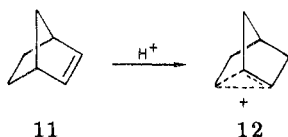**Figure 3.**

be proposed that the high rate of norbornene reflects formation of a stabilized nonclassical norbornyl cation (12).

11   12

The question of bridging in norbornyl cations has been a topic of great interest over a long period of time, and recent publications have claimed to confirm this phenomenon under stable ion conditions[39a] and in solvolysis.[39b] However, extensive experimental work[40a] and a recent theoretical treatment[40b] argue against the importance of bridging in the norbornyl cation, and there will surely be more studies devoted to this system.

The fact that electrophilic additions to norbornenes lead to substantial amounts of unrearranged addition products argues strongly against the intervention of bridging in the transition states for these additions.[41]

(39) (a) G. A. Olah, *Acc. Chem. Res.*, 9, 41 (1976); (b) H. Maskill, *J. Am. Chem. Soc.*, 98, 8482 (1976).

(40) (a) H. C. Brown, *Acc. Chem. Res.*, 6, 377 (1973); *Tetrahedron*, 32, 179 (1976); (b) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. Rzepa, *J. Am. Chem. Soc.*, 99, 377 (1977).

(41) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, 97, 5521 (1975).

We attribute some of the high reactivity of 11 to the unsymmetrical distortion of the molecule, so that the lobes of the p orbitals on the exo face of norbornene contain excess electron density and are vulnerable to electrophilic attack (Figure 3). This argument is supported by theoretical studies.[42]

Recalculation of the correlation appeared desirable because of the greatly increased number of reactivities available since the correlation was formulated. We have tested eq 9 with a set of 29 of the alkenes whose rates seemed to us most reliable using a revised value of σ_p^+ of -0.83 measured by us[29] for EtO. This gave a correlation coefficient of 0.980 with $\rho = -10.7$ and $C = -8.96$. When all of the 96 points were included, the corresponding values were 0.938, -10.5, and -8.92, respectively. Thus, the correlation line defined by all the points was essentially the same as that determined by the selected points but with more scatter in the former case. The group of selected points consisted of those 1,1-disubstituted compounds for which reliable rate constants measured in water were available, excluding substituted styrenes, hydrocarbons with steep acidity dependences, and crowded phosphates. Many other substituents remain to be tested, but so far eq 9 appears to be a reliable guide to the rates and mechanism of alkene hydrations.

(42) S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, 98, 4054 (1976).

Preferential Solvation and the Role of Solvent in Kinetics. Examples from Ligand Substitution Reactions

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In the kinetic literature, an embarrassing ambiguity has plagued many distinguished authors. When a reaction seems to demand participation of a solute *and* a solvent molecule in a way parallel to bimolecular gas-phase reaction, the question arises: can a second-order rate constant be calculated by dividing an observed first-order rate constant by the molar concentration (or the activity) of the solvent?

Such second-order rate constants are frequently calculated, but the authors usually express some malaise. This malaise arises from the fact that a careful

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analysis of the concept of molecularity and its scope and limits for solution have not yet been finally given. This Account will support the claim[1] that such second-order solvolysis rate constants are not useful. The problem just described is not a minor matter. It is symptomatic of a lack of clarity concerning some fundamental aspects of solution kinetics.

Similarly, *mixed solvent* studies in kinetics do not readily clarify hypotheses concerning the mechanistic role of one solvent component. At risk of a bad pun, mixed solvents are a kineticist's troubled waters. Nonetheless, for practical and theoretical reasons, mixed solvents continue to be widely used. They are, after all, of synthetic and even industrial significance.

Our present purpose is to examine certain concepts and to discuss experiments that clarify the issues indicated above. No claim is made that all the difficulties

(1) C. H. Langford, *J. Chem. Educ.*, 46, 577 (1969).

will be straightened out. This is a "prolegomena". The attempt here is to set out the frame of reference for the concept of molecularity and, since molecularity is a structural concept, to develop guidelines for understanding the *use* of a structural model as opposed to a continuum model for reactions in solution. The illustrations chosen will be drawn mainly from transition-metal complex systems. This reflects only our personal interests. The conceptual scheme is not limited to inorganic reactions.

Encounters and Multistep Mechanisms: Generality of First-Order Kinetics

In a reaction between two solutes, the first step is diffusion together of the reactants. This is unlike a gas-phase collision in that it has a *minimum duration* governed by the "cage" effect of surrounding solvent, since two solutes in contact are constrained by the solvent cage to experience the equivalent of a series of 10 to 100 "hard-sphere collisions", even in the absence of an attractive force. The term *"encounter"* is used in solution kinetics to replace the term "collision" of gas-phase kinetics. The complex of two molecules which are nearest neighbors within a solvent cage is described as an *encounter complex*. (In the specific field of coordination chemistry, the term outer-sphere complex is equivalent.) Eigen's elegant work on ultrasonic absorption of solutions of divalent metal sulfates[2] provided the first experimental demonstration that the formation and dissociation of encounter complexes are well-defined, elementary steps.

One of the most useful notions for simplification of kinetic schemes is the pseudoequilibrium approximation which may be applied when the reverse of an elementary reaction step is substantially faster than the succeeding step in a mechanism. For any reaction with a rate-determining step slow compared to diffusion (in water at 25 °C, $t_{1/2} \leq \sim 10^{-8}$ s), the pseudoequilibrium approximation holds for the formation and dissociation of the encounter complex. Labeling the pair of solute molecules A and B as E when they are nearest neighbors and within a solvent cage, i.e., an *encounter complex*, we write for a simple mechanism:

$$A + B \underset{}{\overset{K_E}{\rightleftharpoons}} E$$

$$E \overset{k_1}{\rightarrow} products \tag{1}$$

where K_E is an *equilibrium constant* governing formation of the encounter complex, and k_1 is the rate constant for the rate-determining *first-order* process by which the encounter complex is converted into products.

If concentrations of A and B are small, and K_E is not large (the most common case), the rate law for mechanism 1 is given by eq 2. An experimental second-order

$$rate = K_E k_1 [A][B] \tag{2}$$

rate constant, k_2, determined in these circumstances is then interpretable as equal to $K_E k_1$.

If K_E can be determined experimentally or theoretically, the second-order rate constant (k_2) for reaction of A with B can be interpreted in terms of K_E and a *first-order rate constant*, k_1. This provides an approach

to the problem of comparing reactions differing in kinetic order. Second-order rate constants, k_2, for reactions slow with respect to diffusion may be reduced to first-order reactions by eq 3.

$$k_1 = k_2/K_E \tag{3}$$

The best articulated examples of this approach are metal complex formation reactions. The *second-order* rate constant for formation of a complex between a solvated metal ion, e.g. $Ni(OH_2)_6^{2+}$, and a ligand, L, may be compared to the solvent-exchange first-order rate constant of the solvated metal ion to establish that the rate-determining step involves rupture of the metal-solvent bond.[3] The argument is developed from the similarity of k_1 (calculated according to eq 3) to the experimental *first-order* solvent-exchange rate constant, k_{ex}. In most cases, the value of K_E is derived theoretically from an equation due to Fuoss[4] (who derived it from a hard-sphere statistical mechanical equilibrium model) and Eigen[5] (who derived it from consideration of the formation and dissociation of an encounter complex controlled by diffusion). The Fuoss–Eigen equation is

$$K_E = \frac{4\pi N_0 a^3}{3000} \exp[-U/kT] \tag{4}$$

where a is an adjustable distance of closest approach between A and B, N_0 is Avogadro's number, and U is the interaction potential between A and B at the distance of closest approach, a.

It has been possible to evaluate some K_E's experimentally when K_E corresponds to an ion association constant. Most results can be brought into agreement with the Fuoss–Eigen theory in both aqueous and nonaqueous media of high dielectric constant. However, there is some kinetic evidence that K_E can be sensitive to solvent parameters other than dielectric constants. Since K_E is fundamental, we digress to consider that evidence.

The most direct kinetic evidence for a dependence of K_E on parameters other than simple charge and dielectric constant comes from studies by Caldin and Bennetto[6] on the complex-formation reactions of bipyridine with hexasolvonickel(II) complexes in a variety of solvents. The detailed explanation of the effects observed by Caldin and Bennetto is the subject of a series of elegant papers by J. F. Coetzee and his collaborators (especially P. K. Chattopadhyay).[7] In these papers, a comparison of the relative reactivities of four ligands (4-phenylpyridine, which has a single simple donor and is the reference point, bipyridine, phenanthroline, and terpyridine) in several solvents clarified two main points. First, in several solvents, there is *stabilization* of the encounter complexes with pyridine-type ligands, especially phenanthroline, by steric effects and by interaction with polarized ligand molecules bound in the first sphere of Ni(II). Second, conversion of the nickel species from NiS_6^{2+} to NiS_5Cl^+

(2) M. Eigen and K. Tamm, *Ber. Bunsenges. Phys. Chem.*, 66, 197 (1962).

(3) R. G. Wilkins, *Acc. Chem. Res.*, 3, 408 (1970).
(4) R. M. Fuoss, *J. Am. Chem. Soc.*, 80, 5059 (1958).
(5) M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, 1, 176 (1954).
(6) E. F. Caldin and H. P. Bennetto, *J. Solution Chem.*, 2, 176 (1974).
(7) (a) P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 15, 400 (1976); (b) J. F. Coetzee and D. M. Gilles, *ibid.*, 15, 405 (1976); (c) J. F. Coetzee and C. G. Karakatsanis, *ibid.*, 15, 3112 (1976).

reduces the discrimination among pyridine-type ligands bound in the outer sphere. Apparently, reduced charge reduces the stabilization of outer-sphere complexes which arose from the direct first-sphere–second-sphere ligand interaction. This work points to the more detailed factors governing K_E which need to be studied.

There is one final problem with factoring by eq 2. An *experimental* K_E refers to an observed encounter equilibrium which may not lie on the path of reaction. But, as long as the interconversion of any two "ion pairs" is *fast* compared to the rate-determining step, only one K_E will be the equilibrium constant determined by experimental methods since all common methods of evaluating equilibrium constants depend on variation of a signal with concentration.

An observed K_E will differ only by a *concentration-independent* factor from the desired constant which may be incorporated as a factor (an entropy term) contributing to k_1 in eq 1. An obvious case is that in which the distribution around various positions in the encounter complex (which might usefully be labeled encounter conformations) is statistical. Then one sees the phenomenon[8,9] of a constant relationship between solvent-exchange rate constants which arise from solvent occupying all encounter positions and values of k_1 for complex formation equal to approximately 0.1–0.2 times solvent exchange because only one site in the outer sphere is a reactive position.

We can now attempt to understand solvolysis. Bimolecular reactions for which K_E values are relatively large are found experimentally[8,9] to follow a rate expression given in eq 5 when the concentration of

$$\text{rate} = k_{obsd}[A] = \frac{k_1 K_E[B]}{1 + K_E[B]}[A] \tag{5}$$

reactant B (eq 1) is chosen in such excess over A to render each experiment pseudo-first-order in A. Expressions of the form (5) give second-order kinetics if $K_E[B] \ll 1$. In that limit, rate = $k_1 K_E[A][B]$. But, the other limit is $K_E[B] \gg 1$ where rate becomes equal to $k_1[A]$. The contention of the present analysis is that any second-order "slow" reaction is an example of eq 5 where $K_E[B] \ll 1$. Thus, it is possible to calculate k_1 if an estimate of K_E can be developed.

However, first-order reactions cannot similarly be rendered second order. Consider the important case of solvolysis where reactant B is a solvent molecule. There is no possibility of the solvent *not* being in encounter with a solute. (It is worth noting that, when a number of solvent molecules, as in a mixed solvent, come into encounter, the single K_E must be replaced by a set comparable to successive formation constants described in ref 14.) Thus, solvolysis reactions are always and inherently governed by the rate expression: rate = $k_1[A]$. *This is the fundamental reason why solvolysis reactions are first order. An encounter complex does not need to be formed, it is there.* It is, consequently, entirely meaningless to attempt to calculate a second-order rate constant for a solvolysis reaction!

A second-order rate constant, k_2, has the interpretation: $k_2 = K_E k_1$. For solvolysis, where encounter cannot be avoided, K_E is meaningless. This answers our

first question. Second-order reactions involving solute reactants may be compared to solvolysis *if and only if* K_E can be estimated so that a k_1 to compare to the first-order rate constant for solvolysis may be estimated. The argument has been developed for a second-order reaction. A similar analysis applies to higher order reactions.

One question answered leaves two interesting ones outstanding: (a) how to characterize the kinetic role of solvent; and (b) how to deal with a situation in which B is neither pure solvent nor a *dilute* component, i.e., a mixed solvent? A starting point for these emerges from the above considerations. We need no external kinetic information beyond k_1 when reactant B is *the* solvent because it then occupies all encounter sites. What we do need (vide infra) is a guide to solvent functions beyond simply being a reactant. When reactant B is a nondilute component of a mixture, we need encounter probability data before k_1 can be extracted. This encounter probability will not usually be characterized by a single simple K_E. What we need is the preferential solvation curve for the solvent mixture (also discussed below).

Solvation: Long Range and Short Range

To begin a discussion of functions of solvents in reactions, we must discuss solvation. Solvation shells are most often discussed in terms outlined in Gurney's influential book[10] as regions A, B, and C. Region A is one of high order imposed by the influence of the solute on nearby solvent molecules. Region C is a region of unaltered bulk solvent which exists, at least in dilute solution. Region B is a "disordered" compromise region which is influenced comparably by the forces exerted by the solute which produce region A near the solute and the solvent–solvent forces which produce region C in the bulk far from the solute. There may be no region B for solvents which have only weak forces producing liquid structure in the bulk region C. In fact, region B may be unique to certain aqueous solutions.

For our mechanistic purposes, an alternative classification is more useful. This is derived from coordination chemistry and views solvation shells as including a *primary* coordination sphere (the nearest neighbors of a solute central atom), a *secondary* coordination sphere (the encounter partners), and, in dilute solution, *bulk* solvent. Correlating the two approaches, one sees that the *primary* coordination sphere is an A region. The bulk region beyond the secondary coordination sphere is assumed to be C. (This assumption is supported by the as yet limited experimental evidence including, notably, Atkinson and Kor's ultrasonic study of $MnSO_4$ association[11].)

Of great interest is the *secondary* coordination sphere since such nearby molecules can play a large role in kinetics. Is it an A or B region? There is not too much unambiguous experimental evidence. Evidence has been gathered for a few systems by NMR with attention either to dipolar coupling between a paramagnetic solute and solvent protons,[12] which reveals relaxation processes dependent upon r^{-6}, or to pseudo-contact shifts induced in secondary-shell solvent molecules by

(8) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, 6, 1379 (1967).
(9) C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, 89, 3141 (1967).

(10) R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill, New York, N.Y., 1953, Chapter 16.
(11) G. Atkinson and S. K. Kor, *J. Phys. Chem.*, 69, 128 (1965).
(12) L. S. Frankel, *J. Phys. Chem.*, 74, 1645 (1970).

unsymmetrical paramagnetic complexes.[13,14] Frankel[12] argues that the charge on a Cr(III) complex determines the orientation of the secondary solvation shell, making it A type. Eaton[13,14] describes neutral Co(II) complexes that induce different A-type orientation of solvent molecules in the secondary coordination sphere suggestive of double-layer phenomena (Co is positively charged, the ligands are negative, and the secondary solvation shell ligands orient the positive ends of their dipoles toward the complex). First-sphere–second-sphere interaction seems to be important as well as charge. Hopefully ^{13}C NMR studies will soon add to our understanding of the structure of second coordination sphere structure.[15] The present evidence is taken to support A-type behavior near transition-metal ions.

The theory of the second coordination sphere has been treated by coordination[16] and adsorption[17] models. The coordination model is preferable, although an error in ref 16, which assumes that activity coefficients in bulk (where solvent–solvent interaction controls) are similar to those in the solvation shell (where solvent–solute interactions control), must be corrected, along lines suggested in ref 17.

These remarks conclude our disaggregation of factors. We now turn to a constructive, rather than analytical, approach and try to develop an account of the effects of solvent molecules in kinetics and the categories of preferential solvation.

Bulk Solvent Effects on Reaction Rates

According to Levich,[18] liquid molecules perform motions of two kinds. On the one hand, they make diffusion jumps from one temporary equilibrium position to another. On the other hand, the molecules take part in the motion of the liquid as a whole, vibrating about the equilibrium positions.

The time interval for diffusion jumps is ca. 10^{-9} s. This interval, corresponding to rearrangement of encounter complexes, is long compared to the time scale for a passage through the transition state which occurs on the time scale of vibrational relaxation.[19] Therefore, molecules near a reaction site may be considered fixed at equilibrium sites about which they may vibrate in a manner qualitatively like those in a crystal lattice. The two kinds of vibrations in a crystal are *acoustic* (where contiguous particles vibrate on the average in the same direction) and *optical* (where, on average, contiguous particles move in opposite directions). It is mainly optical vibrations that produce changes in dipole moment. Much experience suggests that electric polarization of the medium is the most important (possibly dominant) factor in long-range solvent effects on reactions of charged particles. Thus, attention focuses on optical vibrations. The practical consequence for ordinary studies of kinetics in mixed solvents
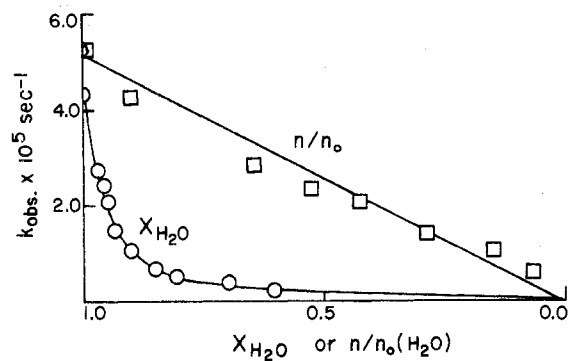

Figure 1. Hydrolysis rates for Cr(NCS)$_6^{3-}$ in water–CH$_3$CN mixtures at 25 °C plotted as a function of mole fraction water (O) and as a function of the NMR determined solvation parameter proportional to the probability of encounter, n/n_0 (□). The straight line represents the expected curve for a simple bimolecular process.

of this analysis is twofold: (a) long-range effects will be *relatively small compared to those of second-sphere solvent* molecules, and (b) these effects may depend on factors related more to the measurable *refractive index* than to dielectric constant.

Specific Solvent Effects: Solvent as Reactant

We turn now to solvent molecules in the first and second coordination spheres of a reactive site. There are two classes of such effects. The *first* and simpler is one associated with the traditional notion of *molecularity*. It is that the solvent molecule may act as a reaction partner in a way entirely analogous to a second molecule, not a solvent component, in a classic bimolecular process or, indeed, as it would in the low P gas-phase analogue of the reaction in solution. For example, the solvent molecule might function as a two-electron donor (or acceptor) toward a central atom in substitution or as one-electron donor (or acceptor) with respect to the central atom in a redox process.

A clean example of the solvent acting as reactant with secondary roles minimized is observed in the solvolysis of Cr(NCS)$_6^{3-}$.[20] The reaction is shown in eq 6 with

$$Cr(NCS)_6^{3-} + H_2O \rightarrow Cr(NCS)_5OH_2^{2-} + SCN^- \qquad (6)$$
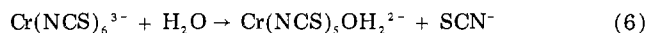
water as a reactant. There are similar reactions with several alcohols, dimethylformamide, and pyridine which proceed at very nearly the same rate in all these materials as solvents. This lack of variation is a clear indication that solvent effects arising from factors other than role as reactant are small (and that the reaction is even relatively nonspecific with respect to reactant in the way described as dissociative activation[21]). However, reaction 6 does not proceed at a measurable rate in poorly coordinating solvents such as CH$_3$CN and CH$_3$NO$_2$! The rate of reaction 6 as a function of composition of mixed CH$_3$CN/H$_2$O solvents is shown in Figure 1. This is a striking figure. Consider the points represented by circles. A small amount of CH$_3$CN is remarkably effective in reducing the rate of reactions with H$_2$O. The NMR method for discovering the composition of the second coordination sphere was applied to the problem of this spectacular effect.

(13) D. R. Eaton, *Can. J. Chem.*, **47**, 2645 (1969).

(14) D. R. Eaton and K. L. Chua, *Can. J. Chem.*, **51**, 4137 (1973).

(15) S. O. Chan and D. R. Eaton, *Can. J. Chem.*, **54**, 1332 (1976); G. Kotowycz, *ibid.*, **52**, 924 (1974).

(16) A. K. Covington and J. M. Thain, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1879 (1974), and earlier papers cited therein.

(17) L. S. Frankel, T. R. Stengle, and C. H. Langford, *J. Phys. Chem.*, **74**, 1376 (1970).

(18) V. G. Levich, *Adv. Electrochem. Electrochem. Eng.*, **4**, 249 (1966).

(19) K. J. Laidler, "Theories of Chemical Kinetics", McGraw-Hill, New York, N.Y., 1969, Chapter 3.

(20) S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Am. Chem. Soc.*, **91**, 2236 (1969).

(21) C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York, N.Y., 1965, Chapter 1.

Figure 1 also shows a plot of the rate as a function of the probability of encounter between water and $Cr(NCS)_6^{3-}$. The plot introduces a convenient parameter, n/n_0, which describes the number of water molecules in encounter with $Cr(NCS)_6^{3-}$ in the mixed solvent (n) as compared to the number in encounter with the complex in pure water (n_0). n/n_0 is a quantity which NMR relaxation times yield directly in the case of Cr(III) complexes.[22] n/n_0 compares the probability of encounter between water and $Cr(NCS)_6^{3-}$ in a mixed solvent to the encounter probability (= unity) when all second-sphere sites are occupied by water. If the only role of water in the mechanism of reaction 6 is to function as a new ligand to replace a leaving SCN^- in the rearrangement of the encounter complex, then the observed *first-order* rate constant should be proportional to the encounter probability with water, i.e., n/n_0. This "prediction" is represented by the straight line in the figure, and the experimental points indicate that it is a good account of the facts. (Specialists in ligand substitutions will recognize this as an example of the I_d mechanism.[21])

The solvolysis of $Cr(NCS)_6^{3-}$ is a beautifully simple case. It is one of the sort of textbook examples that serve to illustrate a basic point, the role of encounter, in an uncomplicated way. Nature in general is, of course, not so simple. The reactions of $Cr(NCS)_6^{3-}$ reflect the indifference of this complex to which site in the second coordination sphere an entering solvent occupies. There do not appear to be strong interactions with second-sphere molecules.

The reaction of ligand exchange between dimethyl sulfoxide (Me_2SO) and $Cr(Me_2SO)_6^{3+}$ represents a second and more complex case; it has been studied[23] in mixtures of Me_2SO and the unreactive solvent component CH_3NO_2 by following the growth of proton NMR signals in bulk when the complex is dissolved in Me_2SO. NMR solvation studies are also possible in this system. Here the rate remains constant as Me_2SO is replaced in the solvation shell by CH_3NO_2 *until the last outer sphere* Me_2SO is undergoing replacement by CH_3NO_2 (low n/n_0). Experimentally the exchange rate declines steeply between Me_2SO mole fraction 0.2 and zero. This could indicate (in contrast to the previous case) that the attacking Me_2SO molecule must occupy a unique site in the second coordination sphere where it is more strongly bound than other second-sphere molecules. This second case, where the dependence on Me_2SO concentration is experimentally *undetectable* over a wide range of compositions of $Me_2SO-CH_3NO_2$ mixtures, is *no less* a "bimolecular" reaction than solvolysis of $Cr(NCS)_6^{3-}$. Indeed, its lack of dependence on solvent composition over a wide range may imply specific second-sphere binding at one site. The strong interaction at one site is consistent with (but not proof of) a pathway in which the attacking solvent in the exchange example plays a more important role in determining the energy of the transition state than the attacking solvent in the $Cr(NCS)_6^{3-}$ solvolysis. This is what would be regarded as a more *associative*[21] transition state. (Note in our earlier context that any attempt to calculate the second-order rate constant for
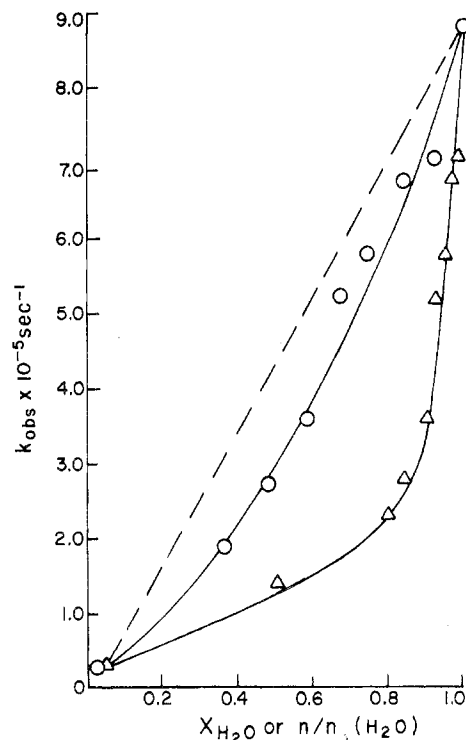
Figure 2. Hydrolysis rates for *trans*-$Cr(NCS)_4(NH_3)_2^-$ in water–CH_3CN mixtures at 25 °C plotted as a function of mole fraction water (△) and as a function of the NMR determined solvation parameter, n/n_0 (O). The broken straight line represents the expected curve for a simple bimolecular reaction free of additional solvent effects.

this reaction would *clearly fail!*)

Now, it should be recognized that this second case, like the first, is relatively simple and subject to fairly straightforward interpretation. In particular, it has been possible to propose (possibly wrongly) a sensible interpretation while considering *only* the role of solvents as the *reactants* engaged in forming or breaking bonds. We cannot expect such simplicity to be very general. The search for illuminating cases must now turn to simpler examples of the effect of second coordination sphere molecules which are not acting as reactants.

Solvation Effects in the Second Coordination Sphere

Given the simplicity of the solvolysis of $Cr(NCS)_6^{3-}$, the reactions of its close relatives are attractive candidates for examination because the degree of added complication may be manageably small. The complex *trans*-$Cr(NCS)_4(NH_3)_2^-$ (the reineckate ion) introduces two NH_3 ligands which may function as H-bond donors to solvents such as water and alcohols. But, it reacts solvolytically with loss of SCN^- like $Cr(NCS)_6^{3-}$ and it preserves a relatively high microsymmetry, D_{4h}. Its solvolytic reactions proceed at closely similar rates in water and alcohols[24] but are retarded by CH_3NO_2 or CH_3CN. Qualitatively, this parallels $Cr(NCS)_6^{3-}$, but quantitative differences are evident.[25]

Figure 2 shows the dependence of hydrolysis rate on the NMR-determined encounter probability parameter, n/n_0, in mixtures of H_2O and CH_3CN. The points represented by circles are rate vs. n/n_0. Here the rate

(22) L. S. Frankel, T. R. Stengle, and C. H. Langford, *Chem. Commun.*, 373 (1965).

(23) C. H. Langford, R. Scharfe, and R. Jackson, *Inorg. Nucl. Chem. Lett.*, **9**, 1033 (1973).

(24) A. W. Adamson, *J. Am. Chem. Soc.*, **80**, 3183 (1958).

(25) V. S. Sastri, R. W. Henwood, S. Behrendt, and C. H. Langford, *J. Am. Chem. Soc.*, **94**, 753 (1972).

of solvolysis falls off somewhat faster than n/n_0 for H_2O. One water is again a reactant, but water molecules in other parts of the solvation shell must also mildly accelerate the reaction. There is an obvious possibility. In a dissociative loss of SCN^-, a transition state of partially reduced coordination number would bind the NH_3 ligands more strongly. This would, of course, render the ammonia protons more acidic and they would be stabilized by H bonding to water.

Fortunately, there is an independent test of the plausibility of this hypothesis. There is a deuterium isotope effect on the reaction rate of approximately two. (This is larger than the effect of changing the solvent from H_2O to CH_3OH.) It is possible to separate the effect of deuteration of the NH_3 ligands from the effect of deuteration of the solvent water. Most of the effect of deuteration is a result of deuteration of the NH_3 ligands and not the solvent, indicating the importance of amine ligand to water H bonding in the transition state.

An example[26] which may be an extension of the nonreactant role of water in solvolysis of *trans*-Cr-$(NCS)_4(NH_3)_2^-$ to an extreme is presented by racemization of optically active $Cr(C_2O_4)_3^{3-}$. Racemization is accomplished by opening one end of an oxalate chelate ring and reclosing it enantiomerically. This reaction is acid catalyzed (presumably by protonation of an oxalate) and is relatively rapid in water and other H-bonding solvents. One end dechelation of oxalate is probably accompanied by temporary coordination of a solvent molecule. The reaction is very slow in Me_2SO. When it is run in mixtures of Me_2SO and H_2O, one expects the two solvents to be *comparable* in ability to mediate the reaction by occupation of a coordination site at chromium. However, only water can effectively H-bond at the various and distinguishable oxygen sites at which it might stabilize a transition state with bond rupture and negative charge developing on oxalate. Experiments reveal the nonintegral relatively high order dependence of rate on n/n_0 for water.[26] Each water displaced from any part of the solvation shell of the complex by Me_2SO leads to sharp rate decreases. This is what our proposed mechanism requires. All oxalate oxygens that H-bond to water are favorable to the transition state.

A more telling example of the role of outer coordination sphere solvent molecules which are not reactants has been reported by Van Meter and Neumann[27] in a discussion of the solvent dependence of racemization of tris(1,10-phenanthroline)iron(II) ion. Many studies of this and related complexes imply that this racemization is an *intramolecular* twist, so that there is no question of release of ligand into bulk solvent or solvent molecules entering the first coordination sphere. Nonetheless, a linear free energy relationship was shown to exist between the free energy of solution of naphthalene (a model of the outer organic part of the ligand) and the logarithm of the racemization rate. Since any reasonable intramolecular racemization mechanism[28] requires a transition state with more open pockets for penetration of second-sphere solvent into the first-sphere ligand region, the positive correlation is im-

pressive. The aromatic ligand is better solvated in the transition state.

There is a further point. Success of the Debye[29] model of molecular tumbling in solution in which the bulk viscosity is used as a surrogate for local molecular barriers suggests a correlation of the barriers to the required *intramolecular* ligand movement with solvent viscosity. This was also seen by Van Meter and Neumann. It serves as a useful corrective to the simplistic hypothesis that all viscosity relationships arise from diffusion jumps. (Another useful corrective to the simple notions advanced throughout this Account is the very complex solvent dependence revealed in our most recent study of a complex formation reaction![30] That case is sufficiently complex that we lapse into silence at this point, our "prolegomena" presented.)

The Study of Preferential Solvation

We have argued that a necessary (but not sufficient) condition for understanding reactions in mixed solvents is to begin with the understanding of encounters which follows from study of preferential solvation and the composition of the second coordination sphere. This information was very hard to derive with any degree of reliability prior to the introduction of NMR methods. (The point is well illustrated in the programs of the international conferences on nonaqueous solvents. In the first conference in 1968, we presented the one paper on this subject. By the fifth conference in 1976, NMR data on preferential solvation arose in the context of almost all discussions of mixed solvents.) This final section describes briefly the NMR studies that are a foundation for the kinetic work.

The two most popular approaches are the solvent relaxation time (T_2) method and the solute chemical shift method introduced in the initial communication of Frankel, Stengle, and Langford.[22] Conceptually the simpler is the solute chemical shift method which is based on the suggestion that chemical shift of a solute nucleus in a mixed solvent will vary linearly with the composition of the solvation shell. The assumption is plausible but difficult to test. It appears from our work,[31,32] contributions of Richards' group,[33] Covington's group,[16] Popov's group,[34] and Bloor and Kidd[35] that the assumption leads to no inconsistencies, but it must be viewed with continuing suspicion because it is difficult to confirm independently.

The solvent relaxation time studies use the effect of paramagnetic solutes such as the Cr(III) complexes mentioned frequently above on the relaxation time of protons on the solvent. The experimentally simple relaxation time to measure, until Fourier transform spectroscopy became popular, was the transverse relaxation time which is determined from line width of continuous-wave absorption signals. Solvent molecules in the second coordination sphere are in rapid exchange on the NMR time scale with solvent molecules in the

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Table I
Excess Line Broadening of ^{1}H NMR Signal of CH_3CN in
CH_3CN-H_2O Mixtures and Values of the Preferential
Solvation Parameter n/n_0 (CH_3CN) for Solvating
$Cr(NCS)_6^{3-}$

Mole fraction CH_3CN	$\Delta\nu$, Hz	n/n_0*
1.000	5.2	1.00
0.757	5.6	0.98
0.447	7.4	0.99
0.391	8.1	1.01
0.342	8.7	1.00
0.257	10.3	0.99
0.188	13.2	1.02
0.129	17.0	0.98
0.104	18.2	0.87
0.087	20.7	0.80
0.058	22.4	0.65
0.041	24.2	0.52
0.037	23.4	0.45
0.018	26.0	0.25

^{a} $[K_3Cr(NCS)_6] = 0.0426$ M.

bulk. The observed relaxation time is an average governed by McConnell's fast exchange equation:[36]

$$\frac{1}{T_{2obsd}} = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}} \tag{7}$$

where T_{2obsd} is the observed average relaxation time, T_{2A} is the relaxation time in the bulk environment, T_{2B} is the relaxation time in the solvation shell (paramagnetic environment), P_A is the probability that a proton is found in the bulk solvent environment, and P_B is the probability that a proton is in the solvation shell environment. The quantity relevant to preferential solvation is P_B. As long as the solute is *dilute*, P_A is approximated as unity and T_{2A} may be measured in the absence of solute. Thus, P_B/T_{2B} may be experimentally evaluated. Only T_{2B} needs to be eliminated. The useful approach is to compare P_B/T_{2B} for a pure solvent to the value for the same protons in a mixed solvent. The ratio of these quantities and knowledge of bulk solvent composition give the parameter n/n_0 introduced above *if T_{2B} is not dependent on solvent composition.* An example is shown in Table I. These data show how increase of CH_3CN in the *solvation shell as compared to bulk* increases line width.

The assumption that T_{2B} is not variable is testable. The preferential solvation curves (n/n_0 function) may
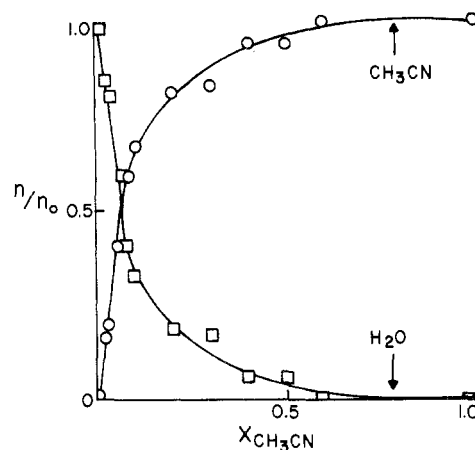
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Figure 3. Preferential solvation of the ion *trans*-$Cr(NCS)_4(NH_3)_2^-$ in acetonitrile–water mixtures as monitored by examination of the proton NMR signals of both CH_3CN and H_2O. Note the agreement between the two measurements indicated by the complementary shape of the two curves.

be determined using protons from both solvent components. If T_{2B} is constant, these curves will be complementary. This test has been satisfactorily met by all published studies using the relaxation time method. Figure 3 illustrates the success of this test for solvation of $Cr(NH_3)_2(NCS)_4^-$.

There is every reason to expect that the relaxation time method will become even more important in the near future. Both the emergence of Fourier transform spectroscopy and the increasing distribution of spectrometers capable of measuring spectra of ^{13}C will favor this approach. T_1 measurements can be expected to displace T_2 measurements. The assumption that T_{2B} is constant has been satisfied for a variety of Cr(III) and Ni(II) complexes, but it cannot be expected to be general to all paramagnetic systems; quite the contrary. However, access to T_1 as well as T_2 and the choice among nuclei offered by multinuclear spectrometers should allow the relaxation time method to be applied to the study of the solvation of the vast majority of paramagnetic metal complexes.