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THE MECHANISM OF OCTAHEDRAL COMPLEX FORMATION BY LABILE METAL IONS*

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CONTENTS

A. INTRODUCTION

The replacement of a solvent molecule bound to a metal ion by another molecule, which may be the same (solvent exchange) or different (complex formation), is one of the fundamental reactions of metal ions in solution. Such reactions are important elementary steps in a wide range of processes. Inner-sphere redox

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* No reprints of this paper are available.

reactions involve an initial substitution step, and catalysis by metal ions often involves a substitution reaction of a solvated ion. Again, in biological systems substitution at a partially or completely solvated metal ion is often an important feature of metalloenzyme or coenzyme function. In less direct ways such substitution processes may be important, for example, when metal ions are transported through and along a membrane of lipid or protein, the membrane, containing potentially coordinating groups, may be regarded as a giant, relatively immobile, polydentate ligand, the metal ion moving from one coordinating site or group of sites to another.

A number of simple mechanistic possibilities arise when the two reactants, solvated ion and solvated ligand, react to give a complex. We note at the outset that it is almost always assumed that the solvation shell of the ligand is orders of magnitude more labile than that of the metal ion. Admitting this assumption we may write the possible ligand interchange mechanisms available to an aquometal ion as in the scheme below.

Possible mechanisms for ligand substitution in an aquocation

$$\underset{\text{solvated ion}}{\mathrm{M(OH_2)}_n^{z+}\,\mathrm{aq}} + \underset{\text{solvated ligand}}{\mathrm{L(OH_2)}_m^{z'-}\,\mathrm{aq}} \longrightarrow \underset{\text{solvated complex}}{\mathrm{ML(OH_2)}_{m+n-p}^{(z-z')+}} + p\mathrm{OH_2}$$

(*A*) Reaction via an intermediate of reduced coordination number

$$\mathrm{M(OH_2)}_n^{z+}\,\mathrm{aq} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \mathrm{M(OH_2)}_{n-1}^{z+}\,\mathrm{aq} + \mathrm{OH_2}$$

$$\mathrm{M(OH_2)}_{n-1}^{z+}\,\mathrm{aq} + \mathrm{L(OH_2)}_m^{z'-}\,\mathrm{aq} \xrightarrow{k_{23}} \mathrm{ML(OH_2)}_{m+n-p}^{(z-z')+}\,\mathrm{aq} + (p\text{–}1)\,\mathrm{H_2O}$$

(*B*) Reaction via an outer-sphere association between ion and ligand

$$\begin{array}{ll} \mathrm{M(OH_2)}_n^{z+}\,\mathrm{aq} + \mathrm{L(OH_2)}_m^{z'-} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} & [\mathrm{M(OH_2)}_n - \mathrm{L(OH_2)}_m\,\mathrm{aq}]^{(z-z')+} \\ & \quad k_{32} \upharpoonleft\!\downharpoonright k_{23} \\ & \quad \mathrm{ML(OH_2)}_{m+n-p}^{(z-z')+}\,\mathrm{aq} \end{array}$$

(*C*) Reaction goes via an associative displacement process

$$\begin{array}{ll} \mathrm{M(OH_2)}_n^{z+}\,\mathrm{aq} + \mathrm{L(OH_2)}_m^{z'-} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} & \left[(\mathrm{H_2O})_{n-1}\mathrm{M}\begin{array}{l} \diagup \mathrm{L(OH_2)}_{m-x} \\ \\ \diagdown \mathrm{OH_2} \end{array}\right]\mathrm{aq} \\ & \qquad\qquad \downarrow k_{23} \\ & \qquad\qquad \mathrm{ML(OH_2)}_{m+n-p}^{(z-z')+}\,\mathrm{aq} \end{array}$$

(*D*) Reaction is preceded by proton transfer from aquocation to ligand prior to the act of substitution

$$\mathrm{M(OH_2)}_n^{z+}\,\mathrm{aq} + \mathrm{L(OH_2)}_m^{z'-}\,\mathrm{aq} \underset{\text{fast}}{\rightleftarrows} \mathrm{M(OH)}\ (\mathrm{OH_2})_{n-1}^{(z-1)+} + \mathrm{HL(OH_2)}_x^{(z-1)-}\ \mathrm{aq}$$

The hydroxocation may then react with the conjugate acid of the ligand by any of the mechanisms *A*, *B*, or *C*.

All these mechanisms show some ligand dependence, even mechanism (*A*) for which the general expression is:

$$k_{\text{obs}} = \frac{k_{12}[\text{M}]}{k_{23}[\text{L}]+k_{21}}$$

General statements of the rate effects of charge, z and z', and metal and ligand size on mechanisms (*A*) and (*C*) are well-documented[1]; such effects on (*B*) are not simple and for (*D*) we note that this mechanism will be favoured by increasing acidity of the aquocation, *i.e.* small size and large z, and by increasing basicity of the ligand.

Often the rate expression for complex formation is the sum of terms such as: Rate $= k[\text{M}]\,[\text{L}]+k'[\text{M}]\,[\text{L}]\,[\text{H}^+]^{-1}+\ldots$ Although each term of such an expression is usually assumed to correspond to a single mechanism there is no *a priori* restriction upon the number of mechanisms and the rate expression as a whole indicates only the minimum number of mechanisms available to the ion. The ion will react by that route having the least activation free energy, $\Delta G^{\pm}$, but if there is more than one route of similar $\Delta G^{\pm}$ then reaction can occur by more than one mechanism simultaneously provided that the latter are consistent with the observed order in metal and ligand. Also, as the ligand is changed the mechanism may well change, *e.g.*, with a series of ligands of increasing basicity we should expect mechanism (*D*) to become progressively more important.

The substantial literature which has accumulated rapidly since 1963–64 when Eigen and Wilkins' review[2] of this topic appeared will be surveyed here, selectively rather than exhaustively. We shall first consider the experimental approach to the problem of complex-formation kinetics, the use of flow and relaxation methods and how data from them are interpreted.

Much of the current interpretation is based on a proposal by Eigen[3] that mechanism (*B*) is operative. The evidence in favour of this path is briefly that (*a*) the observed rate expression is second order; first in metal and first in ligand; and (*b*) the rate at which complexes form is usually similar to the rate of solvent exchange. Since this hypothesis has gained very wide acceptance and has been applied successfully to the majority of recent results, we are led to consider the relation of substitution at a cation to outer-sphere complex formation and the solvent-exchange rate of the solvated ion. We shall then discuss some of the factors which influence the rate of complex formation, and finally attempt to point out the extent to which an exclusive assignment of mechanism may be made.

B. EXPERIMENTAL APPROACHES

The capabilities of the mixer limit the time-range of "flow" techniques and, although modified design is a possibility[5], reactions that are complete in less than one millisecond are usually studied by other methods.

A wide range of relaxation techniques, in which mixing is avoided, has been developed by Eigen and others[4]. For the purpose of complex formation studies an equilibrium mixture of metal, ligand and complex is prepared, and then the physical conditions which control the equilibrium concentrations are suddenly altered by, for instance, a rapid change of temperature or pressure. For a step perturbation of this kind, and small displacements, the rate at which the concentrations of the components linked by a single equilibrium constant is observed to "relax" to the new conditions is of the form

$$\Delta C_n = \Delta C_0 \exp(-t/\tau)$$

where ΔC_n is the displacement of concentration from the final equilibrium value at n sec after the perturbation, and τ is an experimentally determined "relaxation time".

The limiting factor is now the time that the step function takes to perturb the physical property and is usually of the order of 10^{-6} sec. For still faster reactions, a continuously varying perturbation such as ultrasonic waves may be used, to produce rapid changes of pressure within the solution. When the applied frequency is low compared with the rate of reaction, the concentration changes can keep in phase with the sound waves, so there is a large variation in the concentrations with time and no phase lag. At the opposite end of the scale, the reaction is so much slower than the applied signal, that the concentrations of the various components barely change from an average value and the phase lag is very long. The maximum power absorbed by the solution can be shown to be taken when the applied frequency, in radians, $\omega = 1/\tau$, the reciprocal relaxation time[6].

It is an important feature of relaxation techniques that τ is a function of both forward and reverse rate-constants; for example, for the single step reaction of a metal M with a ligand L to give the complex ML:

$$\mathrm{M}+\mathrm{L} \underset{k_{12}}{\overset{k_{21}}{\leftrightarrows}} \mathrm{ML} \tag{1}$$

we may write, at time t:

$$\frac{\mathrm{d}[\mathrm{ML}]}{\mathrm{d}t} = k_{12}[\mathrm{M}]\,[\mathrm{L}] - k_{21}[\mathrm{ML}] \tag{2}$$

At equilibrium:

$$0 = k_{12}[\overline{\mathrm{M}}]\,[\overline{\mathrm{L}}] - k_{21}[\overline{\mathrm{ML}}]$$

Now [M] may be written as $[\overline{\mathrm{M}}]+\Delta\mathrm{M}$, and similarly for [L] and [ML]. Since. from the stoicheiometry of equation (1),

$$\Delta\mathrm{ML} = -(\Delta\mathrm{M}) = -(\Delta\mathrm{L})$$

and we can ignore the term $k_{12}\Delta\mathrm{M}\Delta\mathrm{L}$ for small changes in concentration, equation (2) becomes

$$\frac{\mathrm{d}\Delta\mathrm{ML}}{\mathrm{d}t} = -[k_{12}([\overline{\mathrm{M}}]+[\overline{\mathrm{L}}])+k_{21}]\Delta\mathrm{ML}$$

which may be written in the form

$$\Delta\mathrm{ML}_t = \Delta\mathrm{M}_0 \exp(-t/\tau)$$

where

$$\tau^{-1} = k_{12}([\overline{\mathrm{M}}]+[\overline{\mathrm{L}}])+k_{21} \tag{3}$$

To separate values of k_{12} and k_{23} it is therefore necessary to plot values of τ^{-1} at a variety of concentrations *vs.* $([\overline{\mathrm{M}}]+[\overline{\mathrm{L}}])$ and to obtain the intercept and slope.

When the reaction mechanism involves more than one equilibrium constant, the relationships between τ values and the individual forward and reverse rate constants is not usually as straightforward.

General methods for the determination of concentrations and relaxation times are available[7,8] and, it is interesting to compare the result for the two-step mechanism (*B*) with that derived for the single step reaction (*C*).

$$\mathrm{M}+\mathrm{L} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{X} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{P} \tag{4}$$

In expression (4), X represents some form of intermediate, possibly an ion pair, which may react further to give, as a final product, P, the metal-ligand complex. Four concentration terms are involved, and these are related by two equilibrium constants so there are only two independent concentration terms and two relaxation terms to be determined.

If it is assumed that there is a large difference between the relaxation times and that the rate of formation of the intermediate is considerably greater than its reaction to form product, the two relaxation times may be obtained from expressions for the sum and product of the roots of a quadratic equation and are given[7] approximately by:

$$\begin{aligned}\frac{1}{\tau_1} &= (k_{12}([\overline{\mathrm{M}}]+[\overline{\mathrm{L}}])+k_{21})\\ \frac{1}{\tau_2} &= \frac{K_0 k_{23}([\overline{\mathrm{M}}]+[\overline{\mathrm{L}}])}{1+K_0([\overline{\mathrm{M}}]+[\overline{\mathrm{L}}])}+k_{32}\end{aligned} \tag{5}$$

where $\dfrac{1}{\tau_1} \gg \dfrac{1}{\tau_2}$ and K_0 is the stability constant for the intermediate species $= \dfrac{k_{12}}{k_{21}}$.

The experimental conditions under which complex-formation reactions are usually studied are such that $K_0([\overline{M}]+[\overline{L}])$ is usually considerably smaller than unity. Concentrations are usually in the millimolar range and theoretical estimates of K_0 very seldom exceed 10^3, so the variation of $1/\tau_2$ with concentration reduces to:

$$\frac{1}{\tau_2} = k_{obs}([\overline{M}]+[\overline{L}])+k_{rev} \tag{6}$$

which has the same form as that for the one-step reaction (3). In order to distinguish between a one-step and a two-step mechanism it is necessary, either to detect the faster relaxation time, or to obtain values of K_0 and k_{23} and to investigate the effect on τ_2 when $K_0([\overline{M}]+[\overline{L}])$ is no longer negligible in comparison with unity.

A single study of the latter possibility has been made in labile systems[56] and deviation from second-order behaviour has been found[9] in reactions of anionic complexes of Co(III). Sound absorption measurements have been made on some metal sulphates and equilibria involving associated species were detected[10,11,12]. However it is important to note that the formation of ion pairs does not *necessarily* mean that the substitution pathway proceeds through them[13]. Their occurrence however does suggest that such a mechanism is an attractive possibility since the aquo ion and ligand are held in close proximity. Steric requirements of the ligand might complicate the situation.

An alternative approach is to assume that mechanism (*B*) is operative and to see if observed rate constants give consistent results. When $K_0([\overline{M}]+[\overline{L}]) \ll 1$, a comparison of expressions (5) and (6) gives:

$$k_{obs} = K_0 k_{23} \tag{7}$$

The same expression may be deduced from the results of flow experiments, which have been interpreted in terms of mechanism (*B*).

It is next assumed that k_{23}, the rate at which the associated species loses solvent is equal to the rate of solvent exchange at a free ion since the rate determining step for both processes is thought to be fission of a metal–solvent bond. The value of K_0 can therefore be estimated and compared with known results or a theoretical expression. The methods available for the determination of solvent-exchange rates and outer-sphere association constants are of interest, therefore, and will be discussed in the following sections.

C. THE STABILITY CONSTANT OF THE OUTER-SPHERE COMPLEX

In general values of K_0 have to be estimated although direct measurement is possible in a few cases. The equation (8) derived by Fuoss[14] was the result of statistical argument, and Eigen reached a similar solution from the theory of diffusion-controlled reactions[15].

For a solution of ions carrying unit charges:

$$K_0 = \frac{4\pi \mathrm{N} a^3 \exp{(b)}}{3{,}000} \quad \text{where} \quad b = -\frac{e^2}{aDkT} \tag{8}$$

at infinite dilution.

In this expression, a is the interatomic distance, in cm, N the Avogadro number, e the electronic charge in e.s.u. and D the macroscopic dielectric constant. It is of interest to note that K_0 has a finite value of approximately 0.2 for uncharged ions that are 5 Å apart and values of K_0 for ions carrying multiple charges at higher ionic strengths can be estimated[16] by using

$$b = \frac{z_1 z_2 e^2}{aDkT} - \frac{z_1 z_2 e^2}{DkT(1+\kappa a)}$$

where κ is the Debye–Hückel parameter:

$$\sqrt{\frac{8\pi \mathrm{N} e^2 \mu}{1000 DkT}}$$

and μ is the ionic strength.

While the use of this equation for solutions at ionic strengths as high as 1 M which are employed in temperature-jump experiments is, to say the least, naive*, it is often applied[16–22] to obtain approximate values of K_0 and hence an estimate of k_{23}. Unfortunately, since the distance between metal and ligand in such complexes in solution is unknown, a wide variety of values of K_0 may be obtained through judicious choice of the parameter (a).

It is possible to measure the association constant directly in inert systems from, for example, changes in visible and ultraviolet spectra with changes in the concentration of counter ion. Values[23] of 7 to 70 have been obtained for tripositive cobalt complexes and uninegative ions at infinite dilution in aqueous solution, and a comparable range of values[23] for binegative ions is 1,800 to 2,800. These results may be substituted into equation (8) and give a value of 4 Å to 5 Å for most ions with the possibility of hydroxide and chloride ions coming a little closer to the metal. We may expect that metal–ligand distances in labile systems to be comparable and substitution of 5 Å has been shown to give results in reasonable agreement with the solvent exchange rate[24] when K_0 is substituted into the expression (7). Considerably larger values have, however, been used on occasion[24–26].

The stability constant for ion pairs determined from electrochemical experiments is thought to represent the total concentration of inner- and outer-sphere ion pairs divided by the product of the concentrations of the free ions, and so is not equal to K_0. However, a combination of pressure-jump and sound-absorption

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experiments has led to the suggestion that the contact ion pair is formed in a number of distinct stages[10–12]. It is reasonable to assume that the first step involves the diffusion-controlled approach of free ions and the formation of an outer-sphere ion pair and direct measurement of K_0 has been carried out in aqueous solutions of magnesium and manganese sulphates[26]. Recent ESR measurements on aqueous solutions of manganese halides have also given[27] direct values of K_0. Values obtained by direct experiments[23,26] lie in the range 0.01 to 100 $(\text{mole})^{-1}$ and in any case will be less than values of $K\Sigma$, the formation constant for all associated species determined from conductivity or other measurements. The latter have values of approximately 150 mole^{-1} for 2^+2^- ions and about 50 mole^{-1} for singly charged species at zero ionic strength[28,29], and would have lower values at finite values of μ.

The variation of K_0 with temperature can be calculated from expression (8) from a knowledge of the dielectric constant of the solvent at two temperatures. Calculations of $1/DT$ show that the concentration of associated species in water should increase as the temperature is raised, assuming that the inter-atomic distance does not change. The enthalpy changes for association are positive for a number of metal sulphates[28].

The dependence of K_0 upon ionic strength in very dilute solutions may he calculated from the accepted theory, but in 1M solutions no semi-rigorous theory may be applied. King *et al.*[30] justified the use of a factor of ~10 when the ionic strength is changed from 0.05 to 1M in the association constant of $\text{Co(NH}_3)_6{}^{3+}\cdot\text{Cl}^-$ and stated that the value at 1M is twenty five times less than the value at infinite dilution.

Since values of k_{obs} in Table 2 take values of between 10^{-6} and 10^{+8} $\text{l.mole}^{-1}.\text{sec}^{-1}$, and stability constants for ion pair formation are usually within the range 0.2 to 200 mole^{-1}, the large variation in rate constants for the formation of complexes, must be inherent in k_{23} [see (7)]. The rate of solvent exchange may be related to this quantity and so the determination of exchange rates is relevant.

D. THE RATE OF SOLVENT EXCHANGE

By far the most convenient method for measuring solvent-exchange rates employs nuclear magnetic resonance, although some data have been obtained using an isotope dilution technique.

The width of an NMR line at half height (in a highly homogeneous magnetic field), gives an immediate value of $1/T_2$ where T_2 is the transverse relaxation time and a measure of the speed at which nuclei, which are precessing in phase with an applied radiofrequency field, lose their phase when the signal is removed. In order to become dephased, the nuclei must be subjected to an alternating field of another frequency: and in a pure diamagnetic liquid which does not undergo chemical exchange processes, this can only be generated by the random motion of other nuclei. The ^1H, ^{19}F or ^{31}P resonance spectrum of such a liquid will have sharp peaks because the relaxation time is long.

If a paramagnetic metal ion is added to the liquid, those molecules which solvate the metal will be subjected to a strong alternating magnetic field produced by the unpaired electrons. The resonance spectrum of the coordinated solvent will therefore be much broader than that of the free solvent owing to the increased field and diminished relaxation time. In the event of exchange between bound and free solvent, the value of T_2 for free solvent will also decrease, since it is possible for "in phase" solvent to be coordinated to the metal then "dephased" and returned to the solution, more rapidly than free solvent can he relaxed in the bulk solution[52].

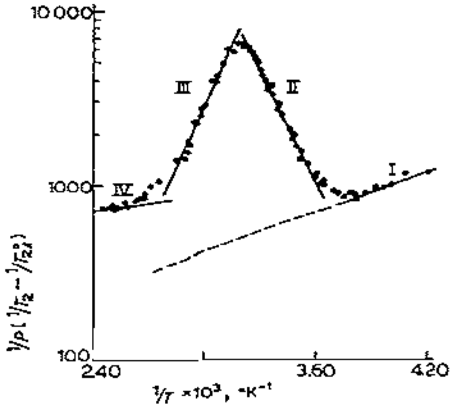

Fig. 1. The contribution by solvent exchange to the line-width of the solvent n.m.r. spectrum as a function of temperature for the system $Ni(ClO_4)_2$ in acetonitrile. Reproduced with permission from D. K. Ravage, T. R. Stengle and C. H. Langford, *Inorg. Chem.*, 6 (1967) 1252.

The contribution by the solvent-exchange process to the line-width may depend either on the rate at which the metal ion can "dephase" the solvent molecule, or on the rate at which solvent can he returned to the solution. However, if the latter is true, the extra broadening should be very sensitive to temperature and obey an Arrhenius equation whereas "dephasing" is much less temperature sensitive.

Fig. 1 illustrates four possible types of temperature effect. In region I there is very little exchange broadening while in region II the amount of broadening is controlled by the chemical exchange rate and each solvent molecule is relaxed before leaving the coordination sphere of the metal ion. Region III occurs as the exchange rate increases to a point when some solvent molecules are not dephased before being returned to the solution and finally in region IV the exchange broadening is determined solely by the rate at which relaxation can occur at the metal ion.

The average time a solvent molecule resides at a coordination site of the metal ion, τ, is simply related to the exchange broadening,

$$\left[\frac{1}{T_2} - \frac{1}{T_{2A}}\right]$$

in region II of Fig. 1:

$$\frac{Pm}{\tau} = \frac{1}{T_2} - \frac{1}{T_{2A}}$$

where Pm is the proportion of coordinated solvent to free, *i.e.*

$$\frac{n[\mathrm{M}]}{[\mathrm{solvent}]}$$

and n is the coordination number of the metal M. The rate constant for exchange of a particular solvent molecule is given by the reciprocal of the average life-time*.

Some of the data from NMR on the rates of solvent exchange have been reviewed[31].

More recent results using NMR, and those of other techniques have been incorporated into Table 1. The NMR method requires a knowledge of the coordination number of the metal ion, and a method of estimating this when separate resonances for coordinated and free solvent cannot be observed has been the subject of controversy[32]. Low temperature studies on mixed solvents[33] have given unequivocal coordination numbers for Mg^{2+}, Al^{3+}, Ga^{3+} and Be^{2+} but separate resonances were not observed for Ca^{2+}, Zn^{2+}, Hg^{2+}, In^{3+}, Y^{3+}, or La^{3+}.

It must also be realised that solvent exchange is only one of several processes which may control the rate of relaxation, and that alternative exchange paths are likely when the probe nucleus is not directly attached to the metal ion. Swift and his coworkers have found that an acid catalysed proton relaxation in aqueous solutions of a number of first row transition elements (notably Cr^{3+}) can be ascribed to proton transfer rather than replacement of the complete water molecule[34].

Some solvent exchange processes have been studied by an isotope dilution method in which an amount of isotopically labelled solvent is added to a solution of the metal salt in solvent of normal isotopic composition. The rate at which the label is incorporated into the free solution from the metal ion may then be recorded, but in practise it is often necessary to carry out the experiment at −100° in order to be able to measure the rate and estimates of minimum exchange rates are fre-

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* It is not immediately apparent that the exchange-rate constant is given by the reciprocal of the average life-time of a coordinated ligand. The exchange process is first order irrespective of its mechanism[37], and the concentration of coordinated solvent which has not undergone chemical exchange after t sec, $C_t = C_0 \exp(-kt)$. The number of atoms exchanging between time t and $t+dt$ is $dc = C_0 k \exp(-kt)\,dt$ and the average life-time of a particular solvent molecule before exchange is given by

$$\int_0^\infty \frac{t[C_0 k \exp(-kt)\,dt]}{C_0} = \frac{1}{k}$$

quently all that can be obtained although solvation numbers can be calculated[35]. Results obtained in this way of the activation enthalpy of cobalt and nickel in methanol do not agree particularly well with NMR data and it has been suggested that some water was present in the system[36].

Rates of solvent exchange may be compared with estimated values of k_{23}, and are found to agree reasonably well; but the uncertainty in K_0 precludes any confident statement on the consistency of these figures with the proposed reaction scheme (*B*) and possibly hides a genuine disparity. A number of assumptions are made when the solvent-exchange rate of a free ion is taken to be the same as k_{23}; the most obvious, and probably the most serious is the assumption that the rate at which solvent leaves the outer-sphere associated complex is identical to that at which it would leave the free ion. Also little is known about the structure of such an intermediate, *e.g.* if the product is formed as soon as the first solvent molecule leaves a coordination site we should use $k_{23} = n \times k_{\mathrm{exch}}$ where n is the coordination number, because the solvent-exchange rate constant usually quoted from NMR studies relates to the rate at which a particular solvent molecule leaves the coordination shell of the solvated ion.

In addition, there are often great differences in the experimental conditions used for solvent-exchange studies and those used to study complex formation. For instance, the temperature ranges and concentration of metal ion are often completely different; and the presence of the large quantity of electrolyte necessary for temperature-jump experiments is almost certain to influence the rate of solvent exchange.

It is useful, nevertheless, to attempt a separation of the experimental rate constants for complex formation into the two independent variables, K_0 and k_{23}, because some factors which appear to influence the rate, may then be expected to have an effect on one and not on the other.

E. TABULATED RATES OF SOLVENT EXCHANGE AND COMPLEX FORMATION

Notes on Tables 1 and 2

(*a*) In Table 1, k is the first-order rate constant for exchange of a particular solvent molecule. The units of k in Table 2 are $\mathrm{l.mole^{-1} \cdot sec^{-1}}$ and both rate constants have been recorded at 25° unless otherwise stated.

(*b*) The methods used are abbreviated: SA = sound absorption, PJ = pressure jump, TJ = temperature jump, SF = stopped flow, EX = solvent extraction technique, LT = observed at a low temperature, ID = isotope dilution method, IE = isotope exchange study. The nucleus is quoted when an NMR technique has been used.

(*c*) Table 2 is arranged with metals in order of increasing atomic weight. Ligands are grouped by charges and placed in order of increasing negative charge.

TABLE 1

RATES OF SOLVENT EXCHANGE

Metal or species	*Solvent*	*Log k* *(sec^{-1})*	*$\Delta H^{\pm}$*	*Coord. no.*		*Method or nucleus*	*Ref.*
Be^{2+}	H_2O	3.5		4		^{17}O	A
		3.5	8			SA	BA
	aq. acetone			4		^{1}H	B
	DMF	2.5	15	4		^{1}H	C
$Be(acac)^{2+}$	DMF	1.3	14			^{1}H	C
Mg^{2+}	H_2O	5.2				SA	BB
$Mg(H_2O)^{2+}$	aq. acetone	6.6	13	6	$(ClO_4)^-$	^{1}H	D
		6.7	14	6	$(NO_3)^-$	^{1}H	D
$Mg(CH_3OH)^{2+}$	CH_3OH/acetone	4.4	12	6		^{1}H	D
Mg^{2+}	CH_3OH	3.6	17	6		^{1}H	E
	CH_3OH	3.5	13	6		ID	F
	DMF	>5	<10			^{1}H	C
	NH_3			5		^{1}H	G
Ca^{2+}	H_2O	8.5			(Est)	SA	BE
Sr^{2+}	H_2O	8.6			(Est)	SA	BE
Ba^{2+}	H_2O	8.9			(Est)	SA	BE
Al^{3+}	H_2O	-0.2				PJ	CP
	H_2O	-0.8	27	6		^{17}O	H
$AlCl_3$	H_2O	6.7	24			^{1}H	I
Al^{3+}	DMSO	-1.3	20	6		^{1}H	J
	DMF	-0.7	18	6		^{1}H, ^{27}Al	K
$Al(acac)^{2+}$	DMF	1.2		4	at 15°	^{1}H	DB
Ti^{3+}	H_2O	5.0	6			^{17}O	L
VO^{2+}	H_2O	2.7	13	4(eq)		^{17}O	M, AY
		11.0		1(ax)		^{17}O	M
$VO(IMDA)^{2+}$	H_2O	4.7				^{17}O	AY
$VO(SS)^{2+}$	H_2O	5.0				^{17}O	AY, N
Cr^{2+}	H_2O	≥ 9.9	3			^{17}O	O
Cr^{3+}	H_2O	-6.3	26	6		ID	P
Mn^{2+}	H_2O	≥ 7.6	8			^{1}H	Q
		≥ 7.5	8			^{17}O	R
		7.6	11			SA	BK
	CH_3OH	6.0	7			ESR	DG
	DMF	6.6				^{17}O	S

(*d*) Abbreviations for reagents mentioned include the following. Tiron: 4,5-dihydroxybenzene-1,3-disulphonic acid. 8-OHQ: 8-hydroxyquinoline. IMDA: iminodiacetate. SS: 5-sulpho-salicylate. DTZ: diphenyl thiocarbazone. *o*CH_3DTZ: ortho methyl DTZ. PAR: 4-(2-pyridylazo)resorcinol. PAD: pyridine-2-azo-dimethylaniline. MNT: maleonitrile dithiolate. NTA: nitrilotriacetate. ACA: apocarbonic anhydrase. 8SQ: 8-mercapto-quinoline. 2M-8SQ: 2-methyl 8MQ. UDA: uramil-*N*,*N*,-diacetate. DTO: dithio-oxalate. TPTZ: 2,4,6,-tripyridyl-5-triazine. DAP: diaminopropionic acid. DAB: diaminobutyric acid. AMP: 2-aminomethyl pyridine. pyc: pyridine 2-carboxylate. pya: pyridine 2-acetate. pydic: pyridine 2,6-dicarboxylate. XO: xylene orange. AN: anthranilate.

TABLE 1 (continued)

Metal or species	*Solvent*	*Log k (sec^{-1})*	*$\Delta H^{\pm}$*	*Coord. no.*		*Method or nucleus*	*Ref.*
Fe^{2+}	H_2O	6.5	8			^{17}O	R
	DMF	4.3				^{17}O	S
Fe^{3+}	H_2O	4.3				^{17}O	T
$Fe(OH)^{2+}$	H_2O	~6				^{17}O	U
Fe^{3+}	DMSO	1.7				^{1}H	CV
$FeCl_3$	H_2O	5.3	10	3		^{17}O, ^{35}Cl	V
Co^{2+}	H_2O	6.4	10	6	Oct–tet eq.	$^{17}O^{1}H$	W, AX
$CoCl_n^{(2-n)+}$	H_2O					^{17}O, ^{35}Cl	X
Co^{2+}	CH_3OH	4.3	14	6		^{1}H	Y
		4.0	12	6		ID	Z
$Co(H_2O)_n^{2+}$	CH_3OH	~5				^{1}H	Y
$CoCl^-$	CH_3OH	7.0	12	4 eq+1 ax.		^{1}H	AA
Co^{2+}	DMF	5.3	7			^{17}O	AB
		5.5	14	6		^{1}H	AC
	CH_3CN	5.2	8	6	$(ClO_4)^-$	^{1}H	AD
		5.2	8	6	$(BF_4)^-$	^{1}H	AE
	NH_3	6.9	11	6		^{14}N	G, AF
$Co(NH_3)_5^{3+}$	H_2O	−5.0	27			ID	AG
$CoCl(en)_2^{2+}$	DMSO	−4.2			at 35°	^{1}H	AH
$CoBr(en)_2^{2+}$	DMSO	−4.1			at 35°	^{1}H	AH
$CoI(en)_2^{2+}$	DMSO	−3.5			at 35°	^{1}H	AH
Ni^{2+}	H_2O	4.4	12			^{17}O	A, R
		4.5	11	6		^{1}H, ^{17}O	AI
	NH_3	5.1	10			^{1}H	AJ
		4.8	11			^{1}H	CZ
		5.2	10			^{14}N	AK
		5.0	11			^{14}N	AL
$Ni(NH_3)^{2+}$	H_2O	5.6	7		at pH 5.7	^{17}O	AM
$NiCl_2$	H_2O	5.4	10		$\mu = 6.5$	^{17}O, ^{35}Cl	AN
Ni^{2+}	CH_3OH	3.0	16			^{1}H	Y
		3.8	13	6		ID	Z
	CH_3CN	3.4	12		$(ClO_4)^-$	^{1}H	AO
		3.6	11		$(ClO_4)^-$	^{1}H	AD
		4.1	12		$(BF_4)^-$	^{1}H	AE
	DMF	3.5	15			^{1}H	AC
		3.8	9			^{17}O	AB
$Ni(NCS)_4^{2-}$	H_2O	6.0	6		$\mu = 6.0$	^{17}O, ^{14}N	AP
Ni^{2+}	DMSO	3.8	8			^{1}H	AQ
Cu^{2+}	H_2O	≥9.9				^{17}O	O, R
	CH_3OH	≥4.0				^{1}H	AR
	DMF					^{1}H	K
Zn^{2+}	H_2O	7.5				SA	CM
Ga^{3+}	H_2O	3.3	6	6		^{17}O	H, AS
		1.3			(Est)	PJ	DN
Y^{3+}	H_2O	8.3			(Est)	SA	CQ
La^{3+}	H_2O	8.7			(Est)	SA	CQ
Ce^{3+}	H_2O	8.7			(Est)	SA	CQ
Sm^{3+}	H_2O	8.9			(Est)	SA	CQ
Eu^{3+}	H_2O	9.0			(Est)	SA	CQ
Gd^{3+}	H_2O	9.6			at 60°	^{17}O	AT
Gd^{3+}	H_2O	9.1			(Est)	SA	CQ

TABLE 2

Metal	*Ligand*	*Log k* *(l . mole^{-1} . sec^{-1})*	*ΔH±* *(kcal. mole^{-1})*	*ΔS±* *(e.u.)*		*Method*	*Ref.*
Dy^{3+}	H_2O	8.8			(Est)	SA	CQ
Dy^{3+}	H_2O	7.8	12			^{17}O	AV
Np(V)	CH_3OH	5.5	8			^{1}H	AU
$Pt(CH_3)_3^+$	H_2O	2.7		3		^{17}O	AW, DH
Pt(II) $(NH_3)_2$	H_2O	~0		2		^{17}O	DH
Au(III) $(CH_3)_2$	H_2O	4.7	7	3		^{17}O	DH
Mg^{2+}	$tiron^{3-}$	6.5				TJ	CF
	8-OH Q	5.5				TJ	BC
$MgUDA^-$	8-OH Q	4.9				TJ	BC
$MgATP^{2-}$	8-OH Q	5.0				TJ	BC
$MgTP^{3-}$	8-OH Q	4.7				TJ	BC
Ca^{2+}	$EDTA^{4-}$	≤9.4			Calc. from exch. rate	^{1}H	BD
	$HEDTA^{3-}$	7.0				^{1}H	BD
Sr^{2+}	$EDTA^{4-}$	8.9				^{1}H	BD
	$HEDTA^{3-}$	5.7				^{1}H	BD
V^{2+}	SCN^-	1.0				F	CW
		1.2				TJ	BF
	ophen	0.5				F	AZ
V^{3+}	SCN^-	2.1				TJ	BF
V^{3+}	SCN^-	2.2	8	−23	Indep $[H^+]$	SF	BH
VO^{2+}	SCN^-	2.2			at 20°	TJ	BJ
	SCN^-	4.1	11	−2		PJ	CO
Ti^{3+}	SCN^-	3.6				—	DM
Mn^{2+}	ophen	5.1			at 11°	SF	BL
	terpy	5.0	6	−15		SF	BL
	β-alanine	4.7				TJ	BM
	Cl^-	7.2	9	+4		ESR	BN
		6.8	14	+19		ESR	DI
MnO_4^{2-}	8-OH Q	2.6				TJ	BO
$Mn(OH)O_3^-$	8-OH Q	6.7				TJ	BO
Fe^{2+}	NO	5.7				TJ	DA
	terpy	4.9	10	−4		SF	BL
	bipy	5.2	11	+1		SF	BL
	TPTZ	5.2				SF	DJ
$Fe(terpy)^{2+}$	terpy	7.0			at 5°	F	BL
$Fe(bipy)^{2+}$	bipy	5.1				F	BL
Fe^{3+}	HF	1.1	9	−24	Recalc. from original data	F	BP
	HN_3	0.6				TJ	BS, BP
	Br^-	1.3			,,	F	BP
	Cl^-	1.0	17	+2	,,	F	BP
	CNS^-	2.1	13	−5	,,	F	BP
	$HC_2O_4^-$	2.9			,,	F	BR
	SO_4^{2-}	3.6	16	~+10		TJ	BQ
	$Fe(CN)_6^{3-}$	3.2	9	+5		TJ	DD
$Fe(OH)^{2+}$	HF	3.5	10	−8		F	BP
	HN_3	3.8	9	−10		TJ	BS, BP
	Br^-	4.4				F	BP
	Cl^-	4.0	13	+4		F	BP
	CNS^-	4.0	10	−8		F	BP
	$HC_2O_4^-$	4.3				F	BR

TABLE 2 (continued)

Metal	*Ligand*	*Log k (l . mole^{-1} . sec^{-1})*	*$\Delta H^{\pm}$ (kcal. mole^{-1})*	*$\Delta S^{\pm}$ (e.u.)*		*Method*	*Ref.*
	SO_4^{2-}	5.3	11	+4		TJ	BQ
Co^{2+}	NH_3	5.0	6	−15		TJ	BT
	ophen	5.5	11	+2		SF	BL
	5-NO_2-ophen	5.2	11	+3		SF	BL
	terpy	4.4	9	−8		SF	BL
	bipy	4.8	10	−8		SF	BL
	DTZ	4.8				EX	CX
	PAD	4.6			at 15°	TJ	BY
	L-carnosine	5.6				TJ	BU
	α-aminobutyrate$^-$	5.4			at 20°	TJ	BV
	β-aminobutyrate$^-$	4.3			at 20°	TJ	BV
	α-alanine$^-$	5.8				TJ	BM
	β-alanine$^-$	4.8				TJ	BM
	murexide$^-$	5.2			at 10°	TJ	BW
	bi-cystein$^-$	5.7				TJ	BX
	cystein^{2-}	6.7			at 20°	TJ	BX
	tiron^{2-}	6.0				TJ	CF
	malonate^{2-}	7.0				TJ	BZ
	tartrate	6.8			pH?	SA	CA
	tiron^{3-}	6.6				TJ	CF
$Co(terpy)^{2+}$	terpy	6.7			at 5°	SF	BL
	PAR	6.9			at 5°	SF	BL
$Co(ophen)^{2+}$	ophen	5.6	13	+11		SF	BL
Ni^{2+}	bipy H^+	1.4				SF	DF
	NH_3	3.2	10	−9		TJ	BT
	2-picolinamide	3.2	12	3		SF	DF
	AMP	3.9				SF	DF
	$NH_2CH_2CONH_2$	3.3				SF	DF
	DAP	3.3				SF	DF
	DAB	3.4				SF	DF
	ornithine	3.3				SF	DF
	lysine	3.6				SF	DF
	5-NO_2-ophen	3.2	14	+3		SF	BL
	PAD	3.6			at 15°	TJ	BY
	α-alanine	4.3				TJ	BM
	β-alanine	4.0				TJ	BM
	glycine$^-$	4.3	11	~0		SF	DF
	digly$^-$	3.5				SF	DF
	trigly$^-$	3.5				SF	DF
	tetragly$^-$	3.6				SF	DF
	asp NH_2^-	3.9				SF	DF
	pyc$^-$	4.3	14	+9		SF	DF
	pya$^-$	4.0	11	−1		SF	DF
	α-aminobutyrate$^-$	4.0				TJ	BV
	β-aminobutyrate$^-$	3.6				TJ	BV
	$HC_2O_4^-$	3.7	14	+7		SF	CC
	bi-cystein$^-$	4.2			at 20°	TJ	BX
	bi-malonate$^-$	3.5	14	+7		TJ	CD
	murexide$^-$	3.5	13			TJ	BW
	DTZ$^-$	3.0				EX	CX, DC

TABLE 2 (continued)

Metal	*Ligand*	*Log k (l . mole^{-1} . sec^{-1})*	*$\Delta H^{\pm}$ (kcal. mole^{-1})*	*$\Delta S^{\pm}$ (e.u.)*		*Method*	*Ref.*
	DTZ*p*F$^-$	3.5				EX	CX, DC
	DTZ*p*Cl$^-$	3.5				EX	CX, DC
	DTZ*p*Br$^-$	4.3				EX	CX, DC
	DTZ*p*I$^-$	5.2				EX	CX, DC
	DTZ*o*CH$_3$$^-$	3.7				EX	CX. DC
	DTZ*p*CH$_3$$^-$	4.4				EX	CX, DC
	DTZ*p*OCH$_3$$^-$	4.8				EX	CX, DC
	DTZ*p*CF$_3$$^-$	4.5				EX	CX, DC
	aspartate^{2-}	4.6				SF	DF
	ama^{2-}	4.6				SF	DF
	pydic^{2-}	4.7	12	+5		SF	DF
	IMDA^{2-}	4.6				IE	DL
	oxalate^{2-}	4.8	14	+12		SF	CC
	succinate^{2-}	5.6	14	+16		PJ	CU
	malonate^{2-}	4.8	15	+14		TJ	CD
		5.3	14	+13		PJ	CU
	cystein^{2-}	5.2			at 20°	TJ	BX
	MNT^{2-}	4.8				SF	CE
	tiron^{2-}	4.9			at 20°	TJ	CF
	DTO^{2-}	4.7				SF	CE
	Me phosphate^{2-}	3.8				TJ	CB
	tiron^{3-}	5.5			at 20°	TJ	CF
	EDTA^{3-}	5.2				SF	DF
	CyDTA^{3-}	5.2				SF	DF
		5.5				SF	DO
	NTA^{3-}	5.6				IE	DK
Ni(ophen 5,6 diMe)$^{2+}$	H dien$^+$	2.6				SF	CH
5 Me	H dien$^+$	2.6				SF	CH
5 H	H dien$^+$	2.5				SF	CH
5 Cl	H dien$^+$	2.5				SF	CH
5 NO$_2$	H dien$^+$	2.5				SF	CH
5 SO$_3$	H dien$^+$	2.8				SF	CH
Ni(bipy)$^{2+}$	bipy	3.7				SF	BL
Ni(terpy)$^{2+}$	terpy	5.3	12	+4		SF	BL
	PAR	4.8				SF	BL
Ni(en)$^{2+}$	NH$_3$	4.1				TJ	CG
Ni(dien)$^{2+}$	NH$_3$	4.6				TJ	CG
Ni(tetren)$^{2+}$	NH$_3$	1.9				TJ	CG
Ni(trien)$^{2+}$	NH$_3$	3.3				TJ	CG
Ni(ophen 5,6 diMe)$^{2+}$	NTA^{3-}	6.6				SF	CH
5 Me	NTA^{3-}	6.5				SF	CH
5 H	NTA^{3-}	6.4				SF	CH
5 Cl	NTA^{3-}	6.4				SF	CH
5 NO$_2$	NTA^{3-}	6.2				SF	CH
5 SO$_3$	NTA^{3-}	6.4				SF	CH
Ni(α-alanine)$^+$	α-alanine$^-$	4.6				TJ	BM
Ni(β-alanine)$^+$	β-alanine$^-$	3.8				TJ	BM
Ni(α-aminobutyrate)$^+$	α-aminobutyrate$^-$	4.2			at 20°	TJ	BV
Ni(β-aminobutyrate)$^+$	β-aminobutyrate$^-$	3.9			at 20°	TJ	BV
NiCl$^+$	Cl$^-$	5.2	11	+4		^{17}O,^{35}Cl	AN

TABLE 2 (continued)

Metal	*Ligand*	*Log k (l . mole⁻¹ . sec⁻¹)*	*ΔH± (kcal. mole⁻¹)*	*ΔS± (e.u.)*		*Method*	*Ref.*
Ni(cystein)	cystein^{2-}	4.4			at 20°	TJ	BX
Ni(malonate)	malonate^{2-}	3.6				TJ	CD
Ni(α-aminobutyrate)$_2$	α-aminobutyrate$^-$	4.5			at 20°	TJ	BV
Ni(β-aminobutyrate)$_2$	β-aminobutyrate$^-$	3.5			at 20°	TJ	BV
Cu^{2+}	bipy	7				SF	BL
	terpy	7.3			at 5°	SF	BL
	PAD	8.0			at 15°	TJ	BY
	L-carnosine	6.5				TJ	CJ
	murexide$^-$	8.1			at 10°	TJ	BW
		7.7	~6	~−3		TJ	CK
	acac$^-$	3.2	5	−27		LT	CL
	gly$^-$	9.6				SF	DE
Zn^{2+}	NH_3	6.5			at 11°	TJ	BT
	terpy	6.1	~8	−4		SF	BL
	bipy	6.0	6	−9		SF	BL
	ophen	6.3	8			SF	BL
	PAD	6.6			at 15°	TJ	BY
	murexide$^-$	7.3			at 10°	TJ	BW
		6.9	6	~−6		TJ	CK
	ACA°	~4	20	~+28		SF	CT
	8SQ	9.5				EX	CX
	2M8SQ	9.1				EX	CX
	DTZ$^-$	6.8				EX	DC
	DTZ$^-$*p*F	7.5				EX	DC
	DTZ$^-$*p*Cl	7.6				EX	DC
	DTZ$^-$*p*Br	8.3				EX	DC
	DTZ$^-$*p*I	6.7				EX	DC
	DTZ$^-$$oCH_3$	6.8				EX	DC
	DTZ$^-$$pCH_3$	8.7				EX	DC
	DTZ$^-$$pOCH_3$	8.4				EX	DC
	DTZ$^-$$pCF_3$	8.3				EX	DC
Cd^{2+}	EDTA	9.0				^{1}H	CN
	ophen	7.0				SF	BL
	terpy	6.5	6	−7		SF	BL
	PAD	7				TJ	BY
	murexide$^-$	8.1				TJ	BW
In^{3+}	SO_4^{2-}	5.4				PJ	DN
	murexide$^-$	6.3			at 12°	TJ	BW
Sc^{3+}		7.6			at 12°	TJ	BW
Y^{3+}		7.2			at 12°	TJ	BW
La^{3+}		7.9			at 12°	TJ	BW
Ce^{3+}		8.0			at 12°	TJ	BW
Pr^{3+}		7.9			at 12°	TJ	BW
Nd^{3+}		8.0			at 12°	TJ	BW
Sm^{3+}		8.0			at 12°	TJ	BW
Eu^{3+}		7.9			at 12°	TJ	BW
Gd^{3+}		7.7			at 12°	TJ	BW
Tb^{3+}		7.5			at 12°	TJ	BW
Dy^{3+}		7.2			at 12°	TJ	BW
Ho^{3+}		7.2			at 12°	TJ	BW

TABLE 2 (continued)

Metal	*Ligand*	*Log k (l . mole^{-1} . sec^{-1})*	*$\Delta H^{\ddagger}$ (kcal/ mole^{-1})*	*$\Delta S^{\ddagger}$ (e.u.)*		*Method*	*Ref.*
Er^{3+}		7.0			at 12°	TJ	BW
Tm^{3+}		7.1			at 12°	TJ	BW
Yb^{3+}		7.1			at 12°	TJ	BW
Lu^{3+}	murexide^{-}	7.4			at 12°	TJ	BW
La^{3+}	oxalate^{2-}	7.9	6	−2		PJ	CY
Nd^{3+}		7.9	6	−2		PJ	CY
Gd^{3+}		7.6	6	−3		PJ	CY
Tb^{3+}		7.4	6	−3		PJ	CY
Er^{3+}		6.8	7	−3		PJ	CY
Tm^{3+}		6.8	7	−3		PJ	CY
Dy^{3+}	AN^{-}	7.2	4	−12		TJ	CR
La^{3+}	XO	6.9				TJ	DP
Ce^{3+}		6.5				TJ	DP
Pr^{3+}		7.1				TJ	DP
Sm^{3+}		6.6				TJ	DP
Gd^{3+}		6.7				TJ	DP
UO_2^{2+}	SCN^-	2.4			at 20°	TJ	CS
	$CH_3CO_2^-$	3.0			at 20°	TJ	CS
	$CH_2ClCO_2^-$	2.1			at 20°	TJ	CS
	SO_4^{2-}	2.3			at 20°	TJ	CS

* For references to Tables 1 and 2 see pp. 70–73

F. FACTORS WHICH INFLUENCE THE RATE OF COMPLEX FORMATION

The amount of data now available is quite considerable, and the results quoted in Table 2 are intended to supplement those of Eigen and Wilkins[2]. The results suggest that although the formation rate is strongly dependent on the nature of the metal ion, it may also be influenced by other factors such as the number and nature of ligands already bound to the central ion, the ionic charges on both reagents, the solvent, and steric effects. These will be discussed in turn, and, where possible, the trends compared with those expected from the ion-pair mechanism.

(i) Nature of the metal

Complex-formation rate constants cover a very wide range whereas the reactions involving a particular metal ion vary at most over a few powers of ten and so the nature of the metal continues to be the main factor determining the overall rate. There is enough agreement between the rates of solvent exchange (Table 1) and the complex-formation rate constants (Table 2) to suggest that the rate determining steps for both reactions may be closely related.

The rates at which particular metal ions exchange solvent molecules have been interpreted in terms of electrostatic, steric and crystal field considerations of the complex and the activated intermediate[31]. Solvation differences between ground state and the intermediate or transition state and the ability of the solvent to stabilise complexes of higher or lower coordination number are also of importance but no single factor can be held responsible for the observed rates[31]. In general, increased nuclear charge on the metal ion, and decreased ionic radius appreciably lower the rate of solvent exchange. Thus while the sodium cations have a water-exchange rate constant of greater than 10^9 sec^{-1}, the analogous figure for magnesium is 10^5 sec^{-1} and that for aluminium 10^{-1} sec^{-1}. Steric factors have been used to explain the large difference in rate between ferric iron and aluminium on the one hand, and the lanthanides on the other since the latter group are capable of expanding their first coordination sphere above six[38], and entropy changes are consistent with this explanation.

One of the more successful relationships for explaining the rate of water exchange at a range of metal ions has been used by Caldin[39] and links a high exchange rate with a low electron density at the perimeter of the ion and hence to a low ratio of nuclear charge to radius. On this basis we should expect exchange rates in the order $La > Y > In > Sc > Ga \approx Fe > Al$ and $Hg > Cd > Ca > Mn > Mg > Be$ from a consideration of their ionic radii[40], and also $Al^{3+} \gg Mg^{2+} \gg Na^+$. Although zinc falls somewhat out of line, and a number of exchange rates have been guessed from complex formation data and an outer-sphere stability constant, quite good agreement is found in most cases.

It will be noted that, with the exception of manganese, the examples do not include any with partially filled *d* orbitals, and so are not susceptible to crystal field effects which could have a strong influence on the solvent-exchange rate. The nature of the metal, in particular its ratio of charge to radius and its crystal-field activation energy, appears to be the major factor in determining the rate of solvent exchange and complex formation, and the remaining parameters may explain variations in observed rates for different complexes of the same metal ion.

There are a few cases where the solvent-exchange rate is greater than the rate at which ligands diffuse through the solution, and these reactions are independent of ligand concentration but alter with varying ligand charges[17], as would be expected for a diffusion controlled process. The reactions of sodium ions with $(EDTA)^{4-}$ and nitrilo triacetate^{3-} are examples of this type.

(ii) Ligands already bound to the metal

If the solvent-exchange rate is simply related to the electron density at the perimeter of the ion, it might be anticipated that the presence of ligands in the coordination sphere of a metal ion would increase the solvent-exchange rate at remaining positions. Ligands are, in general stronger electron donors than the solvent, and would cause the metal ion to receive a larger share of the bonding electrons. This could be expected to result in a slight decrease in the charge on the metal, an increased ionic radius, and hence a faster exchange rate.

Solvent-exchange studies have shown that the presence of a ligand does labilise the remaining solvent molecules in a number of cases. For instance, the rate at which exchange takes place in a methanolic solution of cobalt perchlorate increases on addition of small quantities of water[36] and similar effects have been noted with magnesium[33] and aluminium[41].

However, acceleration of the water-exchange rate in aqueous solutions of nickel chloride has been found on the addition of lithium chloride or lithium perchlorate and has been attributed to salt effects[42].

The rates at which subsequent metal–ligand bonds are formed in a partly substituted complex are also, in general, greater than those for the initial reactions. This acceleration is not caused by any change in formal charge on the metal, but since any outer-sphere association is thought to be ionic in nature, it seems that the effect may be related to alteration of the solvent-exchange rate which is dependent on changes in electron density, caused by metal–ligand bond formation.

The rate at which a second molecule of terpyridine or 4-(2-pyridylazo) resorcinol is added to the mono terpyridyl complex has been found to be about 100 times faster than the rate of formation of the mono complex[43]. The solvent-exchange rate for an aqueous solution of $\mathrm{Ni(terpy)}^{2+}$ is however only 1.5 times that for $\mathrm{Ni(H_2O)_6}^{2+}$ and the increased rate is therefore thought[55] to be due to a large increase in K_0. The ligand is uncharged in this case and the proposed value for the stability constant is remarkably high for a simple dipolar interaction.

Electron-donor properties of the initial complex have been said to control the rates at which a series of mono-5-substituted *o*-phenanthroline complexes of nickel(II) react with nitrilotriacetate[19]. The rates increased by a factor of two when the electron withdrawing nitro group on *o*-phenanthroline was replaced by a methyl group. Steric considerations are not thought to be important because the substituents are remote, and an identical ratio (of $k_{\mathrm{CH_3}}:k_{\mathrm{NO_2}}$) was found when a positively charged ligand was used instead of $(\mathrm{NTA})^{3-}$, suggesting that while the association constant is sensitive to ionic charge, the solvent-exchange rate may depend more on the local electron density experienced by the metal–solvent bond[*].

---

[*] A factor of two in a rate constant indicates a change in $\Delta G^{\ddagger}$ of ~0.5 kcal/mole, and this small effect may arise from a number of other sources such as changes in solvation energy.

(iii) The charge on metal and ligand

The rates of reaction of aquo nickel ions with ligands of various charges illustrates quite clearly the dependence of rate on the charge of the ligand:

Ligand	*Log k*	*Ref.*	*Ligand*	*Log k*	*Ref.*
NH_3	3.2	BT	α-alanine$^-$	4.3	BM
5-NO_2ophen	3.2	BL	glycine$^-$	4.3	2
imidazole	3.7	2	bioxalate$^-$	3.7	CC
bipy	3.3	2	SCN^-	3.7	2
succinate^{2-}	5.6	CU	NTA^{3-}	5.6	DK
malonate^{2-}	4.8	CD	$HP_2O_7{}^{3-}$	6.3	2
cystein^{2-}	5.2	BX			
MNT^{2-}	4.8	CE	$HP_3O_{10}{}^{4-}$	6.8	2

However, when the central atom is coordinated to a variety of charged ligands (such as EDTA), and the rate at which a remaining solvent molecule is replaced by an uncharged ligand is recorded, little difference is observed, even when the number of solvent molecules is the same[44]. The charge effect would therefore seem to result from alterations in K_0 rather than the solvent-exchange rate, because the latter would be expected to depend on ionic charge whereas variation with the product of the charges is found.

Support for this proposal is found in the very high rates of formation found[45] in reactions involving highly charged species such as polyphosphate^{4-} or nitrilo triacetate^{3-} when equation (8) suggests values of 10^2 to 10^3 for K_0, and in the slow rates found[19] with the diethylenetriamine species (Hdien$^+$).

(iv) Solvent

Observation of rates of formation in methanol has provided some results that are difficult to account for by any one-step mechanism, but are consistent with the Eigen mechanism. It was found that some ligands (*e.g.* MNT^{2-}) reacted more rapidly in methanol than in water whereas for others, (*e.g.* *o*-phen) the opposite was true[46]. The lower dielectric constant for methanol would give larger values of K_0 than those found in aqueous solution, especially for highly charged ions. Solvent exchange on the other hand, is faster for water than methanol and so zero- and perhaps singly-charged ligands could be expected to react faster in water while ligands with two or more negative charges should be faster in methanol. A dissociative (S_N1) production of a 5-coordinated intermediate would be expected to show higher rate constants in methanol than in water irrespective of the nature of the ligand, because of the weaker metal–solvent bond[46].

The rate of complex formation has been found to depend on the macroscopic dielectric constant of the solvent and plots of log k_{obs} versus $1/D$ are linear under certain circumstances[47,48]. The energy of activation can be split into two components, $E = E_T + E_D$ where E_T is a function of the dielectric constant and E_D represents the activation energy of the reaction at a fixed dielectric constant. E_T is a linea rfunction of $\log D$ and has a remarkably low value in the reaction of acetonlyacetone with copper(II) in methanol/water mixtures[48].

(v) Chelate conformational effects

At comparable ionic strengths, substitution rates of coordination with multidentate ligands have been found to be almost the same as those of related monodentate complexes. For example:

Metal	*Ligand*	*Log k_{obs} (25°)*	*$\Delta H^{\pm}$*	*Ref.*
Ni	NH_3	3.2	10	BT
	py	3.7	13	2
	phen	3.6	14	2
	terpy	3.1	13	2

The overall rate appears to be largely determined by the rate of formation of the first metal–ligand bond and subsequent bonds are formed more rapidly, possibly because of an increased solvent-exchange rate. However, some chelate systems such as β-aminobutyric acid or β-alanine, react more slowly than the corresponding α-compounds, and the difference has been shown to be more pronounced in manganese than in cobalt and least noticeable in nickel[49]. An interpretation of these results is that although under normal circumstances second and subsequent bonds are formed more rapidly than the first, a bidentate ligand may take some time to "swing round" to the bonded position if it is inhibited sterically. If this time is greater than the average residence time of a solvent molecule, the second bond may no longer be formed as soon as the corresponding solvent molecule leaves the metal and separate relaxations for complex formation and ring closure are observed under favourable conditions[57]. Systems in which solvent loss is rapid are more susceptible to this effect in agreement with the observations on manganese, cobalt and nickel. The formation of a complex of copper with L-β-alanyl–histidine, (a seven-membered-ring chelating ligand) has also been shown to be much slower than for most copper compounds but the formation of the analogous cobalt complex is "normal"[50].

This work provides a useful pointer to the mechanism of formation of multidentate complexes which takes place at lower rates than with simpler ligands. The striking specificity demonstrated by metal ions in a wide variety of biological environments may also depend to some extent upon the greater sensitivity of labile complexes to conformational factors of this kind.

G. EVIDENCE RELEVANT TO THE MECHANISM OF COMPLEX FORMATION

We have seen that the effects of factors such as the nature of metal, ligand and solvent *etc*., may be accounted for by the proposed "dissociative intermediate", mechanism (*B*). Additional data, which may be discussed in terms of this mechanism can be obtained from studies of inert systems, sound absorption experiments and activation enthalpy data.

(i) Sound absorption experiments

Studies of ultrasonic absorption have given some interesting results particularly in the study of M^{2+} sulphates. Atkinson and Kor[11], have stated that a total of three relaxation processes can be detected in aqueous solutions of magnesium and manganese sulphate, but this has been disputed[12]. There seems little doubt that the two uncontested chemical relaxations involve diffusion-controlled approach of the metal and anion, and solvent exchange at the metal ion. The intermediate relaxation has been attributed to solvent exchange at the anion[26] on the grounds that identical values have been obtained in solutions of magnesium, manganese and cobalt sulphates.

The value of the rate constant proposed to represent loss of water from sulphate ion is 7×10^7 sec^{-1}. This value seems remarkably slow in comparison with the solvent-exchange rates typical of large positively charged ions and is less than that attributed to water exchange at rare earth metals in solutions of lanthanide sulphates[40]. The single relaxation times observed for the lanthanides give rate constants which vary with the ionic radius of the individual metals, and cannot arise entirely from solvent exchange at the sulphate ion.

If it is assumed that the rate of solvent exchange at the ligand is more rapid than at the metal, the detailed path of mechanism (*B*) may be written:

$$\mathrm{M(solv)+L(solv)} \underset{k_{12}}{\overset{k_{21}}{\leftrightarrows}} \mathrm{M(solv)\,(solv)L} \underset{k'_{12}}{\overset{k'_{21}}{\leftrightarrows}} \mathrm{M(solv)L} \underset{k_{23}}{\overset{k_{32}}{\leftrightarrows}} \mathrm{ML}$$

where non-participating solvent molecules have been omitted. The pre-equilibrium constant in (7), K_0, then represents $\dfrac{k_{12}k'_{12}}{k_{21}k'_{21}}$ and the extra step would not influence the observed kinetic behaviour appreciably and would remain undetected.

(ii) Comparison with inert systems

The rates of anation of cobalt(III) and chromium(III) complexes have been extensively studied. Results from these systems are fully reported elsewhere[1] and are usually explained on the basis of dissociation followed by competition between ligand and solvent for the five coordinated intermediate[9]. At high ligand concentrations, ligand consumes the intermediate as it is formed and first-order kinetics with no ligand-concentration-dependent term is observed. In more dilute solutions, the solvent becomes a more effective competitor and second-order rate constants are found.

It has been pointed out that the experimental results are also consistent with mechanism (*B*) and the formation of an associated species as intermediate[51]. Second order kinetics are observed when $K_0[\mathrm{L}] \ll 1$ and first order when the converse is true. Equally, however, it should be recognised that the mechanism (*A*) is consistent with most rapid reactions.

The choice between the mechanisms reduces to an argument as to whether the intermediate is five-coordinated, or an outer sphere associated species, and possibilities for distinguishing which is operative will be discussed later.

(iii) Enthalpy of activation

Those rate constants that are accompanied by enthalpy data usually have values of $\Delta H^{\pm}$ which are similar to, or slightly greater than the enthalpy of activation for the solvent exchange process. (Tables 1 and 2). Calculations of K_0 from equation (8) using experimental values for the bulk dielectric constant at each temperature suggest that $\Delta H°$ in aqueous solution may be given by

$$+2.3 \times \frac{Z_1 Z_2}{(\mathring{a})} \text{ kcal/mole,}$$

where $(\mathring{a})$ is the distance between metal and ligand in angstroms. For reasonable values of $(\mathring{a})$ we can expect $\Delta H°$ to take values of 0.5 to 3.0 kcal/mole, and the major contribution to the overall enthalpy of activation for complex formation would then be that involving solvent loss.

H. CONCLUSION

Most experimental results are consistent with the intuitively satisfying mechanism proposed by Eigen, hut the widespread acceptance of this path (as with any mechanistic assignment for processes for which only kinetic data are available) is based on consistency rather than direct evidence, and few experiments have been designed to test rigorously the proposed mechanism.

On the other hand many values for the rate of solvent exchange at the solvated ion have been obtained from measurements of k_{obs} and estimates of K_0. As we have mentioned earlier, this involves the (probably) drastic assumption that ion-pair formation does not affect the solvent-exchange rate.

So far as the alternative mechanisms, (*A*), (*C*) and (*D*) are concerned, the reasons for dismissing an associative mechanism such as (*C*) seem to be based on the statement that the rates of formation of complexes are practically independent of the nature of ligand[2]. It is true that the metal has a greater influence than that of the ligand, but the results (*e.g.* Table 2, those for nickel(II)) can hardly be said to be completely independent of ligand although little variation in rates is observed with ligands of the same charge.

For mechanism (*A*), it is difficult to see how rates of complex formation numerically greater than the solvent-exchange rate can occur[53], but examples of this may be found in Table 2.

With a basic ligand and with a readily hydrolysable metal ion, it would seem that mechanism (*D*) may well be concerned since, in kinetic terms the reaction between HL^+ and $M(OH_2)_n(OH)^{z+}$ is indistinguishable from that between L and $M(OH_2)^{(z+1)+}$. Attempts to distinguish between these two extreme possibilities involve several assumptions[54].

At least two points would repay further investigation. The rate of solvent exchange at a solvated ion is assumed to be independent of the nature and concentration of the ligand, and exchange rates with various anions could be studied in order to confirm this. Also, mechanism (*C*), could in principle, be distinguished from (*A*) and (*B*) (and also from a mechanism involving unreactive ion pairs[13]) by variation of ligand concentration. (*A*) and (*B*) give rate expressions of the form $k_{obs} = X(1+[Y]L)^{-1}$ at high concentrations, where X and Y are functions of individual rate constants, whereas, for path (*C*), k_{obs} should remain independent of concentration.

Experimental difficulties may, at present preclude accurate study of these points, but the authors feel that a knowledge of the extent to which mechanism (*B*) has been accepted without question might galvanise some further activity in this field.

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