Preferential Solvation in Kinetics. III. Thermal and Photochemical Solvolysis of Reinecke's Ion in Acetonitrile–Water Mixtures[1]

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Abstract: The thermal and photochemical solvolysis reactions of *trans*-$Cr(NH_3)_2(NCS)_4^-$ are considered in relation to solvent composition parameters and the composition of the solvation shell as determined by the nmr method based on solvent-proton line broadening produced by the paramagnetic solute. Thermal solvolysis is found to correlate better with nmr preferential solvation parameters than with either mole fraction, concentration, or activity parameters of the reactive solvent component, H_2O, in CH_3CN-H_2O mixtures. Photochemical solvolysis is not simply related to preferential solvation. This result is recognized to be related to the greater lifetime of photoexcited states compared to encounters in solution. A direct transition state analysis of bimolecular kinetics is compared to a theory considering encounter as a separable equilibrium step.

Kinetics in Mixed Solvents. Mechanistic studies in mixed solvents remain interesting because mixed solvents are of great practical importance in preparative chemistry. However, mechanistic analysis in mixed solvents is difficult. Analysis of a solvolysis reaction, where a solvent component participates directly in the reaction, is especially difficult. Recently[3-5] we have considered the utility of nmr derived data on preferential solvation to answer the first (if difficult) question. "What is the relative probability of encounter of a reactive solute with one or the other of the components of a solvent mixture?" In this paper, we wish to compare the encounter approach based on preferential solvation experiments with more conventional modes of analysis.

Imagine the simple case of a reaction which is reasonably described as bimolecular in solution involving one molecule of a solute MX and one molecule of a reactive component of the solvent S. The reaction may be written both *stoichiometrically and mechanistically* as

$$\mathrm{MX + S \longrightarrow MS + X} \qquad (1)$$

A usual transition state analysis would lead to the following expression.

$$\text{rate} \propto K^{\ddagger}[\mathrm{MX}]a_s(\gamma_{\mathrm{MX}})/\gamma_{\ddagger}) \qquad (2)$$

In eq 2, $K^{\ddagger}$ is the pseudoequilibrium constant of transition state theory, [MX] is the concentration of MX, a_s is the activity of the reactive solvent component, and $(\gamma_{\mathrm{MX}}/\gamma_{\ddagger})$ is the ratio of activity coefficients of the complex MX to that for the transition state. The approach to mixed solvent studies suggested by eq 2 is to correlate rate with activity of the reactive solvent in the hope that γ_{MX} will cancel $\gamma_{\ddagger}$. Unfortunately, the desired cancellation is not frequently found.

Now, any "slow" reaction (one proceeding at a rate at least a few orders of magnitude below the diffusion limit) which is bimolecular may be factored into at least two steps.[6] The first step is the diffusional encounter between the reactants. This step may be treated as an equilibrium step. The encounter complex is then converted to the products in a step which is inherently unimolecular. In eq 3, E designates the encounter complex, K_E the equilibrium constant for encounter, and k_1 the first-order rate constant for conversion of E to products.

$$\begin{aligned} \mathrm{MX + S} &\xrightleftharpoons{K_E} \mathrm{E} \\ \mathrm{E} &\xrightarrow{k_1} \mathrm{MS + X} \end{aligned} \qquad (3)$$

At low concentration of reactants the rate law is K_Ek_1[MX][S] and an observed second-order rate constant would correspond to K_Ek_1. If independent information on encounter can be obtained, then the transition state theory treatment of the slow step (E → products) would be

$$\text{rate} \propto K^{\ddagger}[\mathrm{E}](\gamma_{\mathrm{E}}/\gamma_{\ddagger}) \qquad (4)$$

Symbols in eq 4 have meanings parallel to those in eq 2. [E] is the concentration of encounter complex and $(\gamma_{\mathrm{E}}/\gamma_{\ddagger})$ is the ratio of activity coefficients of encounter complex to transition state.

Although the point is yet to be extensively tested, it seems likely that γ_{E} will cancel $\gamma_{\ddagger}$ much more frequently than γ_{MX} will cancel $\gamma_{\ddagger}$ because E is stoichiometrically identical with the transition state. Hence, the approach to mixed solvents suggested by eq 4 is to estimate the variation of [E] as the solvent composition varies and then to apply kinetic (transition state theory) analysis *only* to the first-order step, E → products. In the case of reactions of a solute with a solvent component, information on the concentration of encounter complexes (E) is closely related to preferential solvation data which measure the tendency of the reactive solvent to come into encounter with the solute.

The advantages of eq 4 over eq 2 were shown particularly clearly in the study of solvolysis of $Cr(NCS)_6^{3-}$ in CH_3CN-H_2O mixtures.[4] In that case, small amounts of CH_3CN were found to profoundly repress the solvolysis in a composition region where water activity varies by as little as 5%. Explanations based on eq 2

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[1] This work was supported by the National Research Council of Canada and, in part, by the U. S. Air Force Office of Scientific Research. Parts I and II are ref 4 and 5.

[2] Alfred P. Sloan Foundation Research Fellow, 1968–1970.

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[6] (a) I. Amdur and G. G. Hammes, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1966, Chapter 2; (b) C. H. Langford, *J. Chem. Educ.*, **46**, 557 (1969).

required large variation in the ratio ($\gamma_{MX}/\gamma_{\pm}$) in solvent mixtures varying only slightly in gross physical properties such as dielectric constant. Preferential solvation study by nmr revealed that this variation was a consequence of preferential solvation by CH_3CN. In fact, the assumption that E consisted of one $Cr(NCS)_6^{3-}$ and *one* water molecule led to the conclusion that the ratio ($\gamma_E/\gamma_{\pm}$) remained essentially unity in all mixtures. In this report, the slightly more complicated case of Reinecke's ion (*trans*-$Cr(NH_3)(NCS)_4^-$) is considered.

Nmr Study of Preferential Solvation. The protons in the solvation shell around a *paramagnetic* metal complex have short relaxation times which lead to broadened nmr signals in that immediate paramagnetic neighborhood.[7] But, solvent molecules around a complex like *trans*-$Cr(NCS)_4(NH_3)_2^-$ are in fast exchange with those in the bulk solvent where they are not subject to the influence of the paramagnetic solute. A single average nmr signal is observed as described by McConnell's fast exchange equation.[8] Although it is not feasible in this case to obtain a direct measure of the number, *n*, of solvent molecules in the paramagnetic environment (solvation shell), the ratio of the solvation number for a solvent component in a mixed solvent compared to that number in the pure solvent may be obtained.[3-5,7] We designate the ratio n/n_0.

The parameter n/n_0 measures the relative concentration of 1:1 solvent–solute encounters. (The second power of n/n_0 would be proportional to the concentration of 2:1 solvent–solute encounters, etc.) Details of n/n_0 calculation are given in the references.[3,4,7] The main requirement for successful n/n_0 analysis is that the relaxation time of protons in the solvation shell (paramagnetic environment) remains constant as the solvent composition changes. This is tested by the agreement between n/n_0 measurements on protons of both components of the CH_3CN–H_2O mixture.

Experimental Section

Materials. The complexes $K_3Cr(NCS)_6$ and $K[Cr(NH_3)_2(NCS)_4]$, obtained from Alfa Inorganics, Inc., were recrystallized from ethanol and hot water, respectively. Reagent grade acetonitrile from Fisher Scientific and distilled water were used in solution preparation. D_2O was 99.9 atom % from Diaprep Corp.

Kinetics. The rate of aquation was estimated as the rate of SCN^- loss by measurement of free SCN^- spectrophotometrically as the Fe–NCS^{2+} complex in aqueous perchloric acid following a slightly modified standard procedure which we have described[4] on a Gilford Model 240 spectrophotometer. The analytical system was calibrated in each of the solvent mixtures with standard thiocyanate solutions. The thermal reactions of Reinecke's salt were carried out at 50° in completely blackened flasks. All transfer operations were carried out by the light of red "photographic" bulbs only. Reactions in all systems were followed to the release of 25% of 1 equiv of thiocyanate. Spectra of the complex solution at this point were recorded to establish that the nature of the products present was not varying significantly with solvent composition. The complex concentration was 5×10^{-3} *M*. Assuming the release of 2 mol of SCN^- per chromium, first-order rate constants for aquation of Reinecke's complex were evaluated. (This assumption is discussed in ref 3.)

The solvent dependence of the quantum yields was obtained by irradiating 15 ml of the solution of the complex using the optical train described elsewhere,[9] in a 5-cm quartz cell for 20–30 min and determining the liberated SCN^- as Fe–NCS^{2+} complex spectrophotometrically. Chemical actinometry using *trans*-$Cr(NH_3)_2(NCS)_4^-$ in aqueous media[10] before and after irradiation of the complex confirmed the constancy of light intensity. A parallel dark run was conducted for correcting the photochemical rate of aquation.

Studies in D_2O were carried out with and without preliminary recrystallization of the complex from basic D_2O solution to exchange the protons on coordinated ammonia molecules. Thus, isotope effects are reported for $Cr(NH_3)_2(NCS)_4^-$ in D_2O and $Cr(ND_3)_2(NCS)_4^-$ in D_2O.

Spectra and Preferential Solvation. Proton resonances of CH_3CN and H_2O were recorded at 24 and 50° on a JEOL C-60 nmr spectrometer using a solution prepared immediately prior to analysis. These yield consistent preferential solvation curves without correction for solvolysis of $Cr(NH_3)_2(NCS)_4^-$ with the exception of high water content solutions at 50°. As in earlier work,[4,5] it proved possible to obtain qualitative confirmation of the preferential solvation curves from the small solvent dependent shifts of the low-energy ligand field band of $Cr(NH_3)_2(NCS)_4^-$. These visible spectra were recorded on a Cary 14 spectrophotometer.

Results

Tables I and II show the dependence of the thermal and photochemical reactions of *trans*-$Cr(NH_3)_2(NCS)_4^-$ on solvent. Semiquantitative studies of the photochemical reactivity of $Cr(NCS)_6^{3-}$ reported earlier[4] are rendered quantitative by results collected in Table II. It is immediately clear that both thermal and photochemical solvolysis reactions of *trans*-$Cr(NCS)_4(NH_3)_2^-$ are retarded by CH_3CN and that the thermal reaction

Table I. Rate Constants for Aquation of $K[Cr(NH_3)_2(NCS)_4]$ at 50°

H_2O–CH_3CN mixtures, mole fraction of CH_3CN	k (sec^{-1}) $\times 10^5$
0:0	8.84
0.01	7.13
0.03	6.77
0.05	5.76
0.07	5.20
0.10	3.60
0.15	2.76
0.20	2.30
0.25	1.89
0.30	2.17
0.50	1.45
0.95	1.68
1.00	Very slow[a]
D_2O	7.80
Deuterated complex in D_2O	4.74

[a] 2% reaction in 21 hr.

Table II. Quantum Yields for Photoaquation of Thiocyanato Complexes of Chromium(III)

Mole fraction of CH_3CN	*trans*-$Cr(NH_3)_2(NCS)_4^-$ ϕ (5200 Å)	ϕ (3920 Å)	$K_3Cr(NCS)_6$ ϕ (5650 Å)
0.00	0.286	0.316	0.332[a]
0.04	0.267		
0.10	0.234		
0.20	0.218		0.366
0.30	0.192		
0.50	0.178		0.356
0.80	0.182		0.338
1.00	0.164	0.184	0.370

[a] These values are higher than 0.255 quoted by Adamson.[10]

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

(8) H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).

(9) R. D. Wilson, V. S. Sastri, and C. H. Langford, *Can. J. Chem.*, **49**, 679 (1971).

(10) E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).

Table III. Excess Line Broadening of ^1H Nmr Signal of CH_3CH in CH_3CN-H_2O Mixtures

Mole fraction of CH_3CN	0.02	0.030	0.06	0.08	0.10	0.2	0.30	0.40
$\Delta\nu$ obsd (Hz)	5.52	4.80	5.40	5.70	5.58	4.02	3.12	3.00
Mole fraction of CH_3CN	0.50	0.60	1.0					
$\Delta\nu$ obsd (Hz)	2.64	2.52	2.10					

[a] Reinecke's salt = 0.02 *M*, temperature 25°.

is much more solvent sensitive than the photochemical reaction. The earlier report on $Cr(NCS)_6^{3-}$ indicated considerable sensitivity of thermal solvolysis to addition of CH_3CN but claimed that the photoreaction was solvent independent. It is seen from Table II that that claim is essentially correct. Adamson[11] has reported the D isotope effect on thermal solvolysis. Table I shows that this resides primarily in the deuteration of the complex and not the deuteration of the solvent.

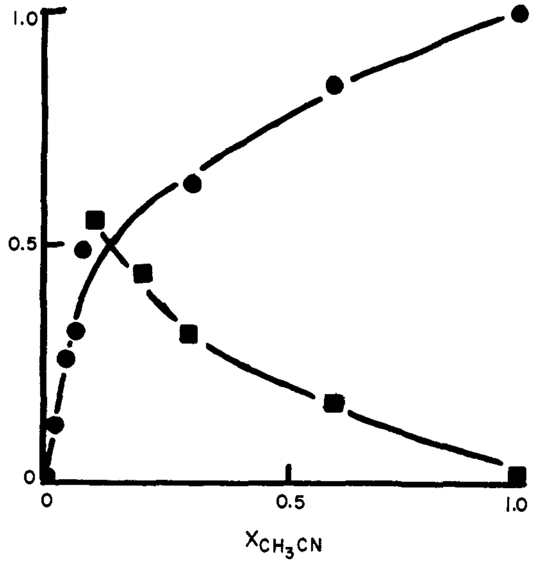

Figure 1. Preferential solvation of *trans*-$Cr(NH_3)_2(NCS)_4^-$ at 50°. Circles show values of n/n_0 derived from nmr line width of CH_3CN protons; squares show values of n/n_0 derived from nmr line width of water protons. n/n_0 is plotted against the mole fraction of CH_3CN.

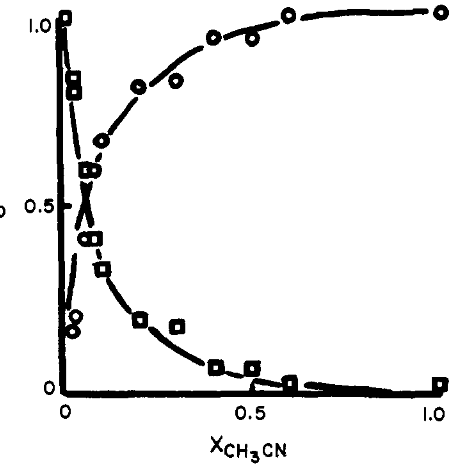

Figure 2. Preferential solvation data at 25°. Symbols as in Figure 1. Note that solvation data from water proton nmr could be obtained in all mixtures at this temperature because solvolysis was slow.

Table III contains typical nmr line broadening data from which n/n_0 values may be derived. Figure 1 shows the nmr derived preferential solvation curves at 50°. At high water concentration, the reaction interfered with determination based on study of the H_2O proton. Figure 2 shows the corresponding curves at 25° where the complete water proton curve is accessible. In both figures the sum of n/n_0 for water (estimated from H_2O proton signals) and n/n_0 for CH_3CN (estimated from CH_3CN proton signals) is within about 10% of unity indicating that the solvation shell populaton changes by a one-for-one substitution of CH_3CN for H_2O and that the approximations of the nmr analysis are satisfactory. Independent semiquantitative confirmation of the preferential solvation of *trans*-$Cr(NCS)_4(NH_3)_2^-$ by CH_3CN is provided by data on the solvent shift of the maximum of the lowest energy ligand field band. It moves about 5 nm from H_2O to CH_3CN. The shift is 4 nm at a mole fraction of 0.15 CH_3CN.

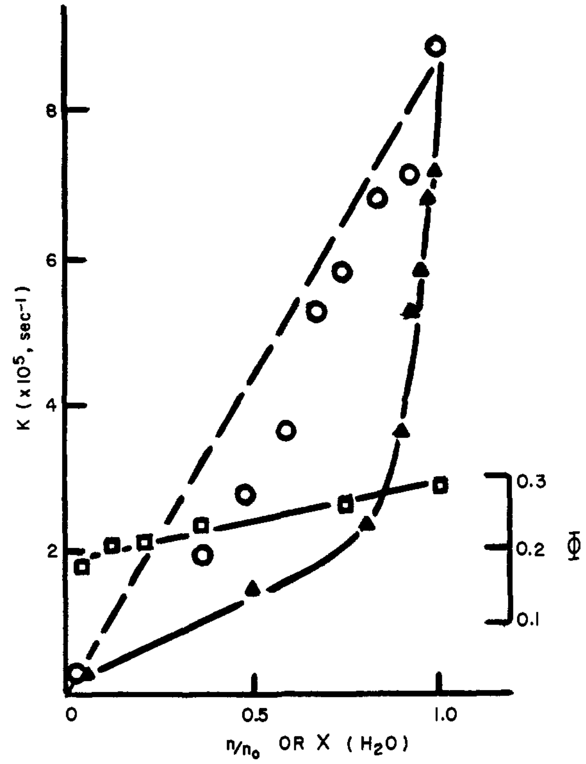

Figure 3. Correlations of reactivity of *trans*-$Cr(NH_3)_2(NCS)_4^-$ with solvent composition. Triangles show the rate constants for thermal solvolysis plotted against the mole fraction of water in the CH_3CN-water mixtures. Circles show these thermal rate constants replotted against the value of n/n_0 for water. The dashed line indicates the ideal behavior for a reaction involving a 1:1 encounter between the complex and a molecule of the reactive solvent, water. Squares show the dependence of the quantum yield for photosolvolysis on the value of n/n_0 for water. (The quantum yield scale is on the right hand axis.)

Figure 3 summarizes the crucial correlations. It presents the dependence of thermal and photochemical

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(11) A. W. Adamson, *J. Amer. Chem. Soc.*, 80, 3183 (1958).

solvolysis rates on the mole fraction of H_2O and on n/n_0 (H_2O) which is the probability that there is a water molecule occupying a given solvation site in the outer sphere of *trans*-$Cr(NH_3)_2(NCS)_4^-$. The correlation with n/n_0 corresponds to the correlation of the rate with the number of 1:1 complex–water encounter species.

Discussion

1. **Thermal Reaction.** The problem is to assess the role of the reactive solvent, water. Following the unelaborated TS theory of eq 2, analysis of the reaction requires information on the activity of the reactive solvent, water. This is available from de Landesberg[12] and was recently reproduced.[4] In the composition range from 0.0 to 0.5 mol fraction CH_3CN water activity is reduced by less than 25%.[4,12] Consequently, it is not easy to attribute the decrease in rate to reduction of activity of the reactive solvent. Instead, one is encouraged to look upon variation of the ratio $\gamma_{MX}/\gamma_{\ddagger}$ as the most important factor, but the origin of this variation is not clear. It does not seem to be simply the change of a bulk parameter-like dielectric constant because the rate decrease is already a factor of 2 in a mixture that is 90 mol % water. A hint at the origin of the variation in $\gamma_{MX}/\gamma_{\ddagger}$ comes from the observation that the rate decrease in the solvolysis reaction is more closely linked to the *rise*[4,12] in the activity of the unreactive CH_3CN component of the solvent mixture.

With this hint, we turn to analysis of the situation *via* eq 4. The simplest assumption would be that the encounter complex consists of one molecule of Cr(III) complex and one molecule of water (the entering ligand), the occupants of other sites in the solvation shell being relatively unimportant. Such an assumption is not unreasonable in this case since Adamson[11] has shown that the reactivity of $Cr(NH_3)_2(NCS)_4^-$ is relatively insensitive to solvent as long as the solvent is solvolytically reactive. If the simple assumption is adequate, a correlation of rate with the population of 1:1 encounter complexes (that is, a correlation with n/n_0) is predicted. The dashed line drawn from the rate in pure water to zero at $n/n_0 = 0$ in Figure 3 represents this prediction. Clearly, there is some departure but the account provided is much nearer the facts than any simple correlation with activity. The small departure from the simple linear relationship may be approached from the point of view of variation of $\gamma_E/\gamma_{\ddagger}$. The rate decrease is a bit more rapid than the decrease in the number of 1:1 $Cr(NH_3)_2(NCS)_4^-$–water encounters in solutions of substantial water content. A second (or third) water molecule may play a helpful (but not essential) role in the transition state as an H-bond acceptor in relation to the NH_3 protons. This suggestion is motivated by the D isotope effect and the simple linear relation between n/n_0 and rate for $Cr(NCS)_6^{3-}$ which has no ammine ligand.[4]

The last suggestions of the previous paragraph are surely speculative but a minimum achievement of the encounter viewpoint is that the concept of a *requirement for encounter between at least one molecule of water and the Cr(III) complex renders manageable the difficult question of the sensitivity of the rate of solvolysis to a small concentration of unreactive solvent.* Use of the data on preferential solvation by CH_3CN disarms the anomaly. Preferential solvation data and the encounter equilibrium approach do not offer complete resolution of the difficulties of kinetics in mixed solvents, but they constitute a valuable first step whenever it is feasible to collect such data.

2. **Photochemical Reaction.** The quartet excited state of a Cr(III) complex is usually assumed to have a lifetime exceeding 10^{-8} sec. This is much longer than the typical lifetime of a particular encounter complex ($\sim 10^{-10}$ sec). Thus, quantum yield need not be limited by a requirement for encounter with a reactive solvent molecule prior to excitation. (The excited state is similar to a "long-lived intermediate" which encounters its final reaction partner after the rate-determining step.) Solvent independence of quantum yield is not improbable and is essentially what is observed in the case of reactions of $Cr(NCS)_6^{3-}$. (Recall that the thermal solvolysis was strictly proportional to n/n_0 (H_2O) in this case.) However, the encounter lifetime explanation of zero solvent dependence for photolysis of $Cr(NCS)_6^{3-}$ can be misleading because it overlooks the photochemical analog of the ratio $\gamma_E/\gamma_{\ddagger}$ which is a matter of the competition among various pathways of relaxation of excited states. Porter and his collaborators[13] have shown, *via* energy transfer experiments, that photolysis of *trans*-$Cr(NH_3)_2(NCS)_4^-$ proceeds primarily from the quartet state but the intersystem crossing to the doublet occurs with a quantum yield near 0.5. A hint as to the nature of the solvent effect is provided by the observation that doublet phosphorescence is a little stronger in CH_3CN than in water.[14]

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[12] V. de Landesbug, *Bull. Soc. Chim. Belg.*, **49**, 59 (1940).

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[14] N. A. P. Kane-Maguire and C. H. Langford, *Chem. Commun.*, 895 (1971).