Kinetics and Mechanism of Metal-ion Complex Formation in Solution

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1 Introduction

There has recently been considerable activity in the field of inorganic reaction kinetics, especially in the area involving the reactions of metal ions.[1–11] With the development of fast-reaction techniques,[12–14] it has become possible to examine in detail systems which had previously been outside the scope of investigators. The use of conventional methods on slower reactions has also helped to extend our knowledge in this field. In addition to the increase in the number of systems studied, the effects on reaction rates of changes in the overall charge of the metal complex, of other ligands in solution, of the nature of the central metal atom, and of solvent, have been examined.[1,3,4] We will limit our discussions to the homogeneous reactions of metal complexes in solution and primarily to the displacement of water molecules from the inner co-ordination sphere of a metal ion and its replacement by a ligand. More detailed reviews are available on dissociation reactions,[1] acidic and basic hydrolyses,[5] and isomerisations.[15]

In this Review, we describe the newer methods available for studies in this field and mechanisms of substitution reactions in general. We then discuss reactions involving metal ions in various stereochemical configurations.

2 Experimental Methods

Until a few years ago, mechanistic studies were restricted mainly to the complexes of Cr^{III}, Co^{III}, Pt^{II}, and Pd^{II}, which undergo substitution slowly and which may

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[1] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', 2nd edn., Wiley, New York, 1967.

[2] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 1962, **4**, 381.

[3] D. R. Stranks, 'Modern Co-ordination Chemistry', ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 78.

[4] R. J. Wilkins, *Quart. Rev.*, 1962, **16**, 316.

[5] N. Sutin, *Ann. Rev. Phys. Chem.*, 1966, **17**, 119.

[6] C. H, Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York, 1966.

[7] J. P. Hunt, 'Metal Ions in Aqueous Solution', Benjamin, New York, 1963.

[8] M. Eigen and R. G. Wilkins, 'Mechanisms of Inorganic Reactions', Amer. Chem. Soc., Advances in Chemistry Series, No. 49, 1965, p. 55.

[9] J. O. Edwards, 'Inorganic Reaction Mechanisms', Benjamin, New York, 1963.

[10] N. Sutin, *Ann. Rev. Nuclear Sci.*, 1962, **12**, 285.

[11] G. H. Nancollas, 'Interactions in Electrolyte Solutions', Elsevier, Amsterdam, 1966.

[12] M. Eigen and L. de Maeyer, in 'Techniques of Organic Chemistry', ed. S. L. Friess, E. S. Lewis, and A. Weissberger, 2nd edn., Interscience, New York, 1963, vol. 8, p. 895.

[13] F. J. W. Roughton and B. Chance, ref. 12, p. 703.

[14] E. F. Caldin, 'Fast Reactions in Solution', Wiley, New York, 1964.

[15] R. G. Wilkins and M. J. G. Williams, ref. 3, p. 174.

be examined by use of conventional techniques. The uses of photometric, electrometric, polarimetric, and isotopic sampling techniques have been fully discussed by Stranks.[3] These methods may be applied where the half-life of the reaction is greater than *ca.* 30 sec., but most transition-metal ions react much faster than this. A summary of 'fast-reaction techniques' is given below; for further detail the reader is referred to more comprehensive reviews.[12,14]

A. Flow Methods.—Despite the development by Hartridge and Roughton[16] of a continuous-flow apparatus over 40 years ago, its application has been confined in the main to the study of biological systems. The rate of formation of $FeS_2O_3^+$ was earlier studied by a simple flow system[17] but the real advances in the study of metal complex formation in solution by use of these methods have taken place within the last 10 years, with the development of the fast-response electronic detectors. Although other systems are also used[14] the most widely employed method is that of stopped flow, where two solutions are forced together through a mixing device; the mixed solution flows along a quartz tube and is abruptly stopped so that the solution comes to rest within a few milliseconds. The rate of flow along the observation tube is such that when the solution is stopped, a segment within 1 cm. of the mixing device has been mixed for only 1—2 milliseconds. Any reaction taking place in this segment of solution is now detected (generally spectrophotometrically); the signal is relayed to an oscilloscope.[18,19] By use of this method, reactions such as the formation and dissociation of Ni^{II} and Fe^{III} complexes[20,21] involving a variety of ligands, with half-lives ranging from milliseconds to several seconds can be conveniently studied. A particular use of this method is in the study of the formation of complexes which occur as intermediates in irreversible reactions. The transient complexes formed in the oxidation of ligands by cobalt(III) and vanadium(V) have been characterised by use of stopped-flow systems.[22–24] Whilst all the reactions cited have been studied by spectral methods, other means of detection have been employed; these have been comprehensively reviewed by Caldin.[14]

B. Relaxation Methods.—These methods, which are used for systems at equilibrium, have been developed by Eigen and his co-workers.[12,25] In these cases the equilibrium is displaced by some external parameter and the readjustment to a new equilibrium position is directly observed. Two main types of physical perturbation have been used.

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[16] H. Hartridge and F. J. W. Roughton, *Proc. Roy, Soc.*, 1923, *A*, **104**, 376.

[17] H. Schmid, *Z. phys. Chem.* (*Leipzig*), 1930, **148A**, 321.

[18] G. Dulz and N. Sutin, *Inorg. Chem.*, 1963, **2**, 917.

[19] J. Hill and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 156

[20] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 1959, 3700, 1960, 2895, 2901.

[21] A. G. Davies and W. M. Smith, *Proc. Chem. Soc.*, 1961, 380.

[22] J. Hill, A. McAuley, and W. F. Pickering, *Chem. Comm.*, 1967, 573.

[23] J. Hill and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 1169.

[24] W. F. Pickering and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 1173.

[25] G. Czerlinski and M. Eigen, *Z. Electrochem.*, 1959, **63**, 652.

(i) *Stepwise or transient methods.* In these, the external parameter is changed stepwise or in the form of a single or repeated pulse followed by a direct (or indirect) observation of the subsequent internal re-equilibration. The dependence of the equilibrium on the particular external parameter largely determines which one is chosen. If the temperature[25] of the solution is changed (at constant pressure), in 10^{-6} sec. a shift in equilibrium will occur if the overall heat of reaction (ΔH) is finite, according to the equation $d(\ln K)/dt = \Delta H/\mathbf{R}T^2$, where K represents the equilibrium constant for the system. Similarly a pressure change at constant temperature[26] or a change in electric field (at constant temperature and pressure)[27] will be effective if the reactions involve a change in volume or electric polarisation respectively. These are thus called the *T*-jump, *P*-jump, and *E*-jump methods respectively. The subsequent internal reorganisation following a single stepwise disturbance may be followed either conductimetrically or spectrophotometrically.

(ii) *Stationary methods.* These are based on the stationary response of the internal chemical variable to periodic perturbation. In principle a steady oscillating function is applied across the solution and from the time lag between the disturbance and the system due to chemical relaxation, the relaxation time and hence the rate constants may be derived. Use has been made of sound waves[12,28] as the oscillating parameter to examine relaxations in $MgSO_4$,[29] $MnSO_4$,[30] and $BeSO_4$.[31]

C. Resonance Techniques.—Both n.m.r. and e.s.r. techniques have been used to study complex formation[32,33] and the aquation of metal ions[34] in solution. These techniques may be applied since the width of the resonance absorption line is related in n.m.r. to the lifetime of the nucleus in a given spin state and in e.s.r. to the lifetime of the paramagnetic species in a given energy state, and any reduction of the lifetime of these states by chemical interaction results in line broadening. Measurements are made of the increase in width of the lines corresponding to one reagent on addition of increasing amounts of the second.

The rates of exchange of several mono- and bi-dentate nitrogen and oxygen donor ligands co-ordinated to Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} have been measured by ^1H n.m.r. line-broadening studies.[35] The technique has also been recently applied to alkaline-earth complexes [36] and to ligand exchange involving phosphine ligands.[37]

[26] H. Strehlow and M. Becker, *Z. Electrochem.*, 1959, **63**, 457.
[27] M. Eigen and L. de Maeyer, *Z. Electrochem.*, 1955, **59**, 986; *Proc. Roy. Soc.*, 1958, **247A**, 505.
[28] M. Eigen, *Discuss. Faraday Soc.*, 1954, **17**, 194.
[29] G. Atkinson and S. Petruccio, *J. Phys. Chem.*, 1966, **70**, 3122.
[30] G. Atkinson and S. K. Kor, *J. Phys. Chem.*, 1965, **69**, 128.
[31] H. Diebler and M. Eigen, *Z. Phys. Chem. (Frankfurt)*, 1959, **20**, 299.
[32] G. Hertz, *Z. Electrochem.*, 1960, **64**, 53.
[33] R. G. Pearson and T. Buch, *J. Chem. Phys.*, 1962, **36**, 1277.
[34] R. E. Connick and R. E. Poulson, *J. Chem. Phys.*, 1959, **30**, 759.
[35] R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, 1964, **86**, 765.
[36] R. J. Kula and D. L. Rabenstein, *J. Amer. Chem. Soc.*, 1967, **89**, 552.
[37] W. De W. Horrocks and L. H. Pignolet, *J. Amer. Chem. Soc.*, 1966, **88**, 5929.

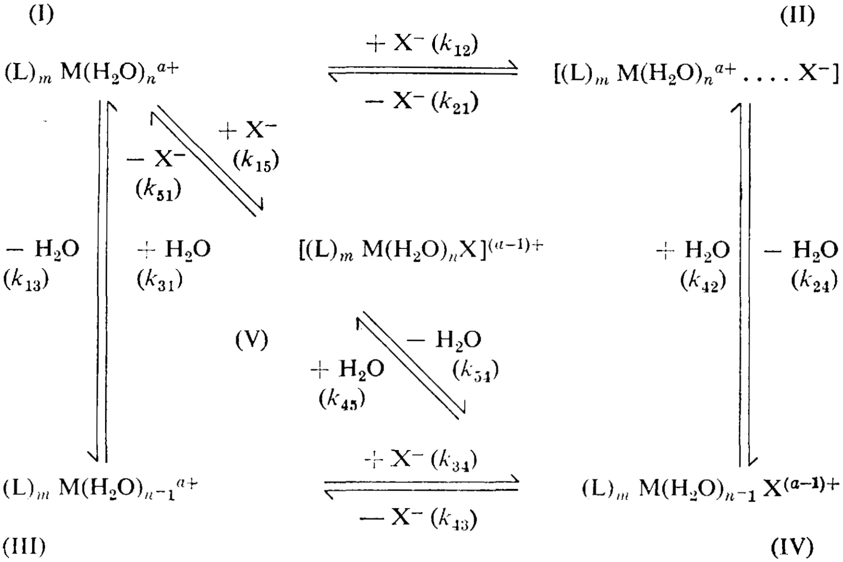
3 Mechanisms

For reactions of the type

$$(L)_mM(H_2O)_n{}^{a+} + X^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} (L)_mM(H_2O)_{n-1}(X)^{(a-1)+} + H_2O \qquad (1)$$

which are considered to take place in a series of steps, two extreme cases of nucleophilic substitution have been described. In the S_N1 displacement the rate-determining step is the removal of a ligand molecule from the inner co-ordination sphere of the complex to yield an intermediate of lower co-ordination number, whereas in bimolecular S_N2 reactions bond-making and-breaking are equally important and the intermediate has an increased co-ordination number. In practise, most reactions conform to neither of these categories, and in such cases a concerted interchange mechanism has been suggested.[6]

A possible reaction Scheme is shown. The route (I) → (III) → (IV) represents



Scheme

the extreme S_N1 condition (the Dissociative mechanism of Langford and Gray[6]). It has been suggested that in the anation reactions of $Co(CN)_5H_2O^{2-}$ (ref. 38) and $Co(NH_3)_5H_2O^{3+}$ (ref. 39) the species $Co(CN)_5{}^{2-}$ and $Co(NH_3)_5{}^{3+}$ are formed as intermediates in this limiting S_N1 mechanism and that these species may discriminate between various nucleophiles. Reactions of the type

$$Co(NH_3)_4SO_3(X)^{n+} + Y \rightarrow Co(NH_3)_4SO_3(Y)^{n+} + X$$

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[38] A. Haim, R. J. Grassi, and W. K. Wilmarth, ref. 8, p. 31; *Inorg. Chem.*, 1967, **6**, 237, 243.

[39] A. Haim and H. Taube, *Inorg. Chem.*, 1963, **2**, 1199.

where X = NH_3, OH^-, NO_2^-, or NCS^- and Y = OH^-, CN^-, NO_2^-, or NCS^- are all thought[40,41] to proceed *via* a mechanism involving the common intermediate $Co(NH_3)_4SO_3^+$.

Route (I) → (V) → (IV) represents the extreme S_N2 mechanism where in the increase in co-ordination number of the intermediate there is a symmetrical arrangement of the incoming and leaving groups. No unequivocal example of this type of reaction is known for octahedral complexes[1] but in the reaction of the square planar Rh^I species [Rh cod (SbR_3) Cl] with amines, *e.g.*

$$[\text{Rh cod }(SbR_3)\text{ Cl}] + \text{pyridine} \rightarrow [\text{Rh cod (pyridine) Cl}] + SbR_3$$

where cod = cyclo-octa-1,5-diene and R = *p*-tolyl, there is strong evidence for the formation of a five-co-ordinate intermediate.[42] Also in the reaction (dien = diethylenetriamine)

$$\text{Pt dien Cl}^+ + CN^- \rightarrow \text{Pt dien CN}^+ + Cl^-$$

there is thought to be little Pt—Cl bond dissociation in the transition state although displacement of the chlorine has occurred to allow Pt—CN interaction to develop.[43]

The third route, (I) → (II) → (IV), involves the formation of an outer sphere ion pair, and studies on the formation of complexes of inert ions such as cobalt(III)[44,45] have shown the importance of such species as intermediates in the formation of inner sphere complexes. The use of fast-reaction techniques has largely substantiated this view that outer sphere complexes are precursors and that there is only partial involvement of the ligand. It has been suggested[6] that this path involves an interchange mechanism which may be dissociative (I_d) or associative (I_a), depending on the nature of the species involved and on the transition state. In the I_d mechanism, the bonding in the transition state is weak to both the incoming and leaving groups, whereas in the I_a case, the entering group interacts (in the bonding) so as to play a part in the energy of the activated complex. In the latter case, the reaction rate is as sensitive to the variation of the entering group as to the variation of that which is leaving, whereas in the former a dependence on the leaving group would be expected. For many complexes in aqueous solution, the rate-determining step is considered to be the rate of elimination of a water molecule from the inner co-ordination sphere of the metal ion and its subsequent replacement by the ligand.

Tobe[46] has also shown the importance of ion pairing in reactions involving non-aqueous solvents. The rate of replacement of water in *trans*-[Co $en_2(H_2O)$

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[40] J. Halpern and R. A. Palmer, Proceedings of 9th International Co-ordination Chemistry Conference, St. Moritz, Switzerland, 1966, p. 354.

[41] J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, 1966, **88**, 2877.

[42] L. Cattalini, A. Orio, R. Ugo, and F. Bonati, *Chem. Comm.*, 1967, 48.

[43] C. H. Langford and H. B. Gray, 'Ligand Substitution Processess', Benjamin, New York, 1965, p. 46.

[44] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, 1963, **75**, 1463.

[45] C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, 1967, **89**, 3141.

[46] M. L. Tobe, in ref. 8, p. 7.

$(NO_2)]^{2+}$ by Cl^-, Br^-, and SCN^- in dimethylformamide, acetone, and sulpholan reaches a limiting value at high ligand concentrations. Under such conditions, the complex ion is considered to be present almost entirely as ion pairs and the reactions can be regarded as rearrangements of the ion aggregates, in that an inner sphere ligand interchanges with an outer sphere. Uni- or bi-molecularity then depends on whether or not the bond making and bond breaking processes are synchronous.

In the Scheme shown, for the path involving the formation of ion pairs, if k_{24} is the rate-determining step, it appears that the substitution is predominantly S_N1 (or I_d) in character. If K_0 ($= k_{12}/k_{21}$) is the equilibrium constant for the formation of the ion pair and if $k_{21} \gg k_{24}$, then the formation and dissociation rates of reaction (1) may be expressed as

$$k_f = k_{24}K_0 + \frac{k_{34} \cdot k_{13}}{k_{31} + k_{34}\ [X^-]} \text{ and } k_d = k_{42} + \frac{k_{43} \cdot k_{31}}{k_{31} + k_{34}\ [X^-]}$$

A possible distinction in the reaction paths has been suggested[5] in that if the route taken is (I) → (III) → (IV) the second term of the rate constants will be more important and a dependence of the rate constants on the concentration of the ligand would thus be observed. If the path is *via* species (I) → (II) → (IV) the first term in each constant will predominate. In this latter case, S_N1-type character would be evident, the first-order rate constant, k_{24}, being expressed as k_f/K_0. A three-step mechanism for complex formation has been suggested:[29] (*a*) the reacting ions come together in a diffusion-controlled process to yield a solvent separated ion pair; (*b*) the fast elimination of a water molecule from the ligand co-ordination sphere occurs; and (*c*) a water molecule is subsequently removed from the inner co-ordination sphere of the cation and replaced by the ligand.

In this mechanism, step (*b*) would depend on the solvent exchange rate of the ligand and step (*c*) on that of the metal ion. By use of ultrasonic techniques, three relaxation frequencies have been shown to occur in the formation of $MnSO_4$ (ref. 29) and $MgSO_4$ (ref. 30). The independence of the metal ion in step (*b*) and of the ligand in step (*c*) have also been demonstrated.[14]

The overall second-order rate constant (k_f) for reaction (1) will be dependent on the charges of the reactants. By calculating the ion-pair equilibrium constant, K_0, however, the rate constant k_{24} may be derived, and thus the reactions of the same metal ion with various ligand types can be compared. The equation[47,48] generally used in this case is

$$K = (4\pi Na^3/3000)e^{-U(a)/kT}$$

where $U(a)$ is the Coulomb energy, N Avogadro's number, k the Boltzmann constant, and a the distance of closest approach of the ions. This distance has

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[47] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

[48] M. Eigen, *Z. Electrochem.*, 1960, **64**, 115.

been taken[49–51] as 5Å. Good evidence for the unimolecular rate-determining step in these reactions has been produced in that whereas k_f varies from $2{\cdot}1 \times 10^6$ l.mole^{-1} sec.$^{-1}$ for reaction[52] of Ni^{2+} with $HP_2O_2^{3-}$ to 5×10^3 for the corresponding reaction[50] with $HC_2O_4^-$, the k_{24} values only vary by a factor of six.

A. Alkali-metal Ions.—These metal ions form complexes faster than any other ions of the Periodic Table. Owing to their low ionic charge and relatively large size, complexes are formed only with strongly interacting ions such as nitrilotriacetate, adenosine triphosphate, and amino-polycarboxylic acid anions.[53] Also since the complexes formed are weak, the rate studies must be carried out at high concentrations, where ionic atmosphere effects or additional ion-pairing may interfere. Sound absorption techniques have been used to determine the rate constants, which are very high: the first-order rate constants for the nitrilotriacetate complexes are given in Table 1. Substitution occurs most rapidly with Cs^+ and slowest for Li^+, which reflects the easier loss of a water molecule from the larger Cs^+ ion. The difference in rates over the series as a whole, however, is less than a factor of 10. It has been shown that the increase in rate on descending the series is a linear function of the ionic radius of the cation,[54] which confirms electrostatic character in the bonding (Figure 1).

In reactions with these multidentate ligands, it has been shown that the rates of the reaction depend to some extent on the nature of the chelating agent. The rate constants do not vary greatly for the formation reaction; the differences in stabilities of the complexes are reflected in the dissociation rates. These differences have been considered to be important in the active transport of ions across biological membranes.[53]

B. Alkaline-earth Ions.—Unlike the Group I ions, the alkaline-earth ions show a considerable variation in reaction rate. Whereas the reactions for divalent strontium and barium ions are almost diffusion controlled, and require to be studied by sound absorption techniques,[8] those of Be^{2+}, Mg^{2+}, and Ca^{2+} are markedly different and may also be examined by the temperature-jump method. [31,55] Values for the rate of water elimination are given in Table 1. No ligand specificity is seen[56] when the anionic charge is varied from -2 to -4, which indicates that the removal of a water molecule from the primary co-ordination sphere of the metal ion is the rate-determining step. There is some evidence[31] that the rate of water substitution in Be^{2+} is hydrogen-ion dependent, which indicates the reaction of a hydrolysed species. The difference in substitution rates between Ca^{2+} and Mg^{2+} is about three powers of 10 magnitude, and may

[49] R. G. Pearson and P. Ellgen, *Inorg. Chem.*, 1967, **6**, 1379.
[50] G. H. Nancollas and N. Sutin, *Inorg. Chem.*, 1964, **3**, 360.
[51] F. P. Cavasino, *J. Phys. Chem.*, 1965, **69**, 4380.
[52] G. G. Hammes and M. L. Morrell, *J. Amer. Chem. Soc.*, 1964, **86**, 1497.
[53] M. Eigen, *Pure Appl. Chem.*, 1963, **6**, 97.
[54] M. Eigen and K. Kustin, I.C.S.U. Review, Elsevier, Amsterdam, 1963, vol. 5, p. 106.
[55] H. Diebler, M. Eigen, and G. G. Hammes, *Z. Naturforsch*, 1960, **156**, 554.
[56] M. Eigen, *Adv. Chem. Co-ordination Compounds*, 1961, 371.

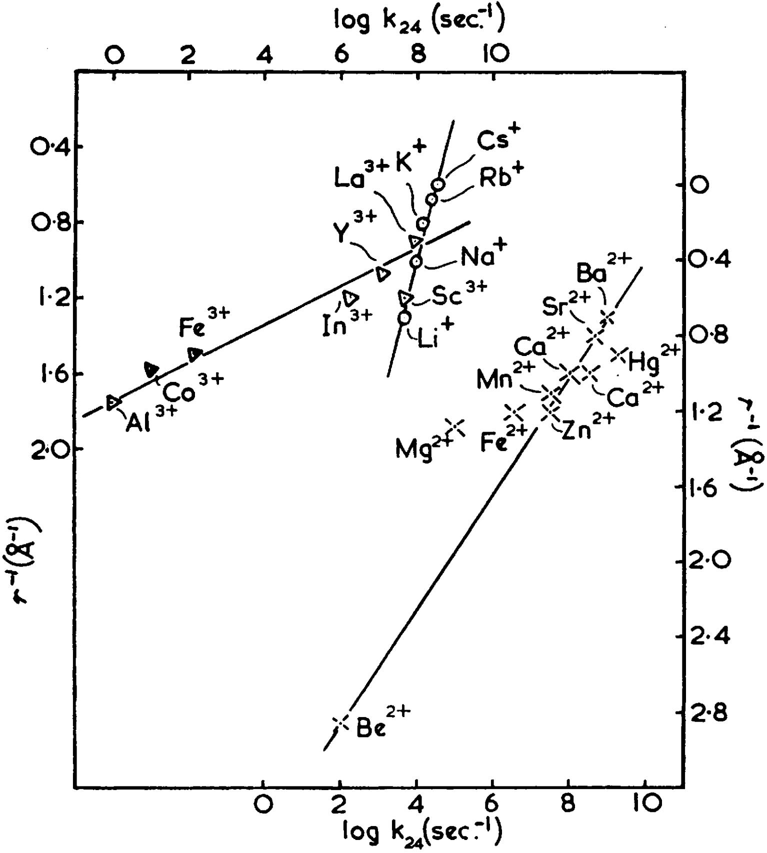

Fig 1 *First-order rate constants for monovalent, divalent, and trivalent cations as a function of ionic size.*

reflect a stronger bonding between the magnesium ion and the substrate. In the case of Ca^{2+}, Ba^{2+}, and Sr^{2+} the bonding is weak and the rates are a linear function of ionic radius, which suggests substantial electrostatic character (Figure 1). The bonding in Mg^{2+} (and Be^{2+}) complexes will, however, be considerably stronger, owing to the greater charge density on the metal ion. The rate differences between Ca^{2+} and Mg^{2+} have significance in the behaviour of these ions as enzymatic activators.[57]

It is of interest to compare these divalent ions with Zn^{2+}, Cd^{2+}, and Hg^{2+}, which have a d^{10} configuration. The order of reactivity of these ions: $Hg^{II} > Cd^{II} > Zn^{II}$ is contrary to the normal order in transition metals and may be explained in the absence of crystal field effects. For these ions, the complexing behaviour would be expected to differ from the alkali metal owing to observed differences in affinity to various ligands and an increasing preference in passing from zinc

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[57] M. Eigen and G. G. Hammes, *Adv. Enzymology*, 1963, **25**, 1.

to mercury(II) for the co-ordination number two. Such differences do not however appear to be too significant, since no ligand specificity is observed. The ions react at rates comparable to those of similarly sized alkaline-earth metal ions,[58] and a dependence of the rate on ionic size is again shown. The rate parameters for these ions follow fairly closely the radial dependence of the alkaline earths.

Reactions of halogen complexes of the type MX^+ and MX_2 ($M = Cd^{II}$, Zn^{II}, or Hg^{II}) with halide ions have been studied by n.m.r.[58] In the case of Cd and Zn, the rates are less than for the aquo-species but for Hg^{II} the reactions are at least as fast. Electric field measurements[59] confirm this in the case of chloromercury complexes. Reactions of the organometallic species MeHgOH with SO_4^{2-}, Cl^-, Br^-, and SCN^-, which are considered to be S_N2 in character show a marked decrease in rate,[60] probably due to the high energy needed to rearrange the molecule from the linear arrangement to the pseudo-octahedral trisubstituted transition state. This process has already been shown to involve a considerable entropy change for the Hg^{II} and Tl^{III} trichloro-complexes.[61,62]

C. Divalent Transition-metal Ions.—(i) *Octahedral complexes.* Most kinetic data refer to the first transition row, where for the divalent ions it is found that the rate data may be represented by the Scheme shown. The rates of exchange of a water molecule for the ions Mn^{II} to Cu^{II} have been found by n.m.r.[63] by Connick and his co-workers and the reactions of these metal ions with widely differing anions indicate that in general the rate of formation of the inner sphere complex is not too dependent on the nature of the incoming ligand. A recent article by Eigen and Wilkins[8] tabulates the formation data for such reactions.

Among divalent metal ions forming octahedral complexes, Co^{2+}, Fe^{2+}, and Mn^{2+} fit reasonably into the radius order shown by the alkaline-earth metals. The rate for Ni^{2+} is however about a power of 10 slower than that for Mg^{2+}, although the ionic radii are about the same, and the value for Cu^{2+} is very high. Few data are available for the early members of the first transition row but the d^3 configuration (V^{2+}) again reacts very slowly. Use has been made of the similarity of the exchange and complex formation rates to construct the order of reactivity of metal ions.[5]

$$V^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+} < Zn^{2+} < Cd^{2+} < Hg^{2+} < Cr^{2+} < Cu^{2+}$$

Figure 2 shows the variation of rate constant k_{24} as a function of the number of d electrons in this series.

The slow rates of Ni^{2+} and V^{2+} may be interpreted in terms of crystal field stabilisation energy,[1] whilst the high rates of Cr^{2+} and Cu^{2+} have been attributed

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[58] H. G. Hertz, *Z. Electrochem.*, 1961, **65**, 36.

[59] M. Eigen and E. M. Eyring, *Inorg. Chem.*, 1963, **2**, 636.

[60] M. Eigen, G. Geier, and W. Kruse, in Essays in Co-ordination Chemistry, Birkhauser Verlag, Basle, 1964, p. 164.

[61] P. K. Gallacher and E. L. King, *J. Amer. Chem. Soc.*, 1960, **82**, 3510.

[62] M. J. M. Woods, P. K. Gallacher, Z. Z. Hugus, E. L. King, *Inorg. Chem.*, 1964, **3**, 1313.

[63] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.

to Jahn–Teller distortion of the octahedral structure. In these cases the axial water molecules are held less rigidly than those in the equatorial positions and exchange more rapidly with the solvent. Also an inversion process in which the axial positions become equatorial and two of the equatorial become axial has been used to describe the exchange process for the equatorial positions.[5] A recent study of the Cr^{2+} ion with bipyridyl[64] has confirmed that the rate of replacement of the axial water molecules is fast but at higher ligand concentrations, a second relaxation effect was slow, probably owing to the reaction between $Cr\,bipy^{2+}$ with a second bipyridyl molecule, with a rate constant of $10^5 M^{-1}$ sec.$^{-1}$ If chelation stabilised the system and prevented rapid interconversion the second reaction would be expected to be slow. No evidence has as yet been seen for a similar second step in the corresponding copper system. There is some evidence, however, that the water replacement in Cu^{II} is relatively slow when chelation prevents the inversion process from occurring.[65,66] The effect of other ligands on the rate of substitution of the remaining co-ordinated water molecules has been investigated for Ni^{II} complexes with N and O donor ligands (L).[67,68] The overall charge of the nickel complexes was varied from + 2 to − 2 and it was found that for the reaction

$$(H_2O)NiL^{y+} + NH_3 \xrightarrow{k_f} (H_3N)NiL^{y+} + H_2O$$

the values of k_f for complexes of the same charge varied markedly with the number of nitrogen atoms attached, which suggested an increase in lability of the complex when nitrogen atoms were co-ordinated rather than the oxygens of carboxylate groups.

In reactions where there is successive replacement of water molecules, *e.g.* in multidentate chelate formation, it is generally considered that the rate of elimination of the first water molecule is the rate-determining step.[69] The effects of the other donor atoms of the chelating agent have also been considered, *e.g.* the increase in rate of formation of nickel(II) polyammine complexes compared with the corresponding monoammine species has been interpreted as the result of internal hydrogen bonding between one nitrogen of the polyammine and a co-ordinated water molecule in an 'internal conjugate base' mechanism.[70] The hydrogen-bond formation is considered to impart at least partial hydroxide character to the co-ordinated water, causing a labilising of an adjacent *cis* water molecule, which is more easily replaced by another non-hydrogen-bonded nitrogen atom. Involvement of this type has also been demonstrated in the formation of the bisterpyridine complexes of Fe^{II}, Co^{II}, and Ni^{II}.[71] Although the

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[64] H. Diebler, personal communication.

[65] D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, 1964, **3**, 382.

[66] D. W. Margerum and R. K. Stenhaus, *J. Amer. Chem. Soc.*, 1965, **87**, 4643.

[67] D. W. Margerum, ref. 8.

[68] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 1088.

[69] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 1962, 4208.

[70] D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891.

[71] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 1966, **5**, 622.

water exchange rate for the Ni terpy^{2+} ion is similar to that of the aquated nickel ion, the rate of formation of the bis-complex from the mono-species is 200 times faster than expected, and it is concluded that either the ammine ligand takes part in an S_N2 attack on the complex ion or it is able to form a strong adduct ($K_0 \gg 1$) prior to formation of the inner sphere complex. If, however, the five-co-ordinate intermediate (see Scheme) were stabilised by the three nitrogen atoms, then some ligand specificity might be expected.

At present there is a dearth of data for reactions in non-aqueous solvents. Most studies to date in these media have been made by use of n.m.r. techniques with Co^{2+} and Ni^{2+} ions. Oxygen-17 data for the *NN*-dimethylformamide (DMF),[72] ^1H data for the methanol,[73] and ^{14}N data for the ammonia exchanges[74] have been obtained. The exchange rate order for both ions is $NH_3 > H_2O > DMF > MeOH$ and a dissociative mechanism has been postulated which is dependent on M—L bond energies, solvation differences between the ground and transition states, and the steric requirements of the different ligands. These conclusions have been confirmed by a study of the Ni^{2+} complexes with phen, tripy, SCN^-, $SeCN^-$, maleonitrilodithiolate, and dithioloxalate, where the k_{24} value in methanol is shown to be about 4 times lower than that in aqueous systems.[75]

(ii) *Five-co-ordinate complexes.* Considerably less work has been carried out on these systems than on the octahedral or square planar complexes. One study[76] involves the reactions of Pt^{II} complexes containing the tetradentate ligand tris-(*o*-diphenylarsinophenyl)arsene (q.a.s.) and either a halide or thiocyanate ion. The nature of the ligand is such as to impose a pseudo-trigonal bipyramidal configuration on the complex. Substitution rates were measured in ethanol. The reactions

$$PtX(qas)^+ + Y^- \rightarrow PtY(qas)^+ + X^-$$

where $Y = CN^-$, thiourea, SCN^-, or I^- were studied by use of a stopped-flow method and extensive ion pairing is considered to take place. The order of reactivity of nucleophiles is similar to that for Pt^{II} square planar complexes with the exception of triphenylphosphine, which reacts more slowly with the five-co-ordinate complex, possibly as a result of steric hindrance. The transition state in these reactions may be quasi-octahedral since stable complexes of the type $[MX_2(qas)]^{2+}$ have been isolated[77,78] and $[RuBr_2(qas)]^{2+}$ has been shown to have bond angles between 82 and 98°.

(iii) *Square planar complexes.* The reaction rates of these complex ions usually depend on the nature and concentration of the reagent and in this respect they differ from octahedral species which generally react through predominantly dissociative processes. By far the most stable complexes are those of Pt^{II} (ref. 2),

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[72] J. S. Babiec, C. H. Langford, and T. R. Stengle, *Inorg. Chem.*, 1966, **5**, 1362.
[73] Z. Lug and S. Meiboom, *J. Chem. Phys.*, 1964, **40**, 2686.
[74] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and P. Hunt, *Inorg. Chem.*, 1965, **4**, 206.
[75] T. J. Connocchioli, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1.
[76] R. G. Pearson, M. M. Muir, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 5521.
[77] G. A Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 1961, 170.
[78] J. G. Hartley, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc.*, 1963, 3930.

and other d^8 systems such as Ni^{II} and Pd^{II} have also been examined, together with Au^{III} (refs. 79, 80), Rh^{I} (refs. 42, 81), and Ir^{I} (ref. 82) species. Although the chemistry of these complexes has been dominated by the *trans* effect,[1] during the last decade considerably more work has been done on their reaction mechanisms.

In the vast majority of cases so far examined, the substitutions are bimolecular displacements and evidence cited[1] to support this includes the fact that in these reactions there is retention of configuration and a rate dependence on the entering ligand, steric effects are important, and five co-ordinate species involving d^8 ions have been isolated. In all cases for reactions of the type

$$PtA_2LX + Y \rightarrow PtA_2LY + X$$

there is retention of configuration. This would be unlikely if a dissociative process occurred, whereas the formation of a five-co-ordinate trigonal bipyramid in the activated complex would explain the observed stereospecificity.

The kinetics for reactions of these complexes obey a two-term rate law, *e.g.* where k_{obs} is the observed rate constant,

$$k_{obs} = k_1 \,[\text{complex}] + k_2 \,[\text{complex}]\,[Y] \qquad (2)$$

where Y is a nucleophile. This has been interpreted[2,6] as two simultaneous reactions, one with the solvent as the incoming nucleophile (k_1) and the second with Y as nucleophilic reactant (k_2). According to equation (2) a plot of k_{obs} against [Y] should be linear with intercept independent of Y. Plots of this type are common for square planar reactions.[2] In general $k_1 \ll k_2$ and is the rate constant for reaction with the solvent, which is then rapidly displaced by Y. The role of solvent as an intermediate has been demonstrated in the following way.[83] The reactions of various nucleophiles with the complex Pt dien H_2O^{2-} were examined, *e.g.*

$$\text{Pt dien } H_2O^{2+} + Y^- \rightarrow \text{Pt dien } Y^+ + H_2O \qquad (3)$$

and then with water as solvent the reactions

$$\text{Pt dien } X^+ + Y^- \rightarrow \text{Pt dien } Y^+ + X^- \qquad (4)$$

were studied. If the first term (k_1) is the solvent reaction, then all the rates for equation (3) should be greater than for equation (4); this was observed.

There are several complexes which do not conform to the two-term law,[84] *e.g.* $[M(Et_4\,\text{dien})X]^{n+}$ where $M = Pt^{II}, Pd^{II}$, or Au^{III} and $X = OH^-, Cl^-$, or Br^-. In this case the four ethyl groups in the triamine may shield the metal from nucleophilic attack and a solvent-assisted dissociation reaction may take place.

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[79] R. L. Rich and H. Tank, *J. Phys. Chem.*, 1954, **58**, 1.
[80] W. H. Baddley and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1087.
[81] A. Wojciki and F. Basolo, *J. Amer. Chem. Soc.*, 1961, **83**, 525.
[82] L. Vaska, *Science*, 1963, **140**, 809.
[83] H. B. Gray and R. J. Olcott, *Inorg. Chem.*, 1962, **1**, 481.
[84] C. F. Weick and F. Basolo, *Inorg. Chem.*, 1966, **5**, 576.

The nature of the intermediate in these reactions is fairly well characterised and an I_a mechanism may hold in most cases. Only in a few cases is there definite evidence for an intermediate,[42] but many five-co-ordinate d^8 complexes are known. Although crystal field considerations would predict a square pyramidal structure in that to go from a square plane to a square pyramid involves less energy than to go to the trigonal bipyramid—the difference is *ca.* 4 Dq units[1]—the trigonal bipyramid is favoured as the structure of the intermediate. In this configuration the mutual repulsion of the five ligands is less than for a square pyramid and strong π-bonding in the trigonal plane may be important. Also the five-co-ordinate rhodium(I)[85] and platinum(II)[86] complexes isolated have trigonal bipyramidal structures.

Thermodynamic parameters involved in these reactions have also been used to yield an insight into the nature of the transition state. Temperature studies[87] of reaction (4) in water indicate that the activation energies fall into two group types for varying X^-. E_a changes in the order $Cl^- \sim Br^- \sim I^- \ll N_3^- \sim NO_2^- < SCN^- < CN^-$. In the case of the halide ions, the rates are almost independent of the leaving group, which suggests that the Pt—X bond rupture is not kinetically important, whereas for the other ligands which are more difficult to displace there is a marked dependence on the leaving group and here the Pt—X bond breaking is considered the rate-determining step, which takes place after the involvement of the incoming ligand. The fact that in all cases studied the entropies of activation are all negative has been interpreted to mean that the transition state is formed with a net increase in bonding.[1] However, a plot of ΔH^* against ΔS^* for both types of ligand gives the same straight line, which suggests a common overall mode of reaction, and that bond formation with the incoming nucleophile is extensive in all cases.

For complexes of the type Pt dien X^+ use of either k_1 or k_2 gives the order of decreasing reactivity of different X groups: $NO_3^- > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$, which parallels both the bond order and the position of these groups in the *trans* effect series.[88]

(iv) *Tetrahedral complexes.* To date, two studies of exchange rates of divalent metal tetrahedral complexes have been made. The exchange of 2-methylpyridine (2-pic) in the reaction

$$\mathrm{Co\,(2\text{-}pic)_2Cl_2 + 2\text{-}pic^* \rightleftharpoons Co(2\text{-}pic)\,(2\text{-}pic^*)Cl_2 + 2\text{-}pic}$$

has been studied[89] at low temperature (— 30 to — 60°) and the triphenylphosphine exchange in $M(PPh_3)_2X_2$ where M = Ni or Co and X = Br or I has been examined at room temperature.[37] When temperature effects are allowed for, the phosphine exchange is slower than that of the pyridine, but in all cases there is a negative entropy of activation, which suggests a five-co-ordinate transition state.

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[85] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

[86] R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stollberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

[87] U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, 1966, **5**, 591.

[88] F. Basolo, H. B. Gray, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 4200.

[89] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1967, **89**, 4319.

The reactions are all second order, which indicates the participation of the free ligand in the activated complex in contrast to the dissociative mechanism for octahedral species.

D. Trivalent Metal Ions.—These ions have been much less studied than the corresponding divalent species. The rates are slower than for the M^{2+} ions, which reflects the greater energy required for the removal of a water molecule in an S_N1 process. Extensive hydrolysis may also take place with those higher charged species and, since some of the ions are oxidants, subsequent internal redox reactions within the complexes may occur.[23,75] The earlier members of the first row have been examined; the low rate for Cr^{3+} is ascribed to ligand field effects.[1] Unlike the M^{2+} ions, however, some of the reactions (*e.g.* those of Fe^{3+}) appear to be dependent on the nature of the ligand;[90] the rate increases with increasing basicity of the anion. The corresponding hydroxy-species react faster than the aquated metal ion.[23,75] The high lability of the cobalt(III) ion may be due to the reaction of a high-spin complex and in this case there appears to be much less ligand specificity. Reactions with malic[23] and thiomalic [91] acids and chloride[75] show k_{24} values differing by less than a factor of 5. In the corresponding thiosemicarbazide[92] reaction the bonding in the complex appears to be through the nitrogen atoms, since the complex formed is stable whereas the others all undergo rapid electron-transfer reactions. The reaction of V^{3+} with SCN^- has recently been examined[93] and the comparatively low activation energy involved attributed to more S_N2 character in this system. Unlike the spin-free Fe^{3+}, V^{3+} has available an orbital which could be involved in bonding with the entering ligand, thus lowering the energy requirements. The reaction rate for Ti^{3+} with thiocyanate is about 40 times greater than for V^{3+} (ref. 64), whilst that for Sc^{3+} with murexide[94] has been measured with a *T*-jump apparatus. The formation rate of the complex between Mn^{3+} and H_2O_2 has been obtained by flow methods.[95] The reactivity of these transition metal ions is, however, quite similar to that of the divalent ion with the same number of *d* electrons (Figure 2). Clearly more data are required to complete the picture but it would appear that Cu^{III}, a d^8 system, should be a fairly inert ion. Temperature-jump methods have also been used to characterise other trivalent cations with a d^0 configuration, *e.g.* La^{3+}, Y^{2+}, In^{3+} (ref. 94). The reaction rates are high but show a linear dependence on the ionic radius (Figure 1).

Complex formation involving these ions appears to be determined largely by the loss of a water molecule in a dissociative mechanism; the order of reactivity of hexa-aquo-ions is $Rh^{3+} < Cr^{3+} < Co^{3+} < V^{3+} \sim Fe^{3+} < Ti^{3+} < Mn^{3+}$. This order is maintained in the trisoxalato-complexes both for racemisation and

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[90] F. Accassina, F. P. Cavasino, and S. D'Alessandro, *J. Phys. Chem.*, 1967, **71**, 2474.

[91] J. Hill and A. McAuley, *J. Chem. Soc.* (*A*), 1968, 2405.

[92] U. D. Gomwalk and A. McAuley, unpublished results.

[93] B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, 1967, **6**, 1948.

[94] G. Geier, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 617.

[95] G. Davies, L. J. Kirchenbaum, and K. Kustin, *Inorg. Chem.*, 1968, **7**, 146.

aquation reactions and agrees with that calculated from crystal field considerations regardless of whether a dissociative or associative pathway is used.[96]

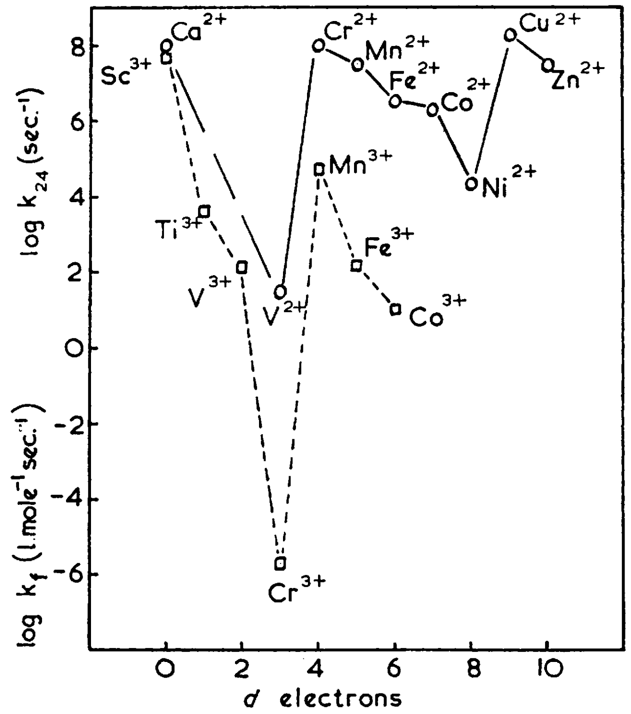

Fig. 2 *Comparison of the rates of divalent and trivalent metal ions with various* d *electron configurations.*

Table 1 *First-order rate constants (k_{24}) for complex formation of various metal ions*

$0^7\ k_{24}$(sec.$^{-1}$)$^{a,\,b}$		k_{24}(sec.$^{-1}$)$^{a,\,c}$		k_{24}(sec.$^{-1}$)	
Li^+	4·7	Be^{2+}	10^2	V^{2+}	30 [d]
Na^+	8·8	Mg^{2+}	10^5	Cr^{2+}	10^8 [d]
K^+	15	Ca^{2+}	10^8	Mn^{2+}	3×10^7 [e]
Rb^+	23	Sr^{2+}	5×10^8	Fe^{2+}	3×10^6 [e]
Cs^+	35	Ba^{2+}	9×10^8	Co^{2+}	2×10^6 [e]
		Cd^{2+}	5×10^9	Ni^{2+}	2×10^4 [e]
		Hg^{2+}	3×10^9	Cu^{2+}	2×10^8 [e]
		Pb^{2+}	6×10^8	Zn^{2+}	3×10^7 [d]

[a] Ref. 8. [b] Reaction with nitrilotriacetate. [c] At 25°. [d] Ref. 64. [e] Calculated from K_0 values derived from expression (2) by use of data from ref. 8.

[96] R. W. Oliff and A. L. Odell, *J. Chem. Soc.*, 1964, 2417.

Table 2 *Rate constant (k_f) for complex formation involving trivalent metal ions*

Al^{3+}	1 [a]	Ti^{3+}	$4\cdot0 \times 10^3$ [c,d]	Ce^{3+}	9·5 [h]	Tb^{3+}	3·0
Sc^{3+}	5×10^7 [b]	V^{3+}	$1\cdot1 \times 10^2$ [c,e]	Pr^{3+}	8·6	Dy^{3+}	1·7
La^{3+}	7×10^7 [b]	Cr^{3+}	$1\cdot8 \times 10^{-6}$ [c,e]	Nd^{3+}	9·3	Ho^{3+}	1·4
Y^{3+}	$1\cdot3 \times 10^7$ [b]	Fe^{3+}	$1\cdot3 \times 10^2$ [c,e]	Sm^{3+}	9·6	Er^{3+}	1·0
In^{3+}	2×10^6 [b]	Co^{3+}	10 [f]	Eu^{3+}	8·2	Tm^{3+}	1·1
		Mn^{3+}	$5\cdot0 \times 10^4$ [g]	Gd^{3+}	5·2	Yb^{3+}	1·1
						Lu^{3+}	1·3

[a] Ref. 54. [b] Ref. 94; at 12°. [c] Reactions with NCS^- ion. [d] Ref. 64; at 8°. [e] Ref. 93. [f] Ref. 23; at 15°. [g] Ref. 95; reaction with H_2O_2. [h] Lanthanide data (× 10^{-7}), from ref. 94.

The investigation of substitution reactions of trivalent metals has been largely dominated by studies on cobalt(III) low-spin complexes.[1,6] The effects of other groups in the co-ordination sphere have been examined and have been used to describe the mechanisms involved. In the case of the anation reaction

$$Co(CN)_5(H_2O)^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(CN)_5{}^{2-} + H_2O$$

$$Co(CN)_5{}^{2-} + X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co(CN)_5X^{3-}$$

there is a dependence of the rate on X^- and these systems are considered to react *via* an S_N1 mechanism.[38] In the case of substitution of N_3^- by NCS^- in $[Co(CN)_5N_3]^{3-}$, however, the intermediate $[Co(CN)_5H_2O]^{2-}$ is not produced first and H_2O and NCS^- compete in reactivity for the $Co(CN)_5{}^{2-}$ species. In the formation of the five-co-ordinate intermediate, it is thought that the negatively charged cyanide ligands produce a high electron density round the cobalt atom which tends to weaken the Co—H_2O bond.[97] A limiting S_N1 mechanism has also been proposed[39] for the anation of $Co(NH_3)_5H_2O^{3+}$, and the complex ion $Cr(OH_2)_5{}^{3+}$ is produced in the substitution reactions[98] of $Cr(OH_2)_5I^{2+}$. In its reaction with Br^- and Cl^- no evidence is seen for the formation of the hexa-aquochromic ion.

For other cobalt(III) complexes the situation is not completely resolved, since many reactions involve hydrolyses where the role of the solvent is not unambiguously known. Attempts have been made to change the nature of the ions being released and to vary the substituents on non-involved ligands but in general no specific conclusions have emerged. In the reactions of a series of chloroammine complexes (am = ammine), the loss of chloride from $Co\,am_2Cl_2{}^+$ is about 100 times faster[99] than for $Co\,am_2(OH_2)Cl^{2+}$, in keeping with a dissociation mechanism.

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[97] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 573, 583.
[98] M. Ardon, *Inorg. Chem.*, 1965, **4**, 372.
[99] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 1955, **59**, 304.

Tobe and his co-workers[100] have examined a series of systems of the type

$$\text{Co en}_2\text{LCl}^+ + H_2O \rightarrow \text{Co en}_2\text{L}(H_2O)^{2+} + Cl^-$$

where L = OH^-, N_3^-, Cl^-, Br^-, NCS^-, NH_3, H_2O, or NO_2^-, and suggested that the mechanism involved is dependent on group L. If L has a tendency to donate electrons to the cobalt atom in some π-interaction, then the Co—Cl bond may be more easily broken and a *quasi*-five-co-ordinate intermediate stabilised. Strongly basic ligands such as OH^- or N_3^- are believed to react *via* an S_N1-type mechanism. Similar effects have been observed with the corresponding bromo-complexes.[101] In all cases there is 100% retention of configuration for *cis* complexes, which supports the mechanism. For electron-withdrawing groups such as NO_2^-, however, there is a withdrawal of electrons from the cobalt atom (to a greater extent in the *trans*- than in the *cis*-isomer), so rendering it more susceptible to attack by the solvent in an S_N2 process. Attempts to clarify the situation by working in non-aqueous solvents have indicated the presence of extensive ion-pairing.[46]

These reactions are probably best described by use of the interchange terminology of Langford and Gray,[6] where the hydroxy-complexes would react by an I_d mechanism and the nitro-species by an I_a reaction. Recently Langford[45] has extended the concept to the formation rates of $Co(NH_3)_5X^{n+}$, with special attention to the reaction rate of the ion pair $Co(NH_3)_5OH_2^{3+} \ldots X^{(3-n)-}$. For all anions so far studied, the reaction rates are similar and are a constant fraction (20%) of the water exchange rate for $Co(NH_3)_5OH_2^{3+}$. The mechanism is considered to be I_d, with the entering and leaving groups weakly bound, but where there is no intermediate of significant lifetime. The anion entry rates appear to be related to the water exchange rate through a statistical factor connected with the probability that an anion is found in an outer co-ordination sphere site when a Co—H_2O dissociation occurs.

That the anion in these reactions is in the transition state in a solvated form has been demonstrated.[102] A plot of log k (rate constant) against pK_{eq} for the reaction

$$Co(NH_3)_5H_2O^{3+} + X^- \rightleftharpoons Co(NH_3)_5X^{2+} + H_2O$$

shows good linearity for X = F^-, $H_2PO_4^-$, Ce^-, Br^-, I^-, or NO_3^-,which indicates that bond breaking is much more important than bond making in the activated complex.

E. Metal Ions in Other Oxidation States.—Substitution reactions of Cr, Mo, and W hexacarbonyls by phosphine and phosphite ligands L in decalin as solvent, *e.g.*

$$M(CO)_6 + L \rightarrow M(CO)_5L + CO$$

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[100] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4803; M. E. Baldwin, S. C. Chan, and M. L. Tobe, *ibid.*, 1961, 4673; M. L. Tobe, *Sci. Progress*, 1960, **48**, 483.

[101] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 5700; C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, 1960, **187**, 477.

[102] C. H. Langford, *Inorg. Chem.*, 1965, **4**, 265.

have been examined.[103] The rate law is of the form

$$\text{rate} = k_1[\mathrm{M(CO)_6}] + k_2\,[\mathrm{M(CO)_6}]\,[\mathrm{L}]$$

and S_N1 and S_N2 mechanisms are proposed to account for the two paths, in that there is a positive ΔS^* for k_1 and a negative ΔS^* for k_2. The S_N2 path is preferred in the order Cr < Mo < W. In the replacement of olefin in dicarbonylcyclopentadienyl(olefin)manganese by amine or phosphine[104] the slow step is the dissociation of the olefin and an S_N1 mechanism is suggested. The reaction of the five-co-ordinate complex $Fe(CO)_4(PPh_3)$ with PPh_3 is also considered to be S_N1,[105] whereas the substitution reaction of $Mn(NO)(CO)_4$ in anhydrous *p*-xylene with PPh_3, $AsPh_3$, and $P(OPh)_3$ are S_N2 processes.[106] This is supported by the negative entropy of activation, which implies a net increase in the bonding in the formation of the transition state, which is considered to be octahedral.

F. Lanthanide Ions.—Few data are available for these ions but studies have been made on some of the sulphates by use of ultrasonic techniques[107] and on the complexes with murexide.[94] The values obtained differ by less than a factor of 10, probably owing to ionic strength and temperature effects. An apparent variation in the data is that whereas the k_f values for the sulphate complexes pass through a minimum at about gadolinium, those of murexide show a minimum at erbium. Ligand field effects for these ions are not considered to be great, owing to deep penetration of the 4*f* electrons into the core of the ion, and increases in stability of less than 10% have been suggested.[108] Attempts to include the rate data for these ions in electrostatic correlations based on a function of the radius (*e.g.* Figure 1) show no linearity, and it is proposed[107] that this is owing to a change in environment of the ion on crossing the series. It is considered that there is an increase of one water molecule in the co-ordination sphere around the middle of the series. In the case of Gd^{3+}, for example, a co-ordination number of 8·5 would mean a distribution of 50% $Gd(H_2O)_9{}^{3+}$ and 50% $Gd(H_2O)_8{}^{3+}$ of approximately equal energy. The reaction step involving the ready loss of the water molecule between these two species would then account for the enhanced reaction rate.

4 Conclusions

The systems most studied to date have involved reactions of transition metals with particular reference to octahedral and square planar substitutions. Emphasis has also been placed largely on the first row of the transition series. While there is a need for development of experiments involving these systems to elucidate reaction mechanisms, there are clearly other areas which will prove fruitful for study. Relatively little work has been done on the second and third row transi-

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[103] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, 1967, **6**, 2083.
[104] R. J. Angelici and W. Loewen, *Inorg. Chem.*, 1967, **6**, 682.
[105] E. E. Siefert and R. J. Angelici, *J. Organometalic Chem.*, 1967, **8**, 374.
[106] H. Wawersik and F. Basolo, *J. Amer. Chem. Soc.*, 1967, **89**, 4626.
[107] N. Purdie and C. A. Vincent, *Trans. Faraday Soc.*, 1967, **63**, 2745.
[108] T. M. Dunn, ref. 3, p. 286.

tion-metal ions,[1] although polymeric species in some cases may prove difficult. The dearth of data available for non-aqueous solvents is apparent, although n.m.r. methods are already being used in this connection.[89] An extension of studies to tetrahedral and five-co-ordinate systems is desirable and here reactions in the organometalllic field may prove helpful. The lanthanides require further investigation as do the non-transition metals. In this respect, studies have been made in silicon complex hydrolyses[109] and in germanium chemistry.[110] The role of metal ions in enzymic systems is another challenging field where the nature of the metal ion may not completely correspond to that in simple model systems.[111–113]

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[109] R. G. Pearson, D. N. Edgington, and F. Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 3234.
[110] R. H. Prince and R. E. Timms, *Inorg. Chim. Acta.*, 1967, **1**, 129.
[111] D. N. Hague and M. Eigen, *Trans. Faraday Soc.*, 1966, **62**, 1236.
[112] P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, 1968, **64**, 977.
[113] R. J. P. Williams, *Roy. Inst. Chem. Rev.*, 1968, vol. 1.