^2: **Vanadium**(III).—Reaction of hexa-aquovanadium(III) with azide takes place by a mechanism with considerable associative character.[136]

d^3: **Chromium**(III).—A general discussion of rates of formation of CrL^{2+} from $[Cr(OH_2)_6]^{3+}$ and from $[Cr(OH)(OH_2)_5]^{2+}$ compares rate constants for reaction with a wide range of ligands L. $[Cr(OH_2)_6]^{3+}$ reacts with a

[186] J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, 1969, **8**, 2124.
[187] C. E. Skinner and M. M. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 1984.
[188] G. C. Lalor and T. Carrington, *J. Chem. Soc.* (*A*), 1969, 2509.
[189] A. McAuley and J. Hill, *Quart. Rev.*, 1969, **23**, 18; D. J. Hewkin and R. H. Prince, *Coordination Chem. Rev.*, 1970, **5**, 45.
[190] H. Strehlow and W. Knocke, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 427.

variety of anions of strong acids at widely different rates, indicating significant incoming-ligand participation in transition-state formation. The slope of the ΔG^0 *vs.* $\Delta G^{\ddagger}$ linear free energy plot also suggests some associative character in the mechanism. In contrast, the range of rates of reaction for $[Cr(OH)(OH_2)_5]^{2+}$ with the same series of ligands is small, suggesting a predominantly dissociative mechanism. Where L is the anion from a weak acid it is difficult to distinguish between the two alternatives $Cr^{3+} + L^- \rightarrow CrL^{2+}$ and $CrOH^{2+} + HL \rightarrow CrL^{2+} + OH_2$; the latter path is thought the more likely, as in the analogous iron(III) case.[191] Kinetics of formation of $[Cr(OH_2)_5(DMSO)]^{3+}$ also indicate considerable associative character in transition-state formation.[115] Kinetics of formation of $[Cr(O_2C\cdot CH_3)(NH_3)_5]^{2+}$ in aqueous acetic acid–sodium acetate solution have been interpreted in terms of parallel S_N1 and S_N1ip pathways; there is ancillary evidence for significant ion-pairing in these solutions.[192] The mechanism of reaction of $[Cr(OH_2)_6]^{3+}$ and of $[Cr(OH_2)_5(MeOH)]^{3+}$ with thiocyanate in aqueous methanol is primarily dissociative, but not $S_N1(lim)$.[193] From these and from a variety of other results there appears to be emerging a general trend for the associative character to be more marked in reactions of $[CrL(OH_2)_5]^{n+}$ than of $[CrL(NH_3)_5]^{n+}$.[191]

The formation of malonate[194] and oxalate[195] complexes from $[Cr(OH_2)_6]^{3+}$ involves rate-determining chromium–water bond breaking in an ion-pair in each case. Activation parameters for these two reactions, for formation of the monoglycine complex, and for water exchange at chromium(III) are all rather similar. The formation of edta complexes of chromium(III) is more complicated, involving several water displacement and chelation steps. Rates and activation parameters are reported[196] for the tridentate to quinquedentate conversion:

$$[CrCl_2(OH_2)(edtaH_3)] \longrightarrow [Cr(OH_2)(edtaH)] + [Cr(OH)(edta)]^-$$

The effects of a variety of anions on chelation steps in the chromium(III)–edta reaction have been studied.[197]

***d*⁴: Ruthenium(IV).**—Effects of added ions (H^+, Li^+, Na^+) on the rates of formation of chloride and bromide complexes of ruthenium(IV) can be explained in terms of the effects of the added cations on solvent structure. Their solvation requirements seem to encourage water loss from the co-ordination shell of the ruthenium(IV).[198]

***d*⁵: Iron(III).**—This is one of the more popular cations for the study of

[191] J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 1554.
[192] D. Banerjea and S. Sarkar, *Z. anorg. Chem.*, 1970, **373**, 73.
[193] R. J. Baltisberger and J. V. Hanson, *Inorg. Chem.*, 1970, **9**, 1573.
[194] D. Banerjea and C. Chatterjee, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3845.
[195] D. Banerjea and S. D. Chaudhuri, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1617.
[196] A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc.* (*A*), 1969, 655.
[197] G. M. Phatak, T. R. Bhat, and J. Shankar, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1305.
[198] A. A. Biryukov, V. I. Shlenskaya, and B. S. Rabinovich, *Russ. J. Inorg. Chem.*, 1969, **14**, 413.

complex formation kinetics. In each case the relative reactivities of $[Fe(OH_2)_6]^{3+}$ and $[Fe(OH_2)_5(OH)]^{2+}$ hereafter referred to as Fe^{3+} and $FeOH^{2+}$, and of the ligand in its protonated and deprotonated forms have to be assessed. As discussed for chromium(III) there is the kinetic ambiguity of $Fe^{3+} + L^-$ *vs.* $FeOH^{2+} + HL$, to be resolved where possible from ancillary evidence. For formation of chloride and bromide complexes new *T*-jump values for the kinetic parameters confirm earlier values obtained by flow techniques.[199] At high ionic strengths formation of $FeCl^{2+}$ is faster, presumably because reduced solvation of the iron(III) species and of the chloride makes their approach to each other somewhat easier.[200] The equilibrium constant for formation of the monohypophosphite complex of iron(III) has been calculated from the quotient of the rate constants for its formation and dissociation.[201] Here, and in the iron(III)–chromate reaction,[202] reaction is primarily between $FeOH^{2+}$ and the ligands.

Several reports concern the formation of organic ligand complexes of iron(III). The variation of rate with ligand concentration in the reaction with mandelic acid [203, 204] is interpreted as a pre-equilibrium ion-pair formation followed by dissociative complex formation within the ion-pair, rather than as simple S_N2 formation.[203] This interpretation is similar to that proffered for formation of malonate [194] and oxalate [195] complexes of chromium(III) (see above). Rates of reaction of iron(III) with a variety of phenols are all very similar, suggesting that iron(III)–water bond breaking is rate determining here also.[205] Sulphosalicylate reacts with $FeOH^{2+}$ by the same rate-determining loss of water from the iron(III).[206] Rates of formation of iron(III) complexes with acetate, monochloroacetate, and propionate have been reported.[207]

d^6: Cobalt(III).—The small dependence of rate of formation of $[Co(N_3)(NH_3)_5]^{2+}$ from $[Co(OH_2)(NH_3)_5]^{3+}$ on azide concentration suggests a dissociative mechanism, probably involving an ion-pair pre-equilibrium [cf. chromium(III) [194, 195] and iron(III) [103, 105] examples]. The estimated equilibrium constant for this is higher than for ion-pair formation with other anions, which suggests specific interaction between the azide and water co-ordinated to cobalt(III).[3] Rates and activation parameters for substitution of the water in *trans*-$[Co(SO_3)en_2(OH_2)]^+$ and *trans*-$[Co(SO_3)(OH)en_2]$ provide a quantitative illustration of the *trans*-labilising effect of sulphite. The formation mechanism involves the generation of

[199] T. Yasunaga and S. Harada, *Bull. Chem. Soc. Japan*, 1969, **42**, 2165.
[200] J. K. Rowley and N. Sutin, *J. Phys. Chem.*, 1970, **74**, 2043.
[201] J. H. Espenson and D. F. Dustin, *Inorg. Chem.*, 1969, **8**, 1760.
[202] J. H. Espenson and S. R. Helzer, *Inorg. Chem.*, 1969, **8**, 1051.
[203] A. D. Gilmour and A. McAuley, *J. Chem. Soc.* (*A*), 1969, 2345.
[204] Z. Andrei, *Studia Univ. Babes-Bolyai, Ser. Chem.*, 1969, **14**, 87 (*Chem. Abs.*, 1969, **71**, 116,945g).
[205] F. P. Cavasino and E. Di Dio, *J. Chem. Soc.* (*A*), 1970, 1151; J. Osugi, H. Nakatani, and T. Fuju, *Nippon Kagaku Zasshi*, 1969, **90**, 529 (*Chem. Abs.*, 1969, **71**, 85,004t).
[206] G. Saini and E. Mentasti, *Inorg. Chim. Acta*, 1970, **4**, 210.
[207] F. Accascina, F. P. Cavasino, and E. Di Dio, *Trans. Faraday Soc.*, 1969, **65**, 489.

$[Co(SO_3)en_2]^+$ as an intermediate.[208] Kinetic investigations of reactions of bridged dicobalt complexes have included two which involve replacement of water by other ligands (see above).[23, 24] A preliminary report of the reaction of $[CoR(DMG)_2(OH_2)]$ with ligands has appeared,[209] and the formation of $[CoCl(DMG)_2(PR_3)]$ from cobalt(II) chloride in ethanolic solution has been described.[210]

d^6: Rhodium(III).—In recent years several workers have suggested a degree of associative character in some substitutions at rhodium(III). Further evidence for some associative character in the ligand interchange mechanism comes from kinetic studies of chloride and bromide replacement of water in $[Rh(NH_3)_5(OH_2)]^{3+}$. The incoming halide groups perhaps offer greater nucleophilic assistance than does incoming water.[211] The *trans*-effects of hydroxide, ammonia, and chloride are fairly similar, but that of water is the lowest yet found for rhodium(III). These effects were derived from kinetic studies of anation of *trans*-$[Rh\,en_2L(OH_2)]^{n+}$. The activation entropy for anation of *trans*-$[Rh\,en_2(OH_2)_2]^{3+}$ is much more positive than that for $[Rh(NH_3)_5(OH_2)]^{3+}$, which is consistent with a greater associative character for the latter.[212] The dependence of the rates of anation on anion concentration suggests a five-co-ordinate intermediate, rather than merely transition-state, for anation of $[RhCl_5(OH_2)]^{2-}$,[213] as for $[IrCl_5(OH_2)]^{2-}$.[148] In these two systems there is no ion-pairing between the complex and the incoming anionic ligand to complicate the kinetics and their interpretation, since the complexes are themselves anionic.

Rates of formation of *cis*-$[RhBr_2\,phen_2]^+$ from rhodium tribromide have been measured in aqueous ethanol and in aqueous acetone. The similarity of these rates suggests that there is no redox catalysis by rhodium(I) species in aqueous ethanol.[144]

d^6: Iridium(III).—There have been two reports on anation at iridium(III), in each case involving replacement of water by chloride. The first case is in $[IrCl_5(OH_2)]^{2-}$,[148] the second is in $[IrCl_3(OH_2)py_2]^0$.[150]

d^6: Iron(II).—Formation of $[Fe(pc)(imidazole)_2]^0$ in DMSO solution involves replacement of the two DMSO molecules which are co-ordinated to the metal in the dissolved iron(II) phthalocyanine $[Fe(pc)(DMSO)_2]^0$. The strong *trans*-labilising effect of imidazole means that it is the replacement of the first DMSO which is rate-determining. A second-order rate law is obeyed over a 6000-fold range of imidazole concentrations, which suggests a bimolecular nucleophilic substitution mechanism rather than the so-called limiting S_N1 mechanism observed for the analogous system cobalt(III)-haematoporphyrin plus thiocyanate. In the iron(II)-phthalo-

[208] D. R. Stranks and J. K. Yandell, *Inorg. Chem.*, 1970, **9**, 751.
[209] A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1970, **92**, 2593.
[210] G. Costa, G. Tauzher, and A. Puxeddu, *Inorg. Chim. Acta*, 1969, **3**, 45.
[211] H. L. Bott, A. J. Poë, and K. Shaw, *J. Chem. Soc.* (*A*), 1970, 1745.
[212] A. J. Poë and K. Shaw, *J. Chem. Soc.* (*A*), 1970, 393.
[213] D. Robb, M. M. de V. Steyn, and H. Krüger, *Inorg. Chim. Acta*, 1969, **3**, 383.

cyanine plus imidazole system both reactants have zero charge so ion-pairing problems are neatly avoided.[214] In the related system of haemin plus imidazole in aqueous ethanolic solution, ion-pairs play a significant role.[215] For discussion of this and other biochemical systems the reader is referred to Part III of this Report.

d^6: Ruthenium(II).—Substitution of water by pyridine in *cis*- or in *trans*-$[Ru(OH_2)_2(NH_3)_4]^{2+}$, as of chloride by pyridine in *cis*- or in *trans*-$[RuCl_2(NH_3)_4]^0$, gives in every case a single isomer. This stereochemical information is unfortunately not sufficient for a choice to be made between a dissociative mechanism with a square-pyramidal transition state and an associative mechanism involving *cis*-attack.[216] The equilibrium

$$[Ru(NH_3)_5(OH_2)]^{2+} + N_2O \rightleftharpoons [Ru(NH_3)_5(N_2O)]^{2+} + H_2O$$

can be forced to the right-hand side by the addition of chromium(II) ions, which very rapidly reduce the nitrous oxide complex to $[Ru(NH_3)_5(N_2)]^{2+}$.[217] The rate of reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with molecular nitrogen is similar to the rate of the previous reaction with nitrous oxide, and to rates of reaction with carbon monoxide, pyridine, and isonicotinamide. The obvious explanation for this similarity of rates is similarity of mechanism, in other words a common dissociative rate-determining step, but the possibility of similar nucleophilicity of these ligands means that an associative process cannot be completely ruled out.[218]

d^6: Platinum(IV).—The first kinetic study of anation at platinum(IV) to be reported involves the reaction of *trans*-$[PtBr(CN)_4(OH_2)]^-$ with bromide. This forms part of an investigation of the oxidation of $[Pt(CN)_4]^{2-}$ by bromine.[219]

d^7: Cobalt(II).—Reactions of molecular oxygen with cobalt(II) complexes involve both substitution and oxidation. As the products seem to be superoxide complexes of cobalt(III) [220] (cf. the recently reported superoxide complexes of palladium [221] and rhodium [222]) rather than molecular oxygen complexes of cobalt(II), it seems more appropriate to discuss these reactions in Part I of this Report.

[214] J. G. Jones and M. V. Twigg, *Inorg. Chem.*, 1969, **8**, 2120; *Inorg. Nuclear Chem. Letters*, 1969, **5**, 333; H. P. Bennetto, J. G. Jones, and M. V. Twigg, *Inorg. Chim. Acta*, 1970, **4**, 180.

[215] B. B. Hasinoff, H. B. Dunford, and D. G. Horne, *Canad. J. Chem.*, 1969, **47**, 3225; N. S. Angerman, B. B. Hasinoff, H. B. Dunford, and R. B. Jordan, *ibid.*, p. 3217.

[216] P. C. Ford and C. Sutton, *Inorg. Chem.*, 1969, **8**, 1544.

[217] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 1969, **91**, 6874.

[218] C. M. Elson, I. J. Itzkovitch, and J. A. Page, *Canad. J. Chem.*, 1970, **48**, 1639.

[219] C. E. Skinner and M. M. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 4405.

[220] D. Diemente, B. M. Hoffman, and F. Basolo, *Chem. Comm.*, 1970, 467; A. G. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55; B. M. Hoffman, D. L. Diemente, and F. Basolo, *ibid.*, p. 61; S. A. Cockle, H. A. O. Hill, and R. J. P. Williams, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 131.

[221] E. W. Stern, *Chem. Comm.*, 1970, 736.

[222] B. R. James and F. T. T. Ng, *Chem. Comm.*, 1970, 908.

Lanthanides.—Complex formation between lanthanides and oxoanions is commonly followed by ultrasonic techniques. Kinetic data are now available on the formation of sulphate complexes for the whole lanthanide series. The mechanism is assumed to be that according to Eigen (cf. Part III), although in many cases only one relaxation time, here assigned to entry of the sulphate into the inner co-ordination sphere of the cation, is observed.[223] The rate-determining step here, and in the formation of nitrate complexes,[224] is said to be water loss from the aquolanthanide cation. Only in the case of Gd^{3+} is there available a water exchange rate to test and confirm this hypothesis. The formation of acetate complexes has been studied mainly for Sm^{3+}, but there are some results for La^{3+}, Ce^{3+}, and Dy^{3+}. Two relaxations are observed, but there is considerable difficulty in interpreting the mechanism unequivocally since it is not certain whether the acetate acts as a mono- or bi-dentate ligand. The most likely assignment of the relaxations is to relatively fast displacement of one water by acetate and then to slower formation of an acetate chelate ring.[225] Difficulties in assigning the appropriate chemistry to observed relaxation times are again encountered in *E*-jump and *T*-jump experiments on scandium(III) perchlorate solutions.[226]

Dimerisation.—The mechanisms of dimerisation of iron(III), vanadium(IV),[135] and uranium(VI)[169] in aqueous solution have been deduced from stopped-flow studies of the kinetics of dissociation of $[FeOH]_2^{4+}$, $[VO(OH)]_2^{2+}$, and $[UO_2(OH)]_2^{2+}$. In each case, formation takes place through reactions of the type $UO_2^{2+} + UO_2(OH)^+ \rightarrow UO_2(OH)UO_2^{3+}$.

Rates of formation, and of dissociation, of dimeric iron(III) complexes of cydta, edta, and hedta have been determined as a function of pH. This represents a contribution to the knowledge of the kinetic behaviour associated with M–O–M and M–OH–M systems, to complement the long-known thermodynamic properties of such complexes.[227] *T*-Jump studies of the dimerisation of iron(III)–edta show one relaxation, ascribed to the equilibrium

$$[Fe(OH)(edta)]^{2-} + [Fe(edta)]^- \rightleftharpoons [Fe_2(edta)_2O]^{4-} + H^+$$

The left to right direction appears to be dissociative in nature.[228]

7 Ligand Exchange and Replacement

Simple Ligands.—*Exchange.* ^{14}N N.m.r. studies of exchange of pyridine with $CoCl_2py_4$, in pyridine solution, indicate a rate constant of 6×10^6 s^{-1}

[223] D. P. Fay, D. Litchinsky, and N. Purdie, *J. Phys. Chem.*, 1969, **73**, 544; D. P. Fay and N. Purdie, *ibid.*, 1970, **74**, 1160; S. S. Bhatti and G. Rai, *Z. Phys. Chem. (Leipzig)*, 1970, **243**, 239.
[224] R. Garnsey and D. W. Ebdon, *J. Amer. Chem. Soc.*, 1969, **91**, 50.
[225] V. L. Garza and N. Purdie, *J. Phys. Chem.*, 1970, **74**, 275.
[226] D. L. Cole, L. D. Rich, J. D. Owen, and E. M. Eyring, *Inorg. Chem.*, 1969, **8**, 682.
[227] R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, 1969, **8**, 1470.
[228] A. D. Gilmour and A. McAuley, *Inorg. Chim. Acta*, 1970, **4**, 158.

at 25·0 °C and activation parameters of 13·2 kcal mol^{-1} and 17 e.u.[229] Exchange of pyridine with $Ni(LL)_2py_2$, where LL = substituted acac, in deuteriochloroform solution follows first-order kinetics. Exchange rates correlate with the Taft σ^* values of the substituents in the acac ligands. Pyridine exchange at $Co(acac)_2py_2$ is considerably faster than at $Ni(acac)_2py_2$, as expected from crystal field considerations.[230]

Exchange of acetylacetone with $Al(acac)_3$ takes place by a mechanism involving intermediates containing monodentate acac in non-aqueous as in aqueous solution.[231] The kinetics of acetate exchange with *trans*-$[Co(OAc)_2en_2]^+$ in acetic acid have been reported.[232]

Replacement. Kinetic aspects of the replacement of acetylacetone in several of its complexes have been reviewed.[233]

The stereochemistry of replacement of chloride in *cis*- or *trans*-$[RuCl_2(NH_3)_4]^0$ by pyridine is consistent both with a dissociative pathway through a square-pyramidal transition state and with an associative pathway involving *cis*-attack by the incoming pyridine.[216]

The first step in the reaction of the cydta complex of cobalt(II) with cyanide is reversible formation of a 1 : 1 seven-co-ordinate adduct. Formation of this adduct follows a second-order rate law and has the extraordinarily low activation energy of 0·8 kcal mol^{-1}. Further reaction to $[Co(CN)_5]^{3-}$ is slow. The rate law for reaction of the 1 : 1 adduct with cyanide is first-order in adduct, second-order in cyanide. Thus the overall reaction is third-order in cyanide, like the related reactions of the edta complexes of cobalt(II) and of nickel(II).[234] The mono-ida and -mida complexes of nickel(II) react with cyanide by rapid reversible addition of two cyanides; the rate-determining step *en route* to $[Ni(CN)_4]^{2-}$ is reaction with a third cyanide. The overall reaction is thus again third-order in cyanide concentration. $[Ni(ida)_2]^{2-}$ and $[Ni(mida)_2]^{2-}$ react slowly with cyanide by parallel dissociative and associative paths; the Ni(ida) and [Ni(ida)(CN)]$^-$ so formed (or their mida analogues) then react rapidly with further cyanide to give $[Ni(CN)_4]^{2-}$.[235] Reaction of $[Ni(trien)]^{2+}$ with cyanide is fifth-order overall; first-order in complex, fourth-order in total cyanide concentration.[236]

Platinum(IV) *Complexes.* Substitution reactions at this d^6 centre are generally ligand replacements, but with the added feature of marked catalysis by platinum(II) compounds. Indeed, this area is as much one of inner-sphere redox reactions as of substitution. Recent kinetic studies include those of substitution at *trans*-$[PtCl_2L_4]^{2+}$, where L = NH_3, amine,

[229] G. D. Howard and R. S. Marianelli, *Inorg. Chem.*, 1970, **9**, 1738.
[230] R. W. Kluiber, R. Kukla, and W. de W. Horrocks, *Inorg. Chem.*, 1970, **9**, 1319.
[231] K. Saito and K. Masuda, *Bull. Chem. Soc. Japan*, 1970, **43**, 119.
[232] A. W. Chester, *Inorg. Chem.*, 1970, **9**, 1746.
[233] R. C. Fay, *Ann. New York Acad. Sci.*, 1969, **159**, 152.
[234] J. P. Jones and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 1486.
[235] L. C. Coombes and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1711.
[236] G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 1125.

or diars,[237] and at $[PtCl_4L_2]$, where L = NH_3 or $MeNH_2$.[238] In this last case the details of the mechanism were probed by studying the effects of added halides on rates. The observed effects were interpreted in terms of the relative stabilities of $[Pt^{II}XL_4]^+$ adducts, with the high catalytic activity of $[Pt(diars)]^{2+}$ ascribed to the particularly high stability of $[PtX(diars)]^+$. Other methods of probing mechanistic details include the study of solvent variation and consequent ion-pairing effects[239] and of the effect of the overall charge on complexes.[240] In the latter work, *cis*-effects on reactivities were examined and found to be, like charge effects, minor.

Replacement of chloride or bromide in *trans*-$[Pt(oxalate)_2X_2]$ by iodide proceeds by reduction to $[Pt^{II}(oxalate)_2]^{2-}$, followed by oxidative addition to give the *trans*-$[Pt^{IV}(oxalate)_2I_2]$ product.[241] Reaction of $[Pt(SCN)_6]^{2-}$ with bases similarly has as its first step formation of $[Pt^{II}(SCN)_4]^{2-}$.[242] The replacement of one bromide by chloride in *trans*-$[Pt(CN)_4Br_2]^{2-}$ and *trans*-$[Pt(NO_2)_4Br_2]$ is catalysed by $[Pt(CN)_4]^{2-}$ or $[Pt(NO_2)_4]^{2-}$. The reactions follow a third-order rate law; the mechanism is the usual inner-sphere redox mechanism of substitution. In the cyanide case there is an additional term independent of chloride concentration in the rate law, indicating a solvent-assisted path.[243] Closely related to these systems is the oxidative addition of bromine to $[Pt(CN)_4]^{2-}$ to give *trans*-$[Pt(CN)_4Br_2]^{2-}$, which has been studied in acid solution by stopped-flow techniques. Here initial fast production of *trans*-$[Pt(CN)_4(OH_2)Br]^-$ is followed by slow displacement of water by bromide, which explains the marked catalytic effect of added bromide on the overall reaction.[219]

Palladium(IV) *Complexes.* Reactions at palladium(IV) resemble those at platinum(IV), although the mechanism of reaction of $PdCl_6^{2-}$ with thiomorpholine (T) is relatively complicated. A series of substitution processes to give $[PdCl_5(OH)]^{2-}$, then $[PdCl_5T]^-$, and then $[PdCl_3(OH)T_2]$ precedes the reduction step to $[PdCl_2T_2]$, which in turn hydrolyses to give the observed $[Pd(OH_2)_2T_2]$ product.[244]

Edta and Related Ligands.—In an earlier paragraph, replacement of cydta by the simple ligand cyanide was reported.[234] In this section we are concerned with the replacement of one ligand of the edta family by another. Such ligand exchange or replacement can occur by completely or partially dissociative processes. The former simply involves complete dissociation of the outgoing ligand before complex formation with the replacing ligand occurs: *e.g.*

[237] A. Peloso, *Gazzetta*, 1969, **99**, 1025; 1970, **100**, 188.
[238] A. Peloso, *Gazzetta*, 1969, **99**, 723.
[239] A. Syamal and R. C. Johnson, *Inorg. Chem.*, 1970, **9**, 265; A. Peloso, B. Corain, and M. Bressan, *Gazzetta*, 1969, **99**, 111.
[240] S. G. Bailey and R. C. Johnson, *Inorg. Chem.*, 1969, **8**, 2596.
[241] A. J. Poë and D. H. Vaughan, *J. Chem. Soc.* (*A*), 1969, 2844.
[242] A. A. Grinberg and S. S. Borzakova, *Russ. J. Inorg. Chem.*, 1969, **14**, 1044.
[243] W. R. Mason, *Inorg. Chem.*, 1969, **8**, 1756; 1970, **9**, 1528.
[244] D. de Filippo, F. Devillanova, and C. Preti, *Inorg. Chim. Acta*, 1969, **3**, 341.

$$\left.\begin{array}{rcl} \text{M–edta} & \longrightarrow & \text{M} + \text{edta} \\ \text{M} + \text{edta*} & \longrightarrow & \text{M–edta*} \end{array}\right\} \quad (1)$$

In the partial dissociation mechanism, association of the incoming ligand with the metal begins before dissociation of the outgoing ligand is complete, giving an intermediate or intermediates in which the cation is bonded to both ligand molecules: *e.g.*

$$\begin{array}{rcl} \text{M–edta} + \text{edta*} & \longrightarrow & \text{edta–M–edta*} \\ & \longrightarrow & \text{edta} + \text{M–edta*} \end{array} \quad (2)$$

A variant of this mechanism is sometimes encountered in which the formation of the mixed ligand complex is preceded by a kinetically distinguishable pre-equilibrium partial dissociation of the starting complex: *e.g.*

$$\text{M}\begin{smallmatrix}\text{L}\\ \text{L}\end{smallmatrix}\!\!\left(\right) \rightleftharpoons \text{M–L–L} + \text{L–L*} \longrightarrow \text{L–L–M–L–L*}$$

$$\longrightarrow \text{L–L} + \text{M}\begin{smallmatrix}\text{L}\\ \text{L}\end{smallmatrix}\!\!\left(\right)^{*} \quad (3)$$

The denticity of the ligands in the intermediates of equations (2) and (3) is difficult to determine, though attempts have been made in certain systems, for example in nitriloacetate exchange.[245] Any of the paths described above may be acid catalysed, as is illustrated in, for example, edta exchange studies.[246]

Systems studied and their reaction mechanisms are listed in Table 4, for ligand exchange, and Table 5, for ligand replacement. It is difficult to pick out general reactivity trends from the assembled results. The partial dissociation path of equation (2) is subject to steric discouragement; complexes of cydta often react only by the complete dissociation path of equation (1) (see Table 5). The importance of steric control is also illustrated by the difference between trien and Me_4trien as entering ligands.[247] The relatively greater stability of five-membered than of six-membered chelate rings (as from aspartate) is also reflected in rates of ligand replacement.[248]

The effect of added ligands on this type of reaction has been studied for the replacement of edta complexed to nickel(II) by Eriochrome Black T.

[245] D. L. Rabenstein and R. J. Kula, *J. Amer. Chem. Soc.*, 1969, **91**, 2492.
[246] T. Asano, S. Okada, K. Sakamoto, S. Taniguchi, and Y. Kobayashi, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2127.
[247] G. K. Pagenkopf and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 2683.
[248] M. Kodama and T. Ueda, *Bull. Chem. Soc. Japan*, 1970, **43**, 419.

Table 4 *Mechanisms of ligand exchange for complexes of the edta family of ligands*

Cation	*Ligand*	*Mechanism*[a]	*Ref.*
Lead(II)	nta	D, DA	245
Nickel(II)	edta	DA	249
Cadmium(II)	nta	D, DA	245
Zinc(II)	nta	D, DA	245
Neodymium(III)	dtpa	DA	250
Lutecium(III)	edta	D(DA)	246

[a] D = *via* complete dissociation path of equation (1); DA = *via* partial dissociation path of equation (2); minor pathways indicated by brackets.

Table 5 *Mechanisms of ligand replacement in edta-type complexes*

Complex	*Incoming ligand*	*Mechanism*[a]	*Ref.*
Cobalt(II)–cydta	ebt		251
–egta	par	DA	252
–nta	cydta		253
Nickel(II)–asp	cydta		248
–asp	dtpa	QDA	248
–cydta	ebt		251
–ida	cydta		253
–ida	dtpa	QDA	248
–ida	edta		253
–ndap	edta	D, DA	254
–ndaip	edta	D, DA	254
–nta	cydta	D	255
–nta	dtpa	DA	256
–tda	cydta	D	254
–tda	edta	D, DA	254
Copper(II)–edta	mnt	D, DA	257
–ndap	cydta	D	258
–nta	cydta	D	258
–nta	mnt	D, DA	257
–par	egta	QDA	259
–trigly	edda	D, DA	247
–trigly	trien	D, DA	247
–trigly	edta	D	247
–trigly	nta	D	247
–trigly	Me_4 trien	D	247
Lanthanide(III)–xyl	edta	D	260

[a] D = *via* complete dissociation path of equation (1); DA = *via* partial dissociation path of equation (2); QDA = *via* pre-equilibrium path of equation (3).

[249] J. D. Carr and C. N. Reilley, *Analyt. Chem.*, 1970, **42**, 51.
[250] T. Asano, S. Okada, and S. Taniguchi, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1287.
[251] M. Kodama, C. Sasaki, and K. Miyamoto, *Bull. Chem. Soc. Japan*, 1969, **42**, 163.
[252] S. Funahashi and M. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 763.
[253] M. Kodama, *Bull. Chem. Soc. Japan*, 1969, **42**, 3330.
[254] M. Kimura, *Bull. Chem. Soc. Japan*, 1969, **42**, 2844.
[255] M. Kimura, *Bull. Chem. Soc. Japan*, 1969, **42**, 2841.
[256] M. Kodama, *Bull. Chem. Soc. Japan*, 1969, **42**, 2532.
[257] D. A. Sweigart and D. G. DeWit, *Inorg. Chem.*, 1970, **9**, 1580.
[258] M. Kimura, *Bull. Chem. Soc. Japan*, 1969, **42**, 3588.
[259] S. Funahashi, S. Yamada, and M. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 769.
[260] E. P. Zhuchenko, L. I. Budarin, and K. B. Yatsimirskii, *Teor. i eksp. Khim.*, 1969, **5**, 507 (*Chem. Abs.*, 1970, **72**, 25,477k).

Here added ammonia or thiocyanate inhibit reaction by forming mixed ligand chelates of some stability.[261]

8 Metal Exchange and Displacement

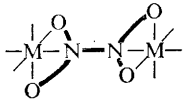
There is the same choice of completely dissociative or concurrent dissociation–association mechanisms here as for ligand replacement when polydentate ligands, especially of the edta type, are involved: *e.g.*

$$\left.\begin{array}{rcl} \text{M–edta} & \longrightarrow & \text{M + edta} \\ \text{M* + edta} & \longrightarrow & \text{M*–edta} \end{array}\right\} \quad (4)$$

or

$$\text{M–edta + M*} \longrightarrow \text{M–edta–M*} \longrightarrow \text{M + edta–M*} \quad (5)$$

The intermediate M–edta–M* of equation (5) may have the structure (20), as suggested for reaction of, *inter alia*, the budta complex of cobalt(II) with zinc(II).[262] Systems studied recently are listed with an indication of their mechanisms, in Table 6 for metal exchange, and in Table 7 for metal replacement. Again, as in the previous section, acid catalysis is an important feature in most systems, and bulky ligands such as cydta influence reaction mechanisms.



(20)

Table 6 *Mechanisms of metal exchange for complexes of edta and related ligands*

Cation	*Ligand*	*Mechanism*[a]	*Ref.*
Cerium(IV)	egta	D, DA	263
Yttrium(III)	dtpa, edta		264
Neodymium(III)	dtpa		264
Europium(II)	dtpa, edta		264

[a] D = *via* complete dissociation path of equation (4); DA = *via* dissociation–association path of equation (5).

Kinetics of displacement of alkaline-earth cations from their cydta complexes by lead(II),[265] or by a variety of other cations including protons,[270] have been suggested as the basis of a differential analytical method for the determination of metal ions.

[261] M. Kodama and K. Miyamoto, *Bull. Chem. Soc. Japan*, 1969, **42**, 833.
[262] H. Ogino, T. Baba, and N. Tanaka, *Bull. Chem. Soc. Japan*, 1969, **42**, 1578.
[263] B. Wiseall and C. Balcombe, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1751.
[264] V. V. Fomin, E. P. Maiorova, and G. A. Leman, *Russ. J. Inorg. Chem.*, 1969, **14**, 1000.
[265] J. B. Pausch and D. W. Margerum, *Analyt. Chem.*, 1969, **41**, 226.

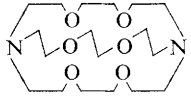
Table 7 *Mechanisms of cation replacement in complexes of ligands of the edta type*

Complex	*Replacing cation*	*Mechanism*[a]	*Ref.*
M(II)[b]–cydta	Lead(II)	D	265
Manganese(II)–cydta	Cobalt(II)	D, DA	266
–cydta	Copper(II)	D, DA	266
Cobalt(II)–budta	Zinc(II)	D	262
–pdta	Zinc(II)	D, DA	262
Cadmium(II)–cydta	Lead(II)	D	267
Ln(III)[b]–cydta	Copper(II)	D	268
Europium(III)–terpy	Terbium(III)	D[c]	269

[a] D = *via* complete dissociation path of equation (4); DA = *via* dissociation–association path of equation (5). [b] M(II) = alkaline earth cation; Ln(III) = lanthanide cation. [c] In nitromethane solution.

The effects of added ions on rates, arising from competitive formation of intermediate mixed complexes, have been described for acetate on the reaction of the edta complex of manganese(II) with cobalt(II),[271] for acetate and phthalate on cobalt(II)–nta plus nickel(II),[272] and for copper(II) or excess lead(II) on cadmium(II)–cydta plus lead(II).[267]

Preliminary kinetic results on cation exchange in cryptates [ligand (21)] show some correlation with thermodynamic parameters, but only go a small way towards the complete elucidation of the mechanism.[273] Metal replacement in complexes of macrocyclic ligands is also illustrated by studies of several metalloporphyrins.[274]



(21)

9 Isomerisation

Chromium(III) and Cobalt(III) Complexes.—Just as copper(II) catalyses aquation of oxalato-complexes of chromium(III) (cf. Section 3, ref. 117), so do a variety of cations catalyse isomerisation of *trans*-$[Cr(oxalate)_2(OH_2)_2]^-$. Rate constants are a function of the charge, radius, and structure of the

[266] M. Kimura, *Nippon Kagaku Zasshi*, 1969, **90**, 1246 (*Chem. Abs.*, 1970, **72**, 71,086e).
[267] G. F. Smith and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 135.
[268] E. Brucher and P. Szarvas, *Magyar Kém. Folyóirat*, 1969, **75**, 405 (*Chem. Abs.*, 1969, **71**, 129,233y).
[269] G. H. Frost and F. A. Hart, *Chem. Comm.*, 1970, 836.
[270] D. W. Margerum, J. B. Pausch, G. A. Nyssen, and G. F. Smith, *Analyt. Chem.*, 1969, **41**, 233.
[271] M. Kimura, *Bull. Chem. Soc. Japan*, 1969, **42**, 404.
[272] M. Kimura, *Bull. Chem. Soc. Japan*, 1969, **42**, 407.
[273] J. M. Lehn, J. P. Sauvage, and B. Dietrich, *J. Amer. Chem. Soc.*, 1970, **92**, 2916.
[274] C. Grant and P. Hambright, *J. Amer. Chem. Soc.*, 1969, **91**, 4195.

added cation; there is a significant variation in activation enthalpies with cation.[275] The particular case of the H^+ cation has been studied in detail; isomerisation rates increase unexpectedly rapidly at high hydrogen ion concentrations. A modified Hammett treatment of the rate-constant variation indicates ligand protonation, for which deuterium solvent effects provide supporting evidence.[276] The pH–rate profile and respective activation parameters have been determined for the pH range covering *trans*-$[Cr(oxalate)_2(OH_2)]^-$, $[Cr(oxalate)_2(OH)(OH_2)]^{2-}$, and $[Cr(oxalate)_2(OH)_2]^{3-}$.[277] Further information germane to isomerisation mechanisms for these complexes is provided by kinetic studies of ligand exchange.[278]

Isomerisation studies of cobalt(III) complexes cover a variety of compounds. The rate law for isomerisation of $[Co(dien)(OH_2)_3]^{3+}$ indicates some isomerisation *via* the hydroxo-cation $[Co(OH)dien(OH_2)_2]^{2+}$. Rates and activation parameters for direct isomerisation of the tris-aquo-complex were determined.[279] Further kinetic results for isomerisation of *cis*- and *trans*-$[Co(OH)_2\,en_2]^+$ in strongly basic solution indicate an intramolecular mechanism.[280] Isomerisation of *cis*-$[CoCl_2(diars)_2]^+$ in methanol is also intramolecular,[281] but isomerisation of *cis*-$[Co(O_2C\cdot CH_3)_2\,en_2]^+$ in acetic acid occupies an intermediate position between intra- and inter-molecularity, for the essential step is solvent-assisted acetate exchange within ion-pairs. This assignment of mechanism results from consideration of kinetics of acetate exchange as well as of isomerisation.[232, 282]

The preceding examples have been of interconversion of geometrical isomers. Conversion of $[Co(SCN)(NH_3)_5]^{2+}$ to its linkage isomer $[Co(NCS)(NH_3)_5]^{2+}$ is intramolecular, as has been demonstrated by tracer experiments. A π-thiocyanate intermediate is possible.[172] Linkage isomerisation in $Ru(NH_3)_5(N_2)^{2+}$ has been investigated qualitatively by tracer techniques. The mechanism again appears to be intramolecular.[283]

Complexes of Acac and Related Ligands.—Isomerisation of complexes of acac and of its fluoro-derivatives tfac and hfac is generally intramolecular. Whether the mechanism involves reversible dissociation of one end of the ligand molecule or simply twisting without any bond breaking, is still a matter for discussion and dispute. The isolation and kinetic study of aquation intermediates containing monodentate en and mono- or

[275] H. Kelm, H. Stieger, and G. M. Harris, *Z. phys. Chem.* (*Frankfurt*), 1969, **67**, 98.
[276] H. Kelm, H. Stieger, and G. M. Harris, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 939.
[277] H. Kelm and G. M. Harris, *Z. phys. Chem.* (*Frankfurt*), 1969, **66**, 8.
[278] H. Stieger, G. M. Harris, and H. Kelm, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 262.
[279] P. Wilairat and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2293.
[280] M. E. Farago, B. A. Page, and C. F. V. Mason, *Inorg. Chem.*, 1969, **8**, 2270.
[281] A. Peloso and G. Dolcetti, *J. Chem. Soc.* (*A*), 1969, 1506.
[282] A. W. Chester, *Inorg. Chem.*, 1969, **8**, 1584.
[283] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 2560.

bi-dentate dien [284] makes the postulation of isomerisation intermediates containing monodentate acac acceptable. Further support is provided by a mass spectrophotometric study of the gas-phase decomposition of several tris-hfac complexes, where loss of the first hfac ligand demonstrably occurs in two distinct stages.[285] Intramolecular isomerisation *via* monodentate diketone intermediates is the mechanism favoured for the mixed ligand complexes $Ga(acac)_2(hfac)$ and $Ga(acac)_2(bzbz)$. As hfac is the weakest of the three chelating ligands the lower activation energy reported for $Ga(acac)_2(hfac)$ is not unexpected.[286] Kinetic measurements in the presence of excess ligands confirm the intramolecularity of isomerisation of *cis*-$[Ti(acac)_2(OR)_2]$. The rate of isomerisation is not a function of concentration of the complex, so a dimeric transition state can be ruled out. Activation energies increase with increasing size of R. This trend disfavours a dissociative mechanism involving intermediates containing monodentate acac, and thus an intramolecular twist is indicated.[287] In alkyltin complexes $Sn(LL)_2R_2$, where LL = acac, hfac, or bzbz, and R = Me, Et, Bu, or Ph, there is rapid ligand rearrangement, but it is not apparent from the n.m.r. results reported whether this is inter- or intramolecular.[288]

Variable temperature n.m.r. studies on $Zr(\pi\text{-}C_5H_5)(tfac)_3$ and $Zr(\pi\text{-}C_5H_5)(hfac)_3$ in acetone or methylcyclohexane solution reveal two coalescence temperatures. Presumably there are two rearrangement processes; mechanistic speculation is minimal in this preliminary report.[289] The compound $SiMe_3(acac)$ is four-co-ordinate and contains unidentate acac. Variable temperature n.m.r. spectra yield values for rate constants and activation parameters for the intramolecular exchange of bonded oxygen atoms of the acac. This reaction presumably proceeds through a five-co-ordinate transition state or intermediate in which two acac-oxygens are attached to the silicon.[290]

Tropolonates are structurally analogous to acac complexes. Their mechanisms of isomerisation or rearrangement can also be monitored by variable temperature ^1H n.m.r. studies.[291]

Inversions.—Currently there is considerable interest in comparing rates of inversion at nitrogen with rates of hydrogen exchange for cobalt(III) and for platinum(II) complexes of ethylenediamine derivatives. Previous work has suggested that, whereas in cobalt(III) systems rates of hydrogen exchange

[284] R. F. Childers, K. G. Vander Zyl, D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 1968, **7**, 749, 2678; G. B. Kauffman, *ibid.*, p. 1694; G. Schwarzenbach and B. Magyar, *Helv. Chim. Acta*, 1962, **45**, 1454; and refs. 106, 176, in this chapter.
[285] R. D. Koob, M. L. Morris, A. L. Clobes, L. P. Hills, and J. H. Futrell, *Chem. Comm.*, 1969, 1177.
[286] T. J. Pinnavaia, J. M. Sebeson, and D. A. Case, *Inorg. Chem.*, 1969, **8**, 644.
[287] D. C. Bradley and C. E. Holloway, *J. Chem. Soc.* (*A*), 1969, 282.
[288] C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, 1969, **8**, 138.
[289] M. Elder, J. G. Evans, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1969, **91**, 1245.
[290] J. T. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.*, 1969, **91**, 5378.
[291] E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, 1969, **91**, 4420.

are much faster than rates of inversion at nitrogen, in platinum(II) complexes these two processes have comparable rates. Further reports on platinum(II) do not fit this generalisation.[292–294] For *N*-methyl derivatives of ethylenediamine, hydrogen-exchange rates are much greater than inversion rates, as in cobalt(III) systems.[293] A similar situation prevails for sarcosine or edda complexes.[294] Inversion at nitrogen in these complexes is thought not to involve participation of platinum *d*-orbitals, in contrast to earlier suggestions of involvement of these orbitals in inversion in similar compounds.[295] Inversion at carbon rather than at nitrogen is involved in glutamate complexes.[296] Isomerisation of the three isomers of β_2[Co(trien){*N*-Me-(*S*)-ala}]$^{2+}$ involves independent inversion at asymmetric nitrogen and carbon.[297] Racemisation (inversion) and hydrogen exchange at nitrogen co-ordinated to platinum(IV), in methyl-substituted ethylenediamine complexes, proceed through a common deprotonated intermediate.[298] Inversion at nitrogen is also the key to reactivity in aquation of the nickel complex of *cis*,*cis*-1,3,5-triaminocyclohexane, described earlier.[161]

The barrier to chelate ring-inversion in [Co en_3]$^{3+}$ in acetone solution was estimated several years ago.[299] Presumably this inversion barrier will be strongly solvent-sensitive, though evidence to support this is scant. The ^{1}H n.m.r. spectrum of [Co en_3]$^{3+}$ in isobutyric acid varies with temperature, but is invariant in several other solvents.[300] Rhodium(III) and platinum(IV) analogues have been reported to invert rapidly, but the n.m.r. spectrum of [Ru en_3]$^{2+}$ shows well-defined fine structure consistent with inversion that is slow on the n.m.r. time scale.[301] The equivalence or non-equivalence of protons in [M en_3]$^{n+}$ cations has been discussed in relation to these variable temperature n.m.r. studies.[302] Though the difference in free energy between various conformations of [Ni en_3]$^{2+}$ is about 300 cal ring^{-1} (say for D-*kkk* → D-*kkk'*), the free energy of activation for interconversion of the enantiomers D-*kkk* to L-*k'k'k'* is as high as 15·7 kcal mol^{-1} at 101 °C. An intramolecular mechanism seems likely.[303]

There remain to report two further examples — inversion at cobalt(II) in the complex Co(acac)$_2$(4,7-diMe phen),[304] and intramolecular rearrangement in edta complexes of uranium.[305]

[292] L. E. Erickson, *J. Amer. Chem. Soc.*, 1969, **91**, 6284.
[293] J. B. Goddard and F. Basolo, *Inorg. Chem.*, 1969, **8**, 2223.
[294] L. E. Erickson, H. L. Fritz, R. J. May, and D. A. Wright, *J. Amer. Chem. Soc.*, 1969, **91**, 2513.
[295] See, *e.g.*, P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1968, **90**, 2293.
[296] L. E. Erickson, A. J. Dappen, and J. C. Uhlenhopp, *J. Amer. Chem. Soc.*, 1969, **91**, 2510.
[297] D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, *Chem. Comm.*, 1969, 581.
[298] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1969, **91**, 5227.
[299] B. M. Fung, *J. Amer. Chem. Soc.*, 1967, **89**, 5788.
[300] H. Yoneda, M. T. Emerson, and Y. Morimoto, *Inorg. Chem.*, 1969, **8**, 2214.
[301] H. Elsbernd and J. K. Beattie, *J. Amer. Chem. Soc.*, 1969, **91**, 4573.
[302] T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, 1970, **9**, 1299.
[303] F. F.-L. Ho and C. N. Reilley, *Analyt. Chem.*, 1970, **42**, 600.
[304] G. N. La Mar, *J. Amer. Chem. Soc.*, 1970, **92**, 1806.
[305] D. L. Ehman and D. T. Sawyer, *Inorg. Chem.*, 1970, **9**, 204.

5
Reactions of Co-ordinated Ligands

Some instances of reactions of co-ordinated ligands have already been mentioned in Chapter 4 of Part II. For example, aquation of nitrito-complexes of chromium(III) takes place by nitrogen–oxygen rather than chromium–oxygen bond fission.[1] Similarly, the acid-catalysed aquation of $[Co(NCO)(NH_3)_5]^{2+}$ involves ligand carbon–nitrogen bond breaking.[2] Mercury(II)[3] and silver(I)[4] assisted aquation of halide complexes, and nitrous-acid-catalysed aquation of azide complexes[5] also involve reaction at the respective co-ordinated ligands as primary steps.

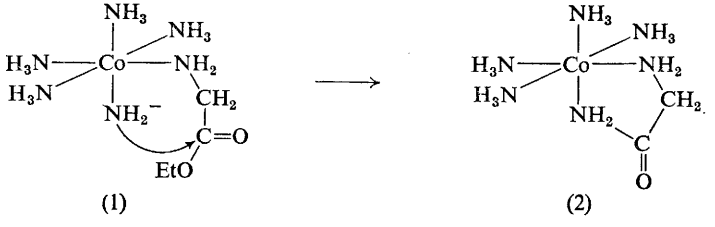
One of the most active areas in research into mechanisms of reactions of co-ordinated ligands is that of transition-metal-catalysed formation and hydrolysis of large organic molecules, for instance Schiff bases derived from amines and carbonyl compounds. In the cases of bis-(8-mercapto-quinoline)nickel(II) reacting with alkyl or aryl halides[6] or of tris-(*o*-benzyl-dithiocarbamato)cobalt(III) with n-propylamine[7] one of the organic reagents is already co-ordinated to the metal ion. More usually, the two organic species and the metal ion are mixed together and the kinetic and mechanistic problem is to determine the nature of the intermediates formed *en route* to the organic product. This is the field of 'template reactions' which, in view of their biochemical significance, are documented in Part III, towards the end of the second chapter. A wider, though qualitative, study of mechanisms of reactions of co-ordinated Schiff bases and related ligands has included ester exchange, racemisation, and hydrolysis of copper(II) complexes.[8]

In the base hydrolysis of β-[Co(glycylglycine) trien]$^{3+}$ the rate of fission of the peptide linkage is over 10^4 times faster than in free glycylglycine.[9] The effects of chelation on rates of ester hydrolysis have been investigated

[1] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1969, 219, 1977.
[2] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1970, **9**, 1567.
[3] *E.g.*, S. C. Chan and S. F. Chan, *J. Chem. Soc.* (*A*), 1969, 202; H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, 1969, **91**, 563; D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 11.
[4] *E.g.*, G. C. Lalor and D. S. Rustad, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3219.
[5] R. C. Thompson and E. J. Kaufmann, *J. Amer. Chem. Soc.*, 1970, **92**, 1540; S. P. Ferraris and E. L. King, *ibid.*, p. 1215.
[6] J. A. Burke and E. C. Brink, *Inorg. Chem.*, 1969, **8**, 386.
[7] J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.
[8] R. D. Gillard and R. Wootton, *J. Chem. Soc.* (*B*), 1970, 364.
[9] R. W. Hay and P. J. Morris, *Chem. Comm.*, 1969, 1208.

for cysteine methyl ester,[10] for histidine methyl ester,[11] for base hydrolysis of glycine esters complexed to cobalt(III),[12] and for Cu(L-valine-*N*-monoacetato) (ester) where ester = methyl leucinate or methyl phenylalaninate.[13] In the last case, the D-amino-acid ester is hydrolysed more rapidly than the L-amino-acid ester; this, therefore, is one of the simplest enzyme models to show stereoselectivity. The difference in rates is paralleled by the difference in stability constants for the complexes of the two stereoisomers. Tracer studies show that hydrolysis of t-butylglycinate complexed to cobalt(III) occurs *via* alkyl–oxygen fission, in contrast to the analogous methyl compound, where hydrolysis proceeds *via* acyl–oxygen fission. This disparity of behaviour exactly parallels that for (uncomplexed) t-butyl acetate, hydrolysed by alkyl–oxygen fission, and primary and secondary acetates, hydrolysed by acyl–oxygen fission; reaction rates are very much faster for the cobalt complexed glycinates than for the acetates.[14] Mercury(II)-assisted hydrolysis of $[CoBr(t\text{-butylglycine})\,en_2]^{2+}$ also results in ester hydrolysis, and again hydrolysis involves alkyl–oxygen bond fission as opposed to the acyl–oxygen fission observed for the ethyl ester complex.[15]

While it is often assumed that in nucleophilic attack at a co-ordinated ligand the nucleophile co-ordinates to the metal prior to its attack at the ligand, this mechanism is rarely unambiguously proved to be correct. Amidolysis of the ethyl ester of glycine complexed to pentamminecobalt(III) has now been shown to be an example of intramolecular nucleophilic attack at a co-ordinated ligand. Loss of a proton from one of the co-ordinated ammonias, giving (1), generates an $-NH_2$ ligand which attacks



(1) (2)

the carbonyl carbon of the ester and displaces OEt^- to give the characterised bidentate glycine imide complex (2).[16] Another example of nucleophilic attack at a co-ordinated ligand, though not this time internal attack, is afforded by the reaction of 3-bromopentane-2,4-dione (or γ-bromoacetylacetone) complexes with thiophenols.[17] The tautomerisation of the enol

[10] R. W. Hay and J. L. Porter, *J. Chem. Soc.* (*A*), 1969, 127.
[11] R. W. Hay and P. J. Morris, *Chem. Comm.*, 1969, 18.
[12] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1969, **91**, 4102.
[13] B. E. Leach and R. J. Angelici, *J. Amer. Chem. Soc.*, 1969, **91**, 6296.
[14] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *Austral. J. Chem.*, 1969, **22**, 2479.
[15] Y. Wu and D. H. Busch, *J. Amer. Chem. Soc.*, 1970, **92**, 3326.
[16] D. A. Buckingham, D. N. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1969, **91**, 3451.
[17] Z. Yoshida, H. Ogoshi, and Y. Shimidzu, *Tetrahedron Letters*, 1969, 2255.

form of pentane-2,4-dione is catalysed by metal ions, through rate-determining attack of hydrated protons at the co-ordinated enolate.[18]

A thorough investigation of ^{18}O-exchange kinetics for $[Co(oxalate)_3]^{3-}$ has shown that, contrary to earlier suggestions that all twelve oxygen atoms exchange, in fact only six exchange with solvent oxygen. Oxygen exchange rates are also reported for related complexes $[M(oxalate)_n(LL)_{3-n}]^{(2n-3)-}$ where M = Co or Cr, and LL = en, bipy, or phen.[19] Oxygen exchange and racemisation rates have been compared for some of these mixed oxalate complexes.[20] Kinetics of oxidation of co-ordinated oxalate, in chromium(III) or rhodium(III) complexes, by cerium(IV) in sulphuric acid indicate stepwise oxidation of the oxalates, with transfer of the first electron rate-determining, as in oxidation of *cis*-$[Cr(oxalate)_2(OH_2)_2]^-$. A bridged or inner-sphere transition state is suggested for the electron-transfer steps. The activation enthalpy is much lower for the chromium(III) complexes than for the rhodium(III).[21] Oxidation of co-ordinated thiocyanate in $[Co(NCS)(NH_3)_5]^{2+}$ by a variety of oxidising agents has been described.[22] Hydration and isomerisation of maleate co-ordinated to chromium(III) has been qualitatively investigated.[23]

The reaction of azide complexes of ruthenium(III) with acid leads to the formation of mono- and di-nuclear nitrogen complexes of the type $[Ru(N_2)(NH_3)_5]^{2+}$ and $[(H_3N)_5RuN_2Ru(NH_3)_5]^{4+}$. Comparison of this behaviour with that of organic azides suggests the intermediacy of metal–nitrene complexes. This hypothesis is supported by the results of trapping experiments using thiourea, diethyl sulphide, and iodide as trapping reagents. The cation *trans*-$[Ir(N_3)_2\,en_2]^+$ behaves similarly, suggesting that iridium–nitrene complexes are also conceivable reaction intermediates, but there is no evidence for the formation of nitrene-containing species from azides of cobalt(III), rhodium(III), platinum(II), or palladium(II).[24] Nitrene intermediates may also be formed in the reaction of the pentacyanocobaltate(II) or hexacyanodinickel(I) ions with organic azides.[25]

Examples of reactions of co-ordinated ligands in square-planar complexes include hydrolysis of *trans*-$[PtCl(CO)(PR_3)_2]$,[26] the reaction of platinum(II)–alkene complexes with ethylamine,[27] and of palladium(II)–alkene complexes with n-butylamine.[28] In the last case there is evidence that the amine co-ordinates to the palladium before attack at the co-ordinated alkene occurs.

[18] J. E. Meany, *J. Phys. Chem.*, 1969, **73**, 3421.
[19] J. A. Broomhead, I. Lauder, and P. Nimmo, *Chem. Comm.*, 1969, 652.
[20] J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, 1970, **9**, 1243.
[21] M. W. Hsu, H. G. Kruszyna, and R. M. Milburn, *Inorg. Chem.*, 1969, **8**, 2201.
[22] A. R. Norris and D. Patterson, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3680.
[23] M. V. Olson and H. Taube, *J. Amer. Chem. Soc.*, 1970, **92**, 3236.
[24] L. A. P. Kane-Maguire, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 4609.
[25] W. C. Kaska, C. Sutton, and E. Serros, *Chem. Comm.*, 1970, 100.
[26] H. C. Clark and W. J. Jacobs, *Inorg. Chem.*, 1970, **9**, 1229.
[27] A. Panunzi, A. de Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, 1970, **92**, 3488.
[28] H. Hirai, H. Saurai, and S. Makishima, *Bull. Chem. Soc. Japan*, 1970, **43**, 1148.

6
Solvent Effects

The arrangement of Chapters 1 to 5 of this Part of this Report by type of compound results in a dispersal of references dealing with the role of the solvent. To remedy this, some of these references have been collected together here, both to illustrate current approaches to determining the role of solvents in inorganic reaction mechanisms and the use of rate-constant variation with solvent composition trends as diagnostic tools.

Solvation is of paramount importance in determining initial-state and transition-state energies and hence reaction rates. Quantitative studies of the effect of solvation on rates of inorganic reactions are relatively uncommon, though in recent months much material has appeared on bimolecular reactions of organotin compounds with mercury halides, which are described in more detail in Chapter 1 of this Part.[1] The importance of solvation in determining reactivity of square-planar complexes has long been recognised. Recently, several studies in non-polar solvents have illustrated the extreme case of non-polar solvents having a negligible effect on reactivity. In other words, values of k_1 in the normal two-term rate law for nucleophilic substitution at d^8 metal centres

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{nucleophile}]$$

which normally vary greatly with solvent, have been shown to be constant for a given reaction in several non-polar solvents. For example, exchange of acac with Pd $acac_2$ has practically the same k_1 value in benzene, anisole, and 1,2-dichloroethane.[2] Again, substitution by Group V bases at $Co(NO)(CO)_3$ follows a similar two-term rate law, with k_1 varying in THF, DMSO, and acetonitrile, but constant in the poor solvents cyclohexane, toluene, and nitromethane.[3]

The ability of polar solvents to solvate ions sometimes has an important effect on the mechanism of a reaction. Thus $N_2Me_4^+.I_2^-$ is an intermediate in the reaction of tetramethylhydrazine with iodine in polar solvents, but

[1] *E.g.*, M. H. Abraham, F. Behbahany, M. J. Hogarth, R. J. Irving, and G. F. Johnston, *Chem. Comm.*, 1969, 117; M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *ibid.*, p. 930; M. H. Abraham, R. J. Irving, and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 199.

[2] K. Saito and M. Takahashi, *Bull. Chem. Soc. Japan*, 1969, **42**, 3462.

[3] G. Cardaci, S. M. Murgia, and A. Foffani, *J. Organometallic Chem.*, 1970, **23**, 265.

not in non-polar.[4] A similar organometallic example is provided by the reaction of the dimer $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ again with iodine, where a cationic intermediate is involved in chloroform but not in n-hexane.[5] Acceleration of the reaction of hyponitrite with dinitrogen tetroxide on addition of a polar solvent is ascribed to the consequent formation of ions from the dinitrogen tetroxide.[6]

Mixed Solvents.—The main value of kinetic studies in mixed solvents is the possibility of following a constant reaction, particularly aquation, in a readily and continuously variable environment. Variation of rate constant with dielectric constant (D) has long been used as a source of evidence concerning mechanisms. Recently, the observation that the slopes of graphs of logarithms of rate constants against the function $(D - 1)/(2D + 1)$ are very different for hydrolysis and for ammonia attack at *trans*-$[PtCl_2(NH_3)_2]$ has been interpreted as indicating different mechanisms, associative for the ammonia attack, dissociative for hydrolysis. Similar plots for hydrolysis of *cis*-$[PtCl_2(NH_3)_2]$ and of $[PtCl_2\,en]$ have similarly been interpreted as evidence for a dissociative mechanism for these complexes also.[7] Other examples of rate *vs.* dielectric constant correlations include those for aquation of *cis*- and of *trans*-$[CoBr(NCS)\,en_2]^+$,[8] of $[Cl(NH_3)_4CoNH_2Co(NH_3)_4(OH_2)]^{5+}$,[9] and of $[CoX(SO_3)\,dmg]^{2-}$ and its protonated-sulphite analogue.[10]

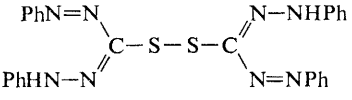
While dielectric constant is obviously an important factor in determining rates, the nucleophilicity of the solvent is also important, hence the preference in some quarters for correlating rates with the solvent parameter Y, or its spectroscopically-based relatives Z or E_T. These empirical parameters incorporate both of these solvent properties. Inorganic reactions studied recently are reported in the Table, which indicates the experimental conditions and gives the respective m values. These values are derived from the defining formula $\log_{10} k/k_0 = mY$, where k is the observed rate constant in the solvent of solvating power Y, k_0 is the rate constant in the reference solvent, and m is characteristic of the reaction — for S_N1 solvolysis of t-butyl chloride m is fixed at 1·00. It is difficult to draw firm conclusions from many m values for inorganic reactions, for there are generally two variables involved in relating them to the organic S_N1 reference value — the actual mechanism of the reaction and the solvation requirements of the centre whence the leaving group departs.

[4] D. Romans, W. H. Bruning, and C. Michejda, *J. Amer. Chem. Soc.*, 1969, **91**, 3859.
[5] D. A. Brown, A. R. Manning, and D. J. Thornhill, *Chem. Comm.*, 1969, 338.
[6] M. N. Hughes and H. G. Nicklin, *Chem. Comm.*, 1969, 80.
[7] V. D. Panasyuk and N. F. Malashok, *Russ. J. Inorg. Chem.*, 1968, **13**, 1405; 1969, **14**, 525, 661; *Dopovidi Akad. Nauk Ukr. R.S.R., Ser. B*, 1969, **31**, 39 (*Chem. Abs.*, 1969, **71**, 33,787f).
[8] V. D. Panasyuk and A. V. Arkharov, *Russ. J. Inorg. Chem.*, 1968, **13**, 1279.
[9] V. D. Panasyuk and E. R. Falendysh, *Russ. J. Inorg. Chem.*, 1969, **14**, 1456; *Dopovidi Akad. Nauk Ukr. R.S.R., Ser. B*, 1969, **31**, 536 (*Chem. Abs.*, 1969, **71**, 64,689e).
[10] G. P. Syrtsova and Nguen Zui Lyong, *Russ. J. Inorg. Chem.*, 1970, **15**, 243; G. P. Syrtsova, L. N. Korletyanu, and Nguen Zui Lyong, *ibid.*, p. 245.

Table *Values of* m *for inorganic reactions*

Bond	*Compound*	*Solvents*	m	*Ref.*
Boron–bromide	$Me_3N.BH_2Br$	dioxan(50—90%)–water	0·59	11
Sulphur–chloride	$Me_2N.SO_2Cl$	acetone(0—80%)–water	0·69	12
Sulphur–sulphur	(1)	ethanol–water	0·44	13
Iron–nitrogen	$Fe(CN)_2\ bipy_2$	ethanol(0—80%)–water	0·2	14
Manganese–bromide	*cis*-$[MnX_2(CO)_4]^-$	1,2-dichloroethane chloroform nitromethane	~ 0·3[a]	15
Carbon–chloride	$Pt(C_2HCl_3)(PPh_3)_2$	methanol; ethanol n-propanol isopropanol t-butanol acetic acid	0·6	16
Tin–carbon and mercury–chlorine	$SnEt_4 + HgCl_2$	methanol–water	0·715	17

[a] Value estimated indirectly *via* $\log k/E_T$ correlation.



(1)

Plots of activation enthalpies against activation entropies for aquation of *trans*-$[CoCl_2\ en_2]^+$ in a range of mixed aqueous solvents [18] and of logarithms of rate constants for aquation against equilibrium quotients for $[CoCl(NH_3)_5]^{2+}$ in aqueous ethanol [19] are both consistent with dissociative mechanisms.

Solvent Structure.—This is often reflected in kinetic parameters. Thus, the rate law for reaction of triphenylchlorosilane with isopropanol in carbon tetrachloride is of order 2·4 with respect to the isopropanol. This suggests that solvent polymers are reactive species in the rate-determining step.[20] The dependence of the rate constants for formation of $[Ni\ bipy]^{2+}$ on solvent fluidity both emphasises the importance of solvent structure in

[11] J. R. Lowe, S. S. Uppal, C. Weidig, and H. C. Kelly, *Inorg. Chem.*, 1970, **9**, 1423.
[12] O. Rogne, *J. Chem. Soc.* (*B*), 1969, 663.
[13] A. M. Kiwan and H. M. N. H. Irving, *Chem. Comm.*, 1970, 928.
[14] J. Burgess, *Chem. Comm.*, 1969, 1422.
[15] F. E. Smith and I. S. Butler, *Canad. J. Chem.*, 1969, **47**, 1311.
[16] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1969, **18**, 199.
[17] M. H. Abraham and G. F. Johnston, *J. Chem. Soc.* (*A*), 1970, 188.
[18] G. C. Lalor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1206.
[19] G. R. H. Jones, R. C. Edmondson, and J. H. Taylor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1752.
[20] A. D. Allen and S. J. Lavery, *Canad. J. Chem.*, 1969, **47**, 1263.

determining rates and suggests that some modification to the general formation mechanism of Eigen (see Part III) may be necessary for its successful extension to non-aqueous solvents.[21] The reaction of Ni^{2+} with 1,10-phenanthroline in aqueous methanol has also been studied.[22]

The effects of anion–solvent interactions on reactivities of cationic complexes and *vice versa* have been described for several systems. Rates of formation of $FeCl^{2+}$ increase at high concentrations of added chloride; reduced solvation of the ions at high ionic strengths is thought to facilitate their approach.[23] The variation of the activation energy for aquation of $[IrCl_6]^{3-}$ with the nature and concentration of added cations is attributed to the orientating effect of the added cations on the water surrounding the complex anion.[24] Effects of added cations on rates of formation of halide complexes of ruthenium(IV) are also attributed to their effects on the structure of the solvent water.[25] A slightly different situation obtains in the reaction of magnesium(II) with oxalate. The rate of reaction is considerably less than would be predicted from the charge : radius quotient for magnesium(II). The explanation proposed is that while larger cations, for which formation rates correlate with radius reciprocals for dipositive cations, influence significantly only the first solvation shell around themselves, the very small magnesium(II) cation exerts an influence on secondary water of solvation as well. This effectively increases the structure of the water in the vicinity and makes loss of water from the primary solvation shell and approach of oxalate more difficult.[26]

It is only rarely possible to probe the composition or structure of secondary solvation shells. One situation where this is possible is $[Cr(NCS)_6]^{3-}$ in solution in aqueous acetonitrile, described in Section 3 of Chapter 4.[27] Control over solvent shell composition in mixed solvents is most readily achieved by the use of mixtures of co-ordinating and non-co-ordinating solvents. Examples of applications of this include the study of DMSO exchange at nickel(II) in DMSO–nitromethane and DMSO–methylene chloride mixtures,[28] and of aquo-ions in methylene chloride.[29]

Molten Salts.—The number of studies of kinetics and mechanisms of inorganic reactions in molten salts is small. The investigation most closely related to the rest of this Report is that of substitution at chromium(III) in

[21] H. P. Bennetto and E. F. Caldin, *Chem. Comm.*, 1969, 599.
[22] M. L. Sanduja and W. MacF. Smith, *Canad. J. Chem.*, 1969, **47**, 3773.
[23] J. K. Rowley and N. Sutin, *J. Phys. Chem.*, 1970, **74**, 2043.
[24] V. I. Kravtsov, E. G. Tsventarnyi, G. P. Tsayun, and V. A. Yusupova, *Russ. J. Inorg. Chem.*, 1970, **15**, 42.
[25] A. A. Biryukov, V. I. Shlenskaya, and B. S. Rabinovich, *Russ. J. Inorg. Chem.*, 1969, **14**, 413.
[26] C.-T. Lin and J. L. Bear, *J. Inorg. Nuclear Chem.*, 1969, **31**, 263.
[27] L. S. Frankel, *J. Phys. Chem.*, 1969, **73**, 3897; 1970, **74**, 1645; L. S. Frankel, C. H. Langford, and T. R. Stengle, *ibid.*, 1970, **74**, 1376; S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, 1969, **91**, 2236.
[28] L. S. Frankel, *Chem. Comm.*, 1969, 1254.
[29] A. J. Leffler, *J. Phys. Chem.*, 1970, **74**, 2810.

molten hydrogen sulphates. Preliminary work on this has been published as the first instalment of a projected series on substitution at both chromium(III) and cobalt(III).[30] Nitrate melts are the most popular solvents; recent reports relate mainly to redox reactions. These include iodide oxidation,[31] oxalate oxidation,[32] the reaction of bromide with bromate and dichromate,[33] and the reaction of iodide with perchlorate.[34] The decomposition of nitrate melts at high temperatures, and the consequent effects on reaction mechanisms in such media, have been described.[35] Oxidation of chloride by iron(III) in molten lithium chloride–potassium chloride eutectic has been studied, and its mechanism compared with those of analogous reactions involving thallium(III) and copper(II).[36] Ultrasonic studies of zinc chloride have covered the range from aqueous solution through to molten salt.[37]

[30] J. A. Duffy and W. J. D. MacDonald, *J. Chem. Soc.* (*A*), 1970, 2066.
[31] R. B. Fulton and H. S. Swofford, *Analyt. Chem.*, 1969, **41**, 2027.
[32] J. M. Schlegal and C. A. Pitak, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2088.
[33] J. M. Schlegal, *J. Phys. Chem.*, 1969, **73**, 4152.
[34] R. M. Pansare, *High Temp. Sci.*, 1970, **2**, 31 (*Chem. Abs.*, 1970, **72**, 104,428y).
[35] R. N. Kust and J. D. Burke, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 333.
[36] I. Sláma and J. Mála, *Coll. Czech. Chem. Comm.*, 1969, **34**, 2134.
[37] G. S. Darbari, M. R. Richelson, and S. Petrucci, *J. Chem. Phys.*, 1970, **53**, 859.

Part III

COMPLEX FORMATION WITH LABILE METALS AND REACTIONS OF BIOCHEMICAL INTEREST

Introduction

In this Part we shall outline the present picture concerning complex formation in solution with labile metal ions, concentrating on work which was published during 1969 and 1970, and then discuss the mechanisms of biochemical reactions which involve metal ions. In the latter Chapter we shall always be interested primarily in the metal, and will also discuss many of the model systems which are so useful in an elucidation of the role of the metal in a complex biochemical situation. Although a discussion of mechanisms of reactions must rest heavily on the results of kinetic studies, we shall not take the two terms to be synonymous and will include other results, especially spectroscopic, where they seem to be particularly pertinent. (However, many spectroscopic and other equilibrium results have not been included because they did not appear to be directly relevant to the discussion.)

The first section of Chapter 2 has been devoted to a discussion of the problem of ion transport through biological membranes. Although this might not, strictly speaking, come under the general title of mechanism of metal action, it is a very important aspect of the role of metals in biological systems because, of course, metal ions have to be able to move selectively through biological membranes. Also, there is increasing evidence for the involvement of particular ions in such membrane-linked phenomena as the action of acetylcholinesterase in nerve cells and muscles. It is also an area in which there has been considerable research activity recently.

1
Complex Formation with Labile Metals

1 Introduction

Metal complex formation in solution can be represented by the general reaction (1), in which a solvent molecule S is replaced in the inner co-ordination sphere by the monodentate ligand X. Metal complexes can be classified as labile or inert, depending on whether or not it is possible to study their reactions kinetically with classical techniques and, until the last 10 or 15 years, a quantitative discussion[1, 2] was possible only for reactions involving such non-labile metals as Cr^{III}, Co^{III}, and Pt^{II}. More recently, the application of such techniques as flow, chemical relaxation, and nuclear magnetic resonance has provided many quantitative results on complex formation of labile metal ions and it is now profitable to discuss some of the finer mechanistic points for these metals also.[3–5]

$$(L)_m M(S)_n^{a+} + X \underset{k_d}{\overset{k_f}{\rightleftharpoons}} (L)_m M(S)_{n-1}(X)^{a+} + S \qquad (1)$$

Reaction (1) may be discussed in terms of the scheme shown in Figure 1 [since the majority of the work on metal complex formation has been done in aqueous solution, the general solvent S in reaction (1) has been replaced by H_2O]. One extreme is the S_N1 pathway (route I) in which the rate-determining step is the removal of a ligand molecule from the inner co-ordination sphere of the complex to give an intermediate of lower co-ordination number. The other extreme is the S_N2 pathway (route IIb), in which the bond-making process is as important as the bond-breaking process and the intermediate has an increased co-ordination number. (A somewhat different nomenclature has been introduced by Langford and Gray,[2] who classify route I as a Dissociative mechanism and route IIb as an Associative mechanism.) A considerable amount of effort has been put

[1] *E.g.* F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.
[2] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965.
[3] M. Eigen and R. G. Wilkins, A.C.S. Advances in Chemistry Series, 1965, No. 49, p. 55.
[4] A. McAuley and J. Hill, *Quart. Rev.*, 1969, **23**, 18.
[5] D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45.

into the task of distinguishing between these two extremes for non-labile metals. For example, it has been suggested [6] that the substitution reactions of $[Co(CN)_5X]^{3-}$ involve the limiting S_N1 mechanism, in which the penta-co-ordinate species $Co(CN)_5^{2-}$ is generated as a reactive intermediate.

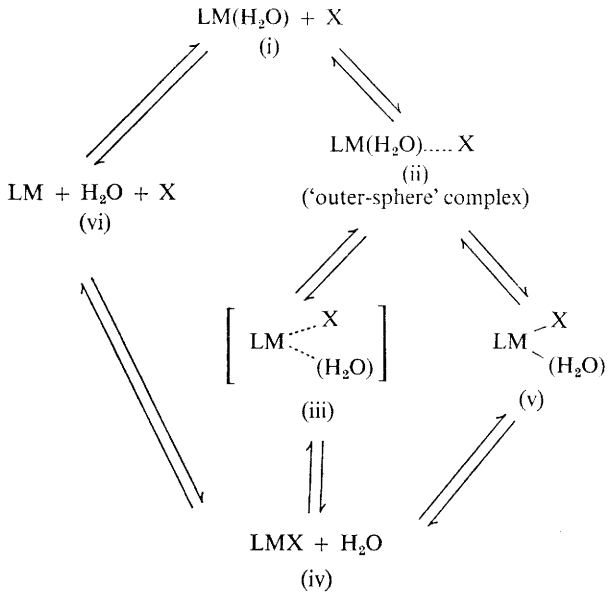


Figure 1 *Formation of metal complexes in aqueous solution. Route* I [(i) ⇌ (vi) ⇌ (iv)] *represents a limiting* S_N1 *mechanism, route* IIa [(i) ⇌ (ii) ⇌ (iii) ⇌ (iv)] *a concerted water-exchange mechanism, and route* IIb [(i) ⇌ (ii) ⇌ (v) ⇌ (iv)] *a limiting* S_N2 *mechanism*

Although the other extreme, the S_N2 mechanism, is thought to be followed in substitution at various square-planar complexes, there is little unequivocal evidence for this type of reaction with octahedral species. The fact is, however, that it has proved exceedingly difficult to differentiate between these two mechanistic extremes in the majority of cases. That being so, it is hardly surprising that the exact mechanism of complex formation at labile metal ions is also somewhat uncertain.

Substitution at a labile metal ion is generally discussed in terms of the mechanism IIa, which was proposed by Eigen [7] as a result of his work with chemical relaxation techniques and discussed further in his review with Wilkins.[3] The hydrated metal ion and the hydrated ligand diffuse together rapidly to form an outer-sphere complex (sometimes called, more specifically, an ion-pair) in which the lone-pairs on the ligand are separated

[6] A. Haim, R. J. Grassi, and W. K. Wilmarth, A.C.S. Advances in Chemistry Series, 1965, No. 49, p. 31.

[7] M. Eigen, *Pure Appl. Chem.*, 1963, **6**, 97.

from the metal ion by the inner co-ordination sphere of the metal. (The water surrounding the ligand, being generally less strongly held than that surrounding the metal, is displaced more readily. This first step can therefore be regarded as a composite one comprising diffusion and water-loss at the ligand.) This is followed by the loss of the water molecule from the inner co-ordination sphere of the metal, coupled with the formation of the M—L bond. As we have indicated, the exact mechanism of complex formation is not known and, indeed, it might even not be meaningful to try and distinguish between an S_N1- and an S_N2-type process at a labile metal ion, since complex formation is almost certainly a concerted process in which water and the incoming ligand change places [*via* (iii)].

Metals can be classified according to the relative rates of steps (i) → (ii) and (ii) → (iv). Group *A* contains metal ions which have a comparatively low charge density at their surface; for example, the alkali metals (including Li^+) and the heavier alkaline earths (Ca^{2+}, Sr^{2+}, and Ba^{2+}). The water molecules are held comparatively weakly, with the result that steps (i) → (ii) and (ii) → (iv) have comparable rates. Group *B* contains metals of intermediate surface charge density, in which the water molecules are held moderately strongly, so that the second step is now rather slower than the first. This group includes many bivalent metals, such as Mg^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}. Group *C* contains metal ions of sufficiently high surface charge density that the water molecules are very strongly held and hydrolysis (*i.e.* splitting of a bound water molecule) can occur before water-loss. This group includes the small, highly-charged ions such as Be^{2+}, Al^{3+}, (probably) Fe^{3+}, and most tetravalent ions. It is the least well understood group since the overall mechanisms may involve quite a number of non-separable steps. Substitution at the hydrolysed ion $M(OH)^{(a-1)+}$ is faster than at the non-hydrolysed ion M^{a+} [in fact $M(OH)^{(a-1)+}$ is usually in group *B*], and so anything which promotes hydrolysis will also promote substitution. In any event, for group *C* the overall rate constant is largely influenced by the nature of the incoming ligand; for example, its basicity. This influence is much less apparent with metals of groups *A* and *B*, except insofar as the formation of second and subsequent bonds with chelating ligands may become rate-determining, as discussed in greater detail below.

Most group *A* metal ions have the d^0 electronic configuration of the rare gases, and the interaction of the metal with a ligand is primarily electrostatic in nature. Because the charge density ($\propto$ charge : radius) is small, the water molecules are weakly held and the rate of their loss is comparable with the diffusion-controlled value of around 10^9—10^{10} s^{-1}. The complex formation rate-constant for an ion in this group is therefore approximately equal to the maximum possible value, unless chelation steps are important, and the stability of the complex is reflected in the dissociation rate constant.

With group *B* metal ions, step (ii) → (iv) is considerably (*i.e.* > 10 times) slower than step (i) → (ii), and so a fast pre-equilibrium step is followed by the rate-limiting loss of a water molecule from the inner co-ordination

sphere. To a first approximation (provided that the concentration of outer-sphere complex is small compared with that of the uncomplexed metal ion), the observed overall formation rate-constant k_f is given by equation (2):

$$k_f = K_{os}\, k_{wl} \qquad (2)$$

where K_{os} is the equilibrium constant for the formation of the outer-sphere complex and k_{wl} is the rate constant for the water-loss process. On this picture, k_{wl} is essentially the rate constant for water exchange at the metal ion, and this can frequently be measured independently by n.m.r.,

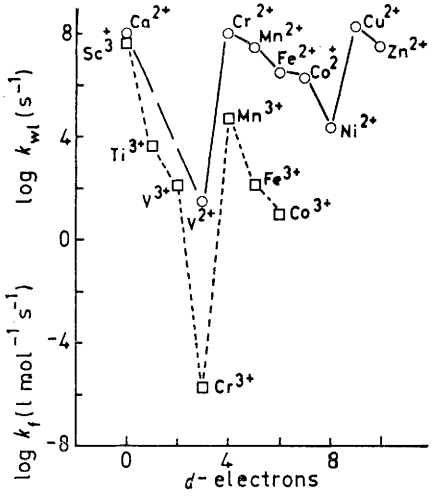


Figure 2 *Comparison of the rate constants for overall complex formation and water exchange, respectively, for di- and tri-valent metal ions with various* d-*electron configurations*
(Reproduced by permission from *Quart. Rev.*, 1969, **23**, 18)

especially when the metal ion is paramagnetic. Unfortunately, it has not yet been possible to measure K_{os} directly in reacting systems, so it has not been possible to confirm the mechanism unequivocally. However, the values of k_f do appear to be more or less typical of the metal and similar in magnitude to the water-exchange rate.

It is found that the forward rate-constant is approximately inversely proportional to the ionic radius for metals of a given charge-type, but the presence of partially-filled *d*-orbitals on the metal ion can cause considerable complication. This effect of *d*-electron configuration on overall formation and water-exchange rate-constants, respectively, for various di- and tri-valent metal ions is shown in Figure 2. The general trend of rates is reminiscent of the crystal-field stabilization diagrams and, indeed, general correlations have been made between substitution rates and crystal-field

activation energies, although the detailed picture has not been satisfactorily explained. Recently, Companion [8] has examined the possibility of improving the CFAE calculations by the use of many-electron methods and improved crystal-field parameters.

The increases in rate constant on going from V^{2+} to Cr^{2+} (d^3 to d^4) and from Ni^{2+} to Cu^{2+} (d^8 to d^9) have been rationalized in terms of the Jahn–Teller effect. Thus, in octahedral Cr^{2+} and Cu^{2+} there are two axial water molecules which are less firmly held than the four equatorial water molecules, and the incoming ligand is assumed to replace the former. The consequence of this is that Cr^{2+} and Cu^{2+} behave more like metals of group *A* than group *B*.

In the next five sections we shall discuss recently published work in the context of mechanism IIa (Figure 1) and the corresponding rate expression, equation (2). It has sometimes proved difficult to decide in which section a given paper should be placed, since the discussions frequently involve aspects which we have treated under various headings. The divisions were chosen with the 'intelligent layman' in mind, and in future Reports it should be possible to avoid this difficulty by a different subdivision of the subject. Data published prior to 1965 have been collected by Eigen and Wilkins [3] and between 1965 and 1970 by Hewkin and Prince.[5]

2 Formation of Outer-sphere Complexes

It is customary to calculate the value of K_{os} from the Fuoss [9] equation; $K_{os} = (4\pi Na^3/3000) \exp[-U(a)/kT]$, where $U(a)$ is the Coulomb energy, N the Avogradro number, k the Boltzmann constant, and a the distance of closest approach of the hydrated metal ion and the ligand, usually taken as 5 Å. Although this formula is only applicable to charged ligands, a similar one has been derived for neutral ligands.[10] It is therefore to be expected that the overall rate of complex formation will increase with the negative charge on the incoming ligand.

The kinetics of outer-sphere ion-pair formation between the sulphate ion and the cobalt(III) species $[Co(NH_3)_6]^{3+}$ and $[Co\,en_3]^{3+}$ have been measured in aqueous solution using the ultrasonic technique. As expected, rates typical of a diffusion-controlled process are found.[11] The electron paramagnetic resonance (e.p.r.) line-broadening technique was used to obtain the thermodynamic parameters for the formation of outer- and inner-sphere complexes between Mn^{II} and dithionite ions.[12] For the formation of the ion-pair, values of $\Delta G^\circ = -1{\cdot}57$ kcal mol^{-1}, $\Delta H^\circ =$

[8] A. L. Companion, *J. Phys. Chem.*, 1969, **73**, 739.
[9] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059; M. Eigen, *Z. Elektrochem.*, 1960, **64**, 115.
[10] *E.g.* M. Eigen, W. Kruse, G. Maass, and L. de Maeyer, *Progr. Reaction Kinetics*, 1964, **2**, 287.
[11] A. Elder and S. Petrucci, *Inorg. Chem.*, 1970, **9**, 19.
[12] L. Burlamacchi and E. Tiezzi, *J. Phys. Chem.*, 1969, **73**, 1589.

3·5 kcal mol^{-1}, and ΔS° = 17·3 e.u. (at 20 °C) were obtained. The results are discussed in the light of the ultrasonic work by Atkinson and Kor [13] on manganese sulphate.

An ingenious application of the n.m.r. technique to the problem of the outer-sphere complex is the subject of a preliminary report by Leffler.[14] He has used methylene chloride as an inert probe to study the ordering of the solvent in the outer co-ordination sphere of the hexaquo-ions of several transition metals which possess unpaired 3*d* electrons. As he points out, a suitable probe for a study of the outer sphere must be completely excluded from the inner sphere under all conditions, and it must be mobile and small enough to diffuse through the bulk solvent to the second co-ordination sphere at a rate which will give the same average distribution as that of the bulk solvent. In other words, it should behave in the same way as the solvent apart from its exclusion from the inner sphere of the metal ion. Methylene chloride and chloroform both fulfil these conditions, although on solubility grounds the former is to be preferred. It is to be hoped that this technique can be developed to monitor the effects of ligands on the outer co-ordination spheres of the metal ions.

In another interesting preliminary communication, Bennetto and Caldin [15] discuss the effect of solvent on the rate of formation of the complex between Ni^{2+} and bipy. They point out that the majority of the evidence in favour of mechanism IIa has been obtained in aqueous solution, and report an extension of previous work in methanol–water mixtures which had suggested that structural features of the solvent are at least as important as the nature of the metal ion in determining k_f. They compare the overall values k_f with the values of solvent exchange k_{wl} [equation (2)], as measured by n.m.r. (Table 1), and it is apparent that K_{os} varies by at

Table 1 *k_f and k_{wl} for* Ni^{II} + bipy *in different solvents*

Solvent	$10^{-3} k_f$ (l mol^{-1} s^{-1})[a]	$10^{-3} k_{wl}$ (s^{-1})	K_{os} (l mol^{-1})
Acetonitrile	4·7	2·8[b]	1·7
Methanol	0·14	1·0[b]	0·14
Dimethylformamide	$0{\cdot}5_4$	7·7[c]	$0{\cdot}07_0$
H_2O	$1{\cdot}6_3$	30[b]	$0{\cdot}05_4$
D_2O	$1{\cdot}0_8$	30[d]	$0{\cdot}03_6$
Dimethyl sulphoxide	$0{\cdot}06_9$	7·5[b]	$0{\cdot}009_2$
Ethylene glycol	$0{\cdot}03_3$	4·4[e]	$0{\cdot}00_8$

[a] From ref. 15. [b] From C. H. Langford and T. R. Stengle, *Ann. Rev. Phys. Chem.*, 1968, **19**, 193. [c] From J. S. Babiec, C. H. Langford, and T. R. Stengle, *Inorg. Chem.*, 1966, **5**, 1362. [d] $k_{wl}^{(D_2O)} = k_{wl}^{(H_2O)}$ is assumed on the basis of data for Mn^{2+} in H. Sprinz, *Z. Naturforsch.*, 1964, **19a**, 1243; J. R. Smithson and T. A. Litovitz, *J. Acoust. Soc. Amer.*, 1956, **28**, 462. [e] R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, 1964, **86**, 765.

[13] G. Atkinson and S. K. Kor, *J. Phys. Chem.*, 1967, **71**, 673.
[14] A. J. Leffler, *J. Phys. Chem.*, 1970, **74**, 2810.
[15] H. P. Bennetto and E. F. Caldin, *Chem. Comm.*, 1969, 599.

least two orders of magnitude over the series. What is more, the difference in enthalpies of activation for the complex formation ($\Delta H_f^{\ddagger}$) and solvent exchange ($\Delta H_s^{\ddagger}$) steps, which should be near zero if the mechanism applies (since the enthalpy change on forming the weak outer-sphere complex should be very small), varies from + 4 ± 1 kcal mol^{-1} in DMSO to − 5 ± 1 kcal mol^{-1} in acetonitrile. Clearly, if their analysis is valid, equation (2) is unsatisfactory, at least for the reaction of Ni^{2+} with bipy in this range of solvents. They do, however, find a good correlation between $\log(k_f/k_{wl})$ and the fluidity of the solvent (defined as the reciprocal of the kinematic viscosity), and they discuss this in terms of the 'open-ness' and 'stiffness' of the liquid matrix.

3 Solvent Exchange at the Metal Ion

In this and the next three sections, we shall only consider work involving the simple, uncomplexed metal ion; the effect of ligands already bound to the metal will be discussed separately in Section 6.

It will be apparent that any attempt to elucidate the mechanism of substitution at labile metal ions must involve itself in a consideration of the kinetics of the solvent exchange process. Since the pioneering work of Swift and Connick,[16] the n.m.r. line-broadening and pulse techniques have been used more and more frequently for this purpose.

Neely and Connick[17] have been able to obtain, for the first time, a direct measurement of the water-exchange rate from hydrated magnesium at room temperature (hitherto, the diamagnetic character of this ion had made it necessary to use indirect methods which required fairly extensive extrapolation procedures, either with respect to temperature or to solvent composition). Using the ^{17}O signal of the water molecules in the first co-ordination sphere and avoiding interference from the bulk solvent by adding sufficient Mn^{2+} to broaden the bulk water resonance to at least ten times that of the bound water signal, they were able to determine an effective first-order exchange rate constant at 25 °C of 5·3 × 10^5 s^{-1} (the observed rate being corrected for a co-ordination number of six). Temperature variation over the range from − 20 to + 23 °C yielded the activation parameters $\Delta H^{\ddagger}$ = 10·2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 2 e.u.

Reuben and Fiat[18] have studied the concentration and temperature dependence of the ^{17}O transverse relaxation time T_2 in aqueous solutions of the perchlorates of Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+}. Lower estimates for the rate constants of water exchange were found to be in the range 0·3—2·6 × 10^7 s^{-1}, and an upper limit of 5 kcal mol^{-1} was estimated for the activation enthalpy of this process. These results are of especial interest in the light of the variation in overall complex formation rate k_f found with the members of the lanthanide series, discussed in Section 5.

[16] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.
[17] J. Neely and R. E. Connick, *J. Amer. Chem. Soc.*, 1970, **92**, 3476.
[18] J. Reuben and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4918.

The comparatively large water-exchange rates for these trivalent ions have been attributed to their having co-ordination numbers greater than six.

An interesting practical point is also made in Reuben and Fiat's paper.[18] They suggest that spherically-shaped samples are preferable for studies involving ^{17}O line-widths in paramagnetic solutions in order to minimize inhomogeneous broadening. They point out that this artefact may be a cause of some of the inconsistencies found in the literature.

Hunt's group have continued to make significant contributions in this field. They have measured[19] the kinetics of NH_3 exchange between solvated Mn^{2+} and the free solvent liquid ammonia, and have found that the rate constant and activation parameters are all strikingly similar to those for the aquo system. The results are, at 25 °C and assuming a co-ordination number of six: $k = 3{\cdot}6 \times 10^7\ s^{-1}$ ($3{\cdot}1 \times 10^7\ s^{-1}$ for Mn_{aq}^{2+}, see ref. 16); $\Delta H^{\ddagger} = 8{\cdot}0$ kcal mol^{-1} (8·1 kcal mol^{-1}); $\Delta S^{\ddagger} = 5$ e.u. (2·9 e.u.). The values in acetonitrile[20] are also rather similar: $k = 1{\cdot}2 \times 10^7\ s^{-1}$; $\Delta H^{\ddagger} = 7{\cdot}25$ kcal mol^{-1}; $\Delta S^{\ddagger} = -1{\cdot}8$ e.u. In contrast,[19] for Co^{2+} and Ni^{2+} the activation enthalpies for the reactions in water and liquid ammonia are very similar, while the rate constants are significantly different, as shown in Table 2. Perhaps, in spite of previous suggestions,[1]

Table 2 *Rate constants and activation enthalpies for solvent exchange*[a]

	k_{wl} (s^{-1})	$\Delta H_{wl}^{\ddagger}$ (kcal mol^{-1})
$Co^{2+} + NH_3$	$7{\cdot}2 \times 10^6$	11
$Co^{2+} + H_2O$	2×10^6	10·4
$Ni^{2+} + NH_3$	$1{\cdot}0 \times 10^5$	11
$Ni^{2+} + H_2O$	$3{\cdot}0 \times 10^4$	11

[a] Data refer to 25 °C; see ref. 19.

crystal field effects are important in determining rates of substitution but not their activation enthalpies?

Separate n.m.r. signals could be obtained from the hydroxy-groups of free and bound ethanol in low-temperature studies on solutions of magnesium perchlorate.[21] From relative intensity measurements below − 60 °C, the solvation number of Mg^{2+} was shown to be six. The rate parameters for the exchange process provide an interesting comparison with those for the aqueous system:[17] $k = 2{\cdot}8 \times 10^6\ s^{-1}$ ($5{\cdot}3 \times 10^5\ s^{-1}$ at 25 °C for H_2O), $\Delta H^{\ddagger} = 17{\cdot}7$ kcal mol^{-1} (10·2 kcal mol^{-1}), $\Delta S^{\ddagger} = 30$ e.u. (2 e.u.).

An n.m.r. study with the Ti^{3+} ion in aqueous and methanol solutions[22] produced the activation enthalpies 6·2 and 3·3 kcal mol^{-1}, and the activation entropies − 15 and − 24 e.u., respectively. Breivogel has measured

[19] M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1969, **91**, 6318.
[20] W. L. Purcell and R. S. Marianelli, *Inorg. Chem.*, 1970, **9**, 1724.
[21] T. D. Alger, *J. Amer. Chem. Soc.*, 1969, **91**, 2220.
[22] A. M. Chmelnik and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4238.

the rates of exchange, together with their activation parameters, for Mn^{2+}, Fe^{2+}, Fe^{3+}, and Cu^{2+} in methanol.[23] He has also studied Fe^{3+} in several solvents [24] and has noted that in water, DMSO, DMF, and acetonitrile the solvent exchange rates are all about 0·006 times the corresponding rate for Ni^{2+}, whereas in methanol and ethanol the solvent exchange rates for Fe^{3+} are twice as large as for Ni^{2+}. This difference in behaviour of the various solvents is attributed to steric effects.

Solvent exchange has also been measured for the vanadyl ion in acetonitrile [25] and for the nickel(II) ion in DMSO.[26]

Frankel has given a preliminary account [27] of studies, involving nickel(II) and cobalt(II) in mixed solvents, which might prove to have far-reaching mechanistic consequences. He found that the ligand exchange kinetics for ML_6^{2+} (where L is DMSO) in pure DMSO, DMSO–nitromethane, and DMSO–methylene chloride mixtures are approximately the same for the individual metals:

	k (s^{-1}, 25 °C)	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
Ni^{2+}	$3·2 \times 10^3$	13·0	3·2
Co^{2+}	$1·7 \times 10^5$	9·6	− 0·4

It was possible to show, by integrating the DMSO peak, that the nitromethane and methylene chloride were both unco-ordinated to the metal ions. The dielectric constant of CH_2Cl_2 is such that the concentration of ion pairs between ML_6^{2+} and ClO_4^-, the counter-ion, would be greatly increased in a DMSO–CH_2Cl_2 mixture compared with pure DMSO. Since the same ligand-exchange parameters were obtained, a mechanism which involves an ion pair is unlikely. The independence of the exchange rate on the ligand concentration, composition, and fluidity is consistent with a dissociative mechanistic pathway.[2] These results provide an interesting comparison with those of Bennetto and Caldin on the nickel(II)–bipyridyl reaction.[15]

4 Complex Formation with Unidentate Ligands

Strehlow and co-workers [28] have given a detailed discussion of the activation energies to be expected for a pure S_N1-type mechanism for metal complex formation (cf. Figure 1) and have concluded that, at least for the small polyvalent cations of group *C* (such as Be^{2+} and Al^{3+}), they would be far higher than those observed experimentally. On the basis of a concerted mechanism of the type shown in Figure 1 (route IIa) the activation energy for these ions is calculated to be about 20 kcal mol^{-1}, compared

[23] F. W. Breivogel, *J. Chem. Phys.*, 1969, **51**, 445.
[24] F. W. Breivogel, *J. Phys. Chem.*, 1969, **73**, 4203.
[25] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 65.
[26] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 2579.
[27] L. S. Frankel, *Chem. Comm.*, 1969, 1254.
[28] H. Strehlow and W. Knoche, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 427; M. Matušek and H. Strehlow, *ibid.*, p. 982.

with the measured value of *ca.* 11 kcal mol^{-1}. In contrast, it would require an energy of about 100 kcal to remove one water molecule from the inner sphere of a Be^{2+} or Al^{3+} ion, and this would therefore be the activation energy for complex formation in an S_N1 mechanism. The kinetic parameters, as measured by the pressure-jump relaxation method, are reported for the formation in water of $BeSO_4$ and $AlFe(CN)_6$.

Several studies involving the formation and dissociation of mono-complexes of iron(III) have been reported. Rowley and Sutin [29] have followed the reaction:

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$$

in solutions containing varying amounts of perchloric acid. The equilibrium constant increases from 5·2 l mol^{-1} at unit ionic strength to 11·0 l mol^{-1} at an ionic strength of 6·0, and it is shown that the large variations in K, ΔH, and ΔS arise almost entirely from changes in the kinetic parameters for the formation rather than the dissociation of the complex. The Cl^- ion is entering the inner co-ordination shell of the hydrated ferric ion more easily as the ionic strength increases; a result which may be rationalized, at least in part, in terms of a decrease in the hydration number of the ions with decreasing H_2O activity. The temperature-jump technique has been used [30] to confirm previous stopped-flow results on the formation of $FeCl^{2+}$ and $FeBr^{2+}$ at moderate ionic strength.

Cavasino and Di Dio [31] have studied the formation of the mono-complexes of iron(III) with some substituted phenols (HA). The only reaction observed involves the hydrolysed metal species:

$$FeOH^{2+} + HA \rightleftharpoons FeA^{2+} + H_2O$$

and all the estimated rate constants for the forward reaction are of the same order of magnitude as those found previously with analogous reactions. The rate constants for the reverse process decrease with decreasing base strength of the departing ligand and follow the Hammett relationship with a reaction constant ρ of $-0{\cdot}33$.

The reactions of Fe^{III} with acetic, propionic, and chloroacetic acids also have 'normal' rate constants.[32]

In spite of a suggestion by Gusenkov [33] that in two- and three-stage mechanisms the maxima observed in the ultrasonic dispersion curves of the reaction mixture may not agree with the eigenvalues from the characteristic equation (both as regards their number and the frequency of the external perturbation), the results of further work with this technique have been reported. Hemmes and Petrucci [34] have reinvestigated the

[29] J. K. Rowley and N. Sutin, *J. Phys. Chem.*, 1970, **74**, 2043.
[30] T. Yasunaga and S. Harada, *Bull. Chem. Soc. Japan*, 1969, **42**, 2165.
[31] F. P. Cavasino and E. Di Dio, *J. Chem. Soc.* (*A*), 1970, 1151.
[32] F. Accascina, F. P. Cavasino, and E. Di Dio, *Trans. Faraday Soc.*, 1969, **65**, 489.
[33] G. N. Gusenkov, *Russ. J. Phys. Chem.*, 1969, **43**, 54.
[34] P. Hemmes and S. Petrucci, *J. Phys. Chem.*, 1970, **74**, 467.

ultrasonic spectra of aqueous copper sulphate and have cleared up some of the controversy regarding earlier reports.

The formation of the complexes between the *m*-benzenedisulphonate ion and Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in anhydrous methanol has been investigated by the pressure-jump technique.[35]

Diebler[36] has measured the rate constants for the formation of the 1 : 1 complexes between Ti^{III} and thiocyanate, and between Mn^{III} and fluoride. Whereas in the former reaction the metal behaves as a normal group *B* ion, in the latter the kinetics could not be unequivocally interpreted.

5 Complex Formation with Chelating Ligands

In this section we shall consider the data which have been presented recently on metal complexation reactions involving bi- and multi-dentate ligands. It has frequently been assumed (and, indeed, there are many

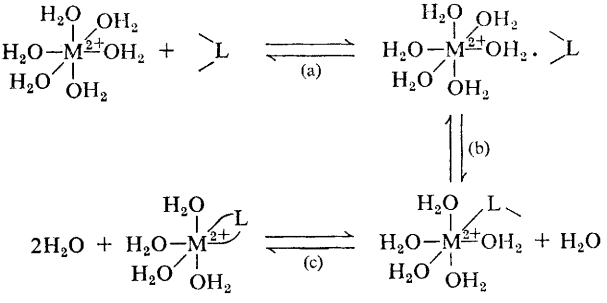


Figure 3 *Mechanism of formation of a complex between a hydrated metal ion* [*e.g.* $M^{2+}(OH_2)_6$] *and a bidentate ligand L*

results which seem to bear this assumption out) that, at least for bidentate ligands reacting with metals of groups *B* and *C*, the rate-determining step in the overall complex-formation process is the formation of the *first* metal–ligand bond. Thus, in the process illustrated in Figure 3, steps (a) and (c) are fast compared with step (b) for most metals. The evidence for this is largely the similarity in overall k_f for reactions of a given metal ion with similar mono- and bi-dentate ligands. It is not necessary to invoke the possible labilizing effect on the remaining solvent molecules of the first metal–ligand bond to explain this (see Section 6) since the formation of this first metal–ligand bond implies the presence of the second binding group in the outer sphere of the metal ion. This leads automatically to a much larger effective K_{os} for the second group than the first, resulting in a higher effective k_f [equation (2)].

In some cases, however, there is a marked difference between the k_f values for mono- and bi-dentate ligands reacting with the same metal ion,

[35] G. Macri and S. Petrucci, *Inorg. Chem.*, 1970, **9**, 1009.
[36] H. Diebler, *Z. phys. Chem. (Frankfurt)*, 1969, **68**, 64.

and in many cases this has been rationalized in terms of ring-size and the nature of the binding groups on the ligand. We shall consider first cases in which it appears that chelate formation is unimportant in determining the value of k_f (though it will, of course, play a large part in determining the dissociation rate-constant k_d and hence the stability constant of the complex), and will then discuss cases in which chelation is important. Several papers, especially those by Kustin's group, will not be referred to in this section, even though they report the formation of 1 : 1 complexes with chelating ligands. These involve primarily reactions of Ni^{2+} and Co^{2+} with amino-acids, and they are mentioned in Section 6 since they are concerned also with the binding of a second and third ligand.

Lin and Bear [37] report a pressure-jump investigation of the formation of magnesium oxalate in water. Rate constants and activation parameters are quoted and discussed in terms of the normal mechanism. The vanadyl–tartaric acid [38] and nickel(II)–8-hydroxyquinoline and –8-hydroxyquinoline-5-sulphonate [39] systems are also reported. An n.m.r. study involving the reaction of $^{19}F^-$ with Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} suggests that the mechanism involves several parallel pathways.[40]

Diebler [41] has studied the reactions between bipy and Cr^{2+} or Cu^{2+} and found them to be sensitive to pH. From the pH-dependence of the relaxation times, he was able to show that the mechanism involves the reaction of the metal ion with either the protonated ($Hbipy^+$) or unprotonated (bipy) form of the ligand. He obtained the overall rate constants given in Table 3

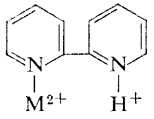
Table 3 *Rate constants for reaction with* bipy *and* $Hbipy^+$

	k_f (l mol^{-1} s^{-1})[a]
Cr^{2+} + bipy	$3{\cdot}5 \times 10^7$
Cr^{2+} + $Hbipy^+$	$6{\cdot}5 \times 10^3$
Cu^{2+} + bipy	$\simeq 4 \times 10^7$
Cu^{2+} + $Hbipy^+$	$2{\cdot}9 \times 10^5$

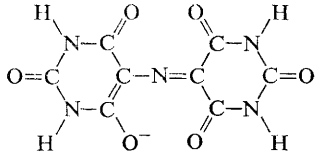
[a] Data for Cr^{2+} refer to 24 °C and ionic strength 0·45, and for Cu^{2+}, 25 °C and 0·30; from ref. 41.

and attributed the large differences between the values for protonated and unprotonated forms of the ligand to the rate-limiting deprotonation of the intermediate (1). The difference in rate constants for Cr^{2+} and Cu^{2+} in their reaction with $Hbipy^+$ can then be explained by the much greater tendency of Cu^{2+} to form stable complexes with ligands which bind through nitrogen atoms. The equilibrium constant for the (rapid) formation of (1) is therefore expected to be larger for Cu^{2+} than for Co^{2+}.

[37] C. T. Lin and J. L. Bear, *J. Inorg. Nuclear Chem.*, 1969, **31**, 263.
[38] K. Kustin and R. Pizer, *Inorg. Chem.*, 1970, **9**, 1536.
[39] W. A. Johnson and R. G. Wilkins, *Inorg. Chem.*, 1970, **9**, 1917.
[40] M. Eisenstadt, *J. Chem. Phys.*, 1969, **51**, 4421.
[41] H. Diebler, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 268.



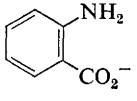
(1)



(2)

Complex formation reactions involving the lanthanides have received a certain amount of attention recently, partly, no doubt, because of the rather subtle changes in chemical and physical properties which are usually observed on going along the series. Some of the earliest kinetic work dates from 1965, when Geier [42] reported the results of his experiments with the mono-anion of purpuric acid [the murexide ion (2)], results which he has recently summarized.[43] The rare-earth metal ions show a characteristic non-linear correlation between log k_{wl} [equation (2)] and the reciprocal ionic radius, which reflects the behaviour of several thermodynamic parameters. He makes three observations on the values obtained. In the first place, the ions all react much more rapidly than expected on the basis of the charge–radius rule found with d^0 and d^5 cations of similar radius (*e.g.* Mg^{2+}, with a radius of 0·78 Å, has a value for k_{wl} of about 10^5 s^{-1}, and Mn^{2+}, with a radius of 0·91 Å, has $k_{wl} \simeq 4 \times 10^6$ s^{-1}. The trivalent lanthanide ions, with radii in the range 0·85—1·1 Å, have overall formation rate constants in the range 10^7—10^8 l mol^{-1} s^{-1}). This point has already been made in Section 3. In the second place, the rate constants only vary within an order of magnitude despite the large variation in ionic radius. Thirdly, there is no simple relationship between rate and ionic radius. Geier discusses these results in terms of the structure of the aquo ions and suggests that the overall rate constants for complex formation are reflecting a labilization of the water molecules in the inner co-ordination shell of the metal ion as the ions increase in size, the loosening of the co-ordination shell being a direct consequence of the raising of the co-ordination number of the metal from six to nine.

Swinehart and co-workers [44] have undertaken a similar study with the anthranilate ion (3) but have obtained a picture which differs in several important respects from that of Geier. Figure 4 gives a comparison of the data for the two systems, and it will be seen that a break occurs between europium and dysprosium for both reactions. However, the regions from



(3)

[42] G. Geier, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 617.
[43] G. Geier, *Chimia* (*Switz.*), 1969, **23**, 148.
[44] H. B. Silber, R. D. Farina, and J. H. Swinehart, *Inorg. Chem.*, 1969, **8**, 819.

lanthanum to europium and from dysprosium to lutetium are not directly comparable. The results with anthranilate do not rule out the possibility that Geier's explanation is correct, but they do suggest the involvement of complicating factors which have not yet been identified. For example, the 'inert' electrolyte [which was $NaClO_4$ at ionic strength 0·2 in the work with (3), but KNO_3 at ionic strength 0·1 in the work with (2)] might be involved in some way. Preliminary results with the lanthanide–acetate system

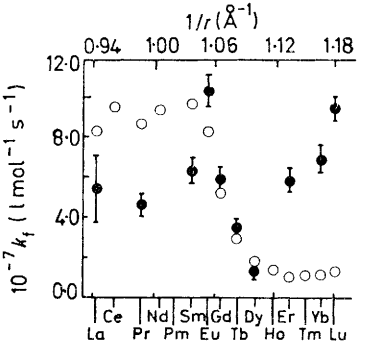


Figure 4 *Comparison of k_f for the reaction of the lanthanides with anthranilate* (●, *ref.* 44) *and murexide* (○, *ref.* 42). *r is the ionic radius of the lanthanide ion*
(Reproduced by permission from *Inorg. Chem.*, 1969, **8**, 819)

suggest [44] that the detailed mechanism of the chelation process may play a role in determining the values of the overall rate constants k_f. Perhaps the measurement of more activation parameters [44] will clarify the situation.

Fay and Purdie [45] have extended their ultrasonic work on aqueous solutions of salts of the lanthanides. They present further evidence to support their contention that they are able to observe directly the last step in the overall complex formation mechanism [*i.e.* step (ii) → (iii) → (iv) in Figure 1]. Activation parameters have also been measured.

Eigen's group have given a general account [46] of the kinetics and mechanism of reactions of main-group metal ions with biological carriers, in which they include the results of a study into the binding of alkali-metal ions with murexide (2); see Chapter 2, Section 1.

Methanol–water mixtures were the solvent in a study involving Ni^{2+} and phen.[47] This work provides an interesting comparison with that of Pearson and Ellgen [48] and Bennetto and Caldin,[15] and it is certain that further work of this type in mixed solvents will lead to a greater understanding of the mechanisms of ligand substitution at labile metal ions.

[45] D. P. Fay, D. Litchinsky, and N. Purdie, *J. Phys. Chem.*, 1969, **73**, 544; D. P. Fay and N. Purdie, *ibid.*, 1970, **74**, 1160.
[46] H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler, *Pure Appl. Chem.*, 1969, **20**, 93.
[47] M. L. Sanduja and W. MacF. Smith, *Canad. J. Chem.*, 1969, **47**, 3773.
[48] R. G. Pearson and P. Ellgen, *Inorg. Chem.*, 1967, **6**, 1379.

Interference from Ring-closure.—In 1966, Kustin, Pasternack, and Weinstock published a paper [49] entitled 'Steric effects in fast metal complex substitution reactions', in which they reported a temperature-jump study involving the nickel(II) and cobalt(II) complexes with α- and β-alanine. With α-alanine, the substitution at cobalt was significantly faster than at nickel, but with the β-isomer, whereas the Ni^{2+} substitution rate was approximately the same as before, substitution at Co^{2+} was significantly slower. The rate constants shown in Table 4 were obtained for the 1 : 1

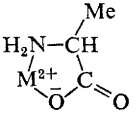
Table 4 *Rate constants for reaction with α- and β-alanines*[a]

	k_f (l mol^{-1} s^{-1})	k_d (s^{-1})
Ni^{2+} + α-alanine	$2{\cdot}0 \times 10^4$	$2{\cdot}2 \times 10^{-2}$
Ni^{2+} + β-alanine	$1{\cdot}0 \times 10^4$	$2{\cdot}3 \times 10^{-1}$
Co^{2+} + α-alanine	$6{\cdot}0 \times 10^5$	32
Co^{2+} + β-alanine	$7{\cdot}5 \times 10^4$	7·5

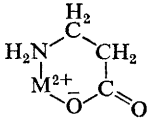
[a] Data refer to 20 °C; from ref. 49.

complexes (data on the 2 : 1, and in some cases the 3 : 1, complexes are also reported).

The data for the formation of the five-membered ring (4) are 'normal': the cobalt rate is about thirty times as large as the nickel rate, and both are consistent with the mechanism described above, in which release of a water molecule from the inner co-ordination sphere of the metal ion is rate-determining. For the six-membered ring (5), the situation is rather different,



(4)



(5)

since the rate constant for Co^{2+} with β-alanine is almost an order of magnitude less than that of Co^{2+} with the α-isomer. Kustin and co-workers suggested that in this system the rate-determining step also involves the ring-closure [step (c) of Figure 3]. Preliminary work on the more labile manganese(II) ion indicated a more drastic retardation of the complex formation process for the six-membered as compared with the five-membered ring, and suggested that with Co^{2+} we have not yet reached the limiting situation in which step (c) is completely rate-determining. Apparently, step (b) is sufficiently slow for nickel that step (c) is not observed. [This is an important point and it explains why the effect had not been described previously except for the alkali metals [50] and other group *A*

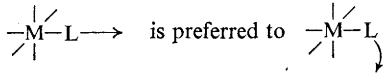
[49] K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, 1966, **88**, 4610.

[50] *E.g.* M. Eigen and G. Maass, *Z. phys. Chem. (Frankfurt)*, 1966, **49**, 163.

metals: most of the published studies on fast metal complex substitution reactions have been concerned with nickel(II).]

The underlying cause for the slowness of step (c) for Co^{2+} and β-alanine is thought to be the difficulty in forming a six-membered ring with an aminocarboxylic acid ligand. The structures of α- and β-alanine are such that, once attachment at the first site has occurred, more energy would be required for β- than for α-alanine to produce attachment at the second site. The effect should therefore involve rather larger contributions to the activation energy for ring-closure than might be expected; one contributing factor might be ring strain and another the additional entropy loss when forming a six-membered chelate ring as compared to a five-membered ring.

Perhaps more light will be shed on the detailed mechanistic aspects of chelate formation by the measurement of activation parameters. The latter is becoming an increasingly worthwhile occupation with the increasing sophistication of chemical relaxation apparatus. In any event, it is a little difficult to rationalize the slower dissociation of the six-membered ring system of Co–β-alanine compared with the five-membered ring of the α-analogue on this picture of ring strain. The question of ring-opening has been discussed by Margerum in several of his papers dealing with the interchange of multidentate ligands between labile metal ions.[51] At the 1964 Kansas conference, he suggested [52] that the reason a chelate bond is so much more difficult to break than a bond involving a non-chelating ligand is that the minimum energy path for the dissociation of a ligand from a metal ion involves a linear displacement rather than an angular displacement, *i.e.*



and only the latter is possible with a chelate. But again, the dissociation results of Kustin *et al.* for the alanines are difficult to explain on this picture since larger chelate rings should be easier to open than smaller ones. It is difficult to avoid the conclusion that more work will have to be done before the mechanism of metal-complex formation and dissociation involving chelating ligands can be said to be completely understood.

Further studies [53] have shown that the steric effect is present in the formation of the analogous complexes with β-aminobutyrate (Table 5).

Makinen, Pearlmutter, and Stuehr [54] have studied the reaction of α- and β-alanine and histidine with Cu^{2+}. As predicted, the chelate effect is

[51] See series entitled 'Multidentate Ligand Kinetics'; Part XIV is G. A. Nyssen and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1814.
[52] D. W. Margerum, A.C.S. Advances in Chemistry Series, 1965, No. 49, p. 75.
[53] A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Amer. Chem. Soc.*, 1967, **89**, 3126.
[54] W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *J. Amer. Chem. Soc.*, 1969, **91**, 4083.

somewhat more pronounced even than with Co^{2+} since Cu^{2+} is inherently the more labile metal. Values of k_f (l mol^{-1} s^{-1}) are: α-alanine $1{\cdot}3 \times 10^9$, β-alanine $2{\cdot}0 \times 10^8$, and histidine $1{\cdot}3 \times 10^7$.

Table 5 *Rate constants for reaction with α- and β-aminobutyrates*[a]

	k_f (l mol^{-1} s^{-1})	k_d (s^{-1})
Ni^{2+} + α-aminobutyrate	$1{\cdot}0 \times 10^4$	$3{\cdot}2 \times 10^{-2}$
Ni^{2+} + β-aminobutyrate	$4{\cdot}0 \times 10^3$	$7{\cdot}0 \times 10^{-2}$
Co^{2+} + α-aminobutyrate	$2{\cdot}5 \times 10^5$	11·0
Co^{2+} + β-aminobutyrate	$2{\cdot}0 \times 10^4$	2·6

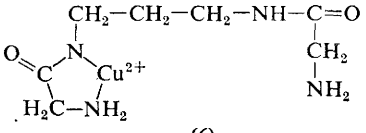
[a] Data refer to 20 °C; from ref. 53.

Similar results have been obtained by Pearson and Anderson [55] for the formation of mono(acetylacetonato)copper(II) in water and methanol. Both the keto and enol tautomers of acac react with Cu^{2+} at rates which are much less than expected for normal substitution. The second-order rate constant for the reaction of the enol form is the same in water and methanol (2×10^4 l mol^{-1} s^{-1}), as expected for a mechanism in which the rate-determining step is the sterically difficult closure of the six-membered ring. For the reaction between the Cu^{II} ion and the keto form of acac, the slow step is thought to be the metal-ion-catalysed proton transfer from the weakly-bound keto tautomer. This suggestion is supported by the increase in rate constant of two orders of magnitude on changing from water (12 l mol^{-1} s^{-1}) to methanol (1300 l mol^{-1} s^{-1}) and the results of deuterium isotope substitution studies.

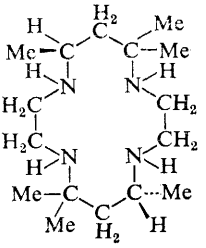
Copper(II) complexes have been the subject of other stopped-flow experiments. In the formation of the complex with *NN'*-diglycylpropylenediamine, it was possible to observe [56] an intermediate which was formed immeasurably rapidly and had an absorption maximum at 670 nm. Two structures (6, and that in which the free amino-group has been protonated) are suggested. It is also shown that the rate of dissociation of the complex is inversely proportional to the square of the hydrogen-ion concentration, and this is explained in terms of a rapid proton addition to one of the amino-groups followed by the slow reaction of a second proton with the co-ordinated amide group. The effect of acetate buffer, which increases the dissociation rate, is also discussed.

Cabbiness and Margerum [57] have given preliminary accounts of the effect of macrocyclic structures on the rate of formation and dissociation of Cu^{2+} complexes. They have compared the rates of reaction of aquocopper with the somewhat flexible fourteen-membered macrocyclic ligand shown (7; also similar macrocycles), with a comparable open-chain polyamine (2,3,2-tet), and with a porphyrin ligand (haematoporphyrin

[55] R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, 1970, **9**, 39.
[56] D. Wagnerová, Th. Kaden, and A. Zuberbühler, *Helv. Chim. Acta*, 1969, **52**, 1776.
[57] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1969, **91**, 6540; 1970, **92**, 2151.



(6)



(7)

IX). At high pH, the macrocycles of type (7) react more slowly than the open-chain ligand by a factor of 10^3—10^4 whereas the more rigid porphyrin is less reactive than the open-chain ligand by a factor of 10^9. The results are discussed in terms of the necessity for multiple desolvation of the metal ion, and it is suggested that twisting or folding of these cyclic ligands is important in the overall complex-formation process.

Hoffmann has discussed in detail the contributions of the various elementary steps to the overall kinetics of complex formation at nickel. By using the pressure-jump technique with conductivity read-out, he has been able to study directly the contributions of steps (b) and (c) (Figure 3) in the reaction with malonate.[58] It was possible to show that the ring-closure step was slower than the departure of the first water molecule from the inner hydration shell of the cation. More recently,[59] he has extended these studies to include several other dicarboxylates and other bidentate ligands containing $-CO_2^-$, $-OH$, and $-NH_2$ groups. By making use of the observation with monodentate ligands that the dissociation rate constant k_d for Ni^{2+} is proportional to the basicity of the departing carboxylate group, he was able to estimate values of k_d for the individual groups of the bidentate ligands. He concludes that, even for Ni^{2+}, ring-closure contributes to the overall k_f since the binding of chelates is slower than that of comparable monodentate ligands. He also concludes, rather surprisingly, that with aminocarboxylates the binding of the carboxylate group occurs first, and is followed by ring-closure involving the amino-group.

Before leaving this aspect of metal complex formation, we might just point out that most of the differences in rate constant to which Hoffmann and co-workers refer are comparatively small. It appears that, at least for systems involving nickel, we have entered the stage reached in discussions of reaction at Co^{III} centres many years ago: the overall pattern appears to be more or less established but many of the finer points are still the subject of healthy debate. In fact, it is even conceivable that Ni^{II} will take over the

[58] U. Nickel, H. Hoffmann, and W. Jaenicke, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 526.

[59] H. Hoffmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 432.

central role in inorganic reaction mechanisms which has been occupied by Co^{III} for so many years, since it does at least have the advantage that a complete kinetic run can be completed within a fraction of a second compared with the several hours or even days required for the more sedate metal.

The Internal Conjugate Base Mechanism.—Also in 1966, Rorabacher [60] reported some temperature-jump data involving the monoammine complexes of Co^{II}, Ni^{II}, and Zn^{II}. The rate constants were discussed in terms of the normal mechanism but they were particularly interesting inasmuch as they suggested that the rates which had been reported previously [61] for the reaction of nickel with polyamines (*e.g.* en) had been unusually high. In the 1966 paper, Rorabacher proposed an internal conjugate base mechanism to explain this acceleration, and this is shown in Figure 5.

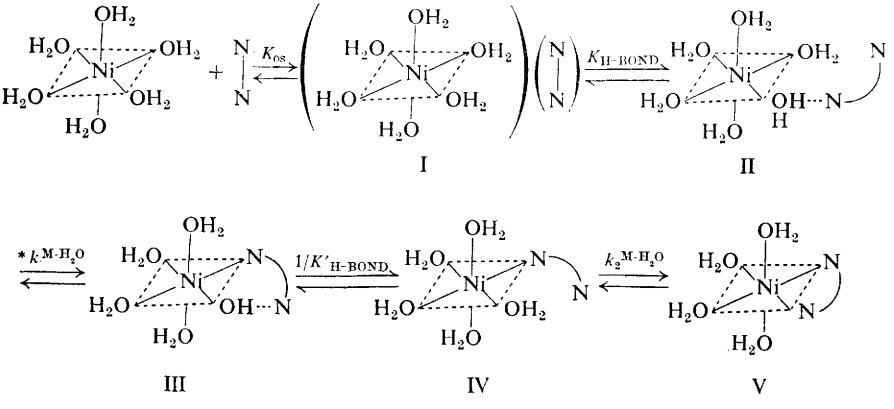


Figure 5 *Internal conjugate base* (ICB) *mechanism, using the reaction of hexaquonickel*(II) *ion with* en *as a model:* I, *outer-sphere complex;* II, *hydrogen-bonded outer-sphere complex;* III, *single-bonded intermediate with hydrogen-bond still intact;* IV, *normal single-bonded intermediate;* V, *normal double-bonded complex;* K_{os} = *equilibrium constant for outer-sphere association;* $K_{H\text{-bond}}$ = *stability constant for hydrogen-bond formation;* $*k^{M-H_2O}$ = *rate constant for enhanced metal–water bond rupture (rate-determining step);* $K'_{H\text{-bond}}$ = *stability constant for hydrogen-bond formation in single-bonded complex;* $k_2^{M-H_2O}$ = *rate constant for metal–water bond rupture in single-bonded complex*
(Reproduced by permission from *Inorg. Chem.*, 1966, **5**, 1891)

If both ammonia and the polyamine ligands are assumed to react with Ni^{2+} according to the normal mechanism (Figure 1), then the enhanced reaction rates in the case of the polyamines must be attributable either to an increase in K_{os} or k_{wl} or both. Since an unprotonated polyamine involves the same electrostatic considerations as does NH_3, the rates of formation of the outer-sphere complexes would presumably be comparable (diffusion-controlled). However, the dissociation rate of the outer-sphere intermediate

[60] D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891.
[61] D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, *Inorg. Chem.*, 1963, **2**, 667.

could be decreased if some means of stabilization were available (*i.e.* K_{os} could be increased through a reduction in the dissociation rate constant). Rorabacher points out that the pK_a values of amines and the aquonickel ion are comparable (of the order of 9—10) and suggests that this stabilization is achieved in the case of the polyamine ligands by hydrogen bonding between a nitrogen donor atom of the incoming ligand and a hydrogen atom of one of the co-ordinated water molecules.

Although ammonia could also participate in this type of hydrogen bond, formation of such a bond would eliminate the potential ability of the same ammonia molecule to co-ordinate with the central metal ion. By contrast, hydrogen-bonded en, or one of the higher polyamines, contains an adjacent nitrogen donor atom within the same molecule which still has the ability to form a co-ordinate bond. Therefore, hydrogen-bond formation between the aquometal ion and the polyamine would effectively increase K_{os} while still promoting the desired reaction. For this type of situation to arise with ammonia, two NH_3 molecules would have to be involved, one to form a hydrogen bond and the other to replace a water molecule in the inner sphere. This would be very unlikely unless the activated intermediate were to have a very long lifetime.

Rorabacher lists [60] the known values for k_f at Ni^{2+} in aqueous solution and points out that all multidentate ligands with pK_a values less than 8 react at rates comparable to those of monodentate ligands, whereas those with pK_a significantly larger than 8 exhibit enhanced formation rate constants. It is of particular interest that protonated species of the polyamines which have pK_a less than 8 (*e.g.* H_2trien^{2+}, $H_3tetren^{3+}$) fail to exhibit enhanced formation rate constants even though two or more unprotonated nitrogen donor atoms are present, whereas $Htrien^+$ (pK_a = 9·2) does.

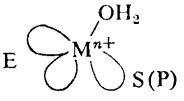
In the original paper,[60] it was pointed out that the ICB mechanism should be applicable to other metal ions, although data were almost non-existent for the reaction of ligands of the type which favour the mechanism with metals other then Ni^{2+}. Recently, it has been shown [62] to be operative in the reactions of Co^{2+} with two branched poly(amino-alcohol) ligands: *NNN'N'*-tetrakis-(2-hydroxyethyl)ethylenediamine (TKED) and *NNN'N'*-tetrakis-(2-hydroxypropyl)ethylenediamine (THPED). A similar result had previously been obtained [63] with the corresponding Ni^{2+} systems. A similar type of acceleration has also been reported [64] in the reaction of Cu^{2+} with en.

6 The Effect of Bound Ligands

In several (though by no means all) enzyme-catalysed reactions which exhibit an absolute requirement for a metal ion, it has been suggested that the

[62] D. B. Rorabacher and D. B. Moss, *Inorg. Chem.*, 1970, **9**, 1314.
[63] D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, 1969, **8**, 1498.
[64] L. J. Kirschenbaum and K. Kustin, *J. Chem. Soc.* (*A*), 1970, 684.

metal M forms a bridge or link between the enzyme E and the substrate S and/or product P. The enzyme, substrate, and product are usually multidentate ligands, and the intermediate EMS (or EMP) is pictured as a double-chelate complex, possibly with one or more water molecules remaining in the inner co-ordination sphere of the metal (8). Since the



(8)

enzymatic turnover must involve at least one complex formation and one dissociation step between a ligand and a metal ion which is already bound in a 1 : 1 complex, a very important question in any discussion involving the role of metals in enzyme action must be: what is the effect of a bound ligand on the kinetics of the subsequent complex formation of the metal? In what ways, if any, are the kinetics and mechanism of the formation of EMS different from those of MS or ME? Not surprisingly, in view of the complexities involved, most of the work which has been done on this problem has been concerned with model systems rather than enzymes themselves. In this section we shall be concerned only with the work which involves these smaller, better-characterized systems.

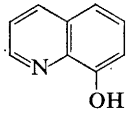
The first paper to concern itself with this problem, amongst others, was probably that by Hammes and Steinfeld,[65] which appeared in 1962. The temperature-jump technique was used to study the binding of one, two, and three molecules of glycine, diglycine, or imidazole to Ni^{II} or Co^{II} in aqueous solution. For the complexes with glycine, the authors found that the formation rate constants (k_f) increased with each successive replacement of the neutral water molecules in the inner co-ordination sphere by the charged glycinate anion, for both Co^{2+} and Ni^{2+}. No such acceleration was found with imidazole and diglycine, however, and the authors came to the very reasonable conclusion that the presence of the negatively-charged carboxylate group in the inner sphere of the metal ion produces a 'drainage' of positive charge from the metal ion and a consequent loosening of the remaining water molecules. They rationalized the diglycine result by suggesting that bonding between this ligand and the metal takes place through the uncharged portions of the ion rather than the carboxylate group. They also predicted that bonding of the first ligand through two or more negatively-charged groups would loosen the water molecules on the metal even more.

Unfortunately, this does not appear to be the case. Indeed, it has been shown, principally by Margerum and co-workers, that even with nickel the factor which influences k_f in this situation is not primarily the charge

[65] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, 1962, **84**, 4639.

on the bound ligand. But before discussing the work with Ni^{2+}, we shall touch on some results which have been published on the ions Mg^{2+} and Mn^{2+}. Besides being of greater interest to biochemists than Ni^{2+}, these metals are simpler in that they are electronically symmetrical (Mg^{2+} being d^0 and Mn^{2+} high-spin d^5).

In 1966, Hague and Eigen [66] reported rate data for the reaction of 8-hydroxyquinoline (oxine, 9) with magnesium and with the complexes



(9)

magnesium–uramil *NN*-diacetate ($MgUDA^-$), –adenosine 5′-triphosphate ($MgATP^{2-}$), and –polytriphosphate ($Mg\,tpp^{3-}$). In all cases the data were consistent with a two-path mechanism in which the magnesium species reacted with either the oxine anion or the oxine molecule.

The rate constants for the formation and dissociation of the complexes involving the monoanion are shown in Table 6. The values of k_f are typical for Mg^{2+} reacting according to the normal scheme (Figure 1). The

Table 6 *Rate constants for the reaction of* 8*-hydroxyquinoline with* Mg^{II} *and* Mn^{II} *species*[a]

	k_f (l mol^{-1} s^{-1})	k_d (s^{-1})
Mg^{2+}	$3{\cdot}8 \times 10^5$	7
$MgUDA^-$	$8{\cdot}0 \times 10^4$	41
$MgATP^{2-}$	$9{\cdot}6 \times 10^4$	54
$Mg\,tpp^{3-}$	$4{\cdot}7 \times 10^4$	6
Mn^{2+}	$1{\cdot}1 \times 10^8$	140
$Mn\,nta^-$	$1{\cdot}9 \times 10^7$	90
$MnUDA^-$	$3{\cdot}6 \times 10^7$	210
$MnATP^{2-}$	$1{\cdot}0 \times 10^6$	35
$Mn\,tpp^{3-}$	$7{\cdot}9 \times 10^5$	80

[a] Data refer to 16 °C; for Mg species from ref. 66, and for Mn species from ref. 67.

presence of the 'innocent' ligand is evidently having very little effect on the rates of both reactions, especially when it is remembered that there are six water molecules available for replacement at hydrated Mg^{2+} but probably only two or three at the metal ion in the other species. In particular, there is no large labilizing effect produced by the highly-charged ATP^{4-} and tpp^{5-} ions; nor is there any large increase in the dissociation rate (the slight increase in k_d caused by UDA^{3-} and ATP^{4-} is probably due to steric crowding with the bulky organic groups). Thus, it appears that the magnesium ion behaves like a uniform positively-charged sphere

[66] D. N. Hague and M. Eigen, *Trans. Faraday Soc.*, 1966, **62**, 1236.

whose charge-density is more or less independent of the nature of the groups bound to it.

This study has recently been extended [67] to the analogous systems involving manganese(II), with somewhat similar results. The rate constants for the formation and dissociation of the complexes with the oxine mono-anion are given in Table 6. Again, the values of k_f are typical for the metal reacting according to the normal scheme (Figure 1) and there is no large labilizing effect due to the presence of the highly-charged 'innocent' ligands in the inner co-ordination sphere of the metal ion. On the contrary, the largest effect is produced by the triphosphate ligands ATP^{4-} and tpp^{5-} and involves a significant *retardation* of the complex-formation process. Thus, whereas the bare Mn^{2+} ion is of the order of 10^3 times more labile than Mg^{2+}, the triphosphate complexes of Mn^{2+} are only about ten times more so.

The reactions of Ni^{2+} have received far more attention than those of any other labile metal, even though ligand field effects are almost certain to produce greater variations in rate constants than those we have seen for magnesium and manganese(II). Nickel(II) has at least three advantages compared with many other labile metals, all of which have contributed to this situation. In the first place, the stability constants are frequently high; in the second place, the values of k_f are generally sufficiently low to allow the reactions to be studied by the stopped-flow technique; and in the third place, the paramagnetic character of nickel coupled with the second factor make it very well suited to n.m.r. solvent-exchange studies. It is the third point which makes nickel a particularly important species in discussions of the mechanism of complex formation at labile metal ions. This is the only metal for which suitable solvent exchange as well as overall complex formation data exist. We shall first discuss the former and then consider the implications of the exchange data on the overall kinetics.

Hunt's group have reported the water-exchange parameters at ammonia- [68] and ethylenediamine-substituted [69] Ni^{2+}; their results are summarized in Table 7 (in all cases, the co-ordination number of Ni^{2+} was taken as six). In general, the remaining water molecules appear to be labilized as the extent of substitution by the other ligands increases, although the activation parameters seem to vary non-systematically.

In contrast, solvent exchange data for aqueous nickel(II)–bipy [70] and –terpy [71] complexes suggest that the ligand is having essentially no effect on the rates, although it affects the activation parameters (see Table 7). It is tempting to ascribe this difference in behaviour between aliphatic and aromatic nitrogen ligands to differences in back π-bonding effects, although no general picture can be given at the present time.

[67] D. N. Hague and M. S. Zetter, *Trans. Faraday Soc.*, 1970, **66**, 1176.
[68] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem., Soc.*, 1970, **92**, 798.
[69] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1969, **91**, 5001.
[70] M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1970, **92**, 2321.
[71] D. Rablen and G. Gordon, *Inorg. Chem.*, 1969, **8**, 395.

Table 7 *Rate constants and activation parameters for water-exchange at substituted* Ni^{II} *species*[a]

	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	*Ref.*
$[Ni(H_2O)_6]^{2+}$	$3{\cdot}6 \times 10^4$	12·3	4	68
$[Ni(H_2O)_5(NH_3)]^{2+}$	$2{\cdot}5 \times 10^5$	10·6	2	68
$[Ni(H_2O)_4(NH_3)_2]^{2+}$	$6{\cdot}1 \times 10^5$	7·8	− 6	68
$[Ni(H_2O)_4\,en]^{2+}$	$4{\cdot}4 \times 10^5$	10·0	10	69
$[Ni(H_2O)_3(NH_3)_3]^{2+}$	$2{\cdot}5 \times 10^6$	10·2	5	68
$[Ni(H_2O)_2\,en_2]^{2+}$	$5{\cdot}4 \times 10^6$	9·1	3	69
$[Ni(H_2O)_4\,bipy]^{2+}$	$4{\cdot}9 \times 10^4$	12·6	5	70
$[Ni(H_2O)_3\,terpy]^{2+}$	$5{\cdot}2 \times 10^4$	10·7	− 1	71
$[Ni(H_2O)_2\,bipy_2]^{2+}$	$6{\cdot}6 \times 10^4$	13·7	9	70

[a] Data refer to 25 °C. Ionic strengths, *etc.*, are different from those to which the data in Table 2 refer (see ref. 70).

Margerum's group have measured the kinetics of overall complex formation at some of these nickel(II) species and have observed similar trends. In a recent paper [72] they have shown that, as the number of co-ordinated nitrogen atoms in nickel–polyamine complexes increases, the value of k_f for the reaction of the aquonickel species with NH_3 increases. Thus, the rate constant for $[Ni\,trien]^{2+}$ is larger than that for $[Ni\,dien]^{2+}$ by a factor of 5 at 8 °C. It is concluded that there is a continuous increase in water lability with increasing number of co-ordinated nitrogen atoms (although this cannot be the whole story since the value of k_f for the complex of the branched tetradentate polyamine tren is larger than that for the complex of the straight-chain isomer trien). This paper is an extension of the one [73] in which it was demonstrated that the charge on the 'innocent' ligand *per se* is of minor importance in determining the overall rate of complex formation.

The substitution of the two water molecules in $[Ni(H_2O)_2\,en_2]^{2+}$ by en has also been studied.[74] The rate of addition of the third en to Ni^{II} is greatly accelerated by the presence of the two co-ordinated en molecules, but the rate constant for ring-closure is similar in magnitude to that for the dissociation of the monodentate en, so that ring-closure contributes to the rate-limiting process (cf. Section 5). Both the unprotonated and monoprotonated forms of en react, and the proposed mechanism is shown in Figure 6. The rate constant for monodentate en-complex formation (k_{14}) is $5{\cdot}5 \times 10^6$ l mol^{-1} s^{-1} and for ring-closure (k_{45}) $2{\cdot}2 \times 10^5$ s^{-1} (at 25 °C). It is thought that ring-closure does not contribute to the overall process for the first and second en molecules.

The solvent exchange studies of Rablen and Gordon [71] have a bearing on some previous results of Wilkins and co-workers,[75] who had found

[72] J. P. Jones, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 1875.
[73] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 1088.
[74] J. P. Jones and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 470.
[75] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1965, **4**, 929; 1966, **5**, 622.

that the formation rates for 1 : 1, 2 : 1, and 3 : 1 complexes of nickel(II) with bipy and phen conformed to the normal picture. In particular, there was no significant effect of previously bound ligands on the rates of subsequent complex formation. However, for terpy, the second ligand molecule reacted two hundred times more rapidly than the first, which

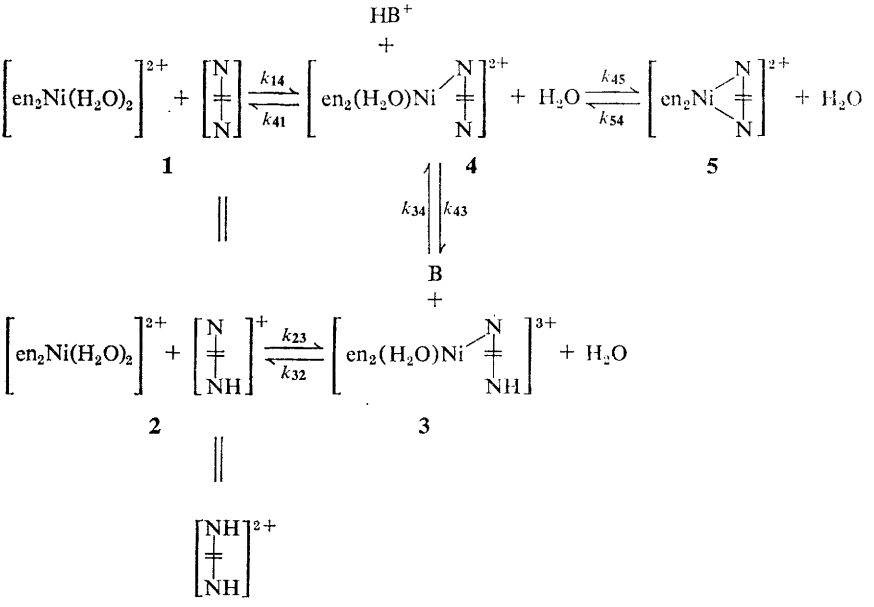


Figure 6 *Proposed mechanism for the reaction of* en *and* Hen$^+$ *with* Ni en$_2$(H$_2$O)$_2^{2+}$, *where* B *and* HB$^+$ *are a base and its conjugate acid in the rapid proton transfer reaction between* 3 *and* 4
(Reproduced by permission from *J. Amer. Chem. Soc.*, 1970, **92**, 470)

had a normal rate constant; this picture was repeated with Fe^{2+} and Co^{2+}. This result had suggested that the co-ordinated terpy labilizes the remaining water molecules, but the results of Rablen and Gordon show that this is not so. Opinion now seems to favour a weak interaction between the two terpy molecules in the mono-terpy complex and the outer-sphere complex, which gives rise to an enhanced value of K_{OS}.

Incidentally, although the overall rate constant for the reaction of $[Ni(H_2O)_2\,bipy_2]^{2+}$ with bipy appeared to be normal,[75] when taken in conjunction with the water-exchange rate [70] it allows a value of 0·015 l mol^{-1} to be calculated for K_{OS}. This is rather lower than the usual value of 0·1 used for neutral ligands. A possible reason for this low value of K_{OS} is apparent if the diaquo species has a *trans*-configuration; indeed, the spatial distribution of substituted ligands around the central metal ion must always be considered when the solvent exchange rates are being compared with k_f values for chelating ligands.

A study by Steinhaus and Margerum,[76] reported in 1966, is also relevant to this discussion. The reactions studied are shown in Figure 7. The substituents X on phen were chosen so as to minimize any steric interference between the two ligands: they were 5-NO_2, 5-Cl, 5-Me, 5,6-diMe, and H. (The reactions with the 5-SO_3^- group were also investigated, but the results

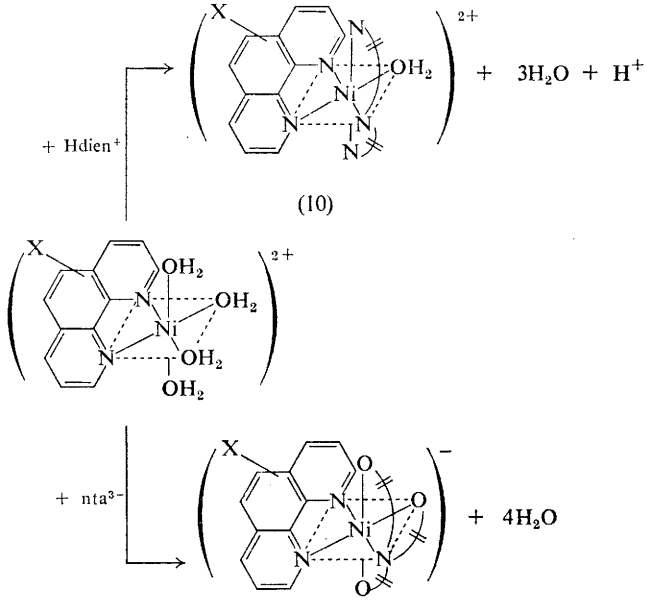


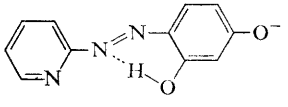
Figure 7 *The reaction of* Ni^{II} *complexes with* $Hdien^+$ *and* nta^{3-}
(Reproduced by permission from *J. Amer. Chem. Soc.*, 1966, **88**, 441)

did not fall in line with the others, presumably because of the difference in charge.) Changes in the formation rates of the mixed complexes (10) and (11) are not large, but they definitely follow Hammett free-energy relationships using the pK values of the substituted 1,10-phenanthrolinium ions. They thus reflect the electron-donating or -withdrawing properties of the substitutents. The Hammett ρ-factors are $-0{\cdot}089$ for the reaction with $Hdien^+$ and $-0{\cdot}264$ for the reaction with nta^{3-}, and the fact that they are negative supports the assignment of the water-loss process on the rate-determining step.

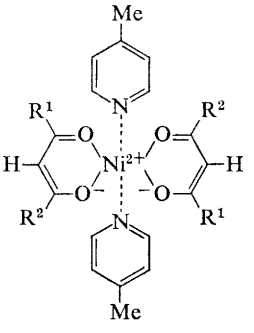
A similar result has been reported by Funahashi and Tanaka [77] for the reaction of (12) with monoacidopenta-aquonickel(II) complexes, $[Ni(H_2O)_5A]^+$, where A^- is OH^-, N_3^-, $CH_3CO_2^-$, and F^-. The effect of

[76] R. K. Steinhaus and D. W. Margerum, *J. Amer. Chem. Soc.*, 1966, **88**, 441.
[77] S. Funahashi and M. Tanaka, *Inorg. Chem.*, 1969, **8**, 2159.

electron donation by the ligand A^- on the rate of complex formation was demonstrated by obtaining a linear plot of log k_f against the function E_A. (The latter is a redox factor defined [78] by the equation $E_A = E^0 + 2{\cdot}60$, where E^0 is the standard redox potential for the process $2A^- \rightleftharpoons A_2 + 2e$.)



(12)



(13)

The kinetics of ligand exchange in bis-(4-picoline) adducts of bis-(β-diketonato)nickel(II) complexes of the type (13) have been studied [79] in deuteriochloroform by an n.m.r. technique. The exchange rates for the process:

$$Ni(AA)_2PP + P^* \rightleftharpoons Ni(AA)_2PP^* + P$$

were independent of the concentration of 4-picoline (P), and electron-withdrawing groups R^1 and R^2 attached to the β-diketone ring slowed down the rate of exchange. Exchange rate-constants correlated with the sum of the Taft σ^* parameters for the substituents, reflecting the results obtained in aqueous systems.

Hoffmann and Yeager [80] have discussed the general problem of the effect of various inner co-ordination sphere ligands on the dissociation rates of nickel(II) complexes, with special reference to the dissociation of the malonate dianion. The opening of the chelate ring appears to be the rate-determining step and the dissociation rate-constants have been compared with the observed shift in the optical absorption peaks for the *d–d* transitions in the various mixed complexes. Hoffmann [81] has also used the pressure-jump technique to measure the kinetics of formation and dissociation of the mono- and bis-thiocyanato-complexes of Ni^{II} in methanol. The overall values of k_f are very similar for the mono- and bis-complexes even though the equilibrium constants differ greatly.

[78] J. O. Edwards, *J. Amer. Chem. Soc.*, 1954, **76**, 1540; 1956, **78**, 1819.
[79] R. W. Kluiber, R. Kukla, and W. deW. Horrocks, *Inorg. Chem.*, 1970, **9**, 1319.
[80] H. Hoffmann and E. Yeager, *Ber. Bunsengesellschaft phys. Chem.*, 1970, **74**, 641.
[81] F. Dickert, H. Hoffmann, and W. Jaenicke, *Ber. Bunsengesellschaft phys. Chem.*, 1970, **74**, 500.

There have been many reports form the Kustin school of the rate constants for formation and dissociation of the complexes between nickel(II) and amino-acids. The reactions are of the type:

$$ML_{n-1} + L \underset{k_{-n}}{\overset{k_n}{\rightleftharpoons}} ML_n$$

(where $n = 1$, 2, and 3) and are usually followed by the temperature-jump method (cf. ref. 65). The reports frequently include the results of parallel studies involving other metals and related types of ligand. The results, which are too numerous to give in detail, also frequently reflect the different behaviour of five- and six-membered chelate rings (see Section 5). The metal ions and ligands involved are given in Table 8.

Table 8 *Reactions of metals with amino-acids*, etc.

Metal	*Ligand*	*Ref.*
Co^{II}, Ni^{II}	arginine	*a*
Co^{II}, Ni^{II}	glycine, di-, tri-, tetra-glycine	*b*
Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}	serine	*c*
Co^{II}, Ni^{II}	picolinic acid	*d*
Co^{II}, Ni^{II}	glycylsarcosine	*e*
Co^{II}, Ni^{II}, Cu^{II}	leucine	*f*
Co^{II}, Ni^{II}, Cu^{II}	sarcosine	*g*

[a] G. Davies, K. Kustin, and R. F. Pasternack, *Internat. J. Chem. Kinetics*, 1969, **1**, 45. G. Davies, K. Kustin, and R. F. Pasternack, *Inorg. Chem.*, 1969, **8**, 1535. [c] R. L. Karpel, K. Kustin, and R. F. Pasternack, *Biochem. Biophys. Acta*, 1969, **177**, 434. [d] A. Kowalak, K. Kustin, and R. F. Pasternack, *J. Phys. Chem.*, 1969, **73**, 281. [e] K. Kustin and R. F. Pasternack, *J. Phys. Chem.*, 1969, **73**, 1. [f] R. F. Pasternack, E. Gibbs, and J. C. Cassatt, *J. Phys. Chem.*, 1969, **73**, 3814. [g] R. F. Pasternack, K. Kustin, L. A. Hughes, and E. Gibbs, *J. Amer. Chem. Soc.*, 1969, **91**, 4401.

A few other studies involving the copper(II) ion have been reported. These include an ultrasonic investigation [82] of aqueous solutions of $CuSO_4$ and $Cu\,en_2(S_2O_3)$ and investigations of consecutive complex formation with α- and β-alanine and histidine (ref. 54) and with en (ref. 64).

Pearson and Sweigart have reported [82] one of the first kinetic studies involving substitution at square-planar nickel(II), in Ni^{II}–dithiolate complexes. They discuss nucleophilic reactivity, leaving group, and *trans* effects, and report that the reactions follow an associative pathway, as expected. The solvent path is not important and, although for Pt^{II} the formation of a five-co-ordinate intermediate may be rate-determining, for Ni^{II} this step is fast compared with subsequent steps. The formation constant of the five-co-ordinate intermediate does, however, markedly affect the overall rates, and it seems that the *trans* effect for nickel(II) operates through the stability of this intermediate.

[82] R. G. Pearson and D. A. Sweigart, *Inorg. Chem.*, 1970, **9**, 1167.

7 Structural Interconversion

In this section we shall mention the few studies which have been concerned with structural interconversion at labile metal ions. They have been involved with cobalt(II) and nickel(II), although it might be mentioned that several groups of workers have apparently been unable to repeat the previously reported [83] study on the octahedral ⇌ tetrahedral transformation of hydrated Co^{2+} and Zn^{2+}.

The kinetics of octahedral ⇌ tetrahedral conversion in nitromethane–pyridine have been reported.[84] The mechanism apparently involves a five-co-ordinate intermediate:

$$Co\,py_4Cl_2 \rightleftharpoons Co\,py_3Cl_2 + py \quad \text{(fast)}$$

followed by:

$$Co\,py_3Cl_2 \rightleftharpoons Co\,py_2Cl_2 + py \quad \text{(rate-determining)}$$

The dependence of the rate parameters for the step:

$$Co\,py_2Cl_2 + py \longrightarrow Co\,py_3Cl_2$$

on the nature of the solvent has been investigated. In nitromethane, the rate constant (ionic strength = 0·1; 25 °C) = $7{\cdot}2 \times 10^4$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 5·4 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = − 18 e.u.; while in pyridine, the quantities are, respectively, $3{\cdot}1 \times 10^3$ l mol^{-1} s^{-1}, 2·6 kcal mol^{-1}, and − 34 e.u. Howard and Marianelli [85] have used ^{14}N n.m.r. to investigate the rapid step in pyridine, and they obtain activation parameters for the loss of a pyridine molecule from $Co\,py_4Cl_2$; $\Delta H^{\ddagger}$ = 13·2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 17 e.u.

Wilkins *et al.*[86] have studied the reaction:

$$\underset{\text{(octahedral)}}{[Ni(L)(H_2O)_2]^{2+}} \rightleftharpoons \underset{\text{(planar)}}{[Ni(L)]^{2+}} + 2H_2O \qquad (3)$$

where L is the quadridentate ligand 2,3,2-tet. This reaction, which is associated with a well-established blue ⇌ yellow colour change, is temperature sensitive, and therefore amenable to investigation by the temperature-jump technique. A relaxation was observed and was attributed to reaction (3), but it was too fast for precise measurement. A lower limit of 10^5 s^{-1} was estimated for the rate constant of interconversion. As the authors point out, this high rate constant resembles that noted for the planar–tetrahedral change observed [87] with certain Ni^{II} complexes. More recently, the latter interconversion has been measured [88] for bis(diphenyl-

[83] T. J. Swift, *Inorg. Chem.*, 1964, **3**, 526.
[84] R. D. Farina and J. H. Swinehart, *J. Amer. Chem. Soc.*, 1969, **91**, 568.
[85] G. D. Howard and R. S. Marianelli, *Inorg. Chem.*, 1970, **9**, 1738.
[86] R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4326.
[87] D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, 1963, **85**, 397.
[88] G. N. LaMar and E. O. Sherman, *Chem. Comm.*, 1969, 809.

methylphosphine)nickel dibromide and di-iodide in deuteriochloroform using ^{1}H n.m.r. line-width ($k \simeq 2 \times 10^3$ s^{-1} at -55 °C for the iodide and $\simeq 1{\cdot}7 \times 10^3$ s^{-1} at -12 °C for the bromide). Other n.m.r. studies [89] give $k = 9{\cdot}0 \times 10^5$ s^{-1} (at 25 °C), $\Delta H^{\ddagger} = 16$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 22$ e.u.

[89] L. H. Pignolet and W. deW. Horrocks, *J. Amer. Chem. Soc.*, 1969, **91**, 3976.

2
Reactions of Biochemical Interest

1 Ion Transport through Biological Membranes

Although there have been many experiments involving the passage of metal and other ions through natural membranes, there is very little understanding of the process at the molecular level. Weiss, in a series of articles,[1] has attempted to show that this and other related problems (such as the passage of action potentials in nerve cells, the sodium pump, and mitochondrial oxidative phosphorylation) are, in fact, variations on a common theme in which an equilibrium is established between opposing dilatory and elastic contractile processes involving polymeric matrices embedded in the membranes. These papers, which incorporate many of the ideas developed by the author during the past 15 years, provide an interesting background to this topic.

In several papers, the coupling of various ion fluxes (*e.g.* H^+ and K^+, K^+ and Ca^{2+}) through membranes has been discussed,[2] and in others the inhibition of ion movement by such agents as the cardiac glycosides has been considered.[3] Baker and Willis[4] have used the fact that inhibition of the Na^+-pump by these compounds is highly specific to measure the number of pumping sites per unit area of membrane. For several types they have found about 10^5 sites per cell and have concluded that red ghost cells, in which only about 200 binding sites (corresponding to approximately one site per square micron of cell surface, a remarkably low density) were found,[5] are exceptional.

The number of chemists interested in the problem of ion transport through cellular membranes has increased markedly in recent years, and the tendency to approach the problem from the molecular standpoint has developed to a large degree because of some remarkable observations with model compounds, such as those reported in the November–December, 1968 issue of *Federation Proceedings*.[6] It has been found that certain macrocyclic antibiotics, such as nonactin, enniatin, and valinomycin,

[1] D. E. Weiss, *Austral. J. Biol. Sci.*, 1969, **22**, 1337, 1355, 1373, 1389.
[2] *E.g.* S. Massari and G. F. Azzoni, *European J. Biochem.*, 1970, **12**, 301; A. Scarpi and G. F. Azzoni, *ibid.*, p. 328.
[3] *E.g.* H. W. Middleton, *Arch. Biochem. Biophys.*, 1970, **136**, 280.
[4] P. F. Baker and J. S. Willis, *Biochim. Biophys. Acta*, 1969, **183**, 646.
[5] J. C. Ellory and R. D. Keynes, *Nature*, 1969, **221**, 776.
[6] *Fed. Proc.*, 1968, **27**, 1250; see also, *e.g.*, *British Medical Bulletin*, 1970, **24**, part 2.

induce in several membrane systems (including mitochondria, erythrocytes, and lipid bilayers) a high degree of permeability with respect to metal ions. Moreover, this permeability is often highly specific inasmuch as one ion is transported through the membrane while another, chemically very similar, ion is not. For example, the macrotetrolides monactin and nonactin possess highly specific K^+ and Rb^+ transport properties,[7] even in the presence of large concentrations of Li^+ and Na^+. Several theories have been advanced to account for the action of these cyclic antibiotics (*e.g.* ref. 6), but there is not yet sufficient experimental evidence to enable a choice to be made between them. Three general mechanisms might be mentioned:

(i) pore formation, in which the active molecule binds to the surface of the membrane and thereby provides an area which offers a lowered energy barrier for the penetration of ions;

(ii) channel formation, in which several active molecules stack together to produce a channel which completely spans the membrane. Either the anhydrous or partially hydrated ionic species pass along the channel, forming intermediate complexes progressively with successive molecules comprising the channel;

(iii) mobile carriers, in which the complexing molecule displaces the hydration sphere of the cation and forms a lipid-soluble complex which diffuses across the membrane; the cation is released at the opposite membrane interface.

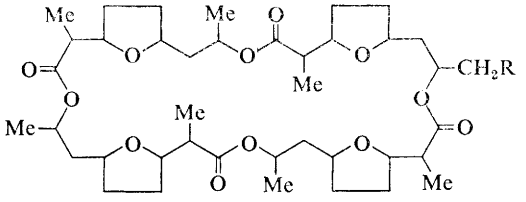
In view of these and other theories, it is important to answer questions concerning the relative affinities of the various antibiotic molecules for different metal ions, the conformations of the macrocycles before and after formation of the ion complexes, the rates of formation and dissociation of the complexes, and so on. In the remainder of this section we shall consider recently published work on this very exciting topic, the starting point being *X*-ray crystal structure determinations of the various complexes.

It had been shown by Dunitz and co-workers [8] in 1967 that the structure of the potassium complex of nonactin (1a) is as shown in Figure 1. The 32-membered ring can be described as resembling the seam of a tennis ball with the K^+ ion at the centre of the ball and the methyl substituents and methylene groups of the furan rings on the outside. More recently, the structure of the K^+ complex of another macrocyclic antibiotic with potassium transport properties, enniatin B (2), has been determined.[9] In this case, the carrier–K^+ complex is in the form of a charged disc with a lipophilic exterior. The authors point out that both molecules are sufficiently large and impenetrable that any counter-ion or polar molecule in

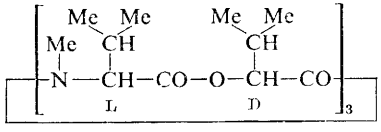
[7] *E.g.* P. Mueller and D. O. Rudin, *Biochem. Biophys. Res. Comm.*, 1967, **26**, 398; Z. Stefanac and W. Simon, *Microchem. J.*, 1967, **12**, 125; H.-K. Wipf and W. Simon, *Biochem. Biophys. Res. Comm.*, 1969, **34**, 707.

[8] B. T. Kilbourn, J. D. Dunitz, L. A. R. Pioda, and W. Simon, *J. Mol. Biol.*, 1967, **30**, 559; M. Dobler, J. D. Dunitz, and B. T. Kilbourn, *Helv. Chim. Acta*, 1969, **52**, 2573.

[9] M. Dobler, J. D. Dunitz, and J. Krajewski, *J. Mol. Biol.*, 1969, **42**, 603.



(1) (a) R = H, (b) R = CH_3



(2)

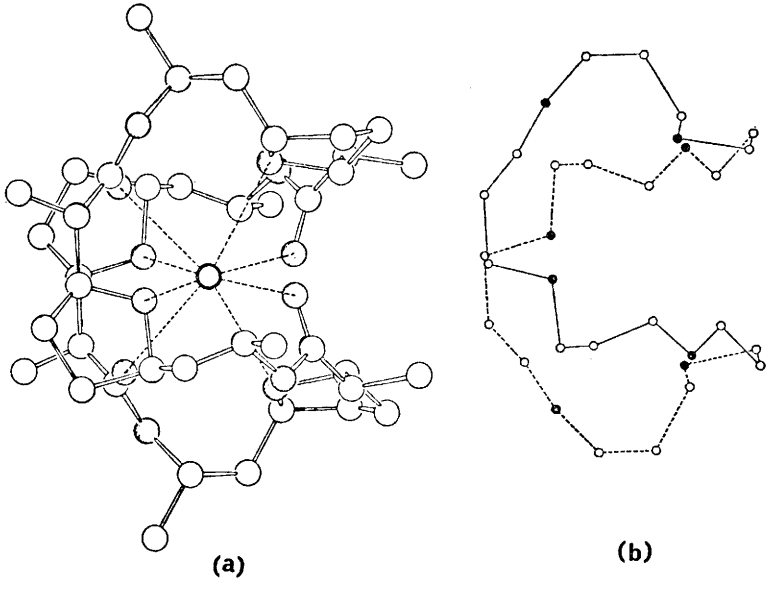
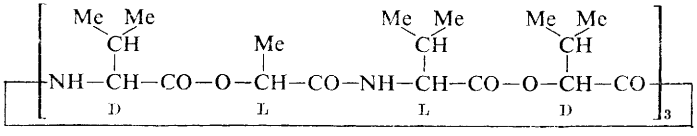


Figure 1 *The nonactin–K^+ complex (a) and the outline of the ring (b) in the complex*

(Reproduced by permission from *J. Mol. Biol.*, 1967, **30**, 559)

the environment will experience a relatively weak electrostatic attraction. They suggest that many of the charged complexes which might be involved in the transport of ions through biological membranes are built along the same lines.

Pinkerton, Steinrauf, and Dawkins [10] have determined the structure of the potassium complex of valinomycin (3). They, also, found that the



(3)

antibiotic is wrapped around the metal ion, with the oxygen atoms of alternate carbonyl groups co-ordinated. The anion, $AuCl_4^-$, is held less specifically in a nearly spherical cavity formed by the top of one valinomycin molecule and the bottom of the next. The authors had found that in order to make the complex, both the proper anion and the proper cation had to be present, and they suggest that some of the biological properties of valinomycin could be explained on the basis of transport of an anion–cation pair into or through the non-aqueous regions of the cell. A similar conclusion had been arrived at by Pressman[11] from considerations based on the biological properties of valinomycin.

Several groups have reported studies in which the conformations of antibiotic–cation complexes in solution are discussed. Russian workers [12] have used n.m.r., i.r., o.r.d., and dipole moment techniques to study valinomycin and its potassium complex in solvents of varying polarity. They suggest that (3) can exist in two forms, in one of which the amide groups form six intramolecular hydrogen bonds and in the other of which only three such bonds are formed; as the solvent polarity increases, so does the proportion of (3) in the latter form. Complexation with K^+ is accompanied by conformational changes in which three formerly outward-facing ester carbonyls become oriented towards the metal ion, which sits in the middle of the ring. Changes in the polarity of the solvent do not affect the shapes of the o.r.d. curve of the complex, suggesting that the latter is quite rigid. A dramatic feature of this conformation is that the K^+ ion and the system of hydrogen bonds which helps to maintain the structure are effectively shielded from solvent action by the hydrophobic branched side-chains at the periphery of the molecule (cf. Figure 1). Similar results are reported for the K^+–enniatin B complex.[13]

[10] M. Pinkerton, L. K. Steinrauf, and P. Dawkins, *Biochem. Biophys. Res. Comm.*, 1969, **35**, 512.

[11] B. C. Pressman in ref. 6, p. 1283.

[12] V. T. Ivanov, I. A. Laine, N. D. Abdullaev, L. B. Senyavina, E. M. Popov, Yu. A. Ovchinnikov, and M. M. Shemyakin, *Biochem. Biophys. Res. Comm.*, 1969, **34**, 803.

[13] Yu. A. Ovchinnikov, V. T. Ivanov, A. V. Evstratov, V. F. Bystrov, N. D. Abdullaev, E. M. Popov, G. M. Lipkind, S. F. Arkhipova, E. Sifremov, and M. M. Shemyakin, *Biochem. Biophys. Res. Comm.*, 1969, **37**, 668.

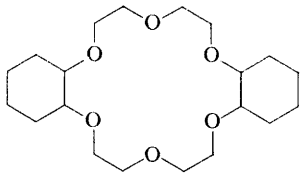
Pressman and co-workers [14] have given a preliminary account of the application of n.m.r. to the study of this conformational change of valinomycin during complexation. Characteristic perturbations of the positions and fine structure of the resonances of the protons of specific groups were observed when (3) complexed with KCNS and CsCNS in deuteriochloroform. Very significantly, the addition of small amounts of water did not affect the structure of the complexes, as judged by the n.m.r. spectra, indicating that the metal is bound to the antibiotic as the bare ion. Preliminary studies were carried out on the rates of complex formation and dissociation using the broadening of the lactate methyl-proton resonances of (3). A measurable rate of transfer of the complexed cation between valinomycin molecules was observed in 80% methanol–20% $CDCl_3$, but no measurable exchange was seen in pure $CDCl_3$ (*i.e.* $\tau^{-1} < 0{\cdot}2\ s^{-1}$). These results have important implications: they suggest that the channel mechanism (ii, above) does not apply, at least in this case. Thus, it is most unlikely that a K^+ ion can shuttle rapidly from molecule to molecule of valinomycin within the low-dielectric interior of the lipid membrane. Ohnishi and Urry [15] have reported the conformation of the K^+–valinomycin complex in methanol.

Prestegaard and Chan [16] have used 220 MHz n.m.r. to investigate the binding of nonactin (1a) to K^+ in [$^2H_6$]acetone and [$^2H_6$]acetone–D_2O mixtures. The conformation of (1a) changes on binding, and it appears that the metal ion has to be stripped of its solvent sheath before the complex will form. The authors suggest that, since the nonactin molecule is quite flexible, it is unlikely that the size of the central aperture is the controlling factor in discriminating between various cations of comparable size. On the other hand, the fact that the ion must lose its water of hydration before the formation of the complex suggests that the hydration energy of the cation may contribute to the cation specificity observed in metabolic behaviour. The study has been extended [17] to include Na^+ and Cs^+, and stability constants have been measured.

Thermodynamic data have also been reported [18] for the binding of the alkali metals with the two isomers of the cyclic polyether 2,5,8,15,18,21-hexaoxatricyclo[20,4,0,$0^{9,14}$]hexacosane (4). The stability order of these metal ions with either isomer is identical to the permeability order for the same metals with the structurally related antibiotics (1b) and (3); *i.e.* $K^+ > Rb^+ > Cs \gg Na^+, Li^+$.

In an important communication,[19] the 1 : 1 complementarity between K^+

[14] D. H. Haynes, A. Kowalsky, and B. C. Pressman, *J. Biol. Chem.*, 1969, **244**, 502.
[15] M. Ohnishi and D. W. Urry, *Science*, 1970, **168**, 1091, which corrects the preliminary communication *Biochem. Biophys. Res. Comm.*, 1969, **34**, 803.
[16] J. H. Prestegaard and S. I. Chan, *Biochemistry*, 1969, **8**, 3921.
[17] J. H. Prestegaard and S. I. Chan, *J. Amer. Chem. Soc.*, 1970, **92**, 4440.
[18] R. M. Izatt, J. H. Rytting, D. P. Nelson, B. L. Haymore, and J. J. Christensen, *Science*, 1969, **164**, 443.
[19] H.-K. Wipf, W. Pache, P. Jordan, H. Zähner, W. Keller-Schierlein, and W. Simon, *Biochem. Biophys. Res. Comm.*, 1969, **36**, 387.



(4)

and antibiotic has been demonstrated by the use of ^{14}C-labelled macrotetrolides: transport of potassium is accompanied by an equal transport of antibiotic molecule.

Eigen and co-workers (see ref. 46, Part III, Chapter 1) have used chemical relaxation methods to study the binding of (1a) and (1b) to Na^+ and K^+ in methanol, using murexide as indicator. Formation rate constants of about 3×10^8 l mol^{-1} s^{-1} were obtained for both metals, making an interesting comparison with the diffusion-controlled value of around 5×10^8 l mol^{-1} s^{-1}. Evidently, the complexity of the ligand has very little effect on k_f (cf. Part III, Chapter 1, Section 5) and, once again, the difference in stability constants (Table 1) for group *A* metals is being reflected in the rate constant

Table 1 *Stability constants of some alkali-metal ion macrotetrolide complexes in methanol*[a]

Ion	*Stability constant K* (l mol^{-1}) *Nonactin*	*Monactin*
Na^+	$(1{\cdot}3 \pm 0{\cdot}2) \times 10^2$	$(1{\cdot}1 \pm 0{\cdot}1) \times 10^3$
K^+	$(5{\cdot}0 \pm 0{\cdot}7) \times 10^3$	$(2{\cdot}5 \pm 1{\cdot}0) \times 10^5$
K_{K^+}/K_{Na^+}	38 ± 5	230 ± 70

[a] Data refer to 30 °C; from L. A. R. Pioda, H. A. Wachter, R. E. Dohner, and W. Simon, *Helv. Chim. Acta*, 1967, **50**, 1373.

for dissociation rather than association. The implications of this result in yielding optimal carrier performance are discussed.

Before leaving the subject of the mechanism of metal-ion transport across membranes, a cautionary result and a by-product of these investigations might be reported. Hall [20] has found that the antibiotic monamycin forms complexes in solution with K^+, Rb^+, and Cs^+, but not with Na^+ or Li^+. However, it seems that their antibacterial action is due to their lytic effects on cell membranes rather than to any ion-transporting properties they may possess. The metal-ion selectivity of nonactin [21] and valinomycin [22] has been put to use in the design of potassium-selective membrane electrodes. These contain the antibiotics as components of the membrane, and can be used to estimate K^+ in the presence of Na^+, for example in human serum.

[20] M. J. Hall, *Biochem. Biophys. Res. Comm.*, 1970, **38**, 590.
[21] L. A. R. Pioda and W. Simon, *Chimia* (*Switz.*), 1969, **23**, 72.
[22] M. S. Frant and J. W. Ross, *Science*, 1970, **167**, 987.

2 Metal Complex Formation

One of the major roles of metals in non-redox biological systems appears to be to act as a bridge between, for example, an enzyme and its substrate. Many papers have appeared during the past two years in which evidence is presented for the formation of such ternary complexes in model systems. We shall take the feasibility of this bridging role for granted and discuss primarily the work which involves the macromolecules themselves.

Suelter [23] has summarized the enzymes catalysed by monovalent cations and has suggested that the data from the various reactions are consistent with a unique interaction of metal with the enzyme and substrate to form a functional ternary complex. While this complex cannot yet be uniquely defined, the pattern of activation suggests that (i) phosphorylation of a carboxy-group or enolate anion, (ii) elimination reactions resulting in a keto–enol tautomer, and (iii) other reactions in which a keto–enol tautomer can be considered as an intermediate, are all candidates for activation by a monovalent cation.

The problem of demonstrating the involvement of a metal ion in a biological reaction has always been a very difficult one, since the most important metals (such as the alkali metals, alkaline-earth metals, and zinc) possess very few convenient 'handles'. The replacement of the native metal by a less retiring one has become a well-established technique, and the n.m.r. work of Cohn and her school on systems in which the paramagnetic Mn^{2+} ion has been substituted for the diamagnetic Mg^{2+} ion needs no introduction. The interaction of transfer-RNA and related compounds with Mn^{2+} has recently been demonstrated [24] by the enhancement of the proton relaxation rate (p.r.r.) technique.

Bryant [25] has used the interaction between Ca^{2+} and ATP to demonstrate that the calcium-43 resonance is a potential probe for investigating the Ca environment in systems where the Ca interactions may be important. The exchange rate of Ca with binding sites is likely to be rapid enough to allow the observation and characterisation of bound calcium when the binding site is a protein, enzyme, or even tissue such as muscle or nerve fibre. As expected, the exchange rate at ATP was too high to permit the evaluation of a rate constant from the T_2 measurements. James and Noggle [26] have used the sodium-23 resonance to study the interaction between Na^+ and transfer-RNA; a stability constant of $10^{2\cdot8}$ was obtained.

In 1966, Stengle and Baldeschweiler [27] described a technique in which the change in the resonance signal of the $^{35}Cl^-$ ion was used to demonstrate

[23] C. H. Suelter, *Science*, 1970, **168**, 789.
[24] M. Cohn, A. Danchin, and M. Grunberg-Manago, *J. Mol. Biol.*, 1969, **39**, 199.
[25] R. G. Bryant, *J. Amer. Chem. Soc.*, 1969, **91**, 1870.
[26] T. L. James and J. H. Noggle, *Proc. Nat. Acad. Sci. U.S.A.*, 1969, **62**, 644; *cf.* their studies with aminocarboxylate complexes of Na^+ in *J. Amer. Chem. Soc.*, 1969, **91**, 3424.
[27] T. R. Stengle and J. D. Baldeschweiler, *Proc. Nat. Acad. Sci. U.S.A.*, 1966, **55**, 1020; see also *J. Amer. Chem. Soc.*, 1967, **89**, 3045.

the displacement of Cl^- from the inner co-ordination sphere of an enzyme-bound metal ion by another ligand. The technique has been extended [28] to $^{81}Br^-$, but it has been found that there is some binding of the bromide ion to proteins such as lysozyme, α-chymotrypsin, and especially serum albumin; a binding which is independent of the metallic sites.

The technique has also been used to obtain further evidence on the binding of zinc to nucleotide diphosphates, and the whole matter of ring-binding in metal–nucleotide di- and tri-phosphate complexes is discussed.[29] The formation of $[Zn(ADP)_2]^{4-}$ is evident, and the results strongly suggest that the zinc ion is chelated between the nucleotide base and phosphate chain in $[Zn(ADP)]^-$ but is chelated only to the phosphate chain in $[Zn(IDP)]^-$.

Further applications of n.m.r. techniques in specific enzyme systems are discussed below. E.p.r. has been used [30] to investigate the bonding of copper(II) in several amino-acid, peptide, and trypsin complexes, and the effects of divalent metal ions on the Raman spectrum of ATP in aqueous solution have also been reported.[31]

The use of thallium-205 as a probe for potassium has been suggested,[32, 33] and Kayne and Reuben [32] have used the broadening between the signals of the two paramagnetic ions thallium(I) and manganese(II) to estimate the distance between the monovalent and bivalent activators in rabbit muscle pyruvate kinase. Several cases of the inhibition of Ca^{2+} transport processes by lanthanides have been reported,[34] and Williams and co-workers [35] have proposed the use of the lanthanides as probes for calcium.

The use of coloured indicators for non-coloured metals is well established, and the bioluminescent protein aequorin has proved a useful addition to the list of Ca^{2+}-sensitive indicators.[36] Recently, the kinetics of several of the steps involved in the Ca^{2+}-aequorin interaction have been reported.[37]

The alkaline phosphatase from *E. coli* is a zinc-containing metalloenzyme comprising two identical subunits. Different groups have claimed that varying numbers of zinc atoms are present in the dimer, but it has recently been demonstrated [38] that there are four, of which only two appear to

[28] M. Zeppezauer, B. Lindman, S. Forsén, and I. Lindqvist, *Biochem. Biophys. Res. Comm.*, 1969, **37**, 137.
[29] J. A. Happe and R. L. Ward, *J. Amer. Chem. Soc.*, 1969, **91**, 4906.
[30] T. H. Crawford and J. O. Dalton, *Arch. Biochem. Biophys.*, 1969, **131**, 123.
[31] L. Rimai, M. E. Heyde, and E. B. Carew, *Biochem. Biophys. Res. Comm.*, 1970, **38**, 231.
[32] F. J. Kayne and J. Reuben, *J. Amer. Chem. Soc.*, 1970, **92**, 220.
[33] J. P. Manners, K. G. Morallee, and R. J. P. Williams, *Chem. Comm.*, 1970, 965.
[34] *E.g.* L. Mela, *Biochemistry*, 1969, **8**, 2481; C. van Breemen and P. de Weer, *Nature*, 1970, **226**, 760.
[35] K. G. Morallee, E. Nieboer, F. J. C. Rossotti, R. J. P. Williams, A. V. Xavier, and R. A. Dwek, *Chem. Comm.*, 1970, 1132.
[36] *E.g.* C. C. Ashley and E. B. Ridgway, *Nature*, 1968, **219**, 1168; O. Shimomura and F. H. Johnson, *Biochemistry*, 1969, **8**, 3991.
[37] J. W. Hastings, G. Mitchell, P. H. Mattingly, J. R. Blinks, and M. van Leeuwen, *Nature*, 1969, **222**, 1047.
[38] C. Lazdunski, C. Petitclerc, and M. Lazdunski, *European J. Biochem.*, 1969, **8**, 510.

participate in the functioning of the enzyme. All four zinc atoms can be replaced by cobalt(II), by manganese(II), and cadmium(II),[38] and by copper(II).[39] Of these reconstituted metalloproteins, only the one containing Co^{II} has significant enzymatic activity, and the kinetic properties of it and the native enzyme have been extensively investigated.[40] Cobalt-substituted alkaline phosphatase possesses characteristic visible absorption bands which are different from those of the free metal.[41] The o.r.d. spectra of the different metallophosphatases are very similar, suggesting little difference in protein structure,[38] and the copper-[39] and manganese-enzymes[42] can be phosphorylated even though they are enzymatically inactive. E.p.r. spectra of the manganese-enzymes indicate the presence of two tightly- and two loosely-bound metal ions,[43] and phosphorus-32 labelling studies on the zinc- and cobalt-enzymes suggest that each active site contains one metal ion of each type.[44] A preliminary report[45] on the application of the halogen ion n.m.r. probe technique mentions a dramatic increase in line-width of the ^{35}Cl signal in the presence of several metallophosphatases; addition of phosphate reduces this broadening. Applebury and Coleman[41] had also found a large change in the c.d. spectrum of the Co^{II}-enzyme in the presence of phosphate. Nayndu and Miles[46] have used steady-state kinetics to show that the substrate of mouse duodenal alkaline phosphatase, when it catalyses the hydrolysis of pyrophosphate, is $[MgP_2O_7]^{2-}$; the enzyme is inhibited by free Mg^{2+}.

N.m.r. has been used to study the active site of other zinc-containing enzymes. In bovine carbonic anhydrase there is a single zinc co-ordination site available for Cl^- interaction, and the latter can be inhibited by CN^- and acetazolamide.[47] ^{35}Cl Resonance has also been used to investigate the environmental differences of the zinc in carbonic anhydrase isozymes[48] and the activation of pyruvate kinase with zinc,[49] and to determine the pK values in cobalt(II)-carbonic anhydrase.[50] It is suggested[51] that, although the pK of aquozinc is about 9, the environment of the zinc ion in carbonic anhydrase B greatly increases the tendency of a zinc-bound water molecule

[39] H. Csopak and K. E. Falk, *F.E.B.S. Letters*, 1970, **7**, 147.
[40] *E.g.* C. Lazdunski and M. Lazdunski, *European J. Biochem.*, 1969, **7**, 294; M. Gottesman, R. T. Simpson, and B. L. Vallee, *Biochemistry*, 1969, **8**, 3776.
[41] M. L. Applebury and J. E. Coleman, *J. Biol. Chem.*, 1969, **244**, 308.
[42] D. Chappelet, C. Lazdunski, C. Petitclerc, and M. Lazdunski, *Biochem. Biophys. Res. Comm.*, 1970, **40**, 91.
[43] C. Lazdunski, C. Petitclerc, D. Chappelet, F. Letevrier, P. Douzou, and M. Lazdunski, *Biochem. Biophys. Res. Comm.*, 1970, **40**, 589.
[44] C. Petitclerc, C. Lazdunski, D. Chappelet, A. Moulin, and M. Lazdunski, *European J. Biochem.*, 1970, **14**, 301; cf. C. Lazdunski, C. Petitclerc, D. Chappelet, and M. Lazdunski, *Biochem. Biophys. Res. Comm.*, 1969, **37**, 744 and ref. 38.
[45] H. Csopak, B. Lindman, and H. Lilja, *F.E.B.S. Letters*, 1970, **9**, 189.
[46] P. R. V. Nayndu and P. L. Miles, *Biochem. J.*, 1969, **119**, 29.
[47] R. L. Ward, *Biochemistry*, 1969, **8**, 1879.
[48] R. L. Ward, *Biochemistry*, 1969, **8**, 2447.
[49] G. L. Cottam and R. L. Ward, *Arch. Biochem. Biophys.*, 1969, **132**, 308.
[50] R. L. Ward and K. J. Fritz, *Biochem. Biophys. Res. Comm.*, 1970, **39**, 707.
[51] S. L. Bradbury, *J. Biol. Chem.*, 1969, **244**, 2002, 2010.

to lose a proton and results in its having a pK value as low as 6·9. The great similarity of the rates of anion binding to liver alcohol dehydrogenase, another zinc enzyme, as compared with carbonic anhydrase has led to a suggestion that the ligands are binding to the zinc ion in the enzyme.[52] The single zinc atom in carboxypeptidase A has been replaced by Mn^{2+} to form CPA(Mn), and the interaction between this and fluoride ion has been studied by means of the broadening induced by the paramagnetic manganese ion on the ^{19}F resonance line.[53] The authors conclude that if the

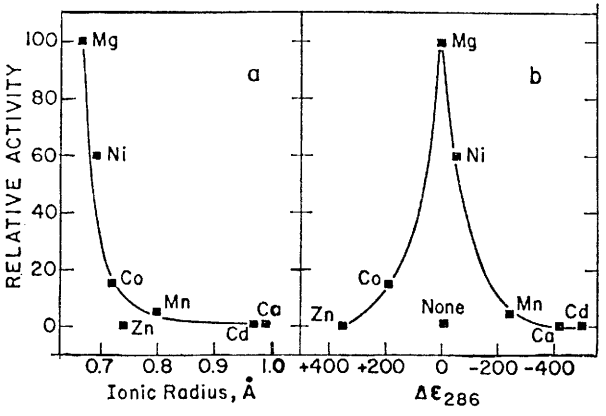


Figure 2 *The relationship between the maximum activity of phosphoglucomutase–metal–glucose phosphate complexes and* (*a*) *the ionic radius of the metal ion, and* (*b*) *the structural change produced on formation of the complex*
(Reproduced by permission from *J. Biol. Chem.*, 1969, **244**, 3754)

metal ion in CPA(Mn) has three protein ligands, as suggested by the X-ray crystal structure of the native zinc enzyme, then the total number of ligands at the metal is five or more.

A bridging role has also been proposed for magnesium in phosphoenolpyruvate carboxy-transphosphorylase, the CO_2-fixing enzymes,[54] and for the various metal activators of phosphoglucomutase.[55] The formation of catalytically active enzyme–metal–glucose phosphate complexes was studied by means of u.v. difference and solvent perturbation spectroscopies. The spectra suggested that the size of a crevice in the enzyme–substrate complex can be either reduced or expanded through binding to the appropriate bivalent metal ion. Furthermore, the crevice size could be correlated with enzymatic activity: the larger the alteration in crevice size on metal binding, the lower the enzymatic activity, no matter whether the change involves a reduction or expansion in size (Figure 2). This correlation with

[52] C. H. Reynolds and J. S. McKinley-McKee, *European J. Biochem.*, 1969, **10**, 474; cf. the rate of binding of bipy to the same enzyme, M. J. Gilleland and J. D. Shore, *Biochem. Biophys. Res. Comm.*, 1970, **40**, 230.
[53] G. Navon, R. G. Shulman, B. J. Wyluda, and T. Yamane, *J. Mol. Biol.*, 1970, **51**, 15.
[54] H. G. Wood, J. J. Davis, and J. M. Willard, *Biochemistry*, 1969, **8**, 3127, 3137, 3145.
[55] E. J. Peck and W. J. Ray, *J. Biol. Chem.*, 1969, **244**, 3754.

ionic radius is interesting in the light of previous unsuccessful attempts to correlate catalytic activity with such factors as metal binding affinity.[56]

The alkaline-earth ions differ greatly in the magnitude of their activation of creatine kinase, which catalyses reaction (1), but it has been shown [57]

$$\text{ATP} + \text{creatine} \rightleftharpoons \text{ADP} + \text{phosphocreatine} \qquad (1)$$

that this difference is not reflected in any large differences in the conformations of the various metal complexes, as evidenced by their e.p.r. spectra. The enzyme was spin-labelled with a nitroxyl free radical, which binds at the two essential SH groups (one for each active site) and it was found that, although the conformation of the enzyme changed on binding the substrate (metal–ADP), the change was similar for Mg, Ca, Sr, or Ba. It was, however, distinctly different for the inhibitory zinc ion. From the magnitude of the spin–spin interaction, the distance between the spin-label and the paramagnetic manganese(II) ion in the complex (spin-labelled creatine kinase)–Mn–ADP was estimated to be in the range 7—10 Å. Temperature-jump studies [58] have confirmed the conformational change concurrent with binding of ADP and ATP and their Mg^{2+}, Mn^{2+}, and Ca^{2+} complexes. The rates of the binding process are quite similar (at 11 °C the rate constant is $2{\cdot}3 \times 10^7$ l mol^{-1} s^{-1} for ADP, and in the range $2—7 \times 10^6$ l mol^{-1} s^{-1} for the metal–ADP complexes), in contrast to most metal complex formation reactions (see Part III, Chapter 1, Section 1) where the second-order rate constants for Mg^{2+}, Mn^{2+}, and Ca^{2+} vary over three orders of magnitude. Although a metal-bridging mechanism is not ruled out, the authors feel that a model in which the cation does not act as a bridge between the enzyme and adenine nucleotide is more likely. A similar conclusion was reached on the basis of earlier results from n.m.r., e.p.r., and steady-state kinetic studies.[59]

Other Mg^{2+}- and Mn^{2+}-activated enzymes in which the metal is thought not to act in a bridging role include yeast hexokinase,[60] yeast enolase,[61] and arginine kinase.[62] The enhancement of p.r.r. by Mn^{2+} and Cu^{2+} has been used to study the interaction of these metal ions with ribonuclease A. The author concludes [63] that, as their concentration is increased, the metal ions first activate the enzyme by binding to the phosphate groups on the substrate (RNA) and then inhibit by blocking the active sites on the enzyme.

[56] W. J. Ray, *J. Biol. Chem.*, 1969, **244**, 3740; E. J. Peck and W. J. Ray, *ibid.*, p. 3748.
[57] J. S. Taylor, J. S. Leigh, and M. Cohn, *Proc. Nat. Acad. Sci. U.S.A.*, 1969, **64**, 219.
[58] G. G. Hammes and J. K. Hurst, *Biochemistry*, 1969, **8**, 1083.
[59] Cf. E. Heyde and J. F. Morrison, *Biochim. Biophys. Acta*, 1969, **178**, 47; M. Cohn, *Quart. Rev. Biophys.*, 1970, **3**, 61.
[60] G. Noat, J. Ricard, M. Borel, and C. Got, *European J. Biochem.*, 1970, **13**, 347; cf. H. F. Fromm, *European J. Biochem.*, 1969, **7**, 385.
[61] D. P. Hanlon and E. W. Westhead, *Biochemistry*, 1969, **8**, 4255.
[62] W. J. O'Sullivan, R. Virden, and S. Blethen, *European J. Biochem.*, 1969, **8**, 562.
[63] T. D. Alger, *Biochemistry*, 1970, **9**, 3248.

3 Reactions Involving Metals in Porphyrins and Related Ring Systems

Haemoglobin, the oxygen-transporting protein of the blood, comprises two pairs of subunits, the so-called α- and β-chains. Each subunit contains a single haem group, the central Fe^{II} of which can combine reversibly with oxygen, so that each haemoglobin molecule can bind up to four oxygen molecules. The affinity of haemoglobin for oxygen increases as the number of oxygen molecules bound increases (*i.e.* $K_4 > K_3 > K_2 > K_1$) and the explanation for this 'co-operativity' has been sought for many years. In an excellent article, Shulman *et al.*[64] discuss the problem in the light of the results of their n.m.r. and e.p.r. experiments. They observed no changes in the haem groups themselves when oxygen was bound to neighbouring haem groups, but they did obtain evidence for changes in the tertiary structure of the protein moiety of the subunits. They suggest that free-energy changes responsible for the co-operative binding of oxygen and other ligands to haemoglobin arise from the dependence of the interaction energy in the protein part of the subunit on the degree of oxygenation, and point out that the term 'subunit interaction' is more appropriate than 'haem–haem interaction' to describe the co-operativity. Incidentally, they found that similar changes in the protein structure occurred when oxygen bound to myoglobin, which resembles a haemoglobin subunit. The results are discussed in terms of Koshland's induced-fit mechanism and Monod's allosteric mechanism, general models which have been set up to explain the phenomenon of co-operativity.

Brunori and Schuster[65] have used the temperature-jump relaxation method to measure the kinetics of ligand binding to sperm whale myoglobin, to the α- and β-chains of human haemoglobin, and to native human and sheep haemoglobins. Whereas the binding of oxygen to myoglobin and the isolated α- and β-subunits is a simple process, exhibiting second-order kinetics, the reaction with the native haemoglobins is complex and only a preliminary analysis is given. Two relaxation times were observed, and the concentration dependence of the longer of these indicates that a bimolecular process is involved. This suggests that the final process by which equilibrium is re-established is not followed by any first-order process, such as a slow intramolecular conformational change. The similarity of the relaxation spectra obtained at different ionic strengths over the range 0·2 to 2·2 mol l^{-1} suggests that the ($\alpha\beta$) dimer is the functionally important unit. (Redox data have also provided support for this hypothesis[66]).

The rates of combination of the isolated chains of human haemoglobin with oxygen have also been measured by flow techniques and by flash

[64] R. G. Shulman, S. Ogawa, K. Wüthrich, T. Yamane, J. Peisach, and W. E. Blumberg, *Science*, 1969, **165**, 251.
[65] M. Brunori and T. M. Schuster, *J. Biol. Chem.*, 1969, **244**, 4046.
[66] M. Brunori, J. F. Taylor, E. Antonini, and J. Wyman, *Biochemistry*, 1969, **8**, 2880.

photolysis in two different laboratories.[67] By and large, the agreement in the results is encouraging, although they sometimes do not agree to within the normal confidence limits of the individual techniques (Table 2; α^{PMB}

Table 2 *Kinetics for the combination of the isolated chains of human haemoglobin with oxygen*[a]

	α^{PMB}	α^{-SH}	β^{PMB}	β^{-SH}
$k \times 10^{-7}$ l mol^{-1} s^{-1} (*T*-jump)	5·5 ± 0·5	4·8 ± 0·5	8·3 ± 1·5	6·5 ± 0·8
$k \times 10^{-7}$ l mol^{-1} s^{-1} (flow)	4·1 ± 0·4	3·7 ± 0·3	—	7·0 ± 0·4
$k \times 10^{-7}$ l mol^{-1} s^{-1} (flash 1)	4·3 ± 0·5	5·7 ± 0·7	4·9 ± 0·4	6·8 ± 0·6
$k \times 10^{-7}$ l mol^{-1} s^{-1} (flash 2)	5·5 ± 0·8	5·5 ± 0·4	7·4 ± 2·0	7·5 ± 1·5
$\Delta H^{\ddagger}$ kcal mol^{-1} (flash 1)	9·1 ± 1·5	8·2 ± 2·2	6·2 ± 1·2	7·6 ± 1·1
$\Delta H^{\ddagger}$ kcal mol^{-1} (flash 2)	10·2 ± 1·3	7·3 ± 3·4	7·5 ± 1·9	8·4 ± 4·3

[a] Data refer to 25 °C and pH 9·1 (*T*-jump) or 20 °C and pH 7·0 (others) and are taken from refs. 65 (*T*-jump) and 67 (others).

and β^{PMB} are chains in which the —SH groups have been blocked by *p*-mercuribenzoate). The rates of the reaction of O_2 with the isolated chains are much greater than of the corresponding reaction with native haemoglobin. This is similar to the situation with carbon monoxide, for which more data have recently been published.[68] The activation energies for these oxygenation reactions are in the range normally associated with reactions having rate constants of such a value.

Gibson [69] has also measured the kinetics of the reaction of oxygen with haemoglobin and has found that, under restricted conditions, the system can be adequately represented by a sequence of four consecutive reversible reactions. He has assigned numerical values to the eight rate constants which permit a satisfactory fit to the rate data for forward and reverse reaction and yield an equilibrium binding curve of the appropriate form. The distribution of rates among the various steps in the sequence requires that co-operativity in oxygen binding be attributed primarily to deviations of the successive dissociation rate constants from their statistical values, and is consistent with the notion that the major change in reactivity occurs after one ligand molecule has dissociated from saturated haemoglobin.

The reactions of haemoglobin derivatives in their oxidised (Fe^{III}) form with ligands have also been studied kinetically. The reactions tend to be

[67] R. W. Noble, Q. H. Gibson, M. Brunori, E. Antonini, and J. Wyman, *J. Biol. Chem.*, 1969, **244**, 3905.

[68] M. Brunori, E. Antonini, C. Phelps, and G. Amiconi, *J. Mol. Biol.*, 1969, **44**, 563; R. D. Gray, *J. Biol. Chem.*, 1970, **245**, 2914; L. J. Parkhurst, G. Geraci, and Q. H. Gibson, *J. Biol. Chem.*, 1970, **245**, 4131.

[69] Q. H. Gibson, *J. Biol. Chem.*, 1970, **245**, 3285.

complex, and k_f values ranging between 2 and 2700 $l\,mol^{-1}\,s^{-1}$ at 20 °C have been reported.[70]

The kinetics of incorporation of metal ions into several water-soluble porphyrins have also been reported.[71]

A preliminary account has been given[72] for peripheral attack on the porphyrin ring during reduction and oxidation of chloroiron(III)octaethylporphyrin. Indeed, although the problem of the detailed mechanism of electron transfer in haem proteins has been the subject of much speculation, little experimental evidence has been collected in support of any of the suggested mechanisms. Kinetic studies have not been very useful except, perhaps, to distinguish the reacting species.

Recently, Kowalsky[73] has attempted to apply the concepts and generalizations developed by Taube and others on electron transfer in metal complexes, to similar processes in haem proteins. He has attempted to use Cr^{2+} as a probe for the mechanism of the oxidation reactions of cytochrome *c*, hoping to determine whether an anion (*e.g.* chloride) bridge between the metal and cytochrome was involved. He found that the chromium(III) produced was tightly bound to the protein, suggesting that the protein itself (or the haem group) had furnished a ligand to the metal during the electron transfer.

Schejter and Aviram[74] studied the reaction of cytochrome *c* with imidazole and observed spectral changes which led them to suggest that the path followed by the electron in its transfer *to* the iron atom in ferricyctochrome *c* is different from that followed in its transfer *from* the iron atom in ferrocytochrome *c*.

Microsomal mixed function oxygenases catalyse the introduction of an oxygen atom from molecular oxygen into an organic substrate according to equation (2),

$$RH + DH_2 + O_2 = ROH + D + H_2O \qquad (2)$$

where DH_2 is a reduced electron-donor. It has been established that cytochrome P-450 is involved in the reduction and activation of molecular oxygen, but a direct investigation of this process has been hampered by the lack of pure enzyme preparations. The problem has been extensively studied in chemical model systems but, so far, none could be regarded as a true model in simulating all the characteristic features of the mixed function oxygenases. Ullrich has recently described[75] a suitable model activator for molecular oxygen, Fe^{II}–2-mercaptobenzoic acid.

[70] Q. H. Gibson, L. J. Parkhurst, and G. Geraci, *J. Biol. Chem.*, 1969, **244**, 4668.
[71] J. Weaver and P. Hambright, *Inorg. Chem.*, 1969, **8**, 167; T. P. Stein and R. A. Plane, *J. Amer. Chem. Soc.*, 1969, **91**, 607; P. Hambright and E. B. Fleischer, *Inorg. Chem.*, 1970, **9**, 1757; P. Hambright, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2449.
[72] C. E. Castro and H. F. Davis, *J. Amer. Chem. Soc.*, 1969, **91**, 5405.
[73] A. Kowalsky, *J. Biol. Chem.*, 1969, **244**, 6619.
[74] A. Schejter and I. Aviram, *Biochemistry*, 1969, **8**, 149.
[75] V. Ullrich, *Z. Naturforsch.*, 1969, **24b**, 699.

Horseradish peroxidase is a protein with a molecular weight of about 40,000 which contains a single protoporphyrin IX haem group. The enzyme catalyses the oxidation of a variety of substrates by H_2O_2 and it is especially interesting in that the mechanism involves species in which the iron atom possesses a formal oxidation state higher than three. The green compound HRP-I, which is formed rapidly on reaction of $Fe^{III}HRP$ with H_2O_2 or alkyl hydroperoxides, has two oxidising equivalents above the Fe^{3+} state, while the red compound HRP-II, formed more slowly from HRP-I in the absence of substrate, retains one oxidizing equivalent above the Fe^{3+} state. In a recent paper,[76] the Mössbauer spectra of these intermediates are discussed. It seems that the iron atoms in HRP-I and HRP-II are in the same oxidation state [presumably (IV)], implying that the extra oxidizing equivalent of the former is localized somewhere other than on the iron centre.

The kinetics of the reaction of ferrous horseradish peroxidase with H_2O_2 have also been reported.[77] The reaction to oxyperoxidase takes place in two steps, the product of the first one being HRP-II. Both stages follow second-order kinetics (first-order with respect to each reactant) and appear to be single-step two-electron oxidations.

The enzymatic transformations catalysed by coenzyme B_{12} can generally be viewed as a double 1,2-shift in which one of the migrating groups is hydrogen.[78] The central role played by the Co—C bond in the catalytic function of the B_{12} coenzymes has been established in recent years and the cleavage of this bond appears to be an intrinsic step in all known B_{12}-dependent reactions. Brodie [79] has recently discussed the mechanism of catalysis by vitamin B_{12} and has suggested that the key transition in all these reactions may be effected merely by changing the position of the cobalt atom relative to the corrin ring: by altering the distance of the Co—N bond, the symmetry of the cobalt and the polarization of the Co—C bond (between $Co^{III}—R^-$ and $Co^{I}—R^+$) and hence its reactivity are changed. It is proposed to test this hypothesis by, amongst other things, c.d. and magnetic resonance experiments with model compounds.

Williams and co-workers [80] have given a preliminary account of kinetic studies on the substitution of co-ordinated carbanions in Co^{III} corrinoids. This group of compounds, which contain the corrin ring of B_{12}, can be prepared with a wide range of carbanions in one of the axial positions of the cobalt atom. In previous papers the authors had studied the effect of the co-ordinated carbanion on the properties of the other ligands in the complex (*i.e.* its *cis* and *trans* effects) and in this work they wished to establish whether reactions which involve the carbanions themselves

[76] T. H. Moss, A. Ehrenberg, and A. J. Bearden, *Biochemistry*, 1969, **8**, 4159.
[77] R. W. Noble and Q. H. Gibson, *J. Biol. Chem.*, 1970, **245**, 2409.
[78] H. G. C. Hogenkamp, *Ann. Rev. Biochem.*, 1968, **37**, 225.
[79] J. D. Brodie, *Proc. Nat. Acad. Sci. U.S.A.*, 1969, **62**, 461.
[80] H. A. O. Hill, J. M. Pratt, S. Ridsdale, F. R. Williams, and R. J. P. Williams, *Chem. Comm.*, 1970, 341.

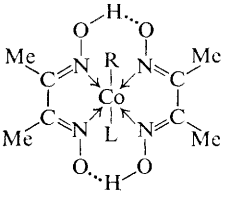
show any regular pattern. The results are discussed in terms of steric and electronic factors, and it is shown that 5,6-dimethylbenzimidazole (the other axial ligand in the cobalamins) exerts a *trans*-labilizing effect relative to H_2O (which is probably the other axial ligand in the cobinamides). The kinetics of the homolytic cleavage of the Co—C bond in cobamide and cobinamide derivatives have been measured[81] by e.p.r. spectrometry, using specially prepared compounds containing a nitroxide spin label.

The fact that the nature of the ligands bound axially to the cobalt atom in the cobalamins and cobinamides profoundly influences the reactivity of the metal has received further confirmation from Hogenkamp and Holmes.[82] They have measured the polarographic half-wave potential of several cobalamins and cobinamides and have shown that the differences in reactivity between the two series cannot be due solely to steric factors.

Schrauzer and Lee[83] have found that the reduction of vitamin B_{12} (containing Co^{III}) by carbon monoxide to vitamin B_{12r} (containing Co^{I}) is initiated by the spontaneous generation of Co^{II} corrin derivatives in aqueous solution. The Co^{II} species is a necessary intermediate and it is subsequently produced by the rapid reduction of B_{12a} by the Co^{I} species formed as the final product. In cases where the self-reduction of the B_{12a} species is impaired through structural modification at the periphery of the corrin ring (such as in B_{12a}-lactam), the reduction by CO does not occur, even in the presence of catalytic amounts of B_{12r}. This reaction represents the first example of a product-autocatalysed reduction of a corrin. It is interesting in the light of the earlier suggestion of Gillard[84] that rapid substitution at Co^{III} complexes by reducing anions might involve Co^{II} intermediates.

Work continues with the vitamin B_{12} model systems which contain two hydrogen-bonded dimethylglyoxime anions in place of the corrin ring, the so-called 'cobaloximes' (5).[85] Sibert and Schrauzer[86] have shown that extracts of the methanogenic bacterium *Methanobacillus omelianskii* can utilize methyl cobaloximes instead of methylcobalamin as substrates for methane production. The efficiency of the substrates depends on the nature of the in-plane and axial ligands, reaching 69% of the specific activity of methylcobalamin in the case of the methylaquo cobaloxime. The authors present preliminary kinetic data for the system and suggest a mechanism for the reductive Co—C bond cleavage in a methane-producing enzyme. They also report[87] the results of B_{12} and B_{12}-model studies in the catalysis of the dehydration of glycols. Schrauzer and Lee[88] have also investigated

[81] T. Buckman, F. S. Kennedy, and J. M. Wood, *Biochemistry*, 1969, **8**, 4437.
[82] H. G. C. Hogenkamp and S. Holmes, *Biochemistry*, 1970, **9**, 1886.
[83] G. N. Schrauzer and L. P. Lee, *Arch. Biochem. Biophys.*, 1970, **138**, 16.
[84] R. D. Gillard, *J. Chem. Soc.* (*A*), 1967, 917.
[85] Cf. G. N. Schrauzer, *Accounts Chem. Res.*, 1968, **1**, 97.
[86] J. W. Sibert and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1970, **92**, 1421.
[87] G. N. Schruazer and J. W. Sibert, *J. Amer. Chem. Soc.*, 1970, **92**, 1022.
[88] G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, 1970, **92**, 1551.



(5)

the oxygen-carrying ability of the cobaloximes(II) and have shown that these compounds, although not sterically hindered, may still serve as models for the oxygen-carrying properties of vitamin B_{12r}.

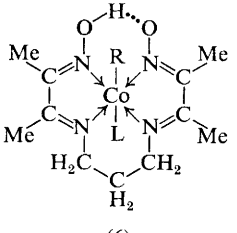
Crumbliss and Wilmarth [89] have measured the kinetics of reaction (3),

$$RCo(DH)_2OH_2 + L \rightleftharpoons RCo(DH)_2L + H_2O \qquad (3)$$

where R is Me, Et, or Pr^i; DH is the dimethylglyoximato monoanion; and L is SCN^-, N_3^-, py, CN^-, or NH_3. They have found that the forward rate constants are approximately invariant, falling in the range 3—50 l mol^{-1} s^{-1} (10 °C, ionic strength = 1·0), even though the equilibrium constants vary between 30 and 10^6 l mol^{-1}. These forward rate constants are larger by a factor of about 10^5 than those obtained [90] in a similar study involving compounds with R = I or NO_2, thus demonstrating the strong kinetic *trans* effect of the alkyl group.

Schrauzer and co-workers,[91] in discussing the origins of the remarkable similarity between the compounds (5) and the B_{12} series, suggest that the properties of the cobalt atom are not specifically dependent on the electronic structure of the vertical π-electron system of the in-plane ligands. The analogy is attributed to the fortuitous identity of the in-plane coordinating strengths of the corrin and the bis(dimethylglyoxime) ligand systems.

Costa, Mestroni, *et al.* have published work involving compounds of the type (6). Although these (L = H_2O or *N*-methylimidazole; R = Me, Et, or C_7H_7) could not be used to replace vitamin B_{12} in a B_{12}-dependent strain of



(6)

[89] A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1970, **92**, 2593.
[90] D. N. Hague and J. Halpern, *Inorg. Chem.*, 1967, **6**, 2059.
[91] G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *J. Amer. Chem. Soc.*, 1970, **92**, 2997.

Lactobacillus leichmanii,[92] they are similar to B_{12} and the cobaloximes inasmuch as the central cobalt atom may pass readily between the oxidation states (I), (II), and (III); the metal–carbon σ-bond in the axial position is also stabilized.[93]

The kinetics of substitution of H_2O in (6; L = H_2O; R = Me, Et, Pr^n, or Ph) by imidazole, benzimidazole, and Ph_3P have been measured [94] in acetone containing 1% water. The nature of the incoming ligand has essentially no effect on the rate, suggesting a limiting S_N1 process, but the R group exhibits a large *trans* effect. The water-loss rate increases in the order Ph < Me < Et < Pr^n, paralleling the order of increasing donor character of R (a similar sequence is observed in organic S_N1 processes). Comparison is made with the results of similar reactions involving Co^{III}-haematoporphyrin and aquocobalamin.

4 Redox Reactions involving Metals in other Biological and Model Systems

It has recently become apparent that iron–sulphur, or non-haem iron, proteins occur widely in animals, plants, and bacteria, and that they play a very important role in such functions as respiration, photosynthesis, and nitrogen-fixation. Both iron–sulphur proteins and cytochromes are electron carriers containing iron, but their active centres are entirely different. Hall and Evans [95] have recently reviewed iron–sulphur proteins, and a discussion on nitrogen fixation held in June 1968 has also been published.[96]

Hemerythrin is a non-haem iron protein which transports oxygen in a few simple invertebrates. The nature of the binding of the oxygen to the iron, and of the iron to the protein, is not fully understood, although the presence of histidine and tyrosine at the active site has recently been demonstrated.[97] Magnetic and spectroscopic data have been used [98] to obtain information about the oxidation states of the two iron atoms at the active site in the oxygenated and oxygen-free proteins.

One of the simplest of the non-haem iron proteins is the rubredoxin from *Clostridium pasteurianum*, which contains one iron atom per molecule and undergoes a reversible one-electron oxidation and reduction. The

[92] N. Stagni, B. de Bernard, G. Costa, and G. Mestroni, *Nature*, 1970, **225**, 942.
[93] G. Costa, G. Mestroni, and E. de Savorgnami, *Inorg. Chim. Acta*, 1969, **3**, 323; cf. G. Costa, G. Mestroni, G. Pellizer, G. Gauzher, and T. Licari, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 515.
[94] G. Costa, G. Mestroni, G. Tauzher, D. M. Goodall, M. Green, and H. A. O. Hill, *Chem. Comm.*, 1970, 34.
[95] D. O. Hall and M. McW. Evans, *Nature*, 1969, **223**, 1342.
[96] *Proc. Roy. Soc.*, 1969, **B172**, 317–441; see also G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1969, **8**, 650.
[97] C. C. Fan and J. L. York, *Biochem. Biophys. Res. Comm.*, 1969, **36**, 365; R. L. Rill and I. M. Klotz, *Arch. Biochem. Biophys.*, 1970, **136**, 507.
[98] M. Y. Okamura, I. M. Klotz, C. E. Johnson, M. R. C. Winter, and R. J. P. Williams, *Biochemistry*, 1969, **8**, 1951; K. Garbett, D. W. Darnall, I. M. Klotz, and R. J. P. Williams, *Arch. Biochem. Biophys.*, 1969, **103**, 419.

iron atom in both oxidation states is high-spin [99] and it has been shown,[100] by *X*-ray crystal structure determination, that the iron is surrounded by the sulphur atoms of four thiol groups in the protein, arranged at the corners of a somewhat distorted tetrahedron.

A possible model for the chromophore of non-haem iron proteins has been described [101] which contains 2-mercaptoethanol, but the rate of uptake of oxygen by the model is higher than would be expected on the basis of a simple reduction of Fe^{III} to Fe^{II} by the mercaptoethanol followed by its reoxidation to Fe^{III}. A rather looser model is mercaptoacetato-bis(ethylenediamine)cobalt(III). The kinetics of the inner-sphere reduction of this and its oxygen analogue by Cr^{II} have been reported.[102] The rate constant (25 °C, ionic strength = 0·1) for $[Co\,en_2(SCH_2CO_2)]^+$ is $> 2 \times 10^6$ l mol^{-1} s^{-1}, and that for $[Co\,en_2(OCH_2CO_2)]^+$ is $9{\cdot}9 \times 10^2$ l mol^{-1} s^{-1}.

An interesting reaction has been reported [103] which might be taken as a model system for biological redox reactions in which the electron activity is transmitted to a remote region of a molecule through several σ-bonds. Ethylene has been produced from monoethylsulphate by reaction with a free radical or oxygen in the presence of a reduced metal ion, in this case Fe^{2+}. The authors propose a 'Taube Bridge' mechanism involving electron activity at a remote site:

$$[R\cdots HCH_2CH_2OSO_2O^-\cdots Fe^{2+}] \longrightarrow RH + CH_2{=}CH_2 + SO_4^{2-} + Fe^{3+}$$

While the yield was rather poor in this case, the mechanism might be very important in more complex biological situations in which the faster competing reactions could be controlled.

An important biological trace element is molybdenum, and it is now well established that it participates in a number of redox reactions, including the oxidation of xanthine and purines and the reduction of nitrate and molecular nitrogen. It seems to be generally accepted that molybdenum is present in the 6+ and 5+ states in the enzymes, probably alternating between the two during active electron transport. Spence [104] has reviewed the biochemical aspects of molybdenum co-ordination chemistry. Kinetic studies have been reported by the same author [105] on a model for nitrate reductase: the $Mo^{V,\,VI}$-catalysed reduction of nitrate by reduced flavin

[99] W. D. Phillips, M. Poe, J. F. Weiher, C. C. McDonald, and W. Lovenberg, *Nature*, 1970, **227**, 574.
[100] J. R. Herriott, L. C. Sieker, L. H. Jensen, and W. Lovenberg, *J. Mol. Biol.*, 1970, **50**, 391.
[101] C. S. Yang and F. M. Huennekens, *Biochemistry*, 1970, **9**, 2127.
[102] R. H. Lane and L. E. Bennett, *J. Amer. Chem. Soc.*, 1970, **92**, 1089,
[103] J. Kumamoto, H. H. A. Dollwet, and J. M. Lyons, *J. Amer. Chem. Soc.*, 1969, **91**, 1207.
[104] J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475.
[105] J. T. Spence, *Arch. Biochem. Biophys.*, 1970, **137**, 287.

mononucleotide. Several papers have been concerned with the role of Mo in milk xanthine oxidase.[106]

The redox properties of copper have received considerable attention. The catalase and peroxidase activity of its complexes, some of which may be regarded as models for the two groups of enzymes, has been reviewed by Sigel.[107]

Sharma and Schubert [108] have investigated the catalatic activity (*i.e.* the catalytic decomposition of H_2O_2 into oxygen and water) of the copper complexes of the monodentate ligand imidazole by means of a differential

$$H_2O_2 \underset{K_1}{\rightleftharpoons} HOO^- + H^+$$

$$[Cu(bipy)]^{2+} + HOO^- \underset{K_2}{\rightleftharpoons} [Cu(bipy)(OOH)]^+$$

$$[Cu(bipy)(OOH)]^+ + H_2O_2 \underset{K_3}{\rightleftharpoons} [Cu(bipy)(OOH)(H_2O_2)]^+$$

} FAST

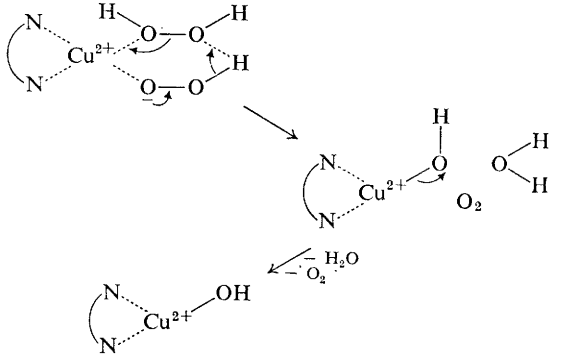


Figure 3 *Proposed mechanism for the decomposition of* H_2O_2 *catalysed by the* Cu^{II}–bipy *complex*

(Reproduced by permission from *J. Amer. Chem. Soc.*, 1969, **91**, 1061)

manometric technique. The kinetic data are consistent with a mechanism involving principally the reaction between Cu im_2^{2+} and the HOO^- anion, and evidence is presented for the involvement of a Cu^{II}–Cu^{I} couple. It is suggested that the species with two nitrogen atoms co-ordinated to the copper provide the lowest-energy path for the reduction of Cu^{II} to Cu^{I}, and that this facilitates the rupture of the oxygen–oxygen bond in $im_2Cu(OOH)^+$ because of an increase in the O—Cu—O bond angle on changing from the Cu^{II} to the Cu^{I} state. A similar intermediate in which the

[106] *E.g.* S. Nakamura and I. Yamazaki, *Biochim. Biophys. Acta*, 1969, **189**, 29; R. C. Bray and T. Vänngård, *Biochem. J.*, 1969, **114**, 725; M. P. Coughlan, K. V. Rajagopalan, and P. Handler, *J. Biol. Chem.*, 1969, **244**, 2658; T. J. Huang and G. P. Haight, *J. Amer. Chem. Soc.*, 1970, **92**, 2336.

[107] H. Sigel, *Angew. Chem. Internat. Edn.*, 1970, **8**, 167.

[108] V. S. Sharma and J. Schubert, *J. Amer. Chem. Soc.*, 1969, **91**, 6291.

peroxide anion acts as a bidentate ligand occupying two adjacent free sites at the copper is also postulated in the corresponding reaction of copper–histidine.[109] In the case of copper–bipy, it has been shown [110] that the rate law is $-\mathrm{d}[H_2O_2]/\mathrm{d}t = k[\mathrm{Cu\ bipy}][H_2O_2]^2/[H^+]$, and the postulated mechanism is given in Figure 3.

Although so many of the studies on copper-containing enzymes point to the importance of Cu^I species, little is known about the complex formation of this ion. This is largely because of the difficulty of preparing aqueous solutions of Cu^I associated with its tendency to disproportionate. Österberg [111] has generated cuprous ions in solutions of ligands (peptides and related compounds) by constant-current electrolysis of a two-phase copper amalgam, and has been able to measure stability constants and redox potentials associated with copper(I) species. The approach of Sigwart *et al.*[112] was to stabilize Cu^+ in aqueous medium by the addition of the non-protophilic ligand CH_3CN, allowing ligand displacement reactions to be investigated as if a stable Cu^I hydrate did exist. Under these conditions, the formation of cuprous complexes with imidazole and its derivatives has been studied in polar solution in the absence of Cu^{II}. It seems that trigonal as well as tetrahedral co-ordination of Cu^I in dilute polar solutions is confined to π- or *d*-acceptor ligands (*e.g.* bipy or methionine) and that otherwise the co-ordination number does not exceed two. Conclusions are drawn on the requirements for redox-active copper in proteins. Zuberbühler [113] has studied the kinetics of the autoxidation of Cu^I complexes with chelating ligands. The reaction is generally very rapid compared with the autoxidation of similar complexes with monodentate ligands, and it appears that steric factors play an important role.

Fungal laccase is a copper-containing oxidase which catalyses the oxidation of *p*-diphenols and related substances (notably aryl amines) by molecular oxygen. It seems that laccase contains two electron-accepting sites other than Type 1 (blue) and Type 2 (non-blue) copper(II), and a mechanism involving the co-operation of several electron-accepting sites has been proposed [114] which is consistent with recent kinetic results.

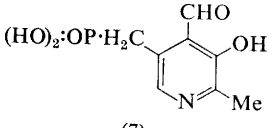
5 Template and Related Reactions

Metal template reactions may be defined as reactions involving ligands which require, or can be significantly enhanced by, a particular geometrical orientation imposed by co-ordination to a metal. Many metal template reactions have resulted in the synthesis of macrocyclic compounds,[115] such

[109] V. S. Sharma, J. Schubert, H. B. Brooks, and F. Sicilio, *J. Amer. Chem. Soc.*, 1970, **92**, 822.
[110] H. Sigel, C. Flierl, and R. Griesser, *J. Amer. Chem. Soc.*, 1969, **91**, 1061.
[111] R. Österberg, *European J. Biochem.*, 1970, **13**, 493.
[112] C. Sigwart, P. Kroneck, and P. Hemmerich, *Helv. Chim. Acta*, 1970, **53**, 177.
[113] A. Zuberbühler, *Helv. Chim. Acta*, 1970, **53**, 669.
[114] B. G. Malmström, A. F. Agrò, and E. Antonini, *European J. Biochem.*, 1969, **9**, 383.
[115] D. H. Busch has reviewed these: *Helv. Chim. Acta*, 1967, A. Werner centennial edition, 174.

as the work by Eschenmoser and his group on corrins.[116] An example of a recent study of template reactions[117] involves the benzilic acid rearrangement of 2,2′-pyridil in the presence of Ni^{II} and Co^{II} acetates, in which it was suggested that the role of the metal ion is twofold: it provides initial electronic activation of a carbonyl group to nucleophilic attack by co-ordination, and a ring-contraction is then brought about largely by a template effect and the formation of a highly stable product.

Several types of enzyme involved in amino-acid metabolism (including aminotransferases and decarboxylases) require pyridoxal phosphate (7, PLP) as co-factor. It has been postulated that all such reactions involve the formation of a Schiff-base intermediate between the amino-acid and (7) as the first step. Simple systems containing metal ion, amino-acid, and



(7)

an analogue of (7) duplicate many of these enzyme reactions, and the first step in these model reactions is the formation of a Schiff-base complex. Hopgood and Leussing[118] have studied the formation of *N*-salicylideneglycinato complexes kinetically and have found two reaction paths, one of which is dependent on the metal ion concentration and the other of which is not. The kinetics for the former suggest that a metal-bridging ternary complex is formed in which the ligands are independently bound and are in rapid equilibrium with the uncomplexed ligands. The rate-determining step is then the condensation of the complexed ligands within the first co-ordination sphere of the metal ion. The order of catalytic activity for the metals tested is Pb $\gg$ Cd $>$ Mn or Mg $>$ Zn $\gg$ Co, Ni, Cu, and the authors presume that the fact that no metal with partially filled *d*-orbitals exhibits reactivity is because ligand field effects cause rigid metal–ligand geometries. The authors propose the term 'promnastic' to describe the behaviour of the metal rather than 'template'. Leussing and Anderson[119] have found that the kinetics of the formation of *N*-pyruvylideneglycinatozinc(II) exhibit similar features.

Leussing and co-workers have studied other enzyme-model systems, such as the dimerization of pyruvate catalysed by Ni^{II} and Zn^{II}.[120] The kinetics and mechanism of the hydrolysis of *N*-salicylideneaniline in the presence of metal ions have also been reported,[121] and Gansow and Holm[122]

[116] *E.g.* A. Eschenmoser, *Quart. Rev.*, 1970, **24**, 366.
[117] D. St. C. Black and R. C. Srivastava, *Austral. J. Chem.*, 1969, **22**, 1439.
[118] D. Hopgood and D. L. Leussing, *J. Amer. Chem. Soc.*, 1969, **91**, 3740.
[119] D. L. Leussing and L. Anderson, *J. Amer. Chem. Soc.*, 1969, **91**, 4698.
[120] D. E. Tallman and D. L. Leussing, *J. Amer. Chem. Soc.*, 1969, **91**, 6253, 6256.
[121] A. C. Dash and R. K. Nanda, *J. Amer. Chem. Soc.*, 1969, **91**, 6944.
[122] O. A. Gansow and R. H. Holm, *J. Amer. Chem. Soc.*, 1969, **91**, 573, 5984.

have given an account of their proton resonance investigations into the equilibria, solute structures, and transamination of pyridoxal–alanine and pyridoxamine–pyruvate with Zn^{II} and Al^{III}. The reaction between pyridoxal phosphate and glutamate in the presence of cupric ions has also been studied kinetically [123] and it seems that the metal acts as a trap for both the Schiff base and an amino-alcohol intermediate.

Several authors have invoked this general type of behaviour for metals in enzyme-model systems [124] and it is likely that research in this area will increase in view of the desire to design model systems for the large group of metal enzymes in which geometrical effects involving the groups bound to the metal ion seem to be important.

[123] M. E. Farago and T. Matthews, *J. Chem. Soc.* (*A*), 1969, 609.

[124] *E.g.* B. S. Cooperman, *Biochemistry*, 1969, **8**, 5005; B. E. Leach and R. J. Angelici, *Inorg. Chem.*, 1969, **8**, 907; M. Munakata, M. Matsui, M. Tabushi, and T. Shigematsu, *Bull. Chem. Soc. Japan*, 1970, **43**, 114.

Part IV

ORGANOMETALLIC COMPOUNDS

1
Substitution and Catalysis

1 Carbonyls, Cyclopentadienyls, and Related Compounds

A general review of exchange and substitution reactions has appeared.[1]

Exchange Reactions.—*Carbon Monoxide.* Two or three years ago the problem of relating carbon monoxide exchange and substitution rates at nickel carbonyl was resolved by a redetermination of the former. This reinvestigation showed up certain deficiencies in the original experimental methods, and led to more accurate kinetic data which were consistent with rate-determining loss of carbon monoxide in both exchange and substitution.[2] Further support for $Ni(CO)_3$ as transition state in these reactions is provided by i.r. evidence for the existence of this species, albeit at 15 K.[3] Parenthetically, there is similar evidence for the existence of $Mn(CO)_3(NO)$, derived from $Mn(CO)_4(NO)$, at very low temperatures.[4] The case of $Co(CO)_3(NO)$ was similar to that of $Ni(CO)_4$, and has been similarly resolved by redetermination of the kinetics of carbon monoxide exchange using modern experimental techniques.[5] For $Co(CO)_3(NO)$, as for $Ni(CO)_4$, carbon monoxide exchange follows the simple first-order rate law,

$$\text{rate} = k_1[\text{carbonyl compound}]$$

but carbon monoxide exchange at the phosphine and phosphite derivatives $Co(CO)_2(NO)(L)$ follows the two-term rate law,

$$\text{rate} = k_1[\text{carbonyl cpd}] + k_2[\text{carbonyl cpd}][CO]$$

with k_1 and k_2 determined by steric and solvation effects.[6]

A long-standing topic of discussion has been the relative reactivities of the *cis*- and *trans*-carbon monoxides in $MnX(CO)_5$. Recently a slightly different system has been studied, carbon monoxide exchange at $Cr(phen)(CO)_4$. Here ^{18}O tracer experiments have revealed a significant difference between rates of exchange of the axial and equatorial CO

[1] F. Basolo, *Chem. in Britain*, 1969, 505.
[2] J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas, and P. M. Henry, *J. Amer. Chem. Soc.*, 1968, **90**, 1925.
[3] A. J. Rest and J. J. Turner, *Chem. Comm.*, 1969, 1026.
[4] A. J. Rest, *Chem. Comm.*, 1970, 345.
[5] J. P. Day, D. Diemente, and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 363.
[6] G. Reichenbach, G. Innorta, and A. Foffani, *Inorg. Chim. Acta*, 1969, **3**, 139.

ligands; exchange at both positions is dissociative in mechanism.[7] Carbon monoxide exchange, both palladium-catalysed and u.v.-initiated, at $Fe(CO)_5$ and $Fe(CO)_4(PPh_3)$ has been monitored by tracer techniques using both ^{13}CO and $C^{18}O$. There is statistical exchange, with no axial–equatorial discrimination, except in the presence of catalytic quantities of trifluoroacetic acid. Then the product distribution suggests simultaneous exchange of two carbon monoxide molecules.[8] Activation parameters for carbon monoxide exchange with $ReX(CO)_5$ are consistent with a dissociative mechanism. Greater difficulty of exchange at $ReX(CO)_5$ than at $MnX(CO)_5$ can be attributed to greater π-bonding to rhenium. At low pressures of carbon monoxide the kinetics suggest the possibility of formation of some $[ReX(CO)_4]_2$ dimer intermediate.[9] Carbon monoxide exchange at $Fe_3(CO)_9Te_2$ takes place by parallel simple and solvent-assisted dissociation paths in alcohols.[10] Rate trends have been qualitatively estimated for exchange at $[RhX(CO)_2]_2$.[11]

Nitric Oxide. Rates of nitric oxide exchange with $CoI(NO)_2(PPh_3)$ in toluene solution[12] are much greater than for nitric oxide exchange with $Co(CO)_3(NO)$ or with $Fe(CO)_2(NO)_2$ in the gas phase.[13] The reaction in toluene is zero-order in nitric oxide concentration, but in the gas phase the reaction is first-order in nitric oxide. A fuller understanding of these rate and rate-law differences may develop when the preliminary report on the solution studies is amplified in the promised full version which will include activation parameters.

Substitution: Carbon Monoxide Replacement.—*Mononuclear Simple Carbonyls.* The majority of studies have involved neutral molecules, but recently substitution by PPh_3 and its chelating analogue $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$ at the cationic species $[Re(CO)_6]^+$ has been described.[14] Reaction of $M(CO)_6$ (M = Cr, Mo, or W) with bis(pentafluorophenyl)phosphine in methylcyclohexane is suggested to proceed by way of homolytic fission of a dinuclear intermediate $(OC)_5{\cdot}M{\cdot}P(C_6F_5)_2{\cdot}P(C_6F_5)_2{\cdot}M(CO)_5$, with subsequent hydrogen abstraction by this intermediate to give the observed product $M(CO)_5{\cdot}PH(C_6F_5)_2$.[15] In this latter case, as in the subsequent reference, the postulated mechanisms are based on products and stoicheiometry rather than on kinetic evidence.

[7] M. Dokiya, R. D. Johnston, and F. Basolo, *Inorg. Chem.*, 1970, **9**, 996.
[8] K. Noack and M. Ruch, *J. Organometallic Chem.*, 1969, **17**, 309.
[9] G. Cetini, O. Gambino, G. A. Vaglio, and R. P. Ferrari, *Inorg. Chem.*, 1969, **8**, 1371.
[10] P. L. Stanghellini, G. Cetini, O. Gambino, and R. Rossetti, *Inorg. Chim. Acta*, 1969, **3**, 651.
[11] B. F. G. Johnson, J. Lewis, P. W. Robinson, and J. R. Miller, *J. Chem. Soc.* (*A*), 1969, 2693.
[12] G. Innorta, S. Pignataro, and A. Foffani, *J. Organometallic Chem.*, 1969, **20**, 284.
[13] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 1969, **8**, 696.
[14] E. W. Abel and S. P. Tyfield, *Canad. J. Chem.*, 1969, **47**, 4627.
[15] M. Green, A. Taunton-Rigby, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1875.

The mechanism of photochemical displacement by thiocyanate of carbon monoxide from $M(CO)_6$ (M = Cr or W) is similar to that previously published for iodide substitution, *viz.*:

$$M(CO)_6 + NCS^- \xrightarrow{h\nu} [M(NCS)(CO)_5]^- + CO$$

$$[M(CO)_5(NCS)]^- + M(CO)_6 \xrightarrow{h\nu} [M_2(NCS)(CO)_{10}]^- + CO$$

Photochemical displacement by cyanide has an analogous first step, but the course of subsequent reaction depends on the solvent. In THF, working with a large excess of the carbonyl, the reaction proceeds as for thiocyanate above, but in methylene chloride solution further cyanide substitution occurs to give a mononuclear product:

$$[M(CN)(CO)_5]^- + CN^- \xrightarrow{h\nu} cis\text{-}[M(CN)_2(CO)_4]^{2-} + CO$$

Cyanide here labilises carbon monoxide, which is not the case in the analogous thermal reaction.[16]

Binuclear Simple Carbonyls. Mechanisms of reactions of the binuclear carbonyls $M_2(CO)_{10}$ continue to be a subject of research and discussion. The most recent paper in this field opens with a useful review of current data and opinions, and offers e.s.r. evidence for the intermediacy of radicals in reaction of $Mn_2(CO)_{10}$ with tributylphosphine or triethylphosphine. Rates of substitution at $Mn_2(CO)_{10}$ by poor nucleophiles are decreased by the presence of an excess of carbon monoxide, are independent of nucleophile concentration, and are associated with large positive activation energies. These, and earlier results reported by other workers, can all be accommodated by a mechanism involving reversible loss of carbon monoxide:

$$Mn_2(CO)_{10} \rightleftharpoons Mn_2(CO)_9 + CO$$

followed by equilibrium with the incoming ligand L:

$$Mn_2(CO)_9 + L \rightleftharpoons Mn_2(CO)_9L$$

While intermediates such as $Mn(CO)_5$ and $(OC)_5Mn(CO)Mn(CO)_5$ might be generated, there is no need to invoke them to explain the kinetic results.[17] However, a comparison of kinetics of substitution at $Re_2(CO)_{10}$ in decalin with earlier results on substitution in this carbonyl and in $Mn_2(CO)_{10}$ has led to the proposal of a general substitution mechanism for these carbonyls in which metal migration to form an intermediate $(OC)_5M(CO)M(CO)_5$ is thought to be the rate-determining step.[18]

Trinuclear Simple Carbonyls. Comparison of kinetic data for Group V ligand replacement and CO exchange at the trinuclear carbonyl $Ru_3(CO)_{12}$ suggests equilibrium loss of one CO molecule as the common initial, and rate-determining, step for both reactions. There is no evidence for radical

[16] J. K. Ruff, *Inorg. Chem.*, 1969, **8**, 86.
[17] H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 113.
[18] L. I. Haines and A. J. Poë, *J. Chem. Soc.* (*A*), 1969, 2826.

intermediates such as $\dot{R}u(CO)_4$, in contrast to the postulated formation of $\dot{M}n(CO)_5$ in reactions of $Mn_2(CO)_{10}$ (*cf.* above). Neither is there evidence for $Ru_3(CO)_{11}L$ or $Ru_3(CO)_{10}L_2$ as significantly stable intermediates *en route* to the observed product $Ru_3(CO)_9L_3$.[19] By contrast, the relative rates for the first three substitutions into $Os_3(CO)_{12}$ are the opposite; indeed $Os_3(CO)_{11}L$ and $Os_3(CO)_{10}L_2$ are readily prepared compounds.[20]

Further information on the detailed mechanism of reaction of $Ru_3(CO)_{12}$ with diphenylacetylene, which results in both displacement of CO by the acetylene and breakdown of the trimeric structure, has been obtained by characterisation of intermediates. The mechanism is slightly different from that observed for the analogous reaction of $Fe_3(CO)_{12}$.[21] Kinetic isotope effects associated with protonation (H, D) of polynuclear carbonyls have been further described.[22]

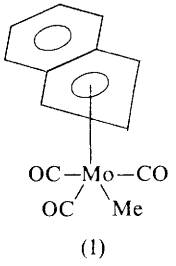
Mononuclear Mixed Ligand Carbonyls. The numerous and varied references which form this section will be mentioned and discussed in Periodic Table order.

The solitary reference to Group V concerns $V(\pi\text{-}C_5H_5)(CO)_4$. An earlier report suggested that the mechanism of reaction of this compound with triphenylphosphine was S_N2. In view of the large size of the cyclopentadienyl ligand this seemed unlikely, and indeed further kinetic work has shown that the rate of substitution by phosphorus bases is independent of nature and concentration of the nucleophile, and that the activation entropy is large and positive. These observations indicate a dissociative mechanism. The activation enthalpy is 55 kcal mol^{-1}, which is extraordinarily large and, allegedly, the largest known for a carbonyl.[23]

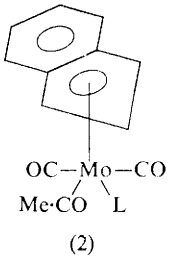
The compounds $M(CO)_4$(diphos), where M = Cr or Mo and diphos = $Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2$, react with ligands (L) in mesitylene to give $M(CO)_3(L)$(diphos). The rate law and activation entropy both suggest reversible loss of carbon monoxide to give a stable five-co-ordinated intermediate as the initial step. Variation of rate with the nature of the ligand L indicates that π-bonding effects are important in the subsequent associative interaction between the five-co-ordinated intermediate and L, for, *e.g.*, n-octylamine reacts only slowly despite its high base strength and the lack of any steric hindrance to its approach to the intermediate.[24] The related compounds $M(CO)_4$(phen) were investigated some years ago, but now the kinetics of reaction of the initial product $M(CO)_3(L)$(phen) with a second molecule of L have been reported.[25] Reaction of

[19] J. P. Candlin and A. C. Shortland, *J. Organometallic Chem.*, 1969, **16**, 289.
[20] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 897.
[21] O. Gambino, G. Cetini, E. Sappa, and M. Valle, *J. Organometallic Chem.*, 1969, **20**, 195.
[22] J. Knight and M. J. Mays, *J. Chem. Soc.* (*A*), 1970, 711.
[23] G. C. Faber and R. J. Angelici, *Inorg. Chem.*, 1970, **9**, 1586.
[24] G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, 1968, **2**, 479.
[25] D. Shrader, E. P. Ross, R. T. Jernigan, and G. R. Dobson, *Inorg. Chem.*, 1970, **9**, 1286.

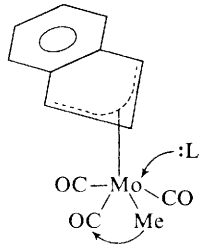
phosphorus ligands (L) with Mo(π-indenyl)Me(CO)$_3$, (1), is faster than with the cyclopentadienyl analogue. The mechanism involves S_N2 attack of L followed by CO insertion into the Mo–Me bond to give (2). The interesting



(1)



(2)



(3)

feature of the π-indenyl ligand is the smallness of the change required to convert it into a π-allyl type of ligand (3), thus leaving more space for S_N2 attack by the incoming ligand.[26] The displacement of carbon monoxide from the dimeric compound [Mo(π-C_5H_5)$(CO)_3]_2$ by P(OR)$_3$ involves an initial simple displacement, but this is followed by a rearrangement of the Michaelis–Arbuzov type to yield a product containing P(O)$(OR)_2$ co-ordinated to the molybdenum.[27]

Reaction of Mo(π-C_5H_5)X$(CO)_3$ with phosphorus bases normally results in loss of carbon monoxide, but when the entering group is $PBu^n{}_2Ph$ or $PBu^n{}_3$ then carbon monoxide or cyclopentadienyl groups are displaced in a ratio dependent on solvent and temperature. Loss of carbon monoxide is dissociative in mechanism here. Dissociative loss, rather than the associative loss often found for M(π-C_5H_5)$(CO)_2$ compounds, can be attributed to the steric crowding around the molybdenum in the present compound.[28]

The mechanism of the photolytic reaction of Mn(π-C_5H_5)$(CO)_3$ with π-interacting ligands such as indene or maleic anhydride depends on the solvent, in that in THF there appears to be a solvated intermediate Mn(π-C_5H_5)$(CO)_2$(THF), whereas in the poorer solvents n-hexane or benzene the intermediate is simply Mn(π-C_5H_5)$(CO)_2$.[29]

The solvent also plays a significant rôle in the reaction of [Fe(π-C_5H_5)$(CO)_2]_2$ with iodine. In chloroform there is evidence for ionic intermediates $\{[Fe(\pi\text{-}C_5H_5)(CO)_2]_2I\}^+X^-$; there is no evidence for such an intermediate in the poorer solvent n-hexane. The product, however, is the same in both solvents—again as in the above Mn example.[30] Rates of carbon monoxide substitution by phosphites in the closely related monomer

[26] A. J. Hart-Davies and R. J. Mawby, *J. Chem. Soc.* (*A*), 1969, 2403.
[27] R. J. Haines, I. L. Marais, and C. R. Nolte, *Chem. Comm.*, 1970, 547.
[28] C. White and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 261.
[29] M. Herberhold and C. R. Jablonski, *Chem. Ber.*, 1969, **102**, 767.
[30] D. A. Brown, A. R. Manning, and D. J. Thornhill, *Chem. Comm.*, 1969, 338.

$Fe(\pi\text{-}C_5H_5)X(CO)_2$ depend on neither nature nor concentration of the incoming ligand, which indicate a dissociative mechanism. The large, positive value of the activation entropy supports this conclusion.[31]

Displacement of carbon monoxide by a Group V base L from $Co(NO)(CO)_3$ [32] and from $Co(NO)(CO)_2L$ [33] follows a two-term rate law of the form:

$$\text{rate} = k_1[Co(NO)(CO)_3] + k_2[Co(NO)(CO)_3][L]$$

Solvent effects on k_1 and k_2 for reaction of $Co(NO)(CO)_3$ have been studied.[34] Effects on k_2 are fairly small and are consistent with the effect of varying dielectric constant on the bimolecular rate-determining step. Values of k_1 for these reactions conducted in the poor solvents cyclohexane, toluene, and nitromethane are similar. This similarity, and the determined activation parameters, are consistent with a dissociative mechanism for this reaction pathway. But k_1 values for reaction in tetrahydrofuran, acetonitrile, and dimethyl sulphoxide are different from the former k_1 values and from each other, indicating an associative mechanism involving the solvent for the k_1 term. The balance between the k_1 and k_2 pathways for substitution in $Co(NO)(CO)_2L$ depends both on the π-bonding and steric characteristics of L. This dependence on the bulk of L is perhaps surprising in view of the tetrahedral stereochemistry and consequent lack of crowding in the substrate.[33] The reverse reaction of $Co(NO)(CO)_2L$ with carbon monoxide has also been studied, so that rates in both directions and equilibrium constants are known for:

$$Co(NO)(CO)_3 + L \rightleftharpoons Co(NO)(CO)_2L + CO$$

These kinetic and thermodynamic results have been discussed in terms of the σ-bonding characteristics of L.[32]

Binuclear Mixed Ligand Carbonyls. Substitution in $Co_2(CO)_6$(alkyne) compounds follows the two-term rate law set out in the previous section, and proceeds by parallel dissociative and associative pathways.[35]

Substitution: Replacement of Other Ligands in Mixed Carbonyls.— Thermodynamic data for the equilibrium

$$W(CO)_5L + L' \rightleftharpoons W(CO)_5L' + L$$

show that bond strengths, and thus the barriers to transition-state formation for an S_N1 substitution mechanism, are determined primarily by σ- rather than by π-interactions.[36] Conversely, chromium–ligand bond

[31] D. A. Brown, H. J. Lyons, A. R. Manning, and J. M. Rowley, *Inorg. Chim. Acta*, 1969, **3**, 346.
[32] G. Innorta, G. Reichenbach, and A. Foffani, *J. Organometallic Chem.*, 1970, **22**, 731.
[33] G. Cardaci, S. M. Murgia, and G. Reichenbach, *Inorg. Chim. Acta*, 1970, **4**, 118.
[34] G. Cardaci, S. M. Murgia, and A. Foffani, *J. Organometallic Chem.*, 1970, **23**, 265.
[35] G. Cetini, O. Gambino, and P. L. Stanghellini, *Rend. Accad. Naz. XL*, 1968, 18, 45 (*Chem. Abs.*, 1970, **72**, 71,104j).
[36] R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, 1969, **8**, 83.

strengths have been estimated from kinetic studies of displacement of ligands L from $Cr(CO)_3L(phen)$, assuming an S_N1 mechanism.[37] The steric course of replacement of X in $Mo(\pi\text{-}C_5H_5)X(CO)_2(PPh_3)$ could be kinetically or thermodynamically controlled;[38] products of replacement of the pyridines in $Cr(CO)_3(py)_3$ by indanes are determined by kinetic factors.[39] This latter case forms an interesting contrast to the reaction of $Cr(CO)_6$ with indanes, where the products are the result of thermodynamic control.[40]

There have been several studies of displacement of bidentate ligands from compounds of the type $M(CO)_4(LL)$. Solvolysis of $M(CO)_4$(7-X-nor), where M = Cr, Mo, or W, and (7-X-nor) = a 7-substituted norbornadiene, occurs *via* dissociation to $M(CO)_4$ plus the norbornadiene.[41] Displacement of dto, (2,2,7,7-tetramethyl-3,6-dithiaoctane), from $M(CO)_4$(dto), where M = Cr, Mo, or W, occurs by reversible dissociation of one end of the dto ligand prior to rate-determining attack by the incoming ligand.[42] Displacement of LL by phosphite from $M(CO)_4(LL)$, where LL = *NNN'N'*-tetramethyl-1,3-diaminopropane or 2,2,8,8-tetramethyl-3,7-dithianonane, occurs by a similar mechanism, although here there is some kinetic evidence for interaction between the incoming and outgoing ligands.[43] The results from these and related references have been interpreted in terms of the nature of the ligand atoms and the size of the chelate rings. In the next example the interest is in the nature of the products as much as in the kinetics, for whereas $M(CO)_4$(diphos) reacts with bases with the displacement of carbon monoxide, the analogous arsenic compound $M(CO)_4$(dpae), where dpae = 1,2-bis(diphenylarsino)ethane, reacts by initial displacement of dpae; the final product is $M(CO)_3L_3$. The variation of rates with L is ascribed, as in the case of the dto complexes mentioned above, to rate-determining attack of L subsequent to reversible opening of the dpae chelate ring. The different mechanisms for these diphos and dpae compounds are consistent with known metal–phosphorus and metal–arsenic bond strengths.[44]

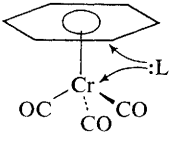
Displacement of arenes from $W(CO)_3$(arene) by trimethyl phosphite, to give $1,2,3\text{-}W(CO)_3[P(OMe)_3]_3$, is a second-order reaction. Reactivities are compared with those for chromium analogues, and for cycloheptatriene analogues. Rate trends cannot be entirely explained in terms of electron-releasing or -withdrawing effects of substituents on the electron density,

[37] G. R. Dobson and L. A. H. Smith, *Inorg. Chem.*, 1970, **9**, 1001.
[38] E. S. Bolton, M. Dekker, G. R. Knox, and C. G. Robertson, *Chem. and Ind.*, 1969, 327.
[39] D. E. F. Gracey, W. R. Jackson, W. B. Jennings, and T. R. B. Mitchell, *J. Chem. Soc.* (*B*), 1969, 1204.
[40] D. E. F. Gracey, W. R. Jackson, C. H. McMullen, and N. Thompson, *J. Chem. Soc.* (*B*), 1969, 1197.
[41] D. F. Hunt, C. P. Lillya, and M. D. Rausch, *Inorg. Chem.*, 1969, **8**, 446.
[42] G. R. Dobson, *Inorg. Chem.*, 1969, **8**, 91.
[43] G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, 1970, **4**, 87.
[44] D. R. Powers, G. C. Faber, and G. R. Dobson, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2970.

and thus on the ease of bimolecular nucleophilic attack, at the central metal atom.[45] The rate law and rate constants for this reaction in the presence of a variety of catalysts have also been reported and discussed in terms of associative mechanisms of substitution.[46]

The displacement of X from *cis*-$[MnX_2(CO)_4]^-$ by a Group V base provides an example both of substitution at a Group VII metal and of substitution at a charged metal carbonyl species. This substitution obeys first-order kinetics and is thought to be dissociative in mechanism. Rate constants in a range of solvents correlate tolerably well with dielectric constants, but better with the solvent parameter E_T.[47] A kinetic study of the cationic Group VIII species $[OsH(CO)_3(PPh_3)_2]^+$ is ruled out by its inertness, both to phosphine exchange and carbon monoxide displacement.[48] Displacement of iodide by nitrogen bases from $[Ir(CO)_2I_4]^-$ has been studied qualitatively.[49]

In nucleophilic substitution reactions of metal carbonyls it is often difficult to decide whether the nucleophile attacks at the central metal or at a relatively positive site on one of the ligands. Such an example is afforded by reaction of hexamethylborazolechromium tricarbonyl (4)



(4)

with phosphites in cyclohexane or dichloromethane solution. The observed second-order kinetics could arise equally well from phosphite attack at the chromium or at the borazole ring. Initial attack at the borazole ring seems the more likely, both in the light of the likely polarisation of the molecule and from a comparison of activation enthalpies for this and similar systems.[50]

In a large number of carbonyls nucleophilic attack seems more likely at the carbonyl-carbon than at the metal. There is often good evidence from products for such attack at the ligand, and these examples are therefore discussed in a later section on reactions of co-ordinated ligands (p. 301).

Substitution: Cyclopentadienyls.—The question of nucleophilic attack at metal or ligand, alluded to in the previous two paragraphs, is also relevant to cyclopentadienyl derivatives. The reaction of nickelocene with triethyl phosphite, in dioxan solution, follows a third-order rate law and has a low activation energy and large negative activation entropy. The rate law

[45] A. Pidcock, J. D. Smith, and B. W. Taylor, *J. Chem. Soc.* (*A*), 1969, 1604.
[46] A. Pidcock, J. D. Smith, and B. W. Taylor, *Inorg. Chem.*, 1970, **9**, 638.
[47] F. E. Smith and I. S. Butler, *Canad. J. Chem.*, 1969, **47**, 1311.
[48] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1969, 1889.
[49] L. Malatesta, M. Angoletta, and G. Caglio, *J. Chem. Soc.* (*A*), 1970, 1836.
[50] E. Deckelmann and H. Werner, *Helv. Chim. Acta*, 1969, **52**, 892.

suggests at least one pre-equilibrium, which makes interpretation of the activation parameters hazardous and prevents a firm choice between attack at nickel or at the ligand.[51] Bimolecular nucleophilic substitution at nickel in nickelocene is thought to be easy.[52]

The rate law and rate constants for photolysis of $Ti(\pi\text{-}C_5H_5)_2S_4$ in benzene, dioxan, and dimethylformamide have been determined radiochemically. The rate law is simple first-order; there is some solvent participation in the reaction in dimethylformamide.[53]

Phosphine and Phosphite Complexes.—The following general scheme is characteristic of reactions of these complexes:

$$ML_4 \rightleftharpoons ML_3 + L$$

$$ML_3 + Y \longrightarrow \text{products}$$

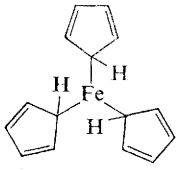
In the reaction of tetrakistriethylphosphitenickel(0) with cyclohexyl isocyanide, in n-hexane or benzene solution, the kinetics are first-order with rates independent of isocyanide concentration. Rates are, however, reduced by the addition of excess triethyl phosphite. Here the forward reaction of the initial equilibrium must be rate-determining, and the second reaction fast. Triethyl phosphite exchange with $Pd[P(OEt)_3]_4$ or $Pt[P(OEt)_3]_4$ also takes place by rate-determining loss of one ligand molecule. Activation energies are in the order Ni < Pd > Pt, as are the stabilities to thermal decomposition of $M(PF_3)_4$. A delicate balance of σ- and π-bonding effects is needed to rationalise this trend.[54]

In many reactions, particularly of phosphine complexes, the above reaction scheme still applies, but with a rapidly established dissociative equilibrium followed by rate-determining reaction of ML_3 with Y. This is the case in oxidative elimination reactions, which are discussed in the oxidative addition section. Sometimes the mechanism and products depend on conditions, as in reaction of $Pt(PPh_3)_4$ with hydroxyacetylenes, where the nature of the solvent, the presence of excess of phosphine, and particularly the stereochemistry of the alkyne, all affect the course of the reaction.[55]

The kinetic behaviour of phosphite, phosphine, and carbonyl complexes has been compared.[56]

Formation and Decomposition Reactions.—Species containing σ-bonded cyclopentadienyl rings have been suggested as intermediates in the synthesis of ferrocene. One such intermediate (5) has now been isolated.[57]

[51] H. Werner, V. Harder, and E. Deckelmann, *Helv. Chim. Acta*, 1969, **52**, 1081.
[52] Yu. A. Ustynyuk, T. I. Voevodskaya, N. A. Zharikova, and N. A. Ustynyuk, *Doklady Akad. Nauk S.S.S.R.*, 1968, **181**, 641.
[53] C. Ungurenaşu and A. Cecal, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1735.
[54] M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1969, **8**, 795.
[55] J. H. Nelson, H. B. Jonassen, and D. M. Roundhill, *Inorg. Chem.*, 1969, **8**, 2591.
[56] F. Basolo, *Trans. N.Y. Acad. Sci.*, 1969, **31**, 676.
[57] M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *J. Amer. Chem. Soc.*, 1969, **91**, 5233.



(5)

The rate law for dimerisation of $RuX_2(CO)_4$, in a range of solvents including nitromethane, 1,2-dichloroethane, chloroform, nitrobenzene, dioxan, and methyl isobutyl ketone, is first-order. The suggested rate-determining step is formation of the five-co-ordinate species $RuX_2(CO)_3$. Rates are affected little by the nature of the solvent, and do not correlate with dielectric constant or co-ordinating ability.[58]

The activation entropy for thermal decomposition of *trans*-$[MnX(CO)_3(PPh_3)_2]$ indicates that manganese–phosphorus bond breaking is rate-determining.[59] The rate law for the decomposition of $CoH(CO)_4$ to $Co_2(CO)_8$ plus hydrogen is second-order in cobalt compound.[60] While this decomposition has previously been studied in the gas phase, this is the first report of decomposition kinetics in the liquid phase. The first step in reaction of $Co_2(CO)_8$ with organomercury halides is solvent-induced disproportionation of the dimeric carbonyl.[61]

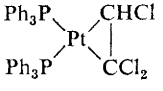
2 Metal–Alkyl and Metal–Aryl Bond Cleavage

Kinetics of acid hydrolysis of a series of pyridiomethyl-carbonyl and -π-cyclopentadienyl derivatives of molybdenum, tungsten, manganese, and iron have been reported. In the case of the 4-pyridiomethyl derivatives the mechanism is dissociative, and may be described either as S_N1 with respect to the metal or S_E1 with respect to the carbon of the pyridiomethyl ligand. For the 3-pyridiomethyl derivatives homolysis is important.[62]

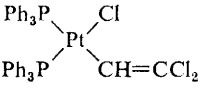
The mechanism of reaction of a variety of triphenylphosphinealkylgold(I) complexes, and of triphenylphosphinetrimethylgold(III), with mercury(II) chloride in a variety of solvents is S_E2. But when the alkyl group is cyano(ethoxycarbonyl)pentyl then the mechanism is dissociative.[63] Decomposition of triphenylphosphine-n-butylcopper must involve initial formation of butene and a transient copper hydride rather than of n-butyl radicals, since no octane can be detected in the ultimate products.[64]

The chloroalkene compound (6) readily isomerises in solution to the vinyl compound (7). Correlation of rate constants with solvent Y values

[58] A. Trovati, A. Araneo, P. Uguagliati, and F. Zingales, *Inorg. Chem.*, 1970, **9**, 671.
[59] H. K. Spendjian and I. S. Butler, *Inorg. Chem.*, 1970, **9**, 1268.
[60] F. Ungváry and L. Markó, *J. Organometallic Chem.*, 1969, **20**, 205.
[61] D. Seyferth and R. J. Spohn, *J. Amer. Chem. Soc.*, 1969, **91**, 3037.
[62] M. D. Johnson and N. Winterton, *J. Chem. Soc.* (*A*), 1970, 511.
[63] B. J. Gregory and C. K. Ingold, *J. Chem. Soc.* (*B*), 1969, 276.
[64] G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, *J. Amer. Chem. Soc.*, 1970, **92**, 1426.



(6)



(7)

indicates a mechanism intermediate between, or involving in parallel, S_N1 loss of chloride from the ligand followed by rapid platinum–chloride bond formation and purely intramolecular movement of chloride from carbon to platinum.[65] The mechanism of hydrolytic degradation of the fluoroalkyne complex $IrCl(CF_3C{\equiv}CCF_3)(PPh_3)_2$ has been discussed in the light of the products observed,[66] and compared with the similar hydrolytic degradation of fluoroalkene complexes of rhodium.[67]

A short review of methods of preparing organometallic compounds by ligand exchange and transfer reactions contains brief comments on mechanisms. The compounds discussed are mainly those containing dienes.[68]

3 Homogeneous Catalysis

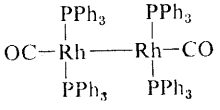
General Features and Reviews.—There have been two general reviews of homogeneous catalysis by transition-metal complexes,[69] plus a number devoted to particular groups of catalytically active compounds. These more specific reviews include articles on catalysis by ruthenium and rhodium compounds,[70] by palladium compounds,[71] and by $IrCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$.[72] General reviews of alkene and alkyne complexes of platinum and palladium include sections on kinetics and reaction mechanisms,[73] while a review of π-complexes as reaction intermediates includes some organometallic examples.[74]

The significance of the Woodward–Hoffmann rules in organometallic chemistry has been discussed, both in general terms,[75] and specifically in relation to the cyclisation of butadiene.[76] Disappointingly, Woodward and Hoffmann's own extensive review of their rules contains no mention of applications to organometallic chemistry.[77] The importance of factors

[65] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1969, **18**, 199.
[66] B. Clarke, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 951.
[67] R. D. W. Kemmitt and D. I. Nichols, *J. Chem. Soc.* (*A*), 1969, 1577.
[68] P. M. Maitlis, *Ann. N.Y. Acad. Sci.*, 1969, **159**, 110.
[69] J. Halpern, *Pure Appl. Chem.*, 1969, **20**, 59; R. Ugo, *Chimica e Industria*, 1969, **51**, 1319.
[70] D. E. Webster and P. B. Wells, *Platinum Metals Rev.*, 1969, **13**, 104.
[71] J. Tsuji, *Accounts Chem. Res.*, 1969, **2**, 144; E. W. Stern, *Trans. N.Y. Acad. Sci.*, 1970, **32**, 66.
[72] W. Strohmeier, *Structure and Bonding*, 1968, **5**, 96.
[73] F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799; U. Belluco, B. Crociani, R. Pietropaolo, and P. Uguagliati, *Inorg. Chim. Acta, Rev.*, 1969, **3**, 19.
[74] D. V. Banthorpe, *Chem. Rev.*, 1970, **70**, 295.
[75] R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, 1969, **47**, 71; F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1969, **91**, 1030.
[76] F. D. Mango, *Tetrahedron Letters*, 1969, 4813.
[77] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

other than orbital symmetry that may be involved in the lowering of barriers to reaction in the presence of transition-metal species has been emphasised, particularly for compounds of metals in d^{10} configurations,[78] and illustrated by the rhodium(I) (d^8) catalysis of the isomerisation of cubane discussed below.[79]

The catalytic efficiency of $RhH(CO)(PPh_3)_2$ for hydrogenation or isomerisation decreases with time, due to gradual formation of the dimer (8)



(8)

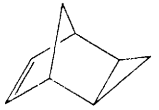
which is not catalytically active.[80] The catalytic activity of $RhCl(PPh_3)_3$ is enhanced by the presence of small amounts of oxygen or of hydrogen peroxide. These oxidants are presumed to oxidise some of the PPh_3 to $OPPh_3$. The latter co-ordinates less strongly to the rhodium than the former thus favouring the product of the active species $RhCl(PPh_3)_2$.[81] Ultimate products of oxidation of $RhCl(PPh_3)_3$ depend on the solvent. Solvent effects and the effects of added oxygen on the catalytic activity of $RhCl(PPh_3)_3$ both for hydrogenation and for isomerisation of alkenes have been described.[82] There has been a similar study of $RhCl(PPh_3)_3$ catalysis of the dehydrogenation of amines to nitriles.[83]

Isomerisation.—Mechanisms of isomerisation of pent-1-ene,[84] hex-1-ene,[85] and hept-1-ene [86] have been discussed, with particular reference to the reduction behaviour of the respective catalysts. Thus there is an induction period for the ruthenium-trichloride-catalysed isomerisation of hex-1-ene since reduction of ruthenium trichloride to the active ruthenium(I) species is slow. There is no induction period for rhodium-trichloride-catalysed isomerisation since reduction to rhodium(I) is rapid.[85] Isomerisation of cyclic alkenes, particularly of the cyclo-octadienes, has attracted some attention.[87-8] There has been discussion on whether the 1,4-isomer is an intermediate in the isomerisation of 1,3-cyclo-octadiene to the 1,5-isomer and *vice versa*; the 1,4-isomer has now been detected in isomerisation of the 1,3-compound catalysed by $PdCl_2$(benzonitrile)$_2$ in benzene solution.[87] Isomerisation

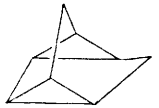
[78] W. T. A. M. van der Lugt, *Tetrahedron Letters*, 1970, 2281.
[79] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515.
[80] M. Yagupsky, C. K. Brown, G. Tagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 937.
[81] H. van Bekkum, F. van Rantwijk, and T. van der Putte, *Tetrahedron Letters*, 1969, 1.
[82] R. L. Augustine and J. F. van Peppen, *Chem. Comm.*, 1970, 495, 497, 571.
[83] J. Blum and A. Fisher, *Tetrahedron Letters*, 1970, 1963.
[84] M. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 941.
[85] H. Hirai, H. Sawai, E.-I. Ochiai, and S. Makishima, *J. Catalysis*, 1970, **17**, 119.
[86] W. Strohmeier and W. Rehder-Stirnweiss, *J. Organometallic Chem.*, 1969, **19**, 417; 1970, **22**, C27.
[87] H. Tayim and A. Vassilian, *Chem. Comm.*, 1970, 630.

catalysed by $[MCl_2(\pi\text{-}C_5Me_5)]_2$ has a complicated mechanism in which π-allyl complexes are likely intermediates.[88] The isomerisation of non-conjugated to conjugated dienes, catalysed by iron carbonyls, proceeds *via* a π-allylhydridoirontricarbonyl intermediate.[90]

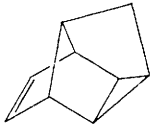
The isomerisation of (9) to (10) is catalysed by the rhodium(I) compounds $RhCl(PPh_3)_3$ or $[RhCl(CO)_2]_2$. It is therefore surprising at first sight that (11) to (12) is not similarly catalysed. However, the reverse reaction (12) to (11) is catalysed by rhodium(I) compounds; the presence of the extra



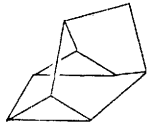
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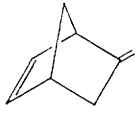
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(11)



(12)

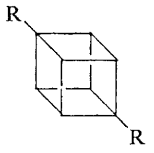


(13)

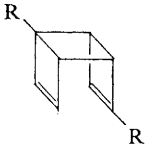
methylene bridge in (11) and (12) seems to have made a large difference to the equilibrium position compared to that of (9) and (10).[91] The isomerisation of (9) to (13) is catalysed by $IrCl(CO)(PPh_3)_2$.[92] Both reactions of (9) may proceed through initial bonding of C=C to iridium or to rhodium. Reaction of hexamethyl Dewar benzene with rhodium trichloride involves isomerisation of the Dewar benzene to a five-carbon ring ligand; the product has pentamethylcyclopentadienyl rings attached to the rhodium.[93]

Isomerisation of cubanes, *e.g.* (14), to diolefins, *e.g.* (15), is forbidden by the Woodward–Hoffmann rules, but is rapid in chloroform or carbon tetrachloride solution in the presence of $[RhCl(nor)]_2$ or of $[RhCl(cod)]_2$. The important question with regard to the mechanism is whether rhodium(I)

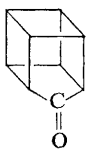
[88] K. Moseley, J. W. Kang, and P. M. Maitlis, *Chem. Comm.*, 1969, 1155.
[89] H. Samejima, T. Mizuta, H. Yamamoto, and T. Kwan, *Bull. Chem. Soc. Japan*, 1969, **42**, 2722.
[90] H. Alper, P. C. LePort, and S. Wolfe, *J. Amer. Chem. Soc.*, 1969, **91**, 7553.
[91] T. J. Katz and S. Cerefice, *Tetrahedron Letters*, 1969, 2509.
[92] H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Amer. Chem. Soc.*, 1969, **91**, 2137.
[93] B. L. Booth, R. N. Haszeldine, and M. Hill, *J. Chem. Soc.* (*A*), 1969, 1299.



(14)

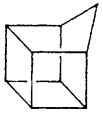


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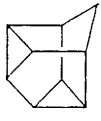


(16)

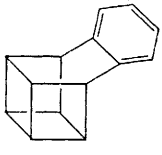
catalysis of breaking the two carbon–carbon bonds is concerted or non-concerted. The latter seems more likely in the light of the ancillary evidence that when isomerisation of cubane is attempted in the presence of $[RhCl(CO)_2]_2$ then carbon monoxide insertion into one carbon–carbon bond to give the ketone (16) is observed. It seems possible that other isomerisations, for instance of quadricyclene or of hexamethylprismane, which are rhodium(I)-catalysed may involve a similar mechanism. Preliminary results indicate that silver(I) catalysis may take an entirely different course.[79] Other examples of silver(I) catalysis of molecular rearrangements include those of homocubane (17) to the pentacyclononane (18)[94]



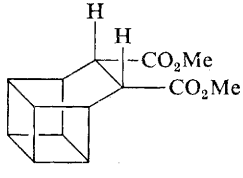
(17)



(18)



(19)



(20)

and of similar isomerisations of benzobasketene (19)[94] and of the ester (20).[94, 95] These processes are discussed in terms of the effects of the interaction of silver(I) and substrate orbitals permitting concerted rearrangements which are Woodward–Hoffmann forbidden. Further reports on the catalysis of isomerisation of esters deal with dimethyl maleate[89] and methyl oleate.[96]

The majority of catalysts mentioned so far have been complexes of rhodium or of iridium. Compounds of the other member of this triad, cobalt, may also catalyse alkene isomerisation. A recent example is provided by the cluster compound $[Co(CO)_2(PR_3)]_n$; the catalytically

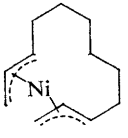
[94] L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, 1970, **92**, 2584.
[95] W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, and D. L. Whalen, *Tetrahedron Letters*, 1970, 787.
[96] R. Lai, E. Ucciani, and M. Naudet, *Bull. Soc. chim. France*, 1969, 793.

active species is believed to be the solvated monomer. The lower activity for this type of compound than of, for instance, $Co(\pi\text{-allyl})(CO)_2(PBu^n{}_3)$ can be ascribed to the greater reluctance of the former to dissociate than of the latter to lose its π-allyl ligand.[97] Compounds of elements elsewhere in the Periodic Table may also be active catalysts, as is illustrated by recently reported catalysis by tungsten compounds.[98]

Disproportionation.—Disproportionation of, for instance, pent-2-ene to but-2-ene plus hex-3-ene, catalysed by $MoCl_2L_2(NO)_2$ in the presence of alkylaluminium chlorides, occurs *via* rapid reversible formation of olefin complexes followed by rate-determining disproportionation. Kinetic results are reported, and the rôle of the metal discussed in terms of the requisite orbital transformations.[99]

The remaining references contain only scant mention of mechanisms. These include disproportionation of cyclohexadienes to benzene and cyclohexene in the presence of a rhodium(I) catalyst,[100] and the disproportionation of methyldisilicon hydrides in the presence of bistriethylphosphine platinum dichloride.[101]

Oligomerisation.—Much detailed discussion, based to a large extent on product characterisation and distribution observations, has appeared on catalysis of olefin oligomerisation by nickel complexes. Thus for the first example π-2-butenylnickel chloride, in contrast to the analogous π-allyl compound, is not a good catalyst for polymerisation of butadiene. But in the presence of trichloroacetate the π-2-butenyl complex does exhibit catalytic activity. This enhancement of activity is ascribed to the intermediacy of charge-transfer complexes.[102] The mechanism of cyclotrimerisation of butadiene has been considerably clarified by the characterisation of an intermediate (21) and determination of the distribution of isomers



(21)

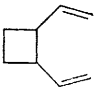
of the cyclododecatriene products as a function of temperature and of the ligands on the nickel.[103] By suitable modification of the nickel catalyst,

[97] G. Pregaglia, A. Andreetta, and G. Ferrari, *Chem. Comm.*, 1969, 590.
[98] J.-L. Hérisson, Y. Chauvin, Nhu Hung Phung, and G. Lefebvre, *Compt. rend.*, 1969, **269**, *C*, 661.
[99] W. B. Hughes, *J. Amer. Chem. Soc.*, 1970, **92**, 532.
[100] K. Moseley and P. M. Maitlis, *Chem. Comm.*, 1969, 1156.
[101] K. Yamamoto, H. Okinoshima, and M. Kumada, *J. Organometallic Chem.*, 1970, **23**, C7.
[102] T. K. Vydrina, E. I. Tinyakova, and B. A. Dolgoplosk, *Doklady Akad. Nauk S.S.S.R.*, 1968, **183**, 1013.
[103] B. Bogdanović, P. Heimbach, M. Kröner, G. Wilke, E. G. Hoffmann, and J. Brandt, *Annalen*, 1969, **727**, 143.

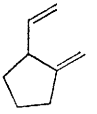
specifically by using tris-*o*-biphenylyl phosphite complexes, butadiene can be made to dimerise rather than trimerise. The discussion of the mechanism is based on the products observed, which are 1-*cis*,5-*cis*-cyclo-octadiene (22), or *cis*-1,2-divinylcyclobutane (23).[104] In the presence of bis(tributylphosphine)nickel halides and butyl-lithium, or of π-allylnickel



(22)



(23)



(24)

bromide dimer and tributylphosphine, butadiene dimerises to 1-vinyl-2-methylenecyclopentane (24). The mechanism of this reaction, the first efficient catalytic route from butadiene to a five-membered ring, is discussed.[105]

Further catalytic systems consist of π-tetramethylcyclobutadienenickel halides plus alkylaluminium halides, with or without phosphorus(III) compounds present as co-catalysts. Kinetics are reported for several olefin oligomerisations catalysed by these mixtures, including the dimerisation of propene[106] and of ethylene.[107] Kinetics of oligomerisations catalysed with the same reagents, save for replacement of the tetramethyl compounds by unsubstituted π-cyclobutadiene analogues, are also reported.[108] These catalyst mixtures have also featured in several co-oligomerisation studies — see below. Propene is selectively dimerised by nickel chloride–phosphine mixtures in the presence of $Al_2Cl_3Et_3$ to 2,3-dimethylbut-1-ene, presumably *via* the usual olefin co-ordination and hydrogen transfer mechanism. The nature of the aluminium compound is important — neither Al_2Cl_6 nor Al_2Et_6 is as effective as $Al_2Cl_3Et_3$, which combines the requisites of Lewis acid and of alkylating power.[109]

Palladium compounds are also useful catalysts for oligomerisation and co-oligomerisation reactions. Dimerisation or co-dimerisation of olefins catalysed by palladium(II) chloride or, better, $PdCl_2(C_6H_5CN)_2$ involves a palladium(II)-hydride intermediate as the catalytically active species.[110] A similar reaction to dimerisation is coupling, *e.g.* of benzene to give biphenyl, which is also catalysed by palladium(II) chloride and proceeds *via* palladium–phenyl σ-bonded species.[111] The nature of intermediates in

[104] W. Brenner, P. Heimbach, H. Hey, E. W. Müller, and G. Wilke, *Annalen*, 1969, **727**, 161.
[105] J. Kiji, K. Masui, and J. Furukawa, *Tetrahedron Letters*, 1970, 2561.
[106] O.-T. Onsager, H. Wang, and U. Blindheim, *Helv. Chim. Acta*, 1969, **52**, 196.
[107] O.-T. Onsager, H. Wang, and U. Blindheim, *Helv. Chim. Acta*, 1969, **52**, 215.
[108] O.-T. Onsager, H. Wang, and U. Blindheim, *Helv. Chim. Acta*, 1969, **52**, 230.
[109] G. G. Eberhardt and W. P. Griffin, *J. Catalysis*, 1970, **16**, 244.
[110] M. G. Barlow, M. J. Bryant, R. N. Haszeldine, and A. G. McKie, *J. Organometallic Chem.*, 1970, **21**, 215.
[111] Y. Fujiwara, I. Moritani, K. Ikegami, R. Tanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 863.

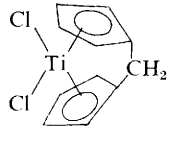
palladium-catalysed reactions has been probed by stereochemical studies involving substituted *endo*- and *exo*-norbornadienes.[112]

Dimerisation of unsaturated nitriles or carbonyls is catalysed by isonitriles in the presence of copper(I) compounds. The mechanisms involve intermediate formation of vinyl or allyl carbanions.[113]

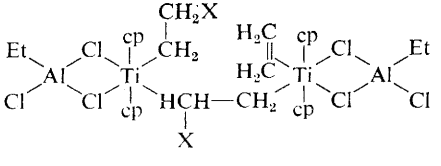
The mechanism of trimerisation of butadiene by a mixed cobalt(II) chloride–aluminium triethyl catalyst has been inferred from the natures of the three products characterised.[114] The determination of the enthalpy of dimerisation of aluminium triethyl provides a useful piece of thermochemical data for quantitative discussion of the rôle and energetics of aluminium triethyl in this type of reaction.[115] Polymerisation of isoprene in the presence of $Fe(acac)_3$–aluminium triethyl–pyridine derivatives mixtures has a negative apparent activation enthalpy, which can be attributed to the instability of the catalytic complex at elevated temperatures.[116] Bis-cyclo-octatetraeneiron(0) is an effective oligomerisation catalyst. The composition of products accessible only by hydrogen migration indicates an oxidative addition–reductive elimination mechanism rather than insertion.[117]

$Mn(acac)_3$ and $Mn(tfac)_3$ catalyse polymerisation of styrene, acrylonitrile, and methyl methacrylate. The reaction sequence is loss of one acac or tfac ligand, co-ordination of the monomer to the manganese, and electron transfer to give manganese(II) and the organic free radical.[118]

The new compound 1,1′-methylenetitanocene dichloride (25) is as effective as its well-known analogue dicyclopentadienyltitanium dichloride in catalysing olefin polymerisation.[119] Further evidence for binuclear



(25)



(26)

intermediates in this type of system is provided by a study of the accelerating effect of added ethylene on polymerisation (and parallel reduction) catalysed by dicyclopentadienyltitanium dichloride. The intermediate (26)

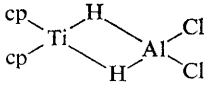
[112] R. Baker, D. E. Halliday, and T. J. Mason, *Tetrahedron Letters*, 1970, 591.
[113] T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *J. Org. Chem.*, 1970, **35**, 670; *Bull. Chem. Soc. Japan*, 1970, **43**, 877.
[114] E. W. Duck, D. K. Jenkins, J. M. Locke, and S. R. Wallis, *J. Chem. Soc.* (*C*), 1969, 227.
[115] J. N. Hay, P. G. Hooper, and J. C. Robb, *Trans. Faraday Soc.*, 1969, **65**, 1365.
[116] H. E. Swift, J. E. Bozik, and C. Y. Wu, *J. Catalysis*, 1970, **17**, 331.
[117] A. Carbonaro, A. Greco, and G. Dall'Asta, *J. Organometallic Chem.*, 1969, **20**, 177.
[118] C. H. Bamford and A. N. Ferrar, *Chem. Comm.*, 1970, 315.
[119] T. J. Katz and N. Acton, *Tetrahedron Letters*, 1970, 2497.

is suggested.[120] The reduction in activity of these Ziegler–Natta catalysts on ageing is ascribed to reduction of the titanium.[121] In fact in some systems catalytic activity increases with reduction to titanium(III), for a balance is involved between the differing requirements of co-ordination of the monomer to the titanium and the subsequent alkyl migration step.[122]

Variable-temperature n.m.r. studies of the soluble Ziegler–Natta catalyst $TiClMe(\pi\text{-}C_5H_5)_2$ plus aluminium trimethyl in benzene solution suggest equilibrium between two adduct species, (27) and (28).[123] Temperature variation of e.s.r. spectral line-widths indicates some dynamic process in



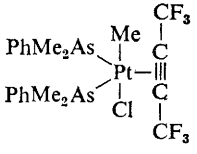
(27) (28)



(29)

THF solutions of $(\pi\text{-}C_5H_5)_2TiH_2AlCl_2$. The low activation energy of *ca.* 4 kcal mol^{-1} seems too low for a bond-breaking process, so intramolecular exchange of positions of the asymmetrical sited bridging protons (29) is suggested as the process responsible.[124]

Alkynes. Homogeneous polymerisation is generally assumed to proceed through complex formation and subsequent insertion, though definitive proof of this pathway is rarely available. This mechanism has been illustrated by the isolation of appropriate intermediates such as (30) for



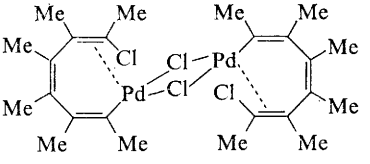
(30)

hexafluorobut-2-yne polymerisation in the presence of some methylplatinum(II) complexes, for instance *trans*-$[PtClMe(AsMe_2Ph)_2]$.[125]

[120] G. Henrici-Olivé and S. Olivé, *J. Organometallic Chem.*, 1969, **16**, 339.
[121] T. Matsuda, T. Furukawa, S. Togo, and T. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 47; *cf.* G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1967, **6**, 690.
[122] R. J. H. Clark and A. J. McAlees, *J. Chem. Soc.* (*A*), 1970, 2026.
[123] K. H. Reichert and M. Mallmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 217.
[124] G. Henrici-Olivé and S. Olivé, *J. Organometallic Chem.*, 1969, **19**, 309.
[125] H. C. Clark and R. J. Puddephat, *Chem. Comm.*, 1970, 92.

Investigation of the nature and activity of catalytic species in copper(I) chloride-promoted dimerisation of acetylene indicates that the mechanism either involves insertion of a C_2H unit into a copper–chlorine bond, or the reaction of C_2H with two copper atoms to give a 3-centre, 2-electron-bonded species.[126] Cyclic oligomerisation of diphenylacetylene in the presence of $AlPh_3$ proceeds through π-complexes as intermediates;[127] benzyne intermediates are suggested, on the basis of observed products, in oligomerisation of but-2-yne and of oct-4-yne in the presence of n-butyl- or *p*-tolyl-chromium compounds.[128]

There are some comments on reaction mechanisms in a recent general review of cyclisation of acetylenic compounds.[129] Trimerisation of but-2-yne and of 1-phenylprop-1-yne catalysed by $PdCl_2$(benzonitrile)$_2$ has been studied; and a mechanism suggested from observed products at various stages. This trimerisation involves successive alkyne complexing and intramolecular insertion stages into Pd–Cl, Pd–C, and Pd–H bonds. This is a variant of one of the four possible cyclotrimerisation mechanisms which have been proposed.[130] The mechanism of reaction of one of the intermediates (31) in this cyclotrimerisation with triphenylphosphine has



(31)

been investigated; one of the reaction pathways involves what is whimsically entitled a 'cyclopropane merry-go-round' process.[131]

Co-addition and Co-oligomerisation.—Nickel and palladium catalysts are again much in evidence. The same π-tetramethylcyclobutadienenickel dichloride plus alkylaluminium halide mixed catalysts which have been investigated in relation to alkene oligomerisation (see above) catalyse co-addition of ethylene and propene. Kinetic results for this reaction are reported.[132] Product analysis and distribution permit postulation of mechanisms of addition of butadiene and but-2-yne to give 4,5-dimethyl-1-

[126] O. N. Temkin, R. M. Flid, G. K. Shestakov, A. Ermakova, G. F. Tikhonov, L. I. Yarovaya, and V. G. Mikhal'chenko, *Kinetika i Kataliz*, 1969, **10**, 1230 (*Chem. Abs.*, 1970, **72**, 59,678s).

[127] J. J. Eisch and R. J. Harrell, *J. Organometallic Chem.*, 1969, **20**, 257.

[128] R. P. A. Sneedon and H. H. Zeiss, *J. Organometallic Chem.*, 1969, **20**, 153.

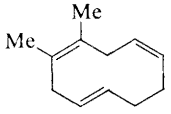
[129] W. Reppe, N. V. Kutepov, and A. Magin, *Angew. Chem. Internat. Edn.*, 1969, **8**, 727.

[130] H. Deitl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 2276.

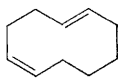
[131] H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 2285.

[132] O.-T. Onsager, H. Wang, and U. Blindheim, *Helv. Chim. Acta*, 1969, **52**, 224.

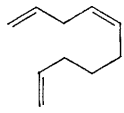
cis-,4-*cis*-,7-*trans*-cyclodecatriene (32),[133] and of butadiene and ethylene to give *cis,trans*-1,5-cyclodecadiene (33) or 1-*trans*-4,9-decatriene (34).[134]



(32)



(33)



(34)

Mixtures containing nickel chloride, aluminium triethyl, and 1,2-bis(diphenylphosphino)ethane (dpe) or 1,2-bis(diphenylphosphino)propane (dpp) catalyse the reaction of ethylene and butadiene to give 1,4,9-decatriene when the ratio of dpe or dpp to nickel is less than 1. However, when more phosphine is present [dpe : Ni > 1 or dpp : Ni = 1·5], 1,4-hexadiene is produced. At higher ratios, dpe : Ni ~ 3, there is little reaction. Such marked discrimination is unusual; even the replacement of these chelating phosphines by triphenylphosphine leads to greatly reduced selectivity.[135]

Palladium(II) compounds are known to be good catalysts for co-additions and co-polymerisations.[136] Recent mechanistic studies include those of the addition of benzene to styrene[137] and to a variety of normal[138] and polar[139] alkenes, catalysed by palladium(II) acetate. Substituents in the benzene do not greatly affect reactivities, but polar groups in the alkene have a large influence, which may well be due to co-ordination of ligating atoms present in such groups to the palladium. The catalytic rôle of palladium(II) chloride or of its benzonitrile complex in co-dimerisation of pairs of alkenes has been described.[110] In palladium-catalysed coupling of π-allyl ligands with a series of substituted acetylacetones there is evidence for anchimeric assistance when the substituents contain units (*e.g.* C=C or O) which can co-ordinate to the palladium at some stage in the reaction sequence.[140]

Addition of ethylene to butadiene is catalysed by cobalt(II) chloride–bidentate diphosphine–aluminium triethyl mixtures [*cf.* similar nickel(II) case above].[141] Addition of butadiene or of 1,1-dimethylallene to norbornadiene is catalysed by iron(0) complexes, for instance the cyclooctene complex.[142]

[133] W. Brenner, P. Heimbach, and G. Wilke, *Annalen*, 1969, **727**, 194.
[134] P. Heimbach and H. Wilke, *Annalen*, 1969, **727**, 183.
[135] Y. Inoue, T. Kagawa, and H. Hashimoto, *Tetrahedron Letters*, 1970, 1099.
[136] See, *e.g.*, R. F. Heck, *J. Amer. Chem. Soc.*, 1968, **90**, 5518, 5526, 5531, 5535, 5538, 5542, 5546; J. M. Davidson and C. Triggs, *J. Chem. Soc.* (*A*), 1968, 1324, 1331.
[137] Y. Fujiwara, I. Moritani, R. A. Sano, H. Tanaka, and S. Teranishi, *Tetrahedron*, 1969, **25**, 4815.
[138] S. Danno, I. Moritani, and Y. Fujiwara, *Tetrahedron*, 1969, **25**, 4809.
[139] S. Danno, I. Moritani, and Y. Fujiwara, *Tetrahedron*, 1969, **25**, 4819.
[140] Y. Takahashi, K. Tsukiyama, S. Sakai, and Y. Ishii, *Tetrahedron Letters*, 1970, 1913.
[141] T. Kagawa, Y. Inoue, and H. Hashimoto, *Bull. Chem. Soc. Japan*, 1970, **43**, 1250.
[142] A. Greco, A. Carbonaro, and G. Dall'Asta, *J. Org. Chem.*, 1970, **35**, 271.

Homogeneous Hydrogenation.—There is considerable interest in the inter-relation between mechanisms of homogeneous and heterogeneous catalysis. In one investigation the homogeneous catalysts were $[RhCl_2(py)_2DMF](BF_4)$ and $[RuCl_2(PPh_3)_3]$. For the latter ruthenium(II) compound rates of homogeneous hydrogenation correlate with complexing constants for the series of alkenes studied, indicating that formation of a ruthenium–alkene complex is the controlling step in hydrogenation by this route. But for the rhodium(III) catalyst, rates of homogeneous hydrogenation are controlled by rates of hydrogen transfer; rates of hydrogenation correlate with heats of *heterogeneous* hydrogenation, which is strongly suggestive of similarity of mechanism.[143] The alternative of complex formation with the alkene *versus* hydrogen transfer as rate-limiting step is a common topic for discussion in mechanisms of homogeneous hydrogenation. Another parallel between homogeneous and heterogeneous catalysis is suggested by the observation that for several complexes of rhodium, iridium, ruthenium, and palladium the mechanism at low olefin concentration involves reaction of the olefin with preformed hydridometal species, but at high olefin concentrations reaction occurs primarily between hydrogen and the metal–olefin complex. This is somewhat reminiscent of the dependence of mechanism on order of adding reagents, and their relative pressures, in heterogeneous hydrogenation.[144] A further link between homogeneous and heterogeneous mechanisms is provided by the study of hydrogenation of $\alpha\beta$-unsaturated carbonyl compounds either in solution in the presence of $RhCl(PPh_3)_3$ or over the usual metal catalysts.[145]

Homogeneous hydrogenation is often claimed to proceed *via* an intermediate in which both the olefin and the hydrogen are co-ordinated to the metal of the catalyst complex, though such hypotheses are rarely supported by the isolation and characterisation of such an intermediate. However, for reduction of activated olefins, for example cyano-olefins, in the presence of $Ir(H)(CO)(PPh_3)_3$, intermediates of the formula $Ir(H)(CO)(PPh_3)_2$(olefin) have been isolated,[146] and the crystal structure of the compound with *trans*-1,2-dicyanoethylene as the olefin has been determined. The mechanistic interest of this crystal structure is that it shows the hydridic-hydrogen conveniently situated *cis* to the co-ordinated olefin ready for transfer.[147]

The 'active' hydrogen in organometallic compounds containing $P(aryl)_3$ ligands may be in the *ortho*-position of a phenyl ring. N.m.r. and deuteriation experiments have now demonstrated rapid equilibrium between such a complex in its initial form, hydrogen, and a σ-phenyl bonded form, both for triphenylphosphine complexes, *e.g.* $RuHCl(PPh_3)_3$, and for several

[143] I. Jardine and F. J. McQuillin, *Chem. Comm.*, 1969, 502.
[144] I. Jardine, R. W. Howsam, and F. J. McQuillin, *J. Chem. Soc.* (*C*), 1969, 260.
[145] H. Simon and O. Berngruber, *Tetrahedron*, 1970, **26**, 161, 1401.
[146] W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, 1969, **91**, 3661.
[147] K. W. Muir and J. A. Ibers, *J. Organometallic Chem.*, 1969, **18**, 175.

triphenyl phosphite compounds. The σ-phenyl-bonded compound has been isolated from the equilibrium involving $RuHCl[P(OPh)_3]_4$.[148] A similar reaction is reported for $IrCl(PR_3)_3$, where R = aryl;[149] this type of reaction has been reviewed.[150]

After these references of general applicability it will be convenient to discuss the large number of specific references to homogeneous hydrogenation of olefins and of other unsaturated molecules in order of the central metal atom in Periodic Table order.

Titanium. Catalyses of hydrogenation of alkenes, alkynes, carbonyl-, and nitro-compounds have been described.[151] The effect of the nature of the ligand L and of the alkene to be reduced on reactivity in catalytic hydrogenation by $Ti(\pi\text{-}C_5H_5)_2L_2$ has been quantitatively studied.[152] The dependence of rate constants on solvent for reduction of decene in the presence of $Ti(\pi\text{-}C_5H_5)Me^+$ is interpreted in terms of electrostatic interaction between the active ionic species and the solvent.[153] There is also a thermochemical report relevant here, and that is of a determination of the heats of mixing of cyclohexene and of hex-1-ene with titanium tetrachloride. The heats of mixing are close to zero, which implies very small heats of complex formation between these alkenes and titanium.[154]

The mechanism of reduction of molecular nitrogen at titanium catalysts continues to be a subject of much research. The inherent complications of these systems, which consist of reagents, catalyst, and co-catalysts, result in a dearth of precise kinetic results, but nonetheless informed speculation on the basis of available kinetic, product, and stoicheiometric knowledge provides useful information about the mechanisms. These have been reviewed in general discussions,[155] while mechanisms have been postulated for specific systems involving catalysis by titanium tetrachloride–aluminium tribromide derivatives,[156] electrolysis in a 1,2-dimethoxyethane solution containing titanium tetraisopropoxide, aluminium trisisopropoxide, and naphthalene,[157] and catalysis by titanium alkoxide–sodium naphthalenide mixtures.[158] In the last case the rôle of titanium(II) in the

[148] G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 1969, **91**, 4990.
[149] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.
[150] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.
[151] *E.g.*, V. V. Abalyaeva and M. L. Khidekel, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, 2087 (*Chem. Abs.*, 1970, **72**, 6540*j*).
[152] R. Stern, G. Hillion, and L. Sajus, *Tetrahedron Letters*, 1969, 1561.
[153] O. N. Babkina, E. A. Grigoryan, F. S. D'yachkovskii, A. E. Shilov, and N. I. Shuvalova, *Russ. J. Phys. Chem.*, 1969, **43**, 984.
[154] B. Hessett and P. G. Perkins, *Chem. and Ind.*, 1970, 747.
[155] G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1969, **8**, 650; E. Bayer and V. Schurig, *Chem. Ber.*, 1969, **102**, 3378.
[156] M. E. Volpin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Schur, *Doklady Akad. Nauk S.S.S.R.*, 1968, **180**, 393.
[157] E. E. van Tamelen and D. A. Seeley, *J. Amer. Chem. Soc.*, 1969, **91**, 5194.
[158] E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, 1969, **91**, 1551; E. E. van Tamelen, B. Åkermark, and K. B. Sharples, *ibid.*, p. 1552.

catalytic process has been clarified. Dicyclopentadienyltitanium dichloride is an effective compound in nitrogen fixation systems; its derivative in which the two cyclopentadienyl rings are joined by a methylene bridge, *viz.* 1,1′-methylenetitanocene dichloride, is also effective.[119]

In most systems, catalytic reduction of molecular nitrogen produces ammonia, but two cases have been reported where hydrogenation of molecular nitrogen takes place without nitrogen–nitrogen bond breaking to give hydrazine. In one case the catalyst contains titanium tetra-alkoxides and sodium naphthalenide,[159] in the other diethyltitanium dichloride and a Grignard reagent.[160] Molecular nitrogen complexes had previously been isolated and characterised in the latter case;[161] the present report describes the production of hydrazine from these complexes on standing.[160]

Chromium. The mechanism of hydrogenation at this rarely studied centre has been probed by product analyses and deuterium tracer experiments. The catalysts used were $Cr(arene)(CO)_3$, which selectively catalyse 1,4-addition to diolefins. Key intermediates are $Cr(H)_2(CO)_3$ and $Cr(H)_2(CO)_3$-(diene).[162]

Ruthenium. The π-benzene–ruthenium(II)–chloride polymer has a catalytic activity comparable with that of $RuCl_2(PPh_3)_3$, though under certain conditions isomerisation is an appreciable side-reaction to catalytic hydrogenation.[163] $Ru(H)(O_2C\cdot CF_3)(PPh_3)_3$ is a selective catalyst for hydrogenation of alk-1-enes. Its selectivity may be attributed to the bulk of the phenyl groups. Its mode of action is the usual one, reversible loss of one triphenylphosphine ligand, co-ordination of and subsequent hydrogen transfer to the alkene, with attack of hydrogen being the rate-determining step. To maintain the expected co-ordination numbers at the metal centre throughout this sequence of reactions it is suggested that the trifluoroacetate acts as a mono- or as a bi-dentate ligand at different stages.[164] The ruthenium(I)–chloride species produced by two-stage reduction of hydrated ruthenium(III) chloride dissolved in dimethyl-acetamide is an active homogeneous hydrogenation catalyst under mild conditions. In the reduction of maleic acid there is no evidence for ruthenium–maleate complex formation; reduction takes place by reversible formation of a hydrido-ruthenium(I) species which transfers its hydrogen to the maleic acid. Kinetic parameters and rate laws were determined both for the ruthenium(III) to ruthenium(I) reduction and for the maleic acid

[159] E. E. van Tamelen, R. B. Fechter, and S. W. Schneller, *J. Amer. Chem. Soc.*, 1969, **91**, 7196.
[160] A. E. Shilov and A. K. Shilova, *Russ. J. Phys. Chem.*, 1970, **44**, 164.
[161] A. E. Shilov, A. K. Shilova, and E. F. Kvashina, *Kinetika i Kataliz*, 1969, **10**, 1402.
[162] E. N. Frankel and R. O. Butterfield, *J. Org. Chem.*, 1969, **34**, 3930; E. N. Frankel, E. Selke, and C. A. Glass, *ibid.*, p. 3936.
[163] I. Ogata, R. Iwata, and Y. Ikeda, *Tetrahedron Letters*, 1970, 3011.
[164] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2610.

hydrogenation.[165] $RuCl_4(bipy)^{2-}$ has also been studied as a catalyst for hydrogenation of maleic acid.[166]

A slightly different system involves reduction of nitrobenzene by hydrogen and carbon monoxide in the presence of $Ru_3(CO)_{12}$, $Ru(CO)_5$, or $Ru(acac)_3$. Here the mechanism suggested involves as a first step oxygen abstraction from the nitrobenzene to give the nitrene PhN as a transient intermediate which can then either pick up hydrogen to give aniline, or pick up carbon monoxide to give phenyl isocyanate which condenses with the aniline to yield diphenylurea as ultimate product. The intermediate nitrene and isocyanate intermediates are probably stabilised to some extent by co-ordination to the ruthenium.[167]

Cobalt. A great diversity of cobalt complexes can act as catalysts for homogeneous hydrogenation. Examples include cyanocobaltate(II) catalysis of the hydrogenation of cinnamate,[168] and $Co(H)_3(PPh_3)_3$, $Co(H)(CO)(PPh_3)_3$,[169] or the cluster compounds $[Co(CO)_2(PR_3)]_n$ [97] as catalysts for alkene hydrogenation. The relatively low reactivity of the monomeric phosphine complexes as catalysts, compared to their rhodium analogues, may be ascribed to a greater reluctance of the cobalt compounds to lose a phosphine ligand to generate the active catalyst.[97] In cyanocobaltate(II) catalysis the mechanism involves radicals, since only one hydrogen atom is attached to $Co(CN)_5^{3-}$. This contrasts with iridium(I) catalysts, which can take up a hydrogen molecule as two hydride ions.

Rhodium. Just as two-electron reduction of ruthenium(III) chloride yields a catalytically active species (see above), so also does reduction of rhodium(III) chloride. In the presence of alcohol and base $RhCl(CO)(PR_3)_2$ can be produced, which catalyses hydrogen transfer from an alcohol (as alkoxide) to olefins.[170] The mechanism of catalysis by these rhodium(I) species $RhX(CO)(PR_3)_2$ is thought to be the same as that for the more widely studied (see below) $IrX(CO)(PR_3)_2$.[171]

Similarly rhodium trichloride reduced by ethanol in the presence of tris-*o*-tolylphosphine gives an active rhodium(I) catalyst $RhCl[(o\text{-tolyl})_3P]_2$, *via* the characterised rhodium(II) intermediate $RhCl_2[(o\text{-tolyl})_3P]_2$. The rhodium(I) in the above three-co-ordinate species can readily abstract a hydrogen atom, even from a second rhodium(I) molecule.[172] Reduction of $RhCl_3(py)_3$ by $NaBH_4$ in DMF yields a catalyst for *trans*-deuteriation of olefins.[173]

[165] B. Hui and B. R. James, *Chem. Comm.*, 1969, 198.
[166] B. Hui and B. R. James, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 367.
[167] F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, 1970, **9**, 342.
[168] M. Takahashi, Y. Hisamatsu, and M. Iguchi, *Nippon Kagaku Zasshi*, 1970, **91**, 46 (*Chem. Abs.*, 1970, **72**, 104,322*j*); J. Basters, H. van Bekkum, and L. L. van Reijen, *Rec. Trav. chim.*, 1970, **89**, 491.
[169] M. Hidai, T. Kuse, T. Hikita, Y. Uchida, and A. Misono, *Tetrahedron Letters*, 1970, 1715.
[170] G. Gregorio, G. Pregaglia, and R. Ugo, *Inorg. Chim. Acta*, 1969, **3**, 89.
[171] W. Strohmeier and W. Redher-Stirnweiss, *Z. Naturforsch.*, 1969, **24b**, 1219.
[172] M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266.
[173] P. Abley and F. J. McQuillin, *Chem. Comm.*, 1969, 1503.

One of the most commonly used catalysts for homogeneous hydrogenation of olefins is $RhCl(PPh_3)_3$; the accepted mechanism involves rate-determining displacement of a solvent molecule (S) by the olefin from $RhClH(PPh_3)_2S$ and subsequent fast transfer of two hydrogen atoms to the complexed olefin to release the product alkane. This mechanism is consistent with relative rates of deuteriation of pairs of *cis*- and *trans*-isomeric olefins.[174] Investigations of hydrogenation and deuteriation of cyclic alkenes and cyclopropyl alkenes confirm the general mechanism outlined above, but indicate several minor modifications. These are that some of the reactions which are considered to be irreversible in the original scheme are in fact reversible equilibria, and that although transfer of both hydrogen atoms from rhodium to the alkene is fast, the two atoms need not be transferred simultaneously.[175] Catalytic hydrogenation of styrenes may involve parallel reactions, one involving simultaneous and the other stepwise transfer of the two hydrogen atoms.[176] It has already been established that rates of homogeneous hydrogenation catalysed by $RhCl(PR_3)_3$ are dependent on the steric properties of the alkenes reduced; it has now been shown that rates, though not selectivity, depend on R.[177]

Two close analogues of $RhCl(PPh_3)_3$ have been studied. Aminophosphine complexes also act as homogeneous hydrogenation catalysts, except when derived from a weakly basic amine.[178] $Rh(NO)(PPh_3)_3$ is also a serviceable catalyst.[179] The dimer $[RhCl(C_8H_{14})_2]_2$ in dimethylacetamide solution acts as a hydrogenation catalyst for maleic acid; the kinetics of this reduction have been briefly reported.[180] The reduction of wet acetone (1% water) is catalysed by solvated $[RhH_2(PPhMe_2)_2]^+$. Although definitive kinetic data are not yet available, there is sufficient information available to suggest a possible mechanism involving co-ordination of the ketone to the rhodium and subsequent transfer of two hydrogen atoms, in other words the analogous mechanism to hydrogenation of alkenes.[181] Dimethyl sulphoxide is also catalytically reduced in the presence of rhodium catalysts, again by transfer of hydrogen within a hydrido-rhodium complex of DMSO.[182]

Iridium. There are several more reports concerning catalysis by the much studied series $IrX(CO)L_2$. Kinetics of hydrogenation, for X = Cl, Br, and I, or L = phosphine or phosphite, have been interpreted in terms of the electron-releasing or -withdrawing effects of the ligands L on the

[174] J. B. Morandi and H. B. Jensen, *J. Org. Chem.*, 1969, **34**, 1889.
[175] A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, 1969, **91**, 672; *J. Org. Chem.*, 1970, **35**, 643; C. H. Heathcock and S. R. Poulter, *Tetrahedron Letters*, 1969, 2755.
[176] G. V. Smith and R. J. Shuford, *Tetrahedron Letters*, 1970, 525.
[177] C. O'Connor and G. Wilkinson, *Tetrahedron Letters*, 1969, 1375.
[178] Y. Chevallier, R. Stern, and L. Sajus, *Tetrahedron Letters*, 1969, 1197.
[179] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 1969, **91**, 5659.
[180] B. R. James and F. T. T. Ng, *Chem. Comm.*, 1970, 908.
[181] R. R. Schrock and J. A. Osborn, *Chem. Comm.*, 1970, 567.
[182] B. R. James, F. T. T. Ng, and G. L. Rempel, *Canad. J. Chem.*, 1969, **47**, 4521.

electron density at the iridium.[183] The equilibrium constants for the uptake of hydrogen:[184]

$$IrX(CO)L_2 + H_2 \rightleftharpoons IrXH_2(CO)L_2$$

and for the analogous interaction with solvent (S):[185]

$$IrX(CO)L_2 + S \rightleftharpoons IrX(CO)L_2S$$

have been reported and discussed. Hydrogenation of dimethyl maleate (dmm) in the presence of $IrX(CO)L_2$ proceeds *via* intermediate formation of $IrX(CO)L_2$(dmm) and $IrXH_2(CO)L_2$(dmm);[186] equilibrium and kinetic results have been reported.[187] In the hydrogenation of alkenes catalysed by $IrH_3(PPh_3)_3$ the active catalyst is in fact $IrH_3(PPh_3)_2$, and there is evidence for the intermediacy of $IrH(PPh_3)_2$ (solvent) species.[188]

In contrast to $RhCl(PPh_3)_3$, which is an effective catalyst, $IrCl(PPh_3)_3$ does not catalyse homogeneous hydrogenation. The explanation for this difference is the much greater reluctance of the iridium compound to lose a molecule of phosphine to generate a catalytically active species.[189]

Nickel. Product analysis gives some information on the catalytic rôle of $Ni(CN)_2L_2^{n-}$, where L = CN, ½ phen, *etc.*, in the hydrogenation and isomerisation of dimethyl maleate and of 1,5-cyclo-octadiene.[190]

Platinum. Linear and cyclic alkenes, except for those containing electronegative substituents, are reduced by *trans*-$[PtClH(PEt_3)_2]$ in acidic ethanol. The deduced rate law and observed products are consistent with two possible mechanisms. Complexing of the alkene to platinum, with subsequent olefin insertion into the platinum–hydrogen bond and final platinum–alkyl bond cleavage, is preferred to the alternative route by way of a platinum(IV) dihydride and subsequent hydrogen transfer to the alkene. The reason for this preference is the known high stability of hydrides of platinum(IV).[191] The same mechanistic sequence is proposed for hydrogenation of ethylene in the presence of platinum(II)–tin(II) catalysts. Activation energies for this hydrogenation conducted in a variety of solvents have been reported.[192] This study amplifies earlier qualitative observations on platinum(II)–tin(II) catalysis of homogeneous hydrogenation.[193]

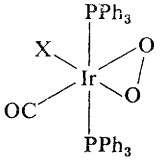
[183] W. Strohmeier and T. Onoda, *Z. Naturforsch.*, 1969, **24b**, 515.
[184] W. Strohmeier and F. J. Müller, *Z. Naturforsch.*, 1969, **24b**, 931.
[185] W. Strohmeier and T. Onoda, *Z. Naturforsch.*, 1969, **24b**, 1185.
[186] W. Strohmeier and T. Onoda, *Z. Naturforsch.*, 1969, **24b**, 461.
[187] W. Strohmeier and T. Onoda, *Z. Naturforsch.*, 1969, **24b**, 1493.
[188] M. Giustiniani, G. Dolcetti, M. Nicolini, and U. Belluco, *J. Chem. Soc.* (*A*), 1969, 1961.
[189] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.
[190] H. Samejima, T. Mizuta, H. Yamamoto, and T. Kwan, *Bull. Chem. Soc. Japan*, 1969, **42**, 2722.
[191] M. Giustiniani, G. Dolcetti, R. Pietropaolo, and U. Belluco, *Inorg. Chem.*, 1969, **8**, 1048.
[192] A. P. Krushch, N. F. Shvetsova, and A. E. Shilov, *Kinetika i Kataliz*, 1969, **10**, 1226 (*Chem. Abs.*, 1970, **72**, 59,648g).
[193] R. W. Adams, G. E. Batley, and J. C. Bailar, *J. Amer. Chem. Soc.*, 1968, **90**, 6051.

Copper. A detailed study of substrates, products, competition, and solvent effects indicates that copper(I) catalysts in the presence of, for instance, 2,4,6-collidine, act as hydrogen transfer agents to unsaturated organic compounds *via* transitory formation of species containing copper–hydrogen bonds.[194]

Hydrogen Exchange.—Hydrogen–deuterium exchange in ethylbenzene is homogeneously catalysed by $[PtCl_4]^{2-}$. A mechanism involving a π-allyl intermediate is suggested in preference to earlier hypotheses of reversible dealkylation or carbonium ion formation.[195] This investigation has been extended over a range of alkylbenzenes[196] and to polycyclic aromatic hydrocarbons.[197] The rates of hydrogen exchange for the polycyclic compounds correlate with double-bond delocalisation energies. Octahedral platinum(IV) intermediates are postulated.

Homogeneous Dehydrogenation.—The first examples of this, the reverse of homogeneous hydrogenation discussed at length above, have been described. A similar range of compounds appear catalytically active, for instance $RhCl(PPh_3)_3$ and *trans*-$IrCl(CO)(PPh_3)_2$.[198] Dehydrogenation of isopropyl alcohol to acetone is catalysed by rhodium trichloride–tin(II) chloride mixtures.[199]

Homogeneous Oxidation.—Iridium(I) complexes catalyse the homogeneous oxidation of styrene and of triphenylphosphine. For oxidation of the latter the mechanism suggested is co-ordination of an oxygen molecule to give (35); intramolecular transfer of the two oxygen atoms then gives two molecules of triphenylphosphine oxide.[200]



(35)

$RhCl(CO)(PPh_3)_2$ catalyses the oxidation of diphenylmethane. The mechanism involves a one-electron transfer step and a hydroperoxide complex intermediate.[201] Analogies have been drawn between homogeneous oxidation at this catalyst with heterogeneous catalytic oxidation.[202]

[194] R. G. R. Bacon and O. J. Stewart, *J. Chem. Soc.* (*C*), 1969, 301; R. G. R. Bacon and S. C. Rennison, *J. Chem. Soc.* (*C*), 1969, 308, 312.
[195] J. L. Garnett and R. S. Kenyon, *Chem. Comm.*, 1970, 698.
[196] R. J. Hodges and J. L. Garnett, *J. Catalysis*, 1969, **13**, 83.
[197] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1969, **73**, 1525.
[198] J. Blum and S. Biger, *Tetrahedron Letters*, 1970, 1825.
[199] H. B. Charman, *J. Chem. Soc.* (*B*), 1970, 584.
[200] K. Takao, Y. Fujiwara, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 1153.
[201] L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organometallic Chem.*, 1970, **22**, 219.
[202] J. Kiji and J. Furukawa, *Chem. Comm.*, 1970, 977.

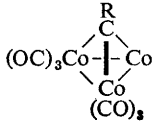
The dimer $[RhCl(C_8H_{14})_2]_2$ in dimethylacetamide solution also catalyses oxidation, of carbon monoxide, of the cyclo-octene ligand, and of the dimethylacetamide. An oxygen complex of rhodium(II) appears, from preliminary e.s.r. results, to be a likely intermediate.[180] Rhodium trichloride itself can also catalyse oxidation of carbon monoxide.[203]

Reaction of $CoH(N_2)(PPh_3)_3$ with nitrous oxide gives triphenylphosphine oxide. This could be considered part of a potentially catalytic cycle for triphenylphosphine oxidation.[204] Acetylacetone complexes of cobalt(II) catalyse oxidation of isopropylbenzene.[205]

Nickel complexes act as catalysts for the oxidation of ditertiary diphosphines.[206] Palladium(0) complexes catalyse the autoxidation of hydrocarbons. The reactivity is sensitive to the nature of the arylphosphine ligands. The mechanism involves intermediate formation of a palladium–molecular oxygen complex.[207]

Hydration and Hydroformylation.—*Ruthenium.* Fluoro-olefins are catalytically hydrated in the presence of chlororuthenate(II) species. Ignorance of the exact nature of the species present in such solutions precludes a precise discussion of the mechanism.[208]

Cobalt. Solvent effects on hydroformylation of propene and of pent-1-ene catalysed by $CoH(CO)_4$ have been investigated by product distribution analysis.[209] Effects of temperature and pressures of hydrogen and carbon monoxide on the mechanism of hydroformylation of propene in the presence of $Co_2(CO)_6(PBu_3)_2$ have similarly been probed by product analysis.[210] The reaction of (36) with methanol or ethanol (R^1OH) produces $CHR(CO_2R^1)_2$.[211]



R = H, CH_3

(36)

Rhodium. Aqueous solutions of aquochlororhodate(III) species catalyse hydration of alkynes, whereas hexachlororhodate(III) does not, so there must be at least one water molecule co-ordinated to the rhodium ready for transfer to the alkyne. Kinetic results are consistent with rate-determining

[203] J. A. Stanko, G. Petrov, and C. K. Thomas, *Chem. Comm.*, 1969, 1100.
[204] Lyong Sun Pu, A. Yamamoto, and S. Ikeda, *Chem. Comm.*, 1969, 189.
[205] I. M. Reibel', A. Ya. Sychev, and L. P. Podgornaya, *Russ. J. Phys. Chem.*, 1970, **44**, 41.
[206] B. Corain, P. Rigo, and M. Bressan, *Chimica e Industria*, 1969, **51**, 386.
[207] E. W. Stern, *Chem. Comm.*, 1970, 736.
[208] B. R. James and J. Louie, *Inorg. Chim. Acta*, 1969, **3**, 568.
[209] Y. Takegami, Y. Watanabe, H. Masada, and T. Mitsudo, *Bull. Chem. Soc. Japan*, 1969, **42**, 206.
[210] F. Piacenti, M. Bianchi, E. Benedetti, and P. Frediani, *J. Organometallic Chem.*, 1969, **23**, 257.
[211] K. Tominaga, N. Yamagami, and H. Wakamatsu, *Tetrahedron Letters*, 1970, 2217.

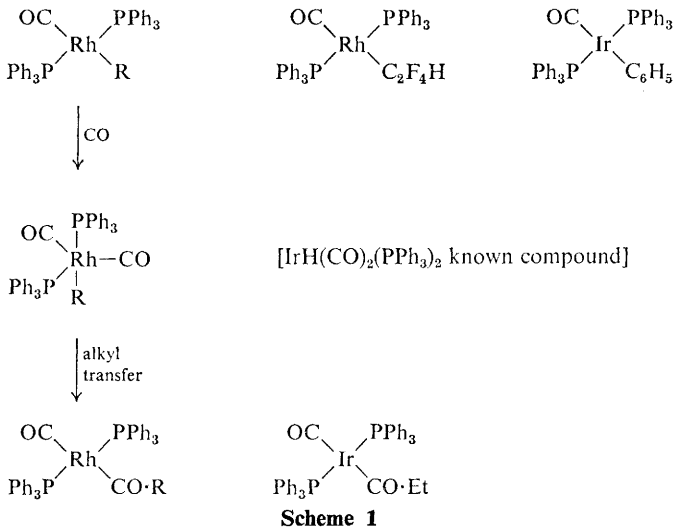
bimolecular attack of the alkyne at rhodium displacing a chloride to give a π-alkyne complex intermediate.[212] The reaction of rhodium trichloride with carbon monoxide in dimethylacetamide is also S_N2, giving initially a rhodium(III) carbonyl. This carbonyl reacts slowly with the water from the rhodium trichloride trihydrate to give $[RhCl_2(CO)_2]^-$, which is the only observable product.[213] The mechanism of formation of $[RhCl_2(CO)_2]^-$ in water may involve intermediate formation of a rhodium–formate complex subsequent to reaction of carbon monoxide with $[RhCl_5(OH)]^{3-}$ or $[RhCl_5(OH_2)]^{2-}$, which are derived from the rhodium trichloride.[214] $[RhCl_4(OH)(CO)]^{2-}$ has been suggested as the carbonyl-containing intermediate, but the isolation of $[RhCl_5(CO)]^{3-}$, which can easily be reduced to a rhodium(I)–carbonyl species, suggests this as a likely alternative.[215]

Kinetic data [216] and characterisation of intermediates [217] provide further insight into the mechanism of hydroformylation catalysed by $RhH(CO)(PPh_3)_3$. Several model intermediates have been prepared. In order to make isolation possible the reactants and catalyst have been somewhat modified. Thus whereas intermediates containing co-ordinated alkyl groups are too unstable for isolation, analogues containing fluoroalkyl, aryl, or benzyl groups can be characterised. Also it is generally easier to isolate iridium analogues than the corresponding rhodium intermediates. Some postulated hydroformylation intermediates and the respective characterised model compounds are set out in Scheme 1 to illustrate this approach to mechanism determination.[218]

Iridium. Iridium analogues of catalytically active rhodium complexes are frequently too stable to function as catalysts, as has been illustrated by the preparation of the iridium model compounds mentioned in the previous paragraph. The mechanism of hydrolytic degradation of fluoro-olefin complexes has been discussed.[66, 67]

Palladium. The dependence of catalytic activity on the composition of the palladium(II) complexes $[Pd(NH_3)_n(OH_2)_{4-n}]^{2+}$ for hydration of acetylene has been assessed; the most active catalyst has $n = 1$.[219] Palladium(II) sulphate catalysis of the hydration of acetylene has been described.[220] The conversion of vinyl chloride to acetal involves addition of alcohol rather than water. It is catalysed by palladium(II) chloride, as well as by ruthenium trichloride or rhodium trichloride.[221]

[212] B. R. James and G. L. Rempel, *J. Amer. Chem. Soc.*, 1969, **91**, 863.
[213] B. R. James, G. L. Rempel, and F. T. T. Ng, *J. Chem. Soc.* (*A*), 1969, 2454.
[214] B. R. James and G. L. Rempel, *Chem. Comm.*, 1967, 158; *J. Chem. Soc.* (*A*), 1969, 78.
[215] J. A. Stanko, G. Petrov, and C. K. Thomas, *Chem. Comm.*, 1969, 1100.
[216] C. K. Brown and G. Wilkinson, *Tetrahedron Letters*, 1969, 1725.
[217] G. Yagupsky, C. K. Brown, and G. Wilkinson, *Chem. Comm.*, 1969, 1244.
[218] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1392.
[219] D. V. Sokol'skii, Ya. A. Dorfman, S. S. Segizbaeva, and I. A. Kazantseva, *Kinetika i Kataliz*, 1969, **10**, 659 (*Chem. Abs.*, 1969, **71**, 54,084q).
[220] D. V. Sokol'skii, Ya. A. Dorfman, S. S. Segizbaeva, and I. A. Kazantseva, *Russ. J. Phys. Chem.*, 1970, **44**, 54.
[221] A. Misono, Y. Uchida, and K.-I. Furuhata, *Bull. Chem. Soc. Japan*, 1970, **43**, 1243.



Scheme 1

Copper. Kinetics of hydration of acetylene in copper(I)–chloride solutions indicate that the catalytically active species are the $[CuCl_2]^-$, $[CuCl_3]^{2-}$, and $[Cu_2Cl_3]^-$ anions.[222]

Decarbonylation.—The mechanism of homogeneous decarbonylation of acetaldehyde to methane catalysed by $[Ru_2Cl_3(PEt_2Ph)_6]^+Cl^-$ has been investigated.[223]

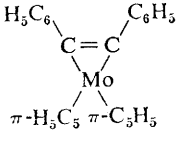
Hydrosilylation.—This reaction is catalysed by the usual homogeneous catalysts.[224] In some cases the mechanism involves insertion of the alkene into a metal–hydrogen bond, as in hydrosilylation of butadiene in the presence of $PdL(PPh_3)_2$, with L = *p*-benzoquinone or maleic anhydride.[225] In other cases concerted addition of the silicon hydride to the carbon–carbon double bond is indicated, as in hydrosilylations catalysed by rhodium(I) catalysts such as $RhCl(PPh_3)_3$.[226] In the reaction of silanes with hex-1-ene in the presence of this catalyst, rates depend on the stability of the intermediate adduct $RhClH(SiR_3)(PPh_3)_2$; such an adduct was isolated in one case.[227] Hydrosilylation of ethylene by trimethylsilicon hydride

[222] G. K. Shestakov, A. Ermakova, V. G. Mikhal'chenko, O. N. Temkin, and R. M. Flid, *Russ. J. Phys. Chem.*, 1970, **44**, 225.
[223] R. H. Prince and K. A. Raspin, *J. Chem. Soc.* (*A*), 1969, 612.
[224] See, *e.g.*, F. de Charentenay, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 787, and refs. therein.
[225] S. Takahashi, T. Shibano, and N. Hagihara, *Chem. Comm.*, 1969, 161.
[226] A. J. Chalk, *J. Organometallic Chem.*, 1970, **21**, 207.
[227] R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J, Chem. Soc.* (*A*), 1969, 683.

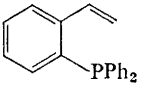
catalysed by $CoH(CO)_4$ probably proceeds through an unstable π-complex.[228]

4 Insertion Reactions

Alkenes and Alkynes.—Many insertion reactions of these compounds into metal–hydrogen bonds have already been mentioned in the previous section on homogeneous catalysis. One reagent wherein insertion is not necessarily followed by hydrogen transfer is $MoH_2(\pi\text{-}C_5H_5)_2$. Thus the dimethyl ester of acetylenedicarboxylic acid inserts into a molybdenum–hydrogen bond to give a product of *cis*-geometry which, surprisingly, liberates the starting ester again on heating. Hexafluorobut-2-yne inserts by a less simple mechanism and is not regenerated on heating. Weaker π-acids, for instance diphenylacetylene, do not insert but rather displace both hydrogens to give compounds of the type (37).[229] Examples of



(37)



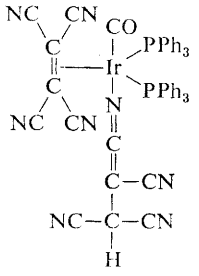
(38)

insertion into platinum–hydrogen bonds include those of the vinyl end of (*o*-vinylphenyl)diphenylphosphine (38) into *trans*-$[PtClH(PPh_3)_2]$,[230] and of dienes into *trans*-$[PtH(NO_3)(PEt_3)_2]$.[231] The relative ease of formation of π-allyl products in the latter case may be attributable to the fact that the nitrate ion is a good leaving group.

In the reaction of $IrH(CO)(PPh_3)_3$ with tetracyanoethylene (tcne) one molecule of tcne inserts into the iridium–hydrogen bond and a second molecule of tcne co-ordinates π-wise to the metal to give the product (39).[232]

Many examples of alkene and alkyne insertion into metal–carbon bonds can also be found in the section on homogeneous catalysis. Other recent examples include the insertion of conjugated dienes into palladium–allyl bonds,[233] olefin arylation in the presence of palladium acetate,[234] and the reaction of ethylene with arylmagnesium halides in the presence of nickel chloride.[235] Reaction of isocyanates with nickel–ethynyl compounds

[228] Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, 1969, **8**, 986.
[229] S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Comm.*, 1969, 1148.
[230] P. R. Brookes and R. S. Nyholm, *Chem. Comm.*, 1970, 169.
[231] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, 1970, 598.
[232] J. S. Ricci, J. A. Ibers, M. S. Fraser, and W. H. Baddley, *J. Amer. Chem. Soc.*, 1970, **92**, 3489.
[233] Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometallic Chem.*, 1969, **16**, 177.
[234] Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, 1969, **91**, 7166.
[235] L. Farady, L. Benczke, and L. Marko, *J. Organometallic Chem.*, 1969, **17**, 107.

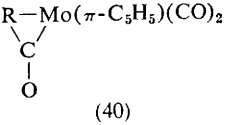


(39)

involves insertion not into the nickel–carbon bond but into a carbon–hydrogen.[236]

Carbon Monoxide.—Again some examples of insertion reactions have already been covered in the hydroformylation section earlier in this chapter. The remaining references to carbon monoxide insertion will be mentioned here in Periodic Table order. In most cases there are no kinetic results, mechanistic suggestions often being based only on product characterisation.

Carbonyl insertion forms an important step in the reaction sequence for substitution into Mo(π-indenyl)$(CO)_3$,[237] and in the reaction of MoR(π-C_5H_5)$(CO)_3$, where R = benzyl or allyl, with phosphorus bases.[238] In this latter reaction the rate is independent of the nature and concentration of the incoming ligand; a plausible transition state is that shown (40). A Group VII example is provided by the reaction of $MnR(CO)_5$



(40)

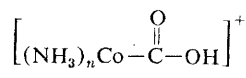
(where R = methyl, acetyl, or phenyl), with alkynes.[239] Another is the reaction of $MnPh(CO)_5$ with the cyclic phosphite $P(O\cdot CH_2)_3C\cdot Et$, which proceeds by carbon monoxide insertion into the manganese–phenyl bond.[240]

Examples of carbonyl insertion reactions involving compounds of Group VIII metals are more common. The reaction of iron pentacarbonyl with the cyclopropylalkene (41) involves both carbonyl insertion and cyclopropane ring opening.[241] Reduction of cobalt(II) to cobalt(0) in aqueous ammonia is thought to involve a carbonyl insertion stage, with

[236] P. Hong, K. Sonogashiri, and N. Hagihara, *Tetrahedron Letters*, 1970, 1633.
[237] A. J. Hart-Davis and R. J. Mawby, *J. Chem. Soc.* (*A*), 1969, 2403.
[238] P. J. Craig and M. Green, *J. Chem. Soc.* (*A*), 1969, 157.
[239] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1970, 308.
[240] B. L. Booth, R. N. Haszeldine, and N. P. Woffenden, *J. Chem. Soc.* (*A*), 1970, 1979.
[241] R. Ben-Shoshan and S. Sarel, *Chem. Comm.*, 1969, 883.



(41)



(42)

intermediates of the type (42).[242] Examples for rhodium are included in the reaction sequences for $Rh(\pi\text{-}C_5H_5)(CO)L$ with alkyl halides,[243] for *trans*-$[RhCl(CO)_2(PR_3)]$ with methyl iodide,[244] and for *trans*-$[RhX(CO)(PR_3)_2]$ again with methyl iodide.[245] These reactions are also mentioned under oxidative addition. Insertions into palladium complexes include those into palladium–chlorine [246] and palladium–allyl [247] bonds. Similar reactions are involved in the carbonylation of olefins [248] and of propargyl compounds [249] with palladium catalysts. Carbon monoxide insertion into nickel–nitrogen bonds occurs after the initial oxidative addition step in the reaction of *N*-monochloroamines with nickel carbonyl.[250]

Further results on the reduction of copper(II) to copper(I) by carbon monoxide indicate parallel reactions involving carbon monoxide insertion into a copper–hydroxide bond, as described for cobalt(II) reduction above, and formation of the stable $Cu(CO)^+$ cation.[251]

Other Molecules.—*Carbon Dioxide.* Carbon dioxide insertion into a rhodium–hydrogen bond seems a likely step in the conversion of mixtures of amines, carbon dioxide, and hydrogen to formamides, catalysed by $RhCl(PPh_3)_3$.[252]

Carbon Disulphide. This can insert into metal–alkyl and into metal–hydrogen bonds; a metal–carbon disulphide π-complex is a possible intermediate.[253]

Isocyanides. Several instances for nickel(II) and palladium(II) complexes have been suggested.[254–256] One interesting feature is that whereas carbon monoxide only inserts once into a given bond, isocyanides can insert repeatedly, providing a potential route for catalytic polymerisation.[254]

[242] H. N. Halvorsen and E. Peters, *Canad. J. Chem.*, 1969, **47**, 2535.
[243] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 243.
[244] P. Uguagliati, A. Palazzi, G. Deganello, and U. Belluco, *Inorg. Chem.*, 1970, **9**, 724.
[245] I. C. Douek and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2604.
[246] V. I. Spitsyn, I. V. Znamenskii, and I. V. Fedoseev, *Doklady Akad. Nauk S.S.S.R.*, 1968, **181**, 668.
[247] S. Imamura and J. Tsuji, *Tetrahedron*, 1969, **25**, 4187.
[248] D. Medema, R. van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, 1969, **3**, 255.
[249] T. Nogi and J. Tsuji, *Tetrahedron*, 1969, **25**, 4099.
[250] S. Fukuoka, M. Ryang, and S. Tsutsumi, *Tetrahedron Letters*, 1970, 2553.
[251] J. J. Byerley and E. Peters, *Canad. J. Chem.*, 1969, **47**, 313.
[252] P. Haynes, L. H. Slaugh, and J. F. Kohnle, *Tetrahedron Letters*, 1970, 365.
[253] D. Commereuc, I. Douek, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1771.
[254] S. Otsuka, A. Nakamura, and T. Yoshida, *J. Amer. Chem. Soc.*, 1969, **91**, 7196.
[255] Y. Yamamoto, H. Yamazaki, and N. Hagihara, *J. Organometallic Chem.*, 1969, **18**, 189.
[256] H. Breil and G. Wilke, *Angew. Chem. Internat. Edn.*, 1970, **9**, 367.

Cyanides. A qualitative report on insertion of cyanides into diethylaluminium compounds has appeared.[257]

Carbenes. The reaction of bistrifluoromethyldiazomethane with transition-metal complexes, for example *trans*-[$PtClH(PEt_3)_2$], is thought to proceed by insertion of $(CF_3)_2C$: into the platinum–hydrogen bond.[258] The reaction of π-allylnickel bromide with ethyl diazoacetate may involve carbene insertion into a nickel–carbon bond;[259] carbene insertion into iron–carbon bonds has also been proposed.[260] Phenyl(bromodichloromethyl)mercury, a known source of $:CCl_2$, reacts with tin(II) halides at least in part by dichlorocarbene insertion.[261] The mechanism of transfer of $:CCl_2$ from trimethyltin trichloroacetate to olefins has been studied by n.m.r. techniques.[262] Dichlorocarbene insertion into carbon–hydrogen bonds of olefins, as well as its addition to the carbon–carbon double bonds, is catalysed by $Fe_2(dtg)(CO)_6$, where dtg is a cyclohexylguanidine derivative.[263] Ethyl diazoacetate reacts with olefins in the presence of $CuX[P(OR)_3]$ to give cyclopropanes; this is addition to the double bond rather than simple insertion. Steric effects on rates indicate an intermediate in which both the olefin and the carbene derived from the diazo-ester are co-ordinated to the copper.[264]

Sulphur Dioxide. The observed products and high rates of insertion of sulphur dioxide into tin–carbon bonds in organotin allenes and alkynes have been interpreted in terms of an electrophilic cleavage mechanism.[265] Such a mechanism is also proposed for sulphur dioxide insertion into mercury–carbon[266] and into lead–carbon[267] bonds. The mechanism of sulphur dioxide insertion into transition metal (Mo, W, or Mn)–carbon bonds is again similar.[268]

Intramolecular Insertion.—This occurs in metal insertion into phenyl-*ortho*-carbon to hydrogen bonds during the intramolecular oxidative addition of triphenylphosphine complexes of iridium(I).[150] Intramolecular insertion also takes place in palladium(II)-catalysed decomposition of vinyl

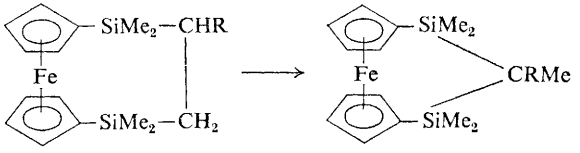
[257] T. Hirabayashi, K. Itoh, S. Sakai, and Y. Ishii, *J. Organometallic Chem.*, 1970, **21**, 273.
[258] J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1872.
[259] I. Moritani, Y. Yamamoto, and H. Konishi, *Chem. Comm.*, 1969, 1457.
[260] M. M. Bagga, G. Ferguson, J. A. D. Jeffreys, C. M. Mansell, P. L. Pauson, I. C. Robertson, and J. G. Sime, *Chem. Comm.*, 1970, 672.
[261] D. Seyferth and F. M. Armbrecht, *J. Organometallic Chem.*, 1969, **16**, 249.
[262] F. M. Armbrecht, W. Tronich, and D. Seyferth, *J. Amer. Chem. Soc.*, 1969, **91**, 3218.
[263] N. J. Bremer, A. B. Cutcliffe, and M. F. Farona, *Chem. Comm.*, 1970, 932.
[264] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.
[265] W. Kitching, C. W. Fong, and A. J. Smith, *J. Amer. Chem. Soc.*, 1969, **91**, 767; C. W. Fong and W. Kitching, *J. Organometallic Chem.*, 1970, **22**, 107.
[266] W. Kitching, B. Hegarty, S. Winstein, and W. G. Young, *J. Organometallic Chem.*, 1969, **20**, 253.
[267] C. W. Fong and W. Kitching, *J. Organometallic Chem.*, 1970, **21**, 365.
[268] J.-L. Roustan and C. Charrier, *Compt. rend.*, 1969, **268**, *C*, 2113.

acetate to acetaldehyde and acetic anhydride,[269] and in hydrogen exchange at $RuH_2(PPh_3)_4$.[270]

As a postscript it should be mentioned that the reaction mechanism for tin(II) halides with $FeI(\pi\text{-}C_5H_5)(CO)_2$ and related compounds does not, as was previously thought, involve insertion.[271]

5 Reactions of Co-ordinated Ligands

Cyclic Alkenes.—*Cyclopentadiene.* It is impossible to draw a satisfactory dividing line between organic and inorganic systems, for what an inorganic chemist regards as the reaction of a co-ordinated organic ligand the organic chemist may regard as the reaction of an organic compound which happens to have a transition-metal-containing substituent. The chemistry of the cyclopentadienyl rings of ferrocene provides a large number of examples to illustrate this. As the majority of these reports appear in organic chemistry journals we shall omit these references, except insofar as the metal plays an exceptionally important rôle in the reaction mechanism. Thus the thermal rearrangement of the organosilicon-bridged ferrocenes (43) to (44) is not

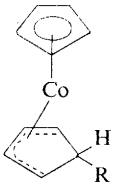


(43) (44)

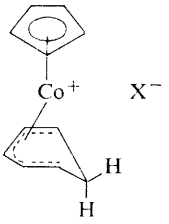
the simple organic rearrangement it may look at first sight, for the iron atom plays a critical rôle in that the transfer of a proton from a bridging methylene group to a non-bonding orbital on the metal, to leave a carbanion bridge, is a key step.[272] Solvolysis of dinitrobenzoate esters of $Fe(\pi\text{-}C_5H_5)(CO)_2$ also involves significant participation by the iron atom.[273]

Similarly the metal–cyclopentadiene bonding is directly involved in the reaction of cobaltocene with benzyl, allyl, or propargyl halides to give the respective compounds (45). These reactions go by a two-step radical mechanism.[274] The conversion of (45), with R = CH_2X and X = Cl, Br, or I, to the salt (46) follows a first-order rate law; rate constants and activation parameters have been determined. The high rates observed are attributed to assistance by the cyclopentadienylcobalt of the heterolysis of the carbon–halogen bond. A plot of logarithms of rate constants

[269] R. G. Schultz and P. R. Rony, *J. Catalysis*, 1970, **16**, 133.
[270] T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1970, **92**, 3011.
[271] M. J. Mays and S. M. Pearson, *J. Chem. Soc.* (*A*), 1969, 136.
[272] M. Kumada, M. Ogura, H. Tsunemi, and M. Ishikawa, *Chem. Comm.*, 1969, 207.
[273] N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, 1970, **92**, 3058, 3065.
[274] G. E. Herberich and E. Bauer, *J. Organometallic Chem.*, 1969, **16**, 301.



(45)

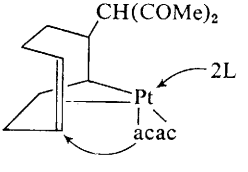


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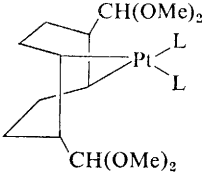
against Grunwald–Winstein Y values has a slope of *ca.* 0·6, which supports the contention that the rate-determining step is not simple carbon–halogen bond dissociation.[275] Loss of cyclopentadiene from $Mo(\pi\text{-}C_5H_5)X(CO)_3$ in reaction with, for instance, tri-n-butylphosphine, may occur by phosphine attack at the cyclopentadienyl ligand rather than at the molybdenum, which is pretty inaccessible to nucleophilic attack.[28]

Higher Cyclic Alkenes. The effect on the reactivity of cyclo-octatetraene [276] and of cycloheptatriene [277] upon co-ordination to $-Fe(CO)_3$ has been investigated. Product analysis indicates that nucleophilic attack of pentafluorothiophenoxide at $Fe(dienyl)(CO)_3^+$ takes place at the dienyl ligand rather than at the iron atom, for the cyclohexa- and cycloheptа- as well as the cyclopenta-dienyl compounds.[278]

The addition of electrophilic dienophiles to cyclo-octatetraene co-ordinated to $-Fe(CO)_3$ or to $-Ru(CO)_3$ does not occur directly, since it is a thermally forbidden process. Rather, the dienophile co-ordinates to the metal, with subsequent transfer to the cycloalkene to give the observed 1 : 1 product.[279] An analogue of the second stage of this mechanism is provided by the transfer of acetylacetone from platinum to the unsaturated ligand in the reaction (47) → (48). This is internal nucleophilic addition of acetyl-



(47)



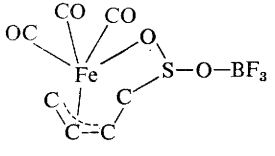
(48)

acetone to the ligand carbon–carbon double bond under the influence of the tertiary phosphine L.[280]

[275] G. E. Herberich and J. Schwarzer, *Chem. Ber.*, 1970, **103**, 2016.
[276] B. F. G. Johnson, J. Lewis, A. W. Parkins, and G. L. P. Randall, *Chem. Comm.*, 1969, 595.
[277] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *Chem. Comm.*, 1969, 1273.
[278] G. R. Knox and A. Pryde, *J. Organometallic Chem.*, 1969, **18**, 169.
[279] M. Green and D. C. Wood, *J. Chem. Soc.* (*A*), 1969, 1172.
[280] B. F. G. Johnson, T. Keating, J. Lewis, M. S. Subramanian, and D. A. White, *J. Chem. Soc.* (*A*), 1969, 1793.

Carbonyls.—It has already been pointed out in the first section of this chapter that the point of attack of a nucleophile at a metal carbonyl may be either at the metal atom or at the carbon atom of the carbonyl ligand. The formation of $[W(NCO)(CO)_5]^-$ as a result of azide attack on $W(CO)_6$ can most simply be attributed to nucleophilic attack at carbonyl-carbon rather than at tungsten;[281] a similar mechanism is suggested for reaction of $Cr(CO)_6$ and of $Mo(CO)_6$ with azides.[282] The cation $[Fe(\pi\text{-}C_5H_5)(CO)_3]^+$ reacts with azides and with hydrazines by initial attack at the carbonyl-carbon, to give $[Fe(\pi\text{-}C_5H_5)(NCO)(CO)_2]$ as product. For reaction with hydrazine and its derivatives in, for instance, benzene solution, there is i.r. evidence for the formation of an intermediate carbazoyl compound $[Fe(\pi\text{-}C_5H_5)(CO\cdot NH\cdot NH_2)(CO)_2]$ which loses ammonia to generate the observed product. Rates for the reaction of $[Fe(\pi\text{-}C_5H_5)(CO)_3]^+$ with azide are very solvent dependent, which is consistent with the proposed mechanism.[283] The products isolated from the reaction of $[Fe(\pi\text{-}C_5H_5)(CO)_2L]^+$ with amines or with methoxide, which give carboxamide $[Fe(\pi\text{-}C_5H_5)(CONH_2)(CO)L]$, or alkoxycarbonyl $[Fe(\pi\text{-}C_5H_5)(CO_2CH_3)(CO)L]$, respectively, also indicate nucleophilic attack at carbonyl-carbon.[284] Reactivities for nucleophilic attack by methyl-lithium or phenyl-lithium at $Fe(CO)_4(PPh_3)$ or at $(CO)_4Co\cdot MPh_3$, where M = Sn or Pb, correlate with carbonyl stretching force constants.[285] The second stage of the reaction of $[IrI_4(CO)_2]^-$ with nitrogen bases provides yet another instance of nucleophilic attack at carbonyl-carbon.[49]

Other Ligands.—Reactions of platinum(II) complexes $PtHX(PR_3)_2$ with azides, which give amido-complexes, may proceed by attack at the co-ordinated hydride.[286] In Friedel–Crafts sulphination of Fe(butadiene)-$(CO)_3$, attack is both at the metal and at the diene ligand, for an *X*-ray study has revealed that the structure of the intermediate is (49).[287]



(49)

Electrophilic attack at the co-ordinated ligand has been demonstrated for acetylacetone complexes of platinum and of palladium.[288] Several reactions

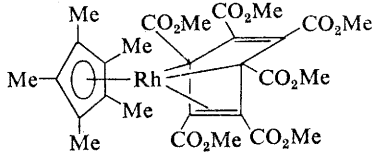
[281] W. Beck, H. Werner, H. Engelmann, and H. S. Smedal, *Chem. Ber.*, 1968, **101**, 2143.
[282] H. Werner, W. Beck, and H. Engelmann, *Inorg. Chim. Acta*, 1969, **3**, 331.
[283] R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, 1969, **91**, 3197.
[284] L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, 1968, **2**, 391.
[285] D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, 1970, **9**, 1691.
[286] W. Beck and M. Bauder, *Chem. Ber.*, 1970, **103**, 583.
[287] M. R. Churchill, J. Wormald, D. A. T. Young, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 7201.
[288] B. F. G. Johnson, J. Lewis, and D. A. White, *J. Chem. Soc.* (*A*), 1970, 1738.

of halogenoalkene and halogenoalkyne complexes of platinum, iridium, and rhodium which have been discussed above may be regarded as reactions of co-ordinated ligands.[65–67] Isocyanate insertion into nickel–ethynyl compounds is also a reaction of a co-ordinated ligand, for the insertion takes place not into a nickel–carbon but into a carbon–hydrogen bond.[236]

6 Isomerisation; Intramolecular Processes

Fluxional Molecules.—The two main areas of interest in current studies of fluxional molecules are the determination of the mechanism, for example whether 1,2- or 1,3-shifts are involved, and the determination of activation parameters. Some values of the latter are given in Table 1.

The first example of a fluxional benzene–metal compound has been reported, the 1,2,3,4-*tetrahapto*benzenerhodium(I) compound (50). The



(50)

free energy of activation for the fluxional motion in dimethyl sulphoxide or in *o*-dichlorobenzene solution is 20—21 kcal mol^{-1} in the range 80—120 °C. The analogous iridium compound does not exhibit fluxional behaviour.[289] Kinetic results are available for another 1,2,3,4-*tetrahapto*-compound, Ru(cot)$(CO)_3$, which is one of the products of reaction between $Ru_3(CO)_{12}$ and cyclo-octatetraene. Computer simulation of ^{1}H n.m.r. spectra suggests that at least 70% of the fluxional rearrangement occurs by a 1,2-shift mechanism.[290] The low-temperature n.m.r. spectrum of the similar compound Os(cot)$(CO)_3$, in carbon disulphide solution, is not first-order so it is not possible to derive kinetic parameters or discuss the mechanism in this case.[291]

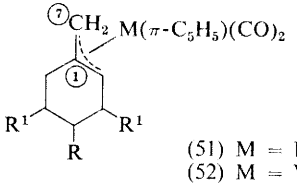
An *X*-ray structural study of *p*-methylbenzylcyclopentadienylmolybdenumdicarbonyl indicates that the benzyl ligand is 1,2,7-*trihapto* (51). Thus variable-temperature n.m.r. spectra of this and related compounds [(51) to (53)] can be interpreted in terms of fluxional behaviour, whose mechanism involves a σ-benzyl intermediate and rotation about the C_1–C_7 bond.[292] In contrast to these benzyl compounds, analogous π-2-thenyl (54) and π-3-thenyl (55) compounds show no evidence for fluxional behaviour in their n.m.r. spectra over a wide range of temperature.[293]

[289] J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 720.
[290] F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Amer. Chem. Soc.*, 1969, **91**, 6598.
[291] M. Cooke, R. J. Goodfellow, M. Green, and J. R. Yandle, *Chem. Comm.*, 1970, 565.
[292] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1969, **91**, 1339.
[293] R. B. King and R. N. Kapoor, *Inorg. Chem.*, 1969, **8**, 2535.

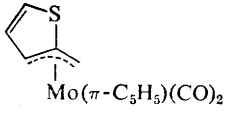
Table 1 *Activation parameters for fluxional molecules*

Fluxional group	*Compound*	*Solvent*	E_a (kcal mol^{-1})	log *A*	*Ref.*
Benzyl	(51)	$CDCl_3$	19·0[a]	16·4[a]	292
Benzyl	(52)	$CD_3 \cdot C_6D_5$	15·9	13·5	292
Benzyl	(53)	$CDCl_3$	18·7	14·9	292
Benzyl	(53)	$CD_3 \cdot C_6D_5$	18·3	14·6	292
Benzyl	(53)	$(CD_3)_2CO$	19·1	14·9	292
Cyclopentadienyl	$Ru(\sigma\text{-}C_5H_5)(\pi\text{-}C_5H_5)(CO)_2$	acetone	9·6	10·0	298
	$Fe(\sigma\text{-}C_5H_5)(\pi\text{-}C_5H_5)(CO)_2$	acetone	8·5	9·8	298
Cycloheptatrienyl	$(\pi\text{-}C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$	$CDCl_3$–$CD_3 \cdot C_6D_5$	13	12·7	302
Cyclo-octatetraene	$Ru(C_8H_8)(CO)_3$	CF_2Cl_2–$CFHCl_2$	9·4	14·0	290

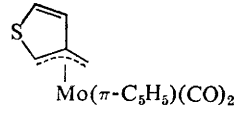
[a] Mean value from observations on two sets of protons.



(51) M = Mo, R = Me, R^1 = H
(52) M = W, R = Me, R^1 = H
(53) M = Mo, R = H, R^1 = Pr^i

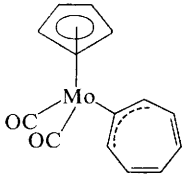


(54)

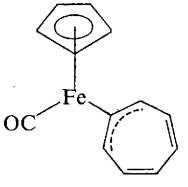


(55)

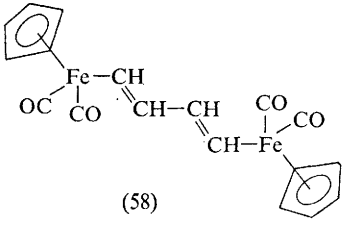
Fluxional behaviour has also been discussed for cycloheptatrienyl compounds of cobalt,[294] molybdenum (56),[294, 295] and iron.[296] The iron compound appears to be *trihapto*, as shown in formula (57), rather than *monohapto* as orginally suggested.[297] Amongst cyclopentadienyl compounds kinetic parameters for $Ru(\sigma\text{-}C_5H_4R)(\pi\text{-}C_5H_5)(CO)_2$, with R = H or Me, and $Fe(\sigma\text{-}C_5H_5)(\pi\text{-}C_5H_5)(CO)_2$ have been determined.[298] The ^{13}C-coupling in the variable-temperature n.m.r. spectra of these molecules suggests a 1,2-shift mechanism.[298, 299] The report of the crystal structure



(56)



(57)



(58)

[294] M. A. Bennett, R. Bramley, and R. Watt, *J. Amer. Chem. Soc.*, 1969, **91**, 3089.
[295] J. W. Faller, *Inorg. Chem.*, 1969, **8**, 767.
[296] D. Ciappenelli and M. Rosenblum, *J. Amer. Chem. Soc.*, 1969, **91**, 6876.
[297] D. Ciappenelli and M. Rosenblum, *J. Amer. Chem. Soc.*, 1969, **91**, 3673.
[298] C. H. Campbell and M. L. H. Green, *J. Chem. Soc.* (*A*), 1970, 1318.
[299] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1969, **91**, 7523.

of $Mo(C_5H_5)_3(NO)$, which has three non-equivalent C_5H_5 ligands, has helped to clarify the kinetic results arising from n.m.r. studies of this compound.[300] A 1,3-shift mechanism, involving the diene rather than the cyclopentadienyl part of the molecule, is suggested for fluxional rearrangement in (58). The evidence is again based on observation of ^{13}C satellite lines in the n.m.r. spectrum.[301]

Examples of fluxional behaviour may also be found in organometallic compounds containing more than one metal atom in the molecule, for example $(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$ [302] and the cluster compound $Ru_3(C_8H_8)(CO)_4$, whose limited solubility unfortunately precludes satisfactory determination of kinetic parameters.[290]

Whereas $Fe(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)(CO)_2$ is fluxional [298, 299] with no evidence for an $h^1 \rightleftharpoons h^5$ equilibrium for the ligands, variable-temperature n.m.r. studies of tetrakiscyclopentadienyltitanium, known from an *X*-ray structure determination to be $Ti(h^1\text{-}C_5H_5)_2(h^5\text{-}C_5H_5)_2$, indicate $h^1 \rightleftharpoons h^5$ rearrangement to be taking place rather than simple fluxional rearrangement involving just the *monohapto*-ligands. Such $h^1 \rightleftharpoons h^5$ rearrangement is easy since there are only 16 electrons formally associated with the titanium in this compound. There is no evidence for similar behaviour in the analogous zirconium and hafnium compounds.[303]

An extension of the normal type of fluxional behaviour is described for the compounds $M(\pi\text{-allyl})[BR(pz)_3](CO)_2$, where M = Mo or W, and $[BR(pz)_3]$ = tris-(1-pyrazolyl)borate, where three types of intramolecular process approximating more or less to fluxional behaviour are postulated.[304]

Fluxional Compounds of sp *Elements.* Fluxional behaviour of analogous derivatives of the *sp* elements has been much studied. The most popular ligands are cyclopentadienyl and indenyl; the popularity of the latter can be attributed to its containing a positional label that is lacking in cyclopentadienyl. Both a 1,2- or a 1,3-shift and slow prototropic rearrangement occurs in cyclopentadienyl derivatives of silicon, germanium, and tin. The corresponding pentamethylcyclopentadienyl compounds also exhibit fluxional behaviour.[305] Both metallotropic and prototropic processes have been reported for methyldichlorosilylcyclopentadiene.[306]

The value of the extra information available from studies of indenyl derivatives is illustrated by the disentangling of fluxional behaviour and

[300] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 1969, **91**, 2528.
[301] C. H. Campbell and M. L. H. Green, *Chem. Comm.*, 1970, 1009.
[302] F. A. Cotton and C. R. Reich, *J. Amer. Chem. Soc.*, 1969, **91**, 847.
[303] J. L. Calderon, F. A. Cotton, B. G. de Boer, and J. Takats, *J. Amer. Chem. Soc.*, 1970, **92**, 3801.
[304] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 3183.
[305] A. Davison and P. E. Rakita, *Inorg. Chem.*, 1970, **9**, 289.
[306] N. M. Sergeyev, G. I. Avramenko, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1970, **22**, 63, 79.

isomerisation of indenyl derivatives of the Group IV elements silicon,[307–310] germanium,[309, 311] and tin.[310, 312] Both processes contribute to the temperature variation of ^1H n.m.r. spectra of these compounds. Sometimes trapping experiments, designed to trap dienic intermediates with dienophiles such as tetracyanoethylene[308] or maleic anhydride,[309] have been performed to establish the mechanism of the isomerisation (migration) process. N.m.r. studies have established the fluxional character of indenyl–mercury compounds.[313, 314] The contrast between fluxional behaviour being observed for bisindenylmercury but not for Fe(indenyl)(π-C_5H_5)$(CO)_2$ is ascribed to the availability of 6*p* orbitals on mercury permitting facile formation of a transition state of increased co-ordination number.[313]

Restricted Rotation.—There has been discussion of internal rotation of the arene ring in compounds of the type Cr(arene)$(CO)_3$. This is variously reported as being too fast and too slow to observe by n.m.r. spectroscopy, while another school of thought maintains that it may not be possible to extract kinetic data from variable-temperature n.m.r. spectra for these compounds should it prove possible to obtain such spectra.[315] Internal rotation may also be important in bis-dicarbollyl compounds of nickel and platinum, whose structures bear a resemblance to that of ferrocene.[316] A simpler example of internal rotation is provided by that about the methyl-carbon to manganese bond in Mn$(CH_3)(CO)_5$, which has been probed by i.r. spectroscopy.[317]

Some kinetic parameters for restricted rotation in rhodium–olefin complexes were reported some time ago.[318] These values have recently been revised, and parameters for related rhodium compounds determined.[319] Activation parameters have also been determined for some platinum–olefin complexes. Here intramolecularity of mechanism is proved by the persistence of ^{195}Pt–^1H coupling and the lack of change in the n.m.r. spectra of the non-olefinic ligands with varying temperature. The rôles of *p* and *d* orbitals both in fixing the preferred orientation of the olefin perpendicular to the co-ordination square around the platinum and in the rotational process, are discussed. Wide-line n.m.r. spectra indicate some

[307] A. Davison and P. E. Rakita, *J. Organometallic Chem.*, 1970, **21**, P55.
[308] A. J. Ashe, *Tetrahedron Letters*, 1970, 2105.
[309] R. B. Larrabee and B. F. Dowden, *Tetrahedron Letters*, 1970, 915.
[310] A. Davison and P. E. Rakita, *J. Organometallic Chem.*, 1970, **23**, 407.
[311] Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1970, **22**, 361.
[312] P. E. Rakita and A. Davison, *Inorg. Chem.*, 1969, **8**, 1164; W. Kitching and B. F. Hegarty, *J. Organometallic Chem.*, 1969, **16**, P39.
[313] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1969, **91**, 3178.
[314] W. Kitching, B. F. Hegarty, and D. Doddrell, *J. Organometallic Chem.*, 1970, **21**, 29.
[315] G. Barbieri and F. Taddei, *Chem. Comm.*, 1970, 312; W. R. Jackson, W. B. Jennings, and R. Spratt, *ibid.*, p. 593.
[316] L. F. Warren and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1970, **92**, 1157.
[317] A. B. Dempster, D. B. Powell, and N. Sheppard, *J. Chem. Soc.* (*A*), 1970, 1129.
[318] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217; 1967, **89**, 5377.
[319] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

residual motion of the co-ordinated olefin even in the solid state.[320] This study has been extended from chloro- to bromo-derivatives; free energies of activation for olefin rotation are surprisingly insensitive to the steric and σ- and π-bonding differences that must exist between analogous chlorides and bromides.[321] Activation parameters for olefin rotation in the compounds mentioned in this paragraph are collected together in Table 2.

Table 2 *Activation parameters for rotation of co-ordinated olefins*

Rotating olefin	*Compound*	*Solvent*	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	*Ref.*
Ethylene	$Rh(\pi\text{-}C_5H_5)(C_2H_4)_2$	CH_2Cl_2	14·4	(log A = 12·5)	319
Ethylene	$Rh(\pi\text{-}C_5H_5)(C_2H_4)(SO_2)$	liq. SO_2	11·6	(log A = 12·3)	319
Ethylene	$Rh(\pi\text{-}C_5H_5)(C_2H_4)(C_2F_4)$	$CDCl_3$	13·0	(log A = 13·6)	319
trans-But-2-ene	$Pt(Cl)(acac)(C_4H_8)$	$CDCl_3$	12·9	− 8·5	320
Tetramethylethylene	$Pt(Cl)(acac)(C_6H_{12})$	$CDCl_3$	10·3	− 12	320
trans-But-2-ene	$Pt(Br)(acac)(C_4H_8)$	$CDCl_3$	10·1	− 19·2	321

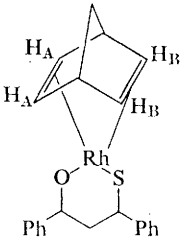
Isomerisation; Pseudorotation.—^{19}F and ^{13}C n.m.r. studies of the trigonal-bipyramidal molecules PF_5 and $Fe(CO)_5$ respectively indicate that all five fluorine or carbon atoms are equivalent at all accessible temperatures. In other words, intramolecular rearrangement, generally termed pseudorotation for this geometry, is rapid on the n.m.r. time scale for these simple molecules. However, the trigonal-bipyramidal compound $Co(CF_3)(PF_3)(CO)_3$ does isomerise at a rate corresponding to n.m.r. frequencies. Two isomers can be detected at low temperatures; their signals coalesce as the temperature rises. The activation enthalpy barrier for interconversion is *ca.* 11 kcal mol^{-1}.[322] Another example of relatively slow pseudorotation is afforded by the ethylene complex $Ir(Cl)(C_2H_4)_4$.[323] There is rapid intramolecular rearrangement within the formally five-co-ordinate compound $Fe(butadiene)(CO)_3$. The proposed mechanism bears a closer resemblance to pseudorotation than to fluxional behaviour despite the authors' use of the latter description.[324] Rapid pseudorotation also seems likely in $IrH(CO)_2(PPh_3)_2$.[325]

Simple octahedral compounds, *e.g.* $C_6H_5 \cdot SF_5$, are rigid even at high temperatures, but several octahedral iron compounds, *e.g.* $H_2Fe[P(OEt)_3]_4$ and $H_2Fe[PPh(OEt)_2]_4$, are non-rigid at high temperatures. This observation, which is effectively of pseudorotation in an octahedral

[320] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 53.
[321] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1653.
[322] C. A. Udovich and R. J. Clark, *J. Amer. Chem. Soc.*, 1969, **91**, 526.
[323] A. van der Ent and T. C. van Soest, *Chem. Comm.*, 1970, 225.
[324] J. D. Warren and R. J. Clark, *Inorg. Chem.*, 1970, **9**, 373.
[325] G. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 725.

complex, is discussed briefly in terms of two possible mechanisms.[326] Barriers to this type of pseudorotation are higher in the ruthenium analogues.[327] Any intramolecular rearrangement of the tetrahedral compound $Co(CO)(NO)(PMe_2Ph)_2$ is slow on the n.m.r. time scale.[328]

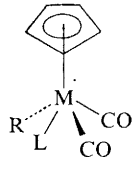
Several modes of rearrangement of the compounds Rh(diolefin)(LL), where diolefin = nor or cod, and LL = dibenzoylmethane (bzbz) or its monothio-derivative (S-bzbz), are possible. Rates of rearrangement of, for instance, Rh(nor)(S-bzbz) can be followed by n.m.r. as the protons in nor are not equivalent when the other ligand is the unsymmetrical (S-bzbz) [see formula (59)]. Equilibrium loss of diolefin or (S-bzbz) is not a



(59)

possible mechanism, but one-ended dissociation of these ligands is possible, as is isomerisation by intermediate formation of a formally five-co-ordinate intermediate incorporating one molecule of solvent or simply by planar ⇌ tetrahedral interconversions. In DMSO, isomerisation *via* solvent co-ordination seems the most likely mechanism.[329]

There have been four investigations of intramolecular *cis* ⇌ *trans* isomerisation in the formally seven-co-ordinate compounds (60) to (63):[330–333]



(60) M = W, R = H, L = CO; see ref. 330

(61) M = W, R = H, L = PMe_3 or $P(OMe)_3$; see ref. 331

(62) M = Mo, R = $PhCH_2$, L = PPh_3; see ref. 332

(63) M = Mo, R = RNC, L = COR; see ref. 333

That isomerisation is intramolecular has been demonstrated by observing ^{13}C and ^{183}W satellite features in the n.m.r. spectra of (60) as a function of temperature,[330] and by noting the lack of dependence of isomerisation rates

[326] F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 1068.
[327] P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 3482.
[328] R. J. Mawby, G. Wright, and D. Ewing, *J. Organometallic Chem.*, 1970, **23**, 545.
[329] H. I. Heitner and S. J. Lippard, *J. Amer. Chem. Soc.*, 1970, **92**, 3486.
[330] J. W. Faller, A. S. Anderson, and Chin-Chun Chen, *Chem. Comm.*, 1969, 719.
[331] P. Kalck and R. Poilblanc, *J. Organometallic Chem.*, 1969, **19**, 115.
[332] J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 1969, **91**, 1550.
[333] Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1970, **43**, 143.

on the concentrations of added ligands.[331, 333] The rate of isomerisation is affected surprisingly little by substituting PMe_3 by $P(OMe)_3$.[331] Factors which may contribute to facile rearrangement in these compounds include the small size of the hydrogen [in (60) and (61)] and the possibility that the cyclopentadienyl ring might become *tri-* or even *mono-hapto* to decrease the steric demands around the metal.

A rather different type of isomerisation process has been observed in compounds $Fe(CO)_3$(olefin), where the olefins included butadiene, 1-methylbutadiene, and 1,4-dimethylbutadiene. At − 78 °C in strong acid there is a proton bonded to the iron, but at higher temperatures proton exchange takes place between this site and the co-ordinated olefin, catalysed by a second proton.[334] Yet another type of isomerisation involving hydrogen movement is that of $Ir(Cl)(PPh_3)_3$, which on heating gives an octahedral hydrido-iridium(III) species, formed by internal oxidative addition involving insertion of the iridium into a phenyl-carbon to hydrogen bond.[335]

Allyl Compounds.—Mechanisms of intra- and inter-molecular rearrangement of π-allyl compounds continue to attract much attention, with a variety of structural modifications being explored in attempts to render the interpretation of variable-temperature ^1H n.m.r. studies as unambiguous as possible. The possible modes of rearrangement have been conveniently summarised [336] and discussed with particular reference to allyl compounds of rhodium, iridium, palladium, and platinum.[337] This latter review emphasises the chemical aspects rather than the spectroscopic methods and the derivation of the kinetic results.

One of the most complicated, but correspondingly most informative, approaches applied to monomeric π-allyl complexes is to study complexes $PdCl(\pi\text{-allyl})L$, where L is an amine $NR^1R^2R^3$ so that its nitrogen atom is in an asymmetric environment and the complex optically active. The molecular processes now include epimerisation as well as simple allyl movements.[338] A simpler approach entails labelling one end of the π-allyl group by substitution,[339] another utilises unsymmetrical phosphines as ligands,[340] while a third imposes some steric constraint by using an allyl complex containing a chelating diphosphine ligand.[341] There is an added advantage in the last system in that equilibrium loss of a diphosphine is very unlikely, whereas equilibrium loss of a monodentate phosphine has been suggested as a possibility in some systems.[338b] Approaching the

[334] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.
[335] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.
[336] D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, 1970, **92**, 3031.
[337] K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta, Rev.*, 1969, **3**, 109.
[338] [a] P. Ganis, G. Maglio, A. Musco, and A. L. Segre, *Inorg. Chim. Acta*, 1969, **3**, 266; [b] J. W. Faller, M. J. Incorvia, and M. E. Thomsen, *J. Amer. Chem. Soc.*, 1969, **91**, 518; [c] J. W. Faller and M. E. Thomsen, *ibid.*, p. 6871.
[339] G. Maglio, A. Musco, and R. Palumbo, *Inorg. Chim. Acta*, 1970, **4**, 153.
[340] P. W. N. M. van Leeuwen and A. P. Praat, *Chem. Comm.*, 1970, 365.
[341] P. W. N. M. van Leeuwen and A. P. Praat, *J. Organometallic Chem.*, 1970, **22**, 483.

problem from a technical rather than a chemical angle, nuclear magnetic double resonance affords additional information, particularly for compounds whose rates of rearrangement are too slow for the normal n.m.r. line-broadening treatment.[341]

Further reports on molecular rearrangements in these π-allyl monomers include those on Pd(π-methallyl)(OAc)(PPh_3)[342] and Pd(π-crotyl)-Cl(2-Me-py),[343] while to link this section with the following one on rearrangements in π-allyl dimers one can mention the rearrangement of Pd(π-methallyl)Cl(PR_3) catalysed by the $[RhCl(cod)]_2$ dimer.[344] Relevant to both is the reported preparation of a five-co-ordinate iridium compound which is a model for five-co-ordinate intermediates postulated for associative rearrangements in these π-allyl systems.[345]

One of the reasons for studying rearrangements in monomeric π-allyl complexes is to gain information which will aid elucidation of the inter- and intra-molecular processes taking place in rearrangements of π-allyl dimers and of chelating diene exchange, particularly those catalysed by Group V bases. Recent contributions to this field include studies of several π-allylrhodium compounds, $[RhCl(cod)]_2$ plus $As[p\text{-}(C_6H_4\cdot NMe_2)]_3$[346] or plus triphenylarsine,[347] and of a range of $[RhCl(diene)]_2$ dimers.[348] In the last case the relationship between kinetic lability and thermodynamic stability was investigated for a series of chelating dienes. The correlation observed between thermodynamic stability and kinetic lability, rather than kinetic inertness, was explained by π-bonding effects. Stabilities and labilities are a function of the geometry and steric requirements as well as of the π-bonding properties of the dienes. Two platinum systems of the type $[PtCl_2(\pi\text{-allene})]_2$ illustrate the extension of these studies to platinum,[349] while investigations of $[PdY(\pi\text{-allyl})]_2$ include the cases of Y = halide or SCN[350] and of X = carboxylate.[351] The rôle of $Fe_2(CO)_9$ in place of the more usual Group V base as catalyst has been studied for rearrangement of $[MCl(\pi\text{-allyl})]_2$, with M = Ni, Pd, or Pt.[352]

[342] P. W. N. M. van Leeuwen and A. P. Praat, *J. Organometallic Chem.*, 1970, **21**, 501.
[343] J. W. Faller and M. J. Incorvia, *J. Organometallic Chem.*, 1969, **19**, P13.
[344] P. W. N. M. van Leeuwen, K. Vrieze, and A. P. Praat, *J. Organometallic Chem.*, 1969, **20**, 219.
[345] H. Yamazaki, M. Takesada, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1969, **42**, 275.
[346] P. W. N. M. van Leeuwen, A. P. Praat, and K. Vrieze, *J. Organometallic Chem.*, 1969, **19**, 181.
[347] P. W. N. M. van Leeuwen, K. Vrieze, and A. P. Praat, *J. Organometallic Chem.*, 1969, **20**, 277.
[348] H. C. Volger, M. M. P. Gaasbeek, H. Hogeveen, and K. Vrieze, *Inorg. Chim. Acta*, 1969, **3**, 145.
[349] K. Vrieze, H. C. Volger, M. Gronert, and A. P. Praat, *J. Organometallic Chem.*, 1969, **16**, P19; K. Vrieze, H. C. Volger, and A. P. Praat, *ibid.*, 1970, **21**, 467.
[350] D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 1108; G. M. Khvostik, I. Ya. Poddubnyi, V. N. Sokolov, and I. Yu. Tsereteli, *Russ. J. Phys. Chem.*, 1969, **43**, 1193.
[351] J. Powell, *J. Amer. Chem. Soc.*, 1969, **91**, 4311; P. W. N. M. van Leeuwen and A. P. Praat, *Rec. Trav. chim.*, 1970, **89**, 321.
[352] A. N. Nesmeyanov, S. P. Gubin, and A. Z. Rubezhov, *J. Organometallic Chem.*, 1969, **16**, 163.

2
Redox Reactions

Many transition metal complexes act as catalysts in homogeneous (and heterogeneous) redox reactions, where a variety of intermediates may be involved. The rôle of the catalyst may be understood as that of stabilising the intermediate states of the corresponding uncatalysed path, this stabilisation being necessarily greater than that of the reactants. Several factors contribute to this catalytic activity, *e.g.* (i) the ability to stabilise a variety of ligands (σ-bonded hydride and alkyl species as well as π-bonded olefines and acetylenes) through co-ordination and (ii), the existence of relatively stable but highly reactive species (d^7, d^8 low-spin complexes) which in some ways may be related to the reactive intermediates in organic chemistry. The driving force for the reactivity of such complexes is in part due to the increased stabilisation of the closed shell 18-valence electron configuration which is achieved in these reactions,[1] *e.g.* five co-ordinate d^7 complexes,

$$2Co^{II}(CN)_5^{3-} + X\text{–}Y \longrightarrow Co^{III}(CN)_5X^{3-} + Co^{III}(CN)_5Y^{3-}$$

and the four co-ordinate d^8 species,

$$Ir^{I}Cl(CO)(PPh_3)_2 + X\text{–}Y \dashrightarrow Ir^{III}Cl(CO)(PPh_3)_2XY$$

where the final products of the reactions have 18 valence electrons and X–Y = HCl, MeI, Br_2, *etc.* Many of the reactions of organometallic species involve oxidative addition with the change in the oxidation number of the central metal ion,[2, 3] the two metals whose compounds are most studied in this type of reaction being rhodium and iridium. Redox reactions of other metals will also be discussed in an attempt to supplement the mechanistic studies described in Part I.

1 Rhodium Complexes

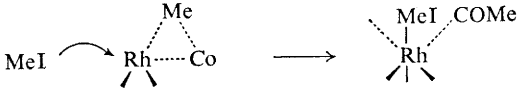
The oxidative addition of iodomethane to *trans*-halogenocarbonylbis-(triarylphosphine)rhodium(I) *trans*-$RhX(CO)L_2$ [where L = PPh_3, $P(p\text{-}MeOC_6H_4)_3$, PEt_3 or $AsPh_3$, and X = Cl] has been studied,[4] the rate

[1] J. Halpern, *Discuss. Faraday Soc.*, 1968, **46**, 7.
[2] R. F. Heck, *Accounts Chem. Res.*, 1969, **2**, 10.
[3] W. H. Baddley, *Inorg. Chem. Acta, Rev.*, 1968, **2**, 7.
[4] I. C. Douek and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2604.

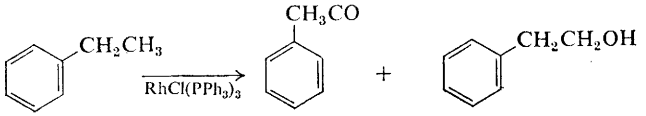
constants being derived for the reaction in iodomethane and other solvents. A subsequent isomerisation of the product takes place *via* a methyl transfer to yield an acetyl complex:

$$\underset{(A)}{\textit{trans}\text{-}RhX(CO)L_2} \underset{}{\overset{MeI}{\rightleftharpoons}} \underset{(B)}{Rh^{III}XI(Me)(CO)L_2} \longrightarrow \underset{(C)}{Rh(X)(COMe)(L_2)}$$

Negative entropies of activation for the forward reaction (A) → (B) are observed (− 29 to − 44 e.u.) the rate decreasing with increasing electron withdrawal from the metal. As in the case of the corresponding iridium system[5] the rate law is second-order, but in the latter system the reaction is neither irreversible nor does it proceed to the second stage. In the isomerisation reaction, where both kinetic and preparative data are available,[6] the mechanism suggested is that the breaking of the Rh–Me bond would be favoured by the formation of a three-centre transition state, the methyl group then being displaced by nucleophilic attack of an incoming solvent molecule:



The extent of reaction is dependent on the solvent involved, the acyl species being formed in acetonitrile and iodomethane whereas in toluene and n-hexane the alkyl complex predominates. In the auto-oxidation of ethylbenzene and related compounds,[6] $RhCl(PPh_3)_3$ has been shown to be a catalyst:



the yields of the ketone and alcohol produced are 20—25% and 6—7% respectively. Both oxido- and hydrido-transition-metal complexes are produced as reactive intermediates. The application of $RuCl_2(PPh_3)_2$ as a catalyst is limited to the oxidation of non-halogenated alkyl arenes and requires the addition of some polyhalogenoalkane.[7]

The synthesis of molecular nitrogen complexes has been achieved by the oxidation of rhodium(I) complexes,[8] by treatment of $Rh(CO)PPh_3(acac)$ with hydrazoic acid in a methylene chloride–pentane mixture at − 60 °C in

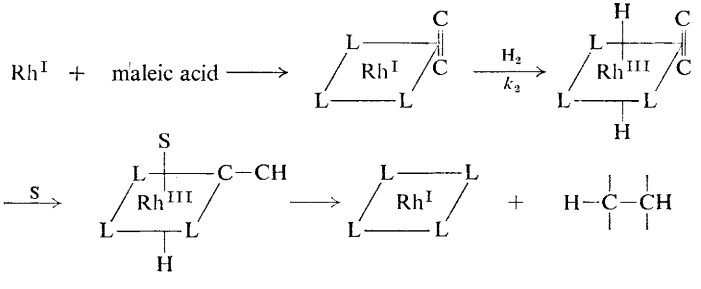
[5] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.
[6] G. Deganello, P. Uguagliati, B. Crociani, and U. Belluco, *J. Chem. Soc.* (*A*), 1969, 2729; P. Uguagliati, A. Palazzi, G. Deganello, and U. Belluco, *Inorg. Chem.*, 1970, **9**, 724.
[7] J. Blum, J. Y. Becker, H. Rosenman, and E. D. Bergmann, *J. Chem. Soc.* (*B*), 1969, 1000.
[8] L. Yu. Ukhin and Yu. A. ShVetsov., *Izvest. Akad. Nauk. S.S.S.R., Ser. Khim*, 1969, 2342.

the presence of dry HCl. The yellow product $Rh_2(N_2)(CO)_2(PPh_3)_2Cl_4$,-$2NH_4Cl$ is rapidly decomposed by water with the liberation of half the bound nitrogen. The formation of the metal–metal bonded dinuclear complex may be described by the scheme:

$$2Rh(CO)PPh_3(acac) + 5HCl + HN_3 \longrightarrow Rh_2(N_2)(CO)_2(PPh_3)_2Cl_4,2NH_4Cl + 2Hacac$$

Tris(triphenylphosphine)chlororhodium(I) has been shown to be an efficient catalyst for the low pressure hydrogenation of alkenes and alkynes.[9] The mechanism[10] involves (a) dissociation of one ligand from the complex, (b) oxidative insertion of rhodium into the hydrogen bond, (c) co-ordination of the alkene with the resulting *cis*-dihydrorhodium(III) complex, and (d) the simultaneous transfer of the bound hydrogens to the alkene. In the reaction with cyclopropyl alkenes,[9] however, the mechanism requires step-wise addition of the bound hydrogens to yield as intermediates either an alkyl–rhodium(III) complex or a cyclopropylcarbinylrhodium species. $Rh(NO)(PPh_3)_3$ has been prepared[11] from the corresponding trichloride in THF and has been shown to be a catalyst for the quantitative reduction of 1-hexene and cyclohexene. In the treatment of cyclohexene with D_2 the product given, $C_6H_{10}D_2$, has an isotopic purity of > 99%, which suggests that the catalyst is stereospecific. In the hydrogenation of *cis*-2-pentene[12] catalysed by the corresponding rhodium(I) chloride, isomerisation to *trans*-2-pentene and 1-pentene takes place, the latter predominating, and occurs about one-third as fast as the hydrogenation. Rhodium(III) halides in dimethylacetamide have been shown to effect hydrogenation of alkanes and, in the reaction with maleic acid in the presence of hydrogen,[13] the kinetic data are consistent with a mechanism involving the formation of a rhodium(I)–maleic acid complex:

$$Rh^{III} + H_2 \longrightarrow Rh^{I} + 2H^{+}$$



[9] C. H. Heathcock and S. R. Poulter, *Tetrahedron Letters*, 1969, 2755.
[10] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.
[11] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 1969, **91**, 5659.
[12] G. C. Bond and R. A. Hillyard, *Discuss. Faraday Soc.*, 1968, **46**, 20.
[13] B. R. James and G. L. Rempel, *Discuss. Faraday Soc.*, 1968, **46**, 48.

where L = Cl, H_2O, or solvent, and S = solvent. A small deuterium isotope effect is observed with the reaction k_2 involving the oxidative addition. In the catalysis of the hydrogen transfer from alcohols or alkoxides to olefins the complexes involved are of the type $Rh(CO)(Cl)(PR_3)_2$, although the reduction from Rh^{III} may proceed further to yield either zero-valent or hydrido-complexes.[14] Carbon monoxide reacts with dimethylacetamide solutions of rhodium(III) chloride[15] to yield initially a monocarbonyl complex *via* an S_N2 mechanism:

$$Rh^{III} + CO \xrightarrow{k_1} Rh^{III}CO$$

the observed rate law is second-order. In the presence of water (or hydroxide), however, this complex decomposes with further uptake of carbon monoxide to form dichlorocarbonylrhodate(I), $Rh(CO)_2Cl_2^-$, the initial step of the reduction process being described as:

$$Rh^{III}CO + OH^- \xrightarrow{k_2} [Rh(CO_2H)] \longrightarrow Rh^{I} + CO_2 + H^+$$

2 Iridium Complexes

The elucidation of the stereochemical course of oxidative addition at iridium(I) has recently been reported.[16] In the addition of alkyl halides,

$$XY + \textit{trans}\text{-}[Ir^{I}(PPh_3)_2(CO)Cl] \longrightarrow [Ir^{III}(PPh_3)_2(CO)Cl(X)(Y)]$$

there is inversion of configuration at the carbon centre strongly indicating an S_N2 reaction. In the corresponding reaction with $MeCHBr\cdot CO_2Et$ as substrate, however,[17] nucleophilic attack by the d^8 system involving the formation of metal–carbon and metal–halide bonds in a concerted process results in retention of configuration at the carbon atom. Solvent effects are also important in the formation of the ultimate products in reactions of this type. In benzene or chloroform, anhydrous hydrogen halides give only *cis*-addition to *trans*-$Ir^{I}(CO)(X)(PR_3)_2$ but in solvating media, such as methanol or acetonitrile, both *cis*- and *trans*-addition takes place.[18] Reactions of alkyl-substituted 3-halopropynes yield a series of σ-allenyl compounds which may be models for intermediates in metal-cation catalysed syntheses of allenes.[19] The large negative entropies of activation for the addition of fluorocyano-olefins to complexes of this type may arise from either large solvation effects in an ionic or polar transition state, or from the precise steric requirements of broadside approach of the olefin to the iridium. Product stereochemistry for these iridium(I) [and

[14] G. Gregorio, G. Pregaglia, and R. Ugo, *Inorg. Chim. Acta*, 1969, **3**, 89.
[15] B. R. James, G. L. Rempel, and F. T. R. Ng, *J. Chem. Soc.* (*A*), 1969, 2454.
[16] J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Comm.*, 1970, 612.
[17] R. W. Johnson and R. G. Pearson, *Chem. Comm.*, 1970, 986.
[18] D. M. Blake and M. Kubota, *Inorg. Chem.*, 1970, **9**, 989.
[19] J. P. Collman, J. N. Cawse, and J. W. Kang, *Inorg. Chem.*, 1969, **8**, 2574.

platinum(0)] oxidative additions would appear to favour a polar transition state.[20] The initial step in the desulphonylation of aromatic sulphonyl halides, which is catalysed by a series of complexes, involves oxidative addition. With the complex $Ir^{I}(CO)(Cl)(PPh_3)_2$, the first product is the complex $Ir^{III}(Cl)_2(SO_2Ar)(CO)(PPh_3)_2$, with subsequent loss of one PPh_3 group, conversion of $ArSO_2$- to separately bonded Ar- and SO_2-ligands, and loss of SO_2.[21] Oxidative additions involving halogenocarbonyl complexes with methyl-substituted phosphines and arsines have been examined[22] and, for species of the type $Ir^{I}(CO)(Cl)(PMe_2Ph)_2$, there is *cis*-addition of oxygen, carbon disulphide, and tetra-cyanoethylene whereas methyl bromide and iodide in benzene solutions give stereospecifically *trans*-addition. The corresponding reactions of chloroformates and allylic halides have been investigated.[23] The relative basicities of complexes of this type with carboxylic acids have been studied[24] by the extent of reaction:

$$\textit{trans}\text{-}[Ir^{I}(CO)Cl(PMePh_2)_2] + HA \rightleftharpoons [Ir^{III}H(CO)(Cl)(A)(PMePh_2)_2]$$

The addition of strong acids (hydrogen halides) may be reversed by bases such as sodium ethoxide. In the presence of glacial acetic acid there is virtually complete conversion to the trivalent iridium species, whereas in a dilute solution of acetic acid in benzene the extent of the conversion may be monitored by the absorbance of the remaining Ir^{I} complex. The good correlation between the degree of conversion and the pK_a of the acid involved is seen to be consistent with the formation of an iridium(III)–hydrido complex. The extent of reaction is also dependent on the phosphine ligand, the effect decreasing in the order $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$. The corresponding arsine complexes are converted to a greater extent since (a) the steric hindrance to the addition of groups to the metal ion is reduced by the greater size of the arsenic and thus its easier accommodation of the three aryl or alkyl groups and (b) since iridium(I) is a 'soft' acid and tertiary arsine is a softer base than the corresponding phosphine, it may be that the electron density around the iridium is increased in the case of the former ligand thus enabling it to undergo oxidative additions, such as protonations, more easily. An example of intramolecular oxidative addition at iridium(I) is afforded by the conversion of $Ir(Cl)(PR_3)_3$ (R = substituted phenyl) to an octahedral iridium(III) hydride on heating.[25] The mechanism involves hydrogen-atom transfer from the *ortho*-position on a phenyl ring to iridium with the formation of an iridium–carbon bond, the small associated kinetic isotope effect being interpreted in terms of a three-centre mechanism.

[20] J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc.* (*A*), 1970, 1847.
[21] J. Blum and G. Scharf, *J. Org. Chem.*, 1970, **35**, 1895.
[22] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128.
[23] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 443, 1560.
[24] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1802.
[25] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

Several examples of oxidative addition reactions of compounds involving group (IV) elements, silicon [26] and germanium,[27] with iridium(I) complexes have been described and reviewed.[28] In the reaction of silicon hydrides $(CH_3)_n(C_2H_5O)_{3-n}SiH$ with bis(bis-1,2-diphenylphosphinoethane)iridium(I), [Ir^I(diphos)$_2$],

$$(CH_3)_n(C_2H_5O)_{3-n}SiH + Ir^I(diphos)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (diphos)_2[(CH_3)_n(C_2H_5O)_{3-n}Si]Ir(H)$$

the rate law for the forward reaction is second-order,[26] the overall heats and entropies of formation of the iridium(III) species being *ca.* − 18 ± 2 kcal mol and − 50 ± 5 e.u. respectively. The values of $\Delta H_1^{\ddagger}$, and $\Delta S_1^{\ddagger}$ are *ca.* 5·7 kcal mol and − 47 e.u. respectively, the marked dependence of reaction rate observed with change in solvent with the corresponding methyl iodide additions being absent in the case of silicon hydride species. The insensitivity of the activation parameters for the forward reaction on the substituents at the silicon suggests a mechanism similar to that described by Chock and Halpern.[5] In the reactions of germanes R_3GeH with $(Ph_3P)_2Ir^I(CO)Cl$ yielding six-co-ordinate dihydro-complexes [27] $(Ph_3P)_2Ir(CO)(H)_2GeR_3$, the mechanism involves intermediate adduct formation:

$$(Ph_3P)_2Ir(CO)Cl + R_3GeH \longrightarrow (Ph_3P)_2(CO)(H)Ir\begin{matrix}Cl\\ \diagdown\\ GeR_3\end{matrix}$$

$$\downarrow -GeR_3Cl$$

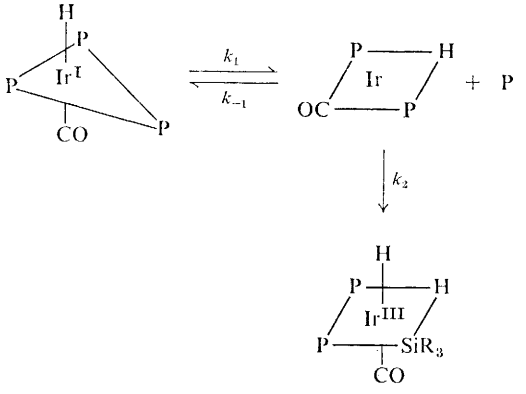
$$(Ph_3P)_2Ir(CO)(H)_2GeR_3 \xleftarrow{+R_3GeH} (Ph_3P)_2Ir(CO)(H).$$

Although oxidation reactions of this type are generally associated with square-planar four-co-ordinate complexes, there are several examples of oxidative addition to five-co-ordinate species. In these systems, however, the mechanism may also be termed as oxidative elimination since the product is six co-ordinate and one of the ligands is displaced. The mechanism of silicon hydride addition to hydridocarbonyltris(triphenylphosphine)iridium(I) has been described,[29] the reaction



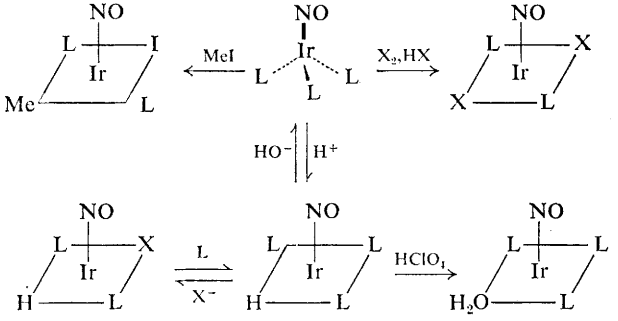
[26] J. Harrod and C. A. Smith, *J. Amer. Chem. Soc.*, 1970, **92**, 2699.
[27] F. Glockling and M. D. Wilvey, *J. Chem. Soc.* (*A*), 1970, 1675.
[28] L. H. Sommer, *Pure Appl. Chem.*, 1969, **19**, 525.
[29] J. F. Harrod, D. F. R. Gilson, and R. Charles, *Canad. J. Chem.*, 1969, **47**, 2205; J. F. Harrod and C. A. Smith, *ibid.*, 1970, **48**, 870.

proceeding *via* a mechanism involving a pre-dissociation of the trigonal bipyramidal species followed by oxidative addition of the silicon hydride:



The activation parameters associated with the dissociation (k_1) reaction are $\Delta H_1^{\ddagger} = 23$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = 15$ e.u.

In the reaction involving the d^{10} species Ir(NO)$(PPh_3)_3$, oxidative elimination occurs, and the resultant complex is a five-co-ordinate tetragonal pyramid:[30]



In the case of the methyl iodide adduct, on reaction with lithium chloride, the corresponding chlorocomplex is produced which suggests that a *trans*-effect may be operative.

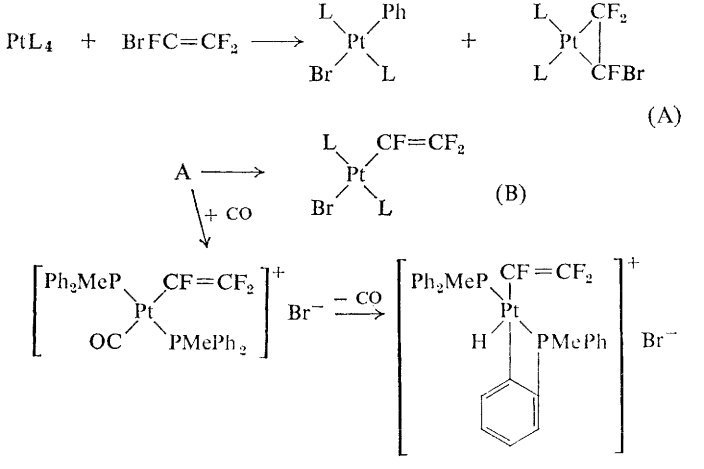
3 Platinum Complexes

The oxidative addition of aldehydes and related species to tetrakis(triphenylphosphine)platinum(0) has been investigated[31] and the product is the square planar platinium(II) diacyl species:

$$Pt^0(PPh_3)_4 \xrightarrow{RCHO} Pt^{II}(COR)_2(PPh_3)_2$$

[30] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 155.
[31] I. Harvie and R. D. W. Kemmitt, *Chem. Comm.*, 1970, 198.

In these oxidations there is no evidence for the formation of six-co-ordinate intermediates. The crystal structure of the complex formed[32] on dissolution of the bis(triphenylphosphine)platinum(0)–ethylenediamine complex in oxygen-saturated toluene has been derived,[33] the two P atoms and the O atoms in the $(PPh_3)_2PtO_2$ unit taking up an essentially planar configuration in the neighbourhood of the platinum atom. The reactions of complexes of the type Pt^0L_4 (where L = Ph_2PMe) with fluorocarbons have been investigated.[34] With bromotrifluoroethylene, one of the products (A) rapidly rearranges to the perfluorovinyl compound (B). On reaction with carbon monoxide, however, there is an intramolecular oxidative addition from $Pt^{II} \rightarrow Pt^{IV}$ involving the cationic platinum carbonyl complex, possibly as the result of electronic interaction between the platinum and the perfluorovinyl group.

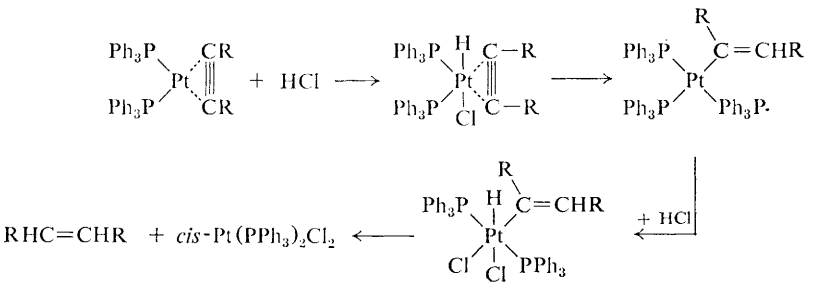


(A)

(B)

It has been suggested that dialkyl mercury complexes react with platinum(II) species in oxidative addition,[35] the nature of the solvent having little effect on the reaction. In the oxidation of tetracyanoplatinate(II) by bromine, the reaction is sufficiently fast to require a rapid-flow device for measurement of the rates.[36] In the absence of added bromide ion the reaction occurs in two steps (a) a rapid interaction to yield the *trans*-bromoaquotetracyanoplatinate(IV) ion and bromide ion followed by (b) the rate-determining replacement of the co-ordinated water molecule by bromide ion. The reaction of $Pt(alkyne)(PPh_3)_2$ with strong acids (HX) is thought[37] to involve two successive oxidative additions,

[32] C. D. Cook and G. S. Jauhal, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 31.
[33] C. D. Cook, P. T. Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, 1969, **91**, 2123.
[34] A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 947.
[35] R. J. Cross and R. Wardle, *J. Chem. Soc.* (*A*), 1970, 840.
[36] C. E. Skinner and M. M. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 4405.
[37] P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1970, **92**, 3825.



although it is possible (though less likely) that the acetylene may dissociate initially to give $Pt(PPh_3)_2$ which then oxidatively adds HCl to give the hydride. Platinum(II)–hydride–HX systems have been shown to reduce olefins [38] under experimental conditions where neither the hydride nor the strong acid react separately with the alkenes:

$$\textit{trans}\text{-}Pt(PEt_3)_2HCl + RCH{=}CHR^1 \xrightarrow{HCl} \textit{trans}\text{-}Pt(PEt_3)_2Cl_2 + RCH_2CH_2R^1$$

In this case there is an oxidative addition after (a) olefin insertion in the Pt–H bond followed by (b) cleavage to yield the Pt^{II}–alkyl complex. Dissociation of the Pt^{IV} complex formed yields the hydrocarbon. Studies on reductive eliminations of this type have been made for other platinum(IV) complexes,[39] *e.g.* the reaction

$$Pt(PEt_3)_2Ph_2I_2 \longrightarrow \textit{trans}\text{-}Pt(PEt_3)_2Ph(I) + PhI$$

takes place on dissolution of the complex in methanol. In the presence of added iodide, however, the reaction is slower and the reaction mechanism is described as (S = solvent):

$$Pt(PEt_3)_2Ph_2I_2 + S \underset{}{\overset{K}{\rightleftharpoons}} [Pt(PEt_3)_2Ph_2I(S)]^+ + I^-$$

$$\downarrow k_1$$

$$\textit{trans}\text{-}Pt(PEt_3)_2Ph(I)$$

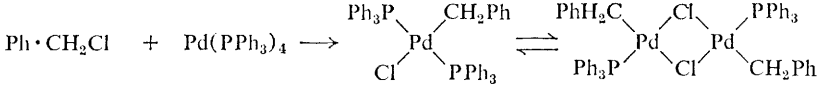
the rate-determining process being the unimolecular reduction of the cationic complex. The fact that substitution of a co-ordinated iodide is seen as a key step in the reduction suggests that a decreased electron density at the central metal atom is the important factor in determining the ease of reductive elimination. This is consistent with the converse, that an increase in the electron density at the metal centre enhances the tendency of d^8 complexes to undergo oxidative addition.

[38] M. Giustiniani, G. Dolcetti, R. Pietropaolo, and U. Belluco, *Inorg. Chem.*, 1969, **8**, 1048.

[39] R. Ettore, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 45.

4 Palladium Complexes

The formation of benzyl palladium(II) complexes from $Pd(PPh_3)_4$ and benzyl chloride have been reported:[40]

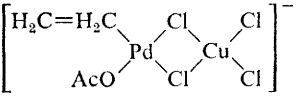


the monomeric *trans*-species is in equilibrium with the dichloro-bridged dimer. In the corresponding reaction with bromotrifluoroethylene,[41] the perfluorovinyl complex *trans*-$(Ph_3P)_2Pd(CF{=}CF_2)Br$ is formed *via* an intermediate similar to that described in the platinum(II) reaction.[34] The formation of palladium(II)[and platinum(II)]–carbon bonds by proton abstraction from quinolines has been described,[42] the reaction between tetrachloropalladate(II) and 8-methylquinoline involving the first example of abstraction from the alkyl group rather than from the aryl. Hydrogen abstraction is also a feature of the homogeneous palladium-catalysed *ortho*-chlorination of azobenzene,[43] where the mechanism proceeds *via* the addition of chlorine to a 2-(phenylazo)phenyl–palladium complex. Intramolecular aromatic substitutions of this type have recently been reviewed.[44]

The oxidation of olefins by palladium salts in non-aqueous solvents has been studied.[45] In the presence of acetic acid, palladous chloride solutions with lithium chloride react with ethylene according to the rate law,

$$\frac{-\,d[C_2H_4]}{dt} = k\frac{[C_2H_4][Pd^{II}][LiOAc]}{[LiCl]^{1-2}}$$

an intermediate of the type $PdCl(OAc)(C_2H_4)(HOAc)$ being involved. This π-bonded ethylene–Pd^{II} complex then rearranges by ligand migration and hydride shift to a σ-bonded acetoxy–ethyl–Pd^{II} species which subsequently decomposes to ethylidene diacetate and vinyl acetate, in proportions dependent on the concentrations of lithium acetate and catalyst present. With palladium(II)–copper(II) catalysts present, both these metal ions are involved, in either a pre-equilibrium or in the transition state, in a complex of the type



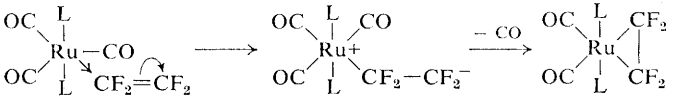
[40] P. Fitton, J. E. McKeon, and B. C. Ream, *Chem. Comm.*, 1969, 370.
[41] A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3023.
[42] G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Comm.*, 1970, 912.
[43] D. R. Fahey, *Chem. Comm.*, 1970, 417.
[44] G. W. Parshall, *Accounts. Chem. Res.*, 1970, **3**, 139.
[45] D. Clark, P. Hayden, and R. D. Smith, *Discuss. Faraday Soc.*, 1968, **46**, 98.

The rôle of the copper(II) ions is to increase the activity of the organo-palladium species, possibly by withdrawal of electrons from the environment of the palladium(II).

5 Miscellaneous Complexes

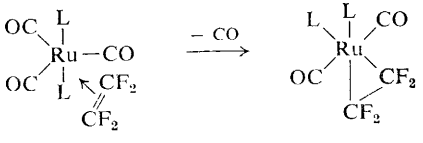
The reaction of the zero-valent osmium complex $Os(CO)_3(PPh_3)_2$ with a series of strong acids (HX) has produced cationic hydrido-species of the type $[Os(H)(CO)_3(PPh_3)_2]X$, where X = Br^-, ClO_4^-, BF_4^-, or PF_6^-.[46] The complexes behave as 1 : 1 electrolytes in nitrobenzene and may be reconverted to the zerovalent complex on the action of base. Ammonia and primary amines (A) react with complexes of the type $[MX_3(PR_3)_3]$, where M = Os or Ru, in ethanol at 20 °C to form the M^{II} species *mer*-$[MX_2(A)(PR_3)_3]$ and acetaldehyde.[47] Secondary and tertiary amines with dimethylphenylphosphine ligands also cause reduction, but in this case the product is an alcohol complex. The reduction is considered to occur *via* formation of a hydride complex since some hydrogen is formed in all reactions and steric factors probably control whether an amine or an alcohol complex is formed.

Although *trans*-$Ru(CO)_3(PPh_3)_2$ does not react with C_2F_4, its phosphite (L) analogue does, by simple carbonyl displacement.[48] Either end-on or sideways-on approach of the fluoro-olefin to the ruthenium is possible; the former is nucleophilic attack by Ru^0 on the olefin,



(B)

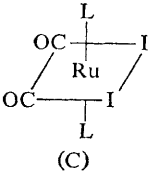
whilst the latter is nucleophilic attack by the olefin at ruthenium,



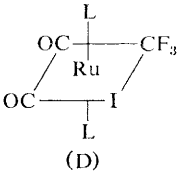
The intermediate (B) is expected to be relatively stable and sufficiently long-lived to permit rotation about the C–C bond. Since the stereochemistry of the olefin is retained in this reaction, the latter is the mechanism favoured. Dodecacarbonyltriruthenium, pentacarbonylruthenium, and tris-(acetylacetonato)ruthenium(III) have been shown to promote the homogeneous reduction of nitrobenzene to aniline in the presence of carbon

[46] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1969, 1889.
[47] J. Chatt, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969, 854.
[48] M. Cooke and M. Green, *J. Chem. Soc.* (*A*), 1969, 651.

monoxide and hydrogen.[49] The mechanism proposed involves the formation of a phenylnitrene intermediate, which is stabilised by bonding to the metal in a dinuclear complex that undergoes either hydrogenolysis to yield aniline or carbonyl insertion and hydrogenolysis to produce 2,2′-diphenylurea. Oxidative elimination of zerovalent ruthenium and iron complexes of the type *trans*-$L_2Ru(CO)_3$ (where L = phosphine or phosphite) with iodine and trifluoroacetic acid have been studied.[50] In the case of the iodine reaction the sole product is (C). Trifluoroiodomethane reacts



(C)



(D)

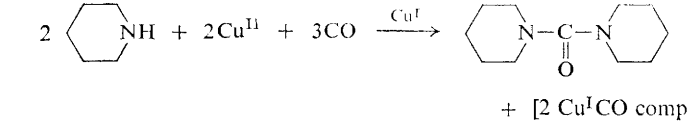
with *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ to form the first σ-bonded trifluoromethyl–ruthenium complex (D). The stereoselectivity of the latter reaction is probably related mechanistically to the former, and may involve nucleophilic attack on the 'positive' iodine of the CF_3I to form a trifluoromethyl anion which rapidly attacks the cationic complex $\{[EtC(CH_2O)_3P]_2Ru(CO_3\}^+$ with displacement of carbon monoxide.

The oxidation of iron(II) porphyrin complexes by organic molecules has been reported.[51] Iron(II)–deuterioporphyrin [$Fe^{II}D$] and its dimethyl ester react rapidly with alkyl halides, quinones, and nitro-compounds. In the case of quinone, the yield of quinol formed is close to 100%. Cyclic amine complexes of nickel(III) have been prepared by the reaction of the corresponding nickel(II) species with nitrosyl tetrafluororate[52] and by electrochemical techniques.[53] The *NN′*-diethyldithiocarbamate (dtc) complexes of nickel(II) and copper(II) have been shown to undergo oxidation by bromine.[54] In carbon disulphide as solvent, the products formed are $Cu^{III}(dtc)Br_2$ and $Ni^{IV}(dtc)_2Br_2$, the latter having a square planar chelated structure. The interaction of the dinitrogen rhenium complex $[Re(N_2)Cl(Ph_2PCH_2CH_2PPh_2)]$ with silver salts and copper(II) and iron(III) chlorides has been shown to yield the corresponding monovalent cationic complex.[55]

Carbon monoxide co-ordinated to copper(I) amine complexes has been found to be much more susceptible to oxidants than is carbon monoxide in

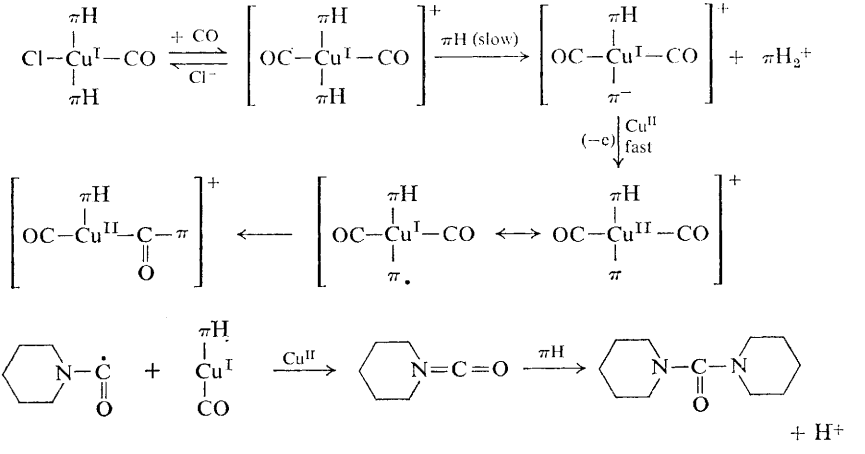
[49] F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, 1970, **9**, 342.
[50] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1969, 2645.
[51] R. S. Wade, R. Havlin, and C. E. Castro, *J. Amer. Chem. Soc.*, 1969, **91**, 7530.
[52] E. K. Barefield and D. H. Busch, *Chem. Comm.*, 1970, 522.
[53] D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611.
[54] Y. Nigo, I. Masuda, and K. Sinra, *Chem. Comm.*, 1969, 476.
[55] J. Chatt, J. R. Dilworth, H. P. Gunz, G. J. Leigh, and J. R. Sanders, *Chem. Comm.*, 1970, 90.

the free state. Use has been made of this in the copper(I)-ion-catalysed oxidative coupling of carbon monoxide and amines:[56]



+ [2 $Cu^{I}CO$ complex]

The reactions are autocatalytic, the copper(I) complexes being readily oxidised to copper(II) by oxygen. If πH = piperidine, an interpretation of the reaction consistent with the kinetics involves the rapid co-ordination of a CO molecule to the copper(I) species:



In methanol, Cl^- and πH^+ ions exhibit a retarding effect. The stabilities of nickel(0)–phosphine complexes have been assessed;[57] these seem to depend more on the size of the phosphine and electronic effects on bond strengths are of secondary importance. In the oxidative addition of aryl halides to nickel(0)–phosphine complexes[58] the reaction appears to proceed *via* an initial slow dissociation step to give $Ni(PR_3)_2$ which then attacks the organic species. The mechanism of oxidative elimination of these nickel species thus contrasts with that for the platinum(0)–phosphines where the dissociation of the ligand is rapid and the rate-determining step is that involving the redox interaction. The oxidation of tetrahedral cobalt(I) complexes with carbon tetrachloride has been described:[59]

$$2Co^{I}Cl(PPh_3)_3 + 2CCl_4 \longrightarrow 2Co^{II}Cl_2(PPh_3)_2 + Ph_3PCl_2 + Ph_3P + C_2Cl_4$$

[56] W. Brackman, *Discuss. Faraday Soc.*, 1968, **46**, 122.
[57] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.
[58] D. R. Fahey, *J. Amer. Chem. Soc.*, 1970, **92**, 402.
[59] M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1969, **3**, 227.

The initial step involves an oxidative addition of CCl_4 to the cobalt(I) species to give an unstable six-co-ordinate cobalt(III) complex which quickly decomposes to yield the stable cobalt(II) derivative. The reduction of cobalt(II) amines by carbon monoxide has been investigated[60] the reaction proceeding in aqueous solution *via* the formation of a cobalt–carbonyl anion $Co(CO)_4^-$. The reactions of $Cr(CO)_6$ and $Mo(CO)_6$ with *N*-methylsalicylideneimine have been shown to involve oxidation of the metal to the + 3 oxidation state, whilst $Mo_2(CO)_{10}$ and $Fe(CO)_5$ with similar nitrogen chelating ligands carrying active protons yield the corresponding M^{II} complexes.[61] Molybdenum hexacarbonyl has also been shown to be oxidised by organic halides.[62] The thermal reaction between $Mo(CO)_6$ and CCl_4 in ethyl acetate involves intermediate formation of $Mo(CO)_5EtOAc$ which is successively oxidised to Mo^{III} and Mo^{V} derivatives, the step $Mo^0 \rightarrow Mo^I$ being mainly responsible for free radical formation. The corresponding reaction with CBr_4 is described in terms of a chain process. Ti^0 and Ti^{II} complexes have been reported active in the fixation–reduction of molecular nitrogen under mild conditions, the overall mechanism for which is extremely complex.[63]

[60] N. N. Halvorson and E. Peters, *Canad. J. Chem.*, 1969, **47**, 2535.
[61] F. Calderazzo, C. Floriani, R. Henzi, and F. L'Eplattenier, *J. Chem. Soc.* (*A*), 1969, 1378.
[62] C. H. Bamford, G. C. Eastmond, and F. J. T. Fildes, *Chem. Comm.*, 1970, 144, 145.
[63] E. E. Van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *J. Amer. Chem. Soc.*, 1969, **91**, 1551.

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Abbreviations for Ligands and Solvents

General

R	alkyl, aryl
L	unidentate ligand
LL	bidentate ligand
LLLL	quadridentate ligand
X	halide

Specific

acac	acetylacetone
acacen	*NN'*-bis(acetylacetonato)ethylenediamine
ADP	adenosine diphosphate
ala	alanine
amp	2-aminomethylpyridine
asp	aspartate
ATP	adenosine triphosphate
bipy	2,2'-bipyridyl
budta	*meso*-butylenediaminetetra-acetate
bzbz	dibenzoylmethane
cod	cyclo-octadiene
cot	cyclo-octatetraene
cyclam	1,4,8,11-tetra-azacyclotetradecane
cydta	cyclohexane-1,2-diaminetetra-acetate
diars	*o*-phenylenebisdimethylarsine
dien	diethylenetriamine
diphos	1,2-bisdiphenylphosphinoethane
DMF	dimethylformamide
dmg	dimethylglyoxime
dmm	dimethyl maleate
DMSO	dimethyl sulphoxide
dopa	dihydroxyphenylalanine
dpae	1,2-bisdiphenylarsinoethane
dpe	1,2-bisdiphenylphosphinoethane
dpp	1,2-bisdiphenylphosphinopropane
dtc	*NN'*-diethyldithiocarbamate
dto	2,2,7,7-tetramethyl-3,6-dithiaoctane
dtpa	diethylenetriaminepenta-acetate
ebt	Eriochrome Black T

edda	ethylenediaminediacetate
edta	ethylenediaminetetra-acetate
egta	ethylene glycol bis-(2-aminoethyl ether)tetra-acetate
en	ethylenediamine
enbig	ethylenebiguanide
epe	*dl*-4-methyl-1,8-diamino-3,6-dithiaoctane
Et_4dien	*NNN″N″*-tetraethyldiethylenetriamine
gly	glycine
hfac	hexafluoroacetylacetone
hist	histamine
hydta	*N*-(2-hydroxyethyl)ethylenediaminetriacetate
ida	iminodiacetate
IDP	inosine diphosphate
im	imidazole
mal	malonate
Me_4trien	*NN′N″N‴*-tetramethyltriethylenetetramine
mida	*N*-methyliminodiacetate
mnt	maleonitriledithiolate
ndaip	nitrilodiaceticisopropionate
ndap	nitrilodiaceticpropionate
nor	norbornadiene
np	naphthalenide anion
NRS	1-nitroso-2-naphthol-3,6-disulphonic acid
nta	nitrilotriacetate
ox	oxalate
par	4-(2-pyridylazo)resorcinol
pc	phthalocyanine
pdta	propylenediaminetetra-acetate
phen	1,10-phenanthroline
pn	propylenediamine
py	pyridine
salen	*NN′*-bis(salicylaldehydo)ethylenediamine
S-bzbz	monothiodibenzoylmethane
tcne	tetracyanoethylene
tda	taurine diacetate
terpy	2,2′,6′,2″-terpyridyl
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-trifluoroacetylacetone
THF	tetrahydrofuran
THPED	*NNN′N′*-tetrakis-(2-hydroxypropyl)ethylenediamine
TKED	*NNN′N′*-tetrakis-(2-hydroxyethyl)ethylenediamine

tn	trimethylenediamine
tpp	tripolyphosphate
trans-14-diene	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene
tren	2,2′,2″-triaminotriethylamine
trenen	4-(aminoethyl)-1,4,7,10-tetra-azadecane
trien	triethylenetetramine
trigly	triglycinate
UDA	uramil diacetate
xyl	xylenol orange