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THE USES OF NUCLEAR MAGNETIC RESONANCE IN THE STUDY OF LIGAND SUBSTITUTION PROCESSES

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CONTENTS

ABBREVATIONS

acac = acetylacetonate
trac = trifluoroacetonylacetonate
dmf = dimethylformamide
dmg = dimethylglycine
dmso = dimethylsulfoxide
gly = glycine

en = ethylenediamine
imda = iminodiacetate
sarc = sarcosine
ss = sulfosalicylate
tpp = triphenylphospine

A. INTRODUCTION

The study of rates and mechanisms of substitution of one ligand of a coordination compound by another has reached an advanced state of sophistication. However, there is an important limitation to such studies which is especially serious for octahedral complexes. A solvent molecule is almost inevitably a participant, either as the entering ligand or as the leaving ligand. This situation brings into the foreground reactions of the type:

$$MS_6+S^* = MS_5S^*+S$$

where M is a metal, S is the solvent, and the asterisk marks an artificial (often experimentally entirely meaningless) distinction between solvent molecules.

The reaction is an exchange process for which no net chemical change occurs. Obviously, usual analytical parameters of the system cannot yield information on the rate. The classical method for coping with the problem (classical is here understood in the common usage meaning "last but one") is the creation of a trivial net chemical reaction by isotopic labeling. Then the rate of redistribution of an isotope may be followed and (within the error of neglect of kinetic isotope effects) the exchange rate inferred. With the recognition that nuclear magnetic resonance absorption (n.m.r.) line shapes depend upon molecular dynamical processes which may include the exchange of nuclei between chemically inequivalent sites, a new tool was brought to bear on the exchange reaction problem. It has proved to be an especially powerful tool in that it is not limited by the requirements of chemical separation and has been applied to ligand exchange processes with rate constants up to 10^9 sec^{-1}. This review recapitulates the theory of the n.m.r. method and considers the role of exchange rates in the analysis of ligand substitution mechanisms.

B. THEORY

(i) *General remarks*

To study fluxes in an equilibrium system, one must examine a property which depends on the behavior of a molecule over a time span which is long compared with the processes giving rise to the vibrational or electronic spectra. The infrared and ultraviolet spectra of an equilibrium mixture are simply superpositions of the spectra of the components of the mixture and do not reflect the dynamic nature of the equilibrium. In radiofrequency spectroscopy, however, the lineshape often depends on relaxation processes which are fairly slow. For example, the width of a proton n.m.r. line in a diamagnetic liquid is dependent upon a transverse relaxation time which may be many seconds long. Should the proton be involved in some reversible chemical transformation which takes place in a time comparable to the relaxation time, the line shape will be modified. Under certain conditions it is possible to determine the rate of the transformation by its effect upon such a lineshape[1].

Given that the n.m.r. spectrum is sensitive to reaction rates, the question at the crux is: "What is the order of magnitude of rates which may be measured?" There is no single simple answer. Whether or not a particular rate can be measured depends on a comparison between the desired rate and the rate of one or more of several possible relaxation processes. In different situations, relaxation times may vary as much as eight powers of ten. Each type of reacting system must be considered as a separate case. Several examples of systems which are important in coordination chemistry are treated here.

(ii) *Basic principles*

First we examine a particularly simple case of chemical exchange from organic chemistry exemplified by the protons of *N,N*-dimethyl-trichloroacetamide, DMTCA, (the subject of Fig. 1[2]). In this molecule, hindered rotation about the C–N bond leads to the methyl protons being divided into two non-equivalent sets based on their positions with respect to the oxygen atom. When the rate of exchange of protons between the two environments (rotation about the C–N bond) is very slow, the resulting spectrum shows two lines, one from each set of protons. As the temperature is raised, the exchange becomes rapid enough to affect the spectrum. At first, the lines are simply broadened. At greater exchange rates, the two lines merge into a single broad line. This point is often called the coalescence temperature. At higher temperatures the line becomes narrower until a limit is reached where further increases in the exchange rate have no effect on the spectrum.

This effect of changing exchange rate on the n.m.r. spectrum is well understood. A simple and straightforward treatment of n.m.r. absorption is based on the Bloch phenomenological equations for the magnetization of the sample[3]. When a sample is placed in a magnetic field, H_0, a magnetization is induced within the material which may be described by a vector M. The observed n.m.r. spectrum is determined by the motion of M under the influence of an applied radiofrequency field, H_1. The Bloch equations are a set of three differential equations which give the variation with time of the three components of the vector M. One component is taken along the direction H_0; it is denoted M_z, and its direction is called the longitudinal direction. The other two components are in a plane perpendicular to H_0 and M_z. The radiofrequency field is applied in this plane. Since the components in this plane vary sinusoidally with time, it is convenient to define the variables u and v as the transverse components of the magnetization which are in phase and 90° out of phase with the impressed radiofrequency field H_1. This definition is equivalent to taking the transverse components of M with respect to a coordinate system rotating at the frequency of H_1 instead of using a set of laboratory fixed axes. In the crossed coil n.m.r. experiment, the absorption signal is proportional to v.

In the rotating coordinate system, the Bloch equations are:

$$\mathrm{d}M_z/\mathrm{d}t = \gamma H_1 v - (M_z - M_0)/T_1 \qquad (1\text{–a})$$

$$\mathrm{d}v/\mathrm{d}t = -\gamma H_1 M_z + (\omega_0 - \omega)u - v/T_2 \qquad (1\text{–b})$$

$$\mathrm{d}u/\mathrm{d}t = -(\omega_0 - \omega)v - u/T_2 \qquad (1\text{–c})$$

where γ is the magnetogyric ratio of the nucleus, ω_0 is the frequency of precession of the nucleus, ω is the frequency of the radiofrequency field, and T_1 and T_2 are the longitudinal (spin-lattice) and transverse (spin–spin) relaxation times respectively. Equation 1–a shows the behavior of M_z to be the result of two opposing processes. The first term on the right describes the interaction between M and H_1. This causes M_z to depart from its equilibrium value. The second term takes into account the effect of spin-lattice relaxation which causes M_z to decay back to its equilibrium value, M_0, with a time constant T_1. Equations 1–b and 1–c result from similar considerations. In particular, the last term in these equations describes the tendency of u and v to decay to their equilibrium values of zero with a time constant T_2.

The microscopic interpretation of T_2 can be seen if one thinks of a sample as a collection of nuclear magnets (spins) which are precessing about the H_0 direction. If they all move in phase with one another, the projections of their moments onto the xy plane will be parallel and add up to a finite value for M_{xy}, which will result in nonzero values for u and v. In the absence of any outside influences, various processes will cause the spins to get out of phase with one another over a period of time. When the phases have been completely randomized, u and v will be zero. This is the process of spin–spin relaxation.

If one sweeps through the spectrum slowly, the steady state conditions apply. The magnetization of the sample changes slowly, and the time derivatives in the Bloch equations may be set equal to zero. The observed signal is the result of the two opposing tendencies; the effect of H_1 in bringing spins together, and the effect of relaxation processes which dephase the spins. This opposition causes the absorption of energy to take place over a range of frequencies, giving the n.m.r. line a finite width which is related in a simple way to the value of T_2.

To include the possibility of chemical exchange between two sites A and B, one sets down the differential equations for the protons of type A and then adds two terms, one of which includes the effect of A type magnetization disappearing as A protons are converted into B protons, the other accounts for the appearance of A type magnetization as B protons are converted into A. Finally, one obtains a total of six equations, three for each type of proton. This treatment was first presented by Gutowsky, McCall, and Slichter[4], and by McConnell[5]. A discussion of it is given in several texts[1]. It is convenient to divide the results of the analysis into several categories depending on the magnitude of the exchange rate, and to discuss each one separately.

Consider a system where the spectrum consists of two isolated narrow lines unmodified by chemical exchange. The widths of the lines are an easily measured parameter of fundamental significance. It can be shown, using the unmodified Bloch equations, that the line widths (in this paper, the full line width at half height) in cycles per second are related to the transverse relaxation times T_2 by[3]:

$$\Delta\nu_A = 1/\pi T_{2A};\ \Delta\nu_B = 1/\pi T_{2B} \tag{2}$$

where the A and B indices refer to the type of proton. The reciprocal of the transverse relaxation time is determined by the rate of physical processes which cause the precessing nuclei to loose phase coherence with each other and hence cause the value of the transverse magnetization (u and v) to decay to zero in the absence of H_1.

When chemical exchange between the two environments is slow but significant, the two lines are broadened slightly, and their widths may be described by the apparent relaxation times T'_{2A} and T'_{2B} where:

$$1/T_{2A}' = 1/T_{2A}+1/\tau_A;\ 1/T_{2B}' = 1/T_{2B}+1/\tau_B \tag{3}$$

τ_A and τ_B are the mean lifetimes of a proton in the environments A and B respectively. These equations adequately describe the line widths as long as the two lines are not so broad as to overlap. This is the condition illustrated by the curve at −3.5° in Fig. 1. The condition is described as the "slow exchange region", in which the line broadening must be small compared to the line separation.

An example of a kinetic study in coordination chemistry using data from the slow exchange region is found in the work of Matwiyoff on the Co^{II}-N,N-dimethylformamide system[6]. At quite low temperatures it was possible to distinguish

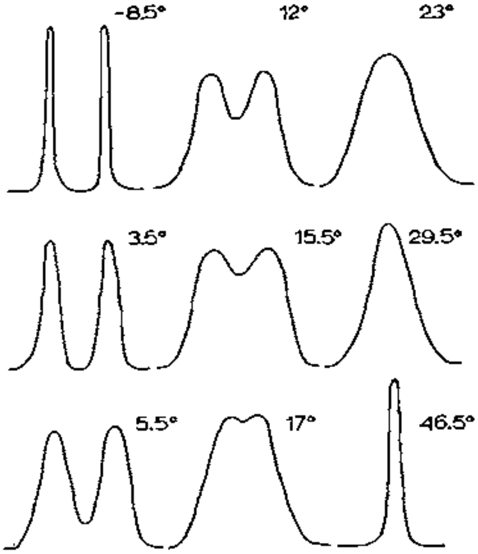

Fig. 1. The proton magnetic resonance spectrum of pure liquid N,N-dimethyltrichloroacetamide (DMTCA) as a function of temperature at 60 MHz. The frequency scale, but not the intensity scale, is the same for all temperatures.

two sets of dimethylformamide (dmf) signals in a solution of Co(dmf)$_6$(ClO$_4$)$_2$ in dmf. One of these originates from dmf in the bulk solvent; it is strong and relatively narrow. The other is from dmf molecules bound to the Co ion; it was broad and weak due to interaction with the paramagnetic ion. Three lines of this second set (corresponding to the three types of protons on dmf) were observed and their widths as a function of temperature are presented in Fig. 2. At the lower temperatures, the exchange of dmf molecules between sites is so slow as to have virtually no effect on the spectrum. The weak temperature dependence of the linewidth is due to the change of the relaxation time T_{2M} (M refers to the environment of the coordination sphere of a metal ion). At higher temperatures, at which $\tau_M{}^{-1}$ becomes significant, the linewidth increases rapidly because of the strong temperature dependence of τ_M. Finally, at temperatures where $1/T$ (the reciprocal of the absolute temperature) < 0.0043, the separate signals from coordinated dmf can no longer be observed. In the intermediate temperature region of Fig. 2, exchange rates may be calculated from equation 3, and a straight line fitted to the temperature dependence yields the activation energy. The results are in excellent agreement with values obtained from other data (*vide infra*).

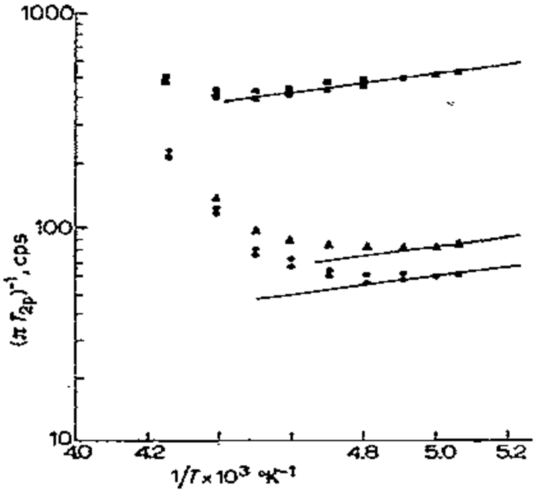

Fig. 2. Temperature dependence of $(\pi T_{2M})^{-1}$ for the formyl and methyl protons in the complex Co(dmf)$_4^{2+}$.

If the spectrum of the bulk solvent protons is examined in the same temperature range, similar behavior is observed. At low temperatures, where exchange is negligible, the solvent proton linewidths also show a very slight temperature dependence. This is illustrated in region I of Fig. 3 which shows another system, the bulk solvent proton resonance of the acetonitrile–Ni$^{\text{II}}$ system over a wide temperature range[7]. The low temperature linewidths of bulk solvent protons are principally determined by long range interactions between the bulk solvent and the metal atom when the metal complex is paramagnetic; this is often called "second

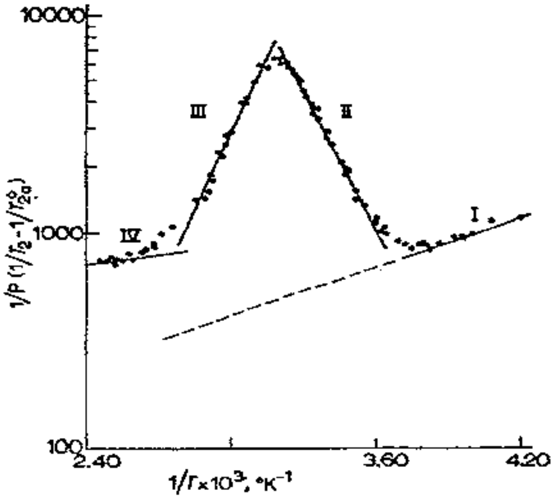

Fig. 3. Temperature dependence of $(1/P_M)\,(1/T_2-1/T_{2A}^0)$ for the protons in CH_3CN solutions of $Ni(CH_3CN)_6^{2+}$ at 56.4 MHz.

sphere broadening", and it depends upon factors similar to those entering into T_{2M}. When the exchange is fast enough to be significant, the linewidth increases rapidly with increasing temperature as shown by region II of Fig. 3. This is the region from which exchange rate data are usually derived since the most accurate results may be obtained. The signal of the bulk solvent protons is strong and its shape is very sensitive to the rate. The exchange rate is usually calculated from the expression:*

$$1/T_2-1/T_{2A}^0 = 1/\tau_A = P_M/\tau_M \tag{4}$$

where the subscript A indicates the bulk solvent phase, and T_{2A}^0 is the relaxation time observed in the pure solvent. This equation ignores the effect of second sphere broadening. If we assume that the second sphere effects observed in region I can be extrapolated to high temperature, the dotted line of Fig. 3 results. Some authors correct their linewidth data by subtracting the extrapolated value of the second sphere broadening, some do not. At present there is not enough evidence to judge the validity of the extrapolation.

Since the linewidths in region II are closely related to τ_M, it is a simple matter to calculate the activation parameters for the pseudo first order exchange reaction from equation(5).

$$k_1 = 1/\tau_M = \frac{kT}{h}\exp\left[-\Delta H^{\neq}/RT+\Delta S^{\neq}/R\right] \tag{5}$$

Many solvent–metal ion systems have been analyzed using these expressions.

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* It can be shown by detailed balancing that:

$$P_A = \frac{\tau_A}{\tau_A+\tau_M};\quad P_M = \frac{\tau_M}{\tau_A+\tau_M}.$$

Thus, for dilute solutions where P_M is small, $\tau_A^{-1} = P_M\tau_M^{-1}$.

(iii) *Relaxation times in paramagnetic solutions*

In solutions of paramagnetic ions, T_{2M} is much smaller than T_{2A} and a simple physical picture of the process leading to region II can be given. If there is no exchange, a solvent will have a relaxation time T_{2A}. However, if the average lifetime of a molecule in the bulk solvent between periods of being bound to a paramagnetic ion is short compared to T_{2A} (*i.e.* $\tau_A \ll T_{2A}$) a second relaxation mechanism may become important. In particular, if the solvent remains coordinated long enough for relaxation to occur ($\tau_M \gg T_{2M}$), it will be relaxed every time it enters that environment. When $\tau_A \ll T_{2A}$, this mechanism predominates, and the relaxation time is simply the mean lifetime of the molecule in the bulk. According to this view, a solvent molecule spends most of its time in the bulk phase, but it will occasionally bind to the metal for a brief period. During this time, it is relaxed (dephased with respect to other nuclei in the sample). Coordination to the metal produces a paramagnetic pulse which alters the phase of the precessing nucleus. This picture (which may be applied to the analysis of Fig. 3) focuses attention on factors other than those which are important to the analysis of Fig. 1. In that figure, $T_{2A} = T_{2B}$, and the most important parameter is the chemical shift between the two environments. In the present case, the difference in relaxation times (T_{2A} and T_{2M}) is paramount, and the same linewidth effects would be observed even if the chemical shift were zero.

If one is to consider both the effects of a relaxation time and a chemical shift, it is necessary to carry out a rigorous solution of the Bloch equations for the system. This was done by Swift and Connick [6], and their results have been used as a guideline by all subsequent workers in the field. For a solution which is dilute in the metal ion, the relaxation time is given by:

$$\frac{1}{T^2} - \frac{1}{T_{2A}} = \frac{P_M}{\tau_M}\left[\frac{T_{2M}^{2-} + (T_{2M}\tau_M)^{-1} + \Delta\omega_M^{\,2}}{(T_{2M}^{\,-1} + \tau_M^{\,-1})^2 + \Delta\omega_M^{\,2}}\right] \tag{6}$$

where T_2 is the experimentally observed relaxation time and $\Delta\omega_M$ is the chemical shift between bulk solvent and the coordination sphere of the metal.

It is convenient to consider the implications of equation (6) for two limiting cases depending on the magnitude of τ_M. If the exchange is not too rapid, we obtain the results discussed earlier with the additional point that the effect of the chemical shift is taken into account. This gives two possibilities. In one case the relaxation of the solvent nuclei in the paramagnetic environment is caused by the chemical shift; in the second case it is brought about by other factors. It is easy to see that a chemical shift will cause relaxation, since a nucleus at a metal ion will precess at a rate different from the nuclei in the bulk solvent. The difference in precession rates will lead to dephasing of the two sets of nuclei, in a time τ_M, the phase difference will be given by $\tau_M\Delta\omega_M$. If the chemical shift is large, and τ_M not too small, equation 6 leads to:

$$\Delta\omega_M{}^2 \gg T_{2M}{}^{-2}, \tau_M{}^{-2}; 1/T_2 - 1/T_{2A} = P_M/\tau_M \tag{7}$$

The same result for the linewidth is obtained when factors other than the chemical shift dominate the relaxation process:

$$T_{2M}{}^{-2} \gg \Delta\omega_M{}^2, \tau_M{}^2; 1/T_2 - 1/T_{2A} = \frac{P_M}{\tau_M} \tag{8}$$

Hence, in this temperature region, the exchange rate can be determined regardless of the relaxation mechanism. This is a fortunate result. The details of the relaxation process are often unclear.

If the exchange rate is rapid compared with the conditions for which equations 7 and 8 are appropriate, the linewidth changes with temperature as shown in regions III and IV of Fig. 3. Here the lifetime in the coordination sphere is too short for relaxation to occur each time the solvent binds to the metal. Since several encounters between solvent and metal are required for relaxation, the linewidth is no longer directly proportional to the exchange rate. As before, there are two possibilities; effects due to chemical shift may predominate, or, if $\Delta\omega_M$ is small, terms depending on T_{2M} will be important. In the former situation we have:

$$\tau_M{}^{-2} \gg \Delta\omega_M{}^2 \gg (T_{2M}\tau_M)^{-1}; 1/T_2 - 1/T_{2A} = P_M\tau_M\Delta\omega_M{}^2, \tag{9}$$

Since the linewidth depends upon τ_M, it will change rapidly with temperature but in a direction opposite to region II. If the chemical shift is independently known, τ_M values and hence the exchange rate can be determined.

Finally when the exchange rate is extremely fast, or the chemical shift is small, we have:

$$(T_{2M}\tau_M)^{-1} \gg T_{2M}{}^{-2}, \Delta\omega_M{}^2; 1/T_2 - 1/T_{2A} = P_M/T_{2M} \tag{10}$$

Here the linewidth no longer depends on the exchange rate, and it varies but slightly with temperature. This is the limiting high temperature region found in most systems; it is generally called the "fast exchange region".

We may now summarize the stages of a typical experimental study. The linewidth of the pure solvent is measured over as wide a temperature range as possible. Then a solution of a paramagnetic ion is studied. The quantity log P_M $(1/T_2 - 1/T_{2A}{}^0)$ is plotted *vs.* reciprocal temperature; the slope of the plot indicates which conditions apply, especially in view of the relatively large values of chemical activation energies. Sometimes, the exchange process is too fast to measure over the entire liquid range of the solvent. Often this difficulty can be circumvented by taking as the probe nucleus the atom directly bound to the metal instead of a proton on the solvent (ligand) molecule. For this atom, $\Delta\omega_M$ is especially large, and T_{2M} is quite small. These conditions extend the applicability of equations 7 through 9. However, the experimental difficulties are often greater since one must deal with "less receptive nuclei" such as ^{14}N and ^{17}O.

A few studies in the literature report linewidth data at room temperature only.

In this case, it is not possible to tell which of the four regions of Fig. 3 is under observation. Usually one is confident that the reaction is too fast to be in region I and calculates an apparent rate constant from equation 7. If the conditions of region II apply, the true rate results. If the reaction is quite fast, and III or IV is appropriate, the experimental linewidth will be less than the linewidth expected for exchange rate control. Then the rate calculated from equation 7 will be less than the true rate. In such studies, a "lower limit" for the exchange rate is usually reported.

(iv) *Chemical shifts in paramagnetic solutions*

The linewidth is not the only parameter which is affected by chemical exchange. Fig. 1 shows a pronounced change in chemical shift as exchange become important. For diamagnetic systems such as the one shown in that figure, it is a common practice to use the separation of the two maxima to calculate the exchange rates at lower temperatures[9]. For dilute solutions of paramagnetic ions, Swift and Connick derived the relationship between the observed chemical shift and the exchange rate. They found that the shift of the solvent signal is given by:

$$\Delta\omega_P = -\Delta\omega_M/\tau_A\tau_M\,[(1/T_{2M}+1/\tau_M)^2+\Delta\omega_M{}^2] \qquad (11)$$

where $\Delta\omega_p$ is the experimental resonance frequency minus the frequency observed in the pure solvent. This quantity does not take bulk susceptibility effects into account; however, measurements are customarily made with respect to an internal standard and no correction is needed. Under certain conditions, equation 11 simplifies in a manner similar to equation 6. In fact the conditions are the same as those stated in 7 through 10.

$$\Delta\omega_M{}^2 \gg T_{2M}{}^{-2}, \tau_M{}^{-2};\ \Delta\omega_P = -P_M\Delta\omega_M{}^{-1}\tau_M{}^{-2} \qquad (12\text{–a})$$

$$T_{2M}{}^{-2} \gg \Delta\omega_M{}^2, \tau_M{}^{-2};\ \Delta\omega_P = -P_M\Delta\omega_M T_{2M}{}^2\tau_M{}^{-2} \qquad (12\text{–b})$$

$$\tau_M{}^{-2} \gg \Delta\omega_M{}^2 \gg (T_{2M}\tau_M)^{-1};\ \Delta\omega_P = -P_M\Delta\omega_M \qquad (12\text{–c})$$

$$(T_{2M}\,\tau_M)^{-1} \gg T_{2M}{}^{-2}, \Delta\omega_M{}^2;\ \Delta\omega_P = -P_M\Delta\omega_M \qquad (12\text{–d})$$

The chemical shift for the fast exchange case is given by 12–c and d. These are analogous to equation 10; no rate data can be obtained, although one can calculate $\Delta\omega_M$ which is used in equation 9. This region is labeled III in Fig. 4. The small temperature dependence follows from the small temperature dependence of the contact shift which makes up the major part of $\Delta\omega_M$. In principle, rate data may be obtained when the conditions for 12–a and 12–b are satisfied. These usually hold only over a short temperature range (region II in Fig. 4). Most workers prefer to use linewidths for rate studies. When exchange is slow, $\Delta\omega_M = 0$, and region I results. One might expect to see a small "second sphere" shift, but if an internal standard is employed, it is shifted by a similar amount and the net result is close to zero.

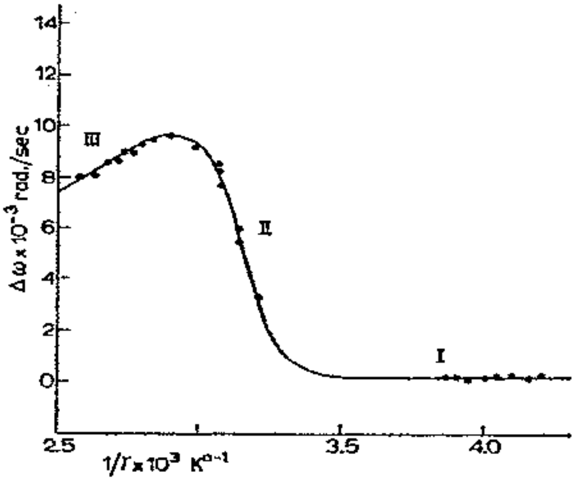

Fig. 4. Temperature dependence of $\Delta\omega_M$ for the protons in CH_3CN solutions of $Ni(CH_3CN)_6^{2+}$ at 56.4 MHz.

(v) *Mechanisms of ion-solvent magnetic interaction*

It is important that none of the above results depend upon the detailed mechanisms of the processes involved in relaxation and chemical shift. There are two types of interaction between a paramagnetic center and a nearby nucleus which can bring about nuclear relaxation. These are the electron spin–nuclear spin magnetic dipole interaction, and the contact term. The first is the simple interaction of two magnetic dipoles across space, while the contact term depends upon the density of the unpaired electron spin at the probe nucleus. Each of these interactions may be controlled by one of several correlation times. The relaxation time is the result of these many competing effects. The proton relaxation in the Mn^{2+}–H_2O system has been thoroughly studied by several workers. The complexity of the problem is nicely illustrated by their results[10].

The chemical shift is also dependent upon two factors, the contact shift and the pseudo-contact shift. The former arises from the same interaction that enters into relaxation. Since it can be related to an electron density, it is useful for extracting information on the nature of binding in a complex[11]. However, the determination of the contact shift from the observed chemical shift $\Delta\omega_M$ is complicated by the additional shift due to the pseudo-contact term. This effect is a result of a magnetic interaction between electron spin, electron orbital angular momentum, and nuclear spin. Its magnitude varies as the inverse cube of the distance and directly with the anisotropy of the g tensor[12].

(vi) *Quadrupolar relaxation*

In the very special case of some labile halide complexes, some fast reactions of diamagnetic complexes may be followed in another way. The relaxation of ^{35,37}Cl, ^{79,81}Br, and ^{127}I (but not ^{19}F) is dominated by the large electric quadrupole moment of the nucleus and its interaction with the electric field gradient[13]. The gradient originates in a non uniformity of the field at the nucleus due to nearby electrons, ions, etc. A free halide ion in solution is symmetrically solvated which gives an almost vanishing field gradient. However, when a halogen is involved in a chemical bond with some covalent character (*e.g.*, HgX_4^{2-}) the field gradient is quite large and a short relaxation time results. A solution of halide complex in the presence of excess halide ion is a system in which there are two environments available to the halogen, the bulk solution where the relaxation time is relatively long, and the coordination sphere where it is extremely short. The situation is quite comparable to the paramagnetic effect on relaxation time.

C. RESULTS OF EXCHANGE STUDIES

A fairly large number of systems have, by now, received attention. So far, relaxation time changes produced by paramagnetic ions have proved most fruitful, but data have been obtained for several diamagnetic systems and in a few cases advantage has been taken of quadrupole relaxation. A majority of the studies have employed proton resonance (probably because of the widespread availability of instrumentation).

Studies vary in complexity from observations at a single temperature which define only a lower limit to the exchange rate to those revealing most of the completetem perature profile of relaxation times discussed earlier in this Review. The Table of results (Table 1) accompanying this section summarizes the available literature through May 1967. Where adequate temperature dependence data were obtained, activation parameters are given in the Table along with rate constants at a specified temperature. In the absence of activation parameters, the reported rate constants are best viewed (conservatively) as lower limits to the exchange rates.

At the present stage of development of kinetic analysis by n.m.r., it is interesting to compare results obtained on a given chemical system as obtained from analysis of resonance lines of different nuclei in the same molecule. The available comparisons emerge from Table I. So far, the results are encouraging. It appears that subtle factors have not been overlooked and that the same exchange rate is inferred from study of each different nucleus. One, as yet unresolved but probably not serious, discrepancy does exist between the activation energy data for dmf exchange derived from ^{1}H and ^{17}O measurements. Where the nucleus under observation is not designated in Table 1, it is ^{1}H.

TABLE 1

RATES OF LIGAND EXCHANGE DETERMINED BY N.M.R. METHODS

Complex	*Ligand*	*Nucleus*	*Log k* sec^{-1} *(25°)*	$\Delta H^{\neq}$	$\Delta S^{\neq}$	*Ref.*
$Cr^{2+}(aq)$	H_2O	^{17}O	9.9	3		33
$Mn^{2+}(aq)$	H_2O	^{17}O	7.5	8	2	8
$Fe^{2+}(aq)$	H_2O	^{17}O	6.5	8		8
$Co^{2+}(aq)$	H_2O	^{17}O	6.0	8		8
$Ni^{2+}(aq)$	H_2O	^{17}O	4.4	12		8
$Cu^{2+}(aq)$	H_2O	^{17}O	9.9	4		33
$Fe^{3+}(aq)$	H_2O	^{17}O	0.6			14
$FeOH^{2+}(aq)$	H_2O	^{17}O	2.6			14
$Gd^{3+}(aq)$	H_2O	^{17}O	9.6*			34
$VO^{2+}(aq)$	H_2O equatorial	^{17}O	2.7	13	−1.5	29, 30
$VO^{2+}(aq)$	H_2O axial	^{17}O	$\sim$11			29
$VO(IMDA)(aq)$	H_2O	^{17}O	4.7			26
$VO(SS)^{-}(aq)$	H_2O	^{17}O	5.0			26
$Ni(NCS)_4(OH_2)_2^{-2}$	H_2O	^{17}O	6.0**	6		28
$FeCl_4^{-}(aq)$	Cl^-	^{35}Cl	5.0			15
$NiCl^{+}(aq)$	Cl^-	^{35}Cl	5.0	10		27
$Ni(NCS)_4(OH_2)_2^{2-}$	NCS^-	^{14}N	5.7	9		28
$Fe(NCS)_4^{-}$	NCS^-	^{14}N	5.0	10	−1.5	25
$Ni(NH_3)_6^{2+}$	NH_3	^{14}N	5.2	10	−1	21
$Co(NH_3)_6^{2+}$	NH_3	^{14}N	6.2	11	10	24
$Ni(aq)^{2+}$	H_2O		4.8	11	1	36
$Ni(NH_3)_6^{2+}$	NH_3		5.2	10	−0.5	35
$Ni(tpp)_2Br_2$	tpp		3.8	5	25	16
$Ni(tpp)_2I_2$	tpp		3.8	7	22	16
$Al(dmso)_6^{3+}$	dmso		−.3	20	4	23
$Ni(dmf)_6^{2+}$	dmf	^{17}O	3.8	9	−9	22
"	"		3.5	15	8	6
$Co(dmf)_6^{2+}$	dmf	^{17}O	5.3	7	−10	22
"	"		5.5	14	13	6
$Fe(dmf)_6^{2+}$	dmf	^{17}O	5.7			31
$Mn(dmf)_6^{2+}$	dmf	^{17}O	6.6			31
$Ni(CH_3CN)_6^{2+}$	CH_3CN		3.4	12	−4	4
$Co(CH_3OH)_6^{2+}$	CH_3OH		5.0	13		17
$Co(CH_3OH)_4(OH_2)_2^{2+}$	CH_3OH		6.3			17
$Co(CH_3OH)_5(OH_2)^{2+}$	CH_3OH		5.8			17
$Co(CH_3OH)_5Cl^{+}$	CH_3OH cis		3.2			18
$Co(CH_3OH)_5Cl^{+}$	CH_3OH trans		2.9			18
$Np(V)(CH_3OH)_n$	CH_3OH		4.9***	8	−8	19
$Co(gly)_3^{-}$	gly		3.8			20
$Fe(gly)_2$	gly		4.3			20
$Ni(sarc)_3^{-}$	sarc		1.8			20
$Co(sarc)_3^{-}$	sarc		2.7			20

* at 60°.

** at 8.0 M KCNS.

*** at 0°.

TABLE 1 – Continued

Complex	*Ligand*	*Nucleus*	*Log k* *sec^{-1} (25°)*	*$\Delta H^{\neq}$*	*$\Delta S^{\neq}$*	*Ref.*
$Ni(dmg)_3^-$	dmg		1.8			20
$Co(dmg)_3^-$	dmg		3.5			20
$Co(en)_3^{2+}$	en		3.7			20
	the following rate constants are 2nd. order (M^{-1} sec^{-1})					
$Co(en)_3^{2+}$	en		3.5			20
$Co(gly)_3^-$	gly		3.7			20
$Fe(gly)_2$	gly		4.6			20
$Ni(sarc)_3^-$	sarc		2.0			20
$Co(sarc)_3^-$	sarc		3.4			20
$Ni(dmg)_3^-$	dmg		2.7			20
$Co(dmg)_3^-$	dmg		3.9			20
Zr acac (in benzene)	acac		1.3			32
Zr tfac (in benzene)	tfac		1.4			32
Hf acac (in benzene)	acac		1.1			32
Hf tfac (in benzene)	tfac		1.6			32
Th acac (in benzene)	acac		2.8			32
Zr acac (in chlorobenzene)	acac		1.9			32
Zr tfac (in chlorobenzene)	tfac		1.7			32
Hf acac (in chlorobenzene)	acac		1.8			32
Hf tfac (in chlorobenzene)	tfac		1.6			32

D. MECHANISTIC IMPLICATIONS OF SOLVENT EXCHANGE RATES

Table 1 contains, chiefly, rate constants for the exchange of solvent molecules between the coordination sphere and the bulk of the solution. Such reactions are *inevitably* first order. They cannot offer opportunities for sophisticated analysis of the rate laws governing ligand substitution. They do not shed light on the question of *stoichiometric mechanism*[37] [*i.e.* the questions of stoichiometric composition of the transition state, reaction intermediates, and the number of elementary steps]. Instead, they may illuminate the *intimate mechanism*[37] of the reaction [*i.e.* the energetics of the activation process] when relative rates in a series of reactions are compared.

Perhaps, the most obvious sequence to explore is the sequence of rates of exchange of a particular solvent as the central metal atom is varied. This approach has been richly developed for the plus two ions of the first row transition metals from Mn^{2+} to Cu^{2+}. First, analysis of aqueous solutions appeared in the important paper of Swift and Connick[8], later information on NH_3, CH_3OH, dmf, and (in part) CH_3CN appeared. In this series, Cu^{2+} is a special case for structural reasons. All other ions form approximately octahedral solvent complexes. Figure 5 displays the pattern of activation free energy ($\Delta G^{\neq}$-proportional to log k) as a function of metal ion. This figure comes tantalizingly close to being informative. It shows a pattern of metal ion dependence strikingly independent of the nature

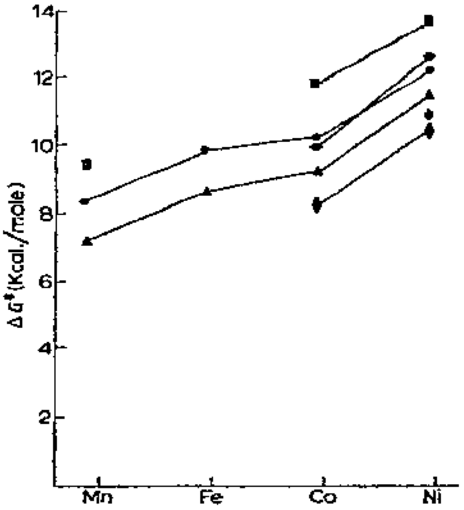

Fig. 5. Free energies of activation for solvent exchange by octahedral 2+ metal ions as a function of metal ion. The solvents are (reading from the top curve) CH_3OH, dmf, H_2O, CH_3CN, NH_3.

of the molecule acting as ligand and solvent. The pattern indicates a general rise in $\Delta G^{\neq}$ with increasing atomic number marked by the irregularities that might be qualitatively rationalized in the language of crystal field theory[8,38]. This pattern suggests an important role for dissociation, breaking of the extant metal-ligand bond, in the formation of the transition state.

An extreme view might be adopted. It could be argued that the process of activation requires nearly complete fission of the extant metal–ligand bond with little or no energetic assistance from the formation of a partial bond to the entering group. The transition state would be imagined as approaching a five coordinate complex with only very weak bonding of the entering or leaving ligands (*d* mechanism[37]). This view is neither ruled out nor persuasively supported by detailed comparison of exchange energetics with either theoretical or experimental estimates of the energetics of formation of five coordinate complexes.

Fig. 6 shows the pattern of "crystal field theory activation energies" calculated for trigonal bipyramidal five coordinate transition states by Basolo and Pearson on the assumption that the spectroscopic parameter 10Dq would remain the same in the five coordinate transition state as in the six coordinate ground state. The predicted activation energies are much too large and indicate a greater variation from metal to metal than is observed. Of course, the model was recognized to be crude on two counts. First, it is not reasonable to assume that the parameter, 10Dq, will be unaffected by a change in the coordination number of the metal; second, any crystal or ligand field treatment must fail to reflect, in any way, variations in sigma bonding involving the metal s and p orbitals.

An alternative comparison of *experimental* quantities has recently become

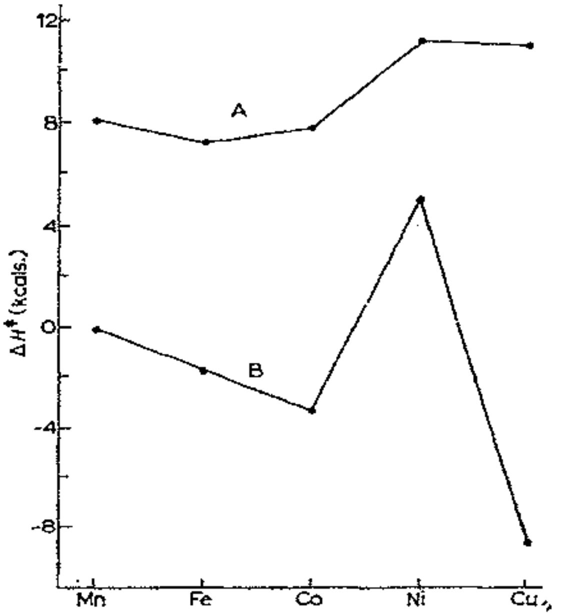

Fig. 6. Activation enthalpies for water exchange by octahedral 2+ metal ions: (A) as observed by Swift and Connick[8], (B) as predicted by a crystal field model assuming a trigonal bipyramidal five coordinate transition state.

possible. It relies on the thermodynamic data on the formation of high spin five coordinate complexes of M^{2+} ions accumulated by Paoletti and Ciampolini[39]. We may define $\Delta H^0 - \Delta H^0(Mn)$ as the enthalpy difference between a five and a six coordinate system minus the corresponding enthalpy difference for the Mn complexes where the five coordinate complex is $M(Me_2tren)Br^+$ and the six coördinate complex is $M(dien)_2^{2+}$ (M = Mn, Fe, Co, Ni; dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$; $Me_2tren = H_2NCH_2CH_2\text{–}N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2NH_2$). Fig. 7 shows $\Delta H^0 - \Delta H^0(Mn)$ plotted for comparison with $\Delta H^{\ddagger} - \Delta H^{\ddagger}(Mn)$, the activation enthalpy for water exchange minus the activation enthalpy for water exchange of the Mn ion, as a function of the metal ion. Note that Fig. 5 implies that the activation parameters would be very similar if data for an amine were available instead of water data. A rough parallelism between the rate and equilibrium curves is seen in Fig. 7. But, the activation parameters are much smaller than the standard enthalpy changes. This comparison may again suggest that bond rupture plays a significant role in the activation process. However, it would seem to imply that a trigonal bipyramid five coordinate complex is not a faithful model of the transition state. But, there is a weakness in the comparison that may vitiate the latter conclusion. Probably, the stable, isolable, high spin, five coordinate complexes arise as a result of steric hindrance. Thus, metal-ligand bond lengths may be longer in the stable five coordinate species than they would be in the "five coordinate" transition state. This could result in a larger enthalpy

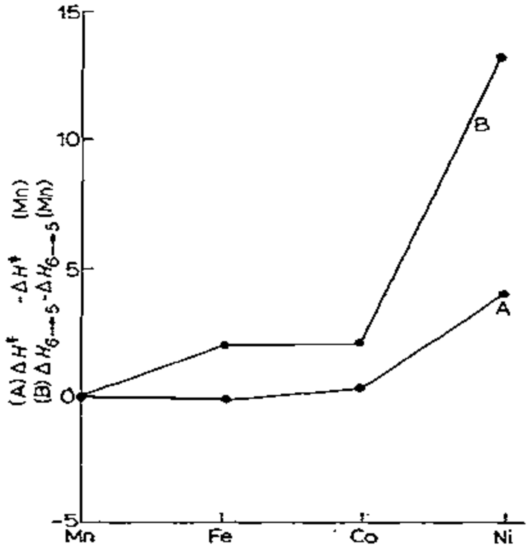

Fig. 7. Activation enthalpies for water exchange relative to that for Mn^{2+}(A), and standard enthalpy change for conversion from six to five coordinate complexes relative to that for Mn^{2+} (B). See text for identification of the particular systems.

difference between "dien" and "Me_2tren" complexes than between six and five coordinate amine or aquo complexes.

Turning from the metal ion, we may examine the variation in exchange rates for a given metal ion as the solvent (and simultaneously the ligand!) is varied. Fig. 5 shows immediately that such variation is small over a significant range of good donor solvents which are also good media for dissolution of electrolytes. The limited range is both surprising and interesting but complicates any attempt at mechanistic interpretation, since exchanging ligand, other ligands, and solvent environment are simultaneously varied. At least the following factors must be considered: (1) metal-ligand bond energies, (2) ligand nucleophilicities, (3) solvation differences between ground and transition states, (4) steric requirements of the ligands, (5) the ability of ligands to provide electronic stabilization to complexes of reduced or increased coordination number. No single factor can be held responsible for the observed order of rates which is (in the case of Ni^{2+})$NH_3 > H_2O >$ dmf $> CH_3CN > CH_3OH$.

The d^4 and d^9, Cr^{2+} and Cu^{2+} ions exchange water molecules at least 100 times faster than the iron group ions discussed above. This phenomenon must be connected with the substantial distortion from octahedral symmetry which is expected (as a consequence of the Jahn–Teller theorem). Two of the water molecules should be bound differently (presumably more weakly) than the other four. The interesting result is that there is only *one* observable rate process. Distinct exchange rates for "axial" and "equatorial" ligands are not observed. Meredith and Connick[33] suggest that an axial to equatorial interconversion occurs faster than the exchange of the more labile (presumably axial) waters. Another extremely fast water exchange is inferred for $Gd(aq)^{3+}$ from ^{17}O measurements. This surprisingly rapid process may reflect the stability of Gd^{3+} complexes of more than one coordination number.

E. COMPARISON OF SOLVENT EXCHANGE RATES WITH OTHER "FAST" RATE PROCESSES

If relationships among solvent exchange rates are difficult to interpret, it does not follow that such rate constants play a small role in understanding ligand substitution processes. Profoundly significant information may be derived from the comparison of solvent exchange rates with the rates of complex formation involving non-solvent ligands. These latter rates are rates of net chemical change and must be derived from other experimental approaches to fast processes. So far, available data are limited (with minor exceptions) to aqueous solutions and have been derived from T-jump, ultrasonic absorption, and flow techniques[40].

Table 2 lists values of second order rate constants for the reactions which may be generally represented:

$$Ni(OH_2)_6{}^{2+} + L^{n-} = Ni(OH_2)_5L^{(2-n)+} + H_2O.$$

This example system displays the characteristic feature of the behaviour of most of the first transition series metal ions among a number of others. The rates of complex formation are very similar, showing little dependence on the *nature* of the ligand L. This result, *by itself*, implies a *dissociative activation process*. If a substitution rate is insensitive to the nature of the entering ligand, that ligand cannot be contributing significantly to stabilization of the transition state. In the absence of entering ligand assistance, the transition state must be reached dissociatively.

The solvent molecule itself is the entering ligand in the exchange reactions studied by n.m.r. techniques. With appropriate assumptions to allow comparison of first and second order rate processes, it does appear that solvent exchange occurs at about the same rate as the complex formation reactions in agreement with the dissociative model (*e.g.* compare Table 2 to the $Ni(aq)^{2+}$ entry in Table 1). But, it must now be recognized that there are two distinct stoichiometric pathways available to a reaction with a *dissociative* activation process (*d* reaction). They are shown in Table 3 using $Ni(OH_2)_6{}^{2+}$ again as a paradigm.

Path I–III–IV (Table 3) involves an intermediate of reduced coordination number which survives long enough in solution to react selectively. It has been called the *D* mechanism[37]. Path I–II–IV involves preassociation of the entering ligand with the complex followed by a ligand interchange between the inner and outer coordination spheres. It has been called an I_d (dissociative interchange)

TABLE 2

SECOND ORDER RATES OF COMPLEX FORMATION OF THE $Ni(OH_2)_6^{2+}$ ION WITH VARIOUS LIGANDS AT 25°
(DATA FROM THE COMPLICATION IN REF. 41)

Complex	*Entering ligand*	*log k (M^{-1} sec^{-1})*
$Ni(OH_2)_6^{2+}$	$HP_2O_7^{3-}$	6.3
	SO_4^{2-}	4.2
	$C_2O_4^{2-}$	4.9
	$HC_2O_4^-$	3.7
	SCN^-	3.7
	NH_3	3.4
	pyridine	3.7

mechanism[37]. The I_d process arises in the context of dissociative activation when the species of reduced coordination number produced by loss of the leaving group is not sufficiently stable to function as a selectively reacting intermediate. If the species of reduced coordination number is highly reactive, it will recombine with the ligand already present in the appropriate position in the outer coordination sphere. (In which case, it becomes operationally impossible to tell whether or not there is actually a minimum in the potential surface for the reaction corresponding to a species of reduced coordination number and consideration of an "intermediate" becomes meaningless.)

TABLE 3

POSSIBLE STOICHIOMETRIC PATHWAYS FOR d SUBSTITUTION PROCESSES
(THE SYSTEM $Ni(OH_2)_6^{2+}$ AS A PARADIGM)

$$\begin{tikzcd}
\text{(I)} & & \text{(II)} \\
Ni(OH_2)_6^{2+} \arrow[rr, shift left, "+L\ (K_a)"] \arrow[d, shift right, "k_{+H_2O}"'] & & Ni(OH_2)_6^{2+}\ldots L \arrow[ll, shift left, "-L"] \arrow[d, shift right, "k'_{-H_2O}"'] \\
Ni(OH_2)_5^{2+} \arrow[rr, shift left, "k_{+L}"] \arrow[u, shift right, "k_{-H_2O}"'] & & Ni(OH_2)_5L \arrow[ll, shift left, "k_{-L}"] \arrow[u, shift right, "k'_{+H_2O}"'] \\
\text{(III)} & & \text{(IV)}
\end{tikzcd}$$

Examination of the rate laws governing formation of $Ni(OH_2)_5L$ by paths I–II–IV and I–III–IV in the presence of excess L so that pseudo – first order kinetics are observed shows that the following equations are obeyed:

$$k_{obs} = k'_{-H_2O}K_a[L]/1+K_a[L] \qquad \text{(I–II–IV)}$$

$$k_{obs} = k_{+L}k_{H_2O}[L]/k_{H_2O}+k_{+L}[L] \qquad \text{(I–III–IV}$$

where k_{obs} is the observed pseudo-first order rate constant and [L] is the concentration of the entering ligand. In both cases, k_{obs} approaches a limit at high [L]. On path I–II–IV, the limit is k'_{-H_2O} reached when K_a[L] is large, or when most of the metal complex is associated with an outer sphere ligand L. On path I–III–IV, the limit is k_{-H_2O} when $k_L[L]$ is much larger than k_{+H_2O}, or L captures essentially 100% of the intermediate formed. On the D path (I–III–IV), the limit k_{-H_2O} should be *identical to the solvent exchange rate* obtained from n.m.r. measurements. On the I_d path (I–II–IV), k'_{-H_2O} should *not* be identical to the solvent exchange rate. If one of s outer sphere ligand sites is occupied by an L molecule, the remaining outer sphere sites (s–1) will be occupied by H_2O. When a dissociative event occurs (activation), the chance that the outer sphere ligand in the correct position for entry is L is only 1/s. s–1/s "dissociative events" lead to water exchange so that k'_{-H_2O} is approximately 1/s *times the rate of solvent exchange obtained from n.m.r. measurements.*

Looking at the rate law for path I–II–IV, it is clear that it is not actually necessary to measure the limiting rate in order to evaluate k'_{-H_2O}. K_a is often an independently accessible quantity. Thus a sufficiently detailed study of kinetics of complex formation with a ligand L may be compared to n.m.r. solvent exchange data to distinguish D from I_d processes. The distinction will require rate constants from n.m.r. work with an uncertainty small compared to a factor of s. So far, it is probable that only the most extensively studied systems (wide temperature range, two different nuclei) can be confidently assumed to meet this requirement. It is also true that experimental values of K_a(as opposed to those calculated from various equations of electrostatic models) are rare. But, the work of Atkinson and Kor[42] suggest that K_a values should be available in many cases from ultrasonic absorption data, and Brintzinger and Hammes[43] were recently able to resolve one indirectly in a T-jump study.

TABLE 4

TWO EXAMPLES OF COMPARISON OF k'_{-H_2O} OR k_{-H_2O} WITH WATER EXCHANGE

Complex	*Entering ligand*	*k (sec⁻¹) at 25°*	*Method*	*Ref.*
$Ni(OH_2)_6^{2+}$	OH_2	2.7×10^4	n.m.r.	8
$Ni(OH_2)_6^{2+}$	$CH_3OPO_3^{2-}$	0.7×10^4	T-jump	43
$Mn(OH_2)_6^{2+}$	OH_2	3.6×10^7	n.m.r.	8
$Mn(OH_2)_6^{2+}$	SO_4^{2-}	4.7×10^7	ultrasonic	42

As an example of what may be expected to emerge, Table 4 exhibits two examples where values of what should be k'_{-H_2O} on the I_d path have been calculated from known K_a. The Ni^{2+} result is very similar to the result reported by Langford and Muir [44] for complex formation reactions of cobalt (III) ammine complexes. It is suggestive of the I_d process with a value of s in the neighborhood of four. (Does this imply a bidentate outer sphere ligand?) The Mn^{2+} result might imply that every waterless event led to sulfate entry. Such a result is consistent with a D path. (Having sulfate in the ion pair may lead to sulfate capturing every intermediate.) In fact, I_d reaction at Ni^{2+} and D reaction at Mn^{2+} is consistent with the greater difficulty of formation of five coordinate Ni^{2+} complexes suggested by

Fig. 8. Of course, this is pure speculation. Studies in appropriate detail are urgently needed.

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