pattern of $NdCl_3$. We also thank personnel of the Argonne Chemical Engineering Division for making available one of the He-recirculating dryboxes. A travel grant to one of us (H. A. Øye) from "Norges Almenvitenskapelige Forskningsråd" is gratefully acknowledged. We are indebted to Mr. T. Hertzberg, Laboratory of Chemical Engineering, Technical University of Norway, Trondheim, for placing his least-squares program at our disposal and for performing the additional programming.

Preferential Solvation and the Mechanisms of Thermal and Photochemical Solvolysis of the Hexathiocyanatochromate(III) Ion in Acetonitrile–Water Mixtures[1]

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Abstract: The nmr method for determining the composition of the solvation shell of a paramagnetic solute introduced by Frankel, Stengle, and Langford has been applied to reveal the strong preference of $Cr(NCS)_4^{3-}$ for CH_3CN in CH_3CN–H_2O mixtures. The rate of loss of the first SCN^- from this complex has been measured as a function of solvent-shell composition. The thermal solvolysis reaction rate decreases linearly with the fraction of water (the reactive solvent) in the solvation shell revealing the requirement for one water molecule as a stoichiometric component of the transition state. Solvolysis by D_2O, methanol, and pyridine proceeds at nearly the same rate as hydrolysis. The corresponding photolysis is nearly independent of solvent-shell composition. A dissociative interchange mechanism for thermal solvolysis would explain these results. The photoexcited state is expected to have a lifetime sufficiently long to allow rearrangement of the solvation shell after "activation."

Any second or higher order solution reaction which proceeds at a rate significantly less than the diffusion control limit may be considered as requiring at least two elementary steps. For example, the solvolytic reaction of a transition metal complex would be

$$MX + S \rightleftarrows E \qquad (1)$$
$$E \longrightarrow MS + X$$

where MX is some substrate complex, S is the reactive solvent species, E is the *encounter*[3] complex, and MS and X are the products. The formation and dissociation of an encounter complex must, under normal circumstances, proceed at a rate approximating diffusional control.[4] Thus, the slow step leading to products does not significantly perturb the equilibrium of the encounter step. If the equilibrium for the encounter may be studied independently, correlation of the reaction rate with the population of encounter complexes between MX and S may reveal the number of solvent molecules, S, required as stoichiometric components of the transition state for product formation.

In a pure solvent, the encounter complex population is clearly invariant, which is the *fundamental* reason for pseudo-first-order kinetics. In a mixed solvent (one "unreactive" component) the population will vary according to the preference of the solute for solvation by one or the other component. In the event that there is a *strong* preference for one solvent component, it may be that the probability of encounter with the reactive component varies significantly without a correspondingly large change in the relevant parameters for the bulk of the solvent (*e.g.*, dielectric constant). Just such a situation seems to arise with respect to solutions of $K_3[Cr(NCS)_6]$ in acetonitrile–water mixtures.[5]

The strong preference in this case is that of $Cr(NCS)_6^{3-}$ for acetonitrile and the reactive solvent is water. The preferential solvation information is derived from studies of the effect of the paramagnetic solute on the nmr relaxation times of protons of the solvent molecules. This method, recently suggested,[5,6] merits brief recapitulation.

The transverse relaxation time, T_2, of the protons on a solvent molecule will be greatly reduced by a paramagnetic solute. In cases of solvation in the outer coordination sphere, this effect depends upon dipolar coupling between the paramagnetic electrons and the protons which enters the relaxation equations with an inverse sixth power distance dependence.[7] As a result, it is a good approximation to partition the solution into a paramagnetic environment (the solvation shell) and a diamagnetic environment (the bulk solvent). When exchange between these two environments is

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[1] We acknowledge support from the National Research Council (Canada) and the Air Force Office of Scientific Research.

[2] To whom correspondence should be addressed at Carleton University; Alfred P. Sloan Fellow, 1968–1970.

[3] A pair of partners trapped in the "solvent cage."

[4] M. Eigen, "Proceedings of the VIIth International Conference on Coordination Chemistry," Butterworth and Co., Ltd., London, 1963, p 97.

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

[6] C. H. Langford and J. F. White, *Can. J. Chem.*, 47, 3049 (1967).

[7] A. Carrington and A. McLachlan, "Introduction to Magnetic Resonance," Harper & Row, New York, N. Y., 1967, Chapter 11.

rapid (as it will be when the solvation shell is the outer coordination sphere), McConnell's equation applies.[8]

$$\frac{1}{T_2} = \frac{P_D}{T_{2D}} + \frac{P_M}{T_{2M}} \tag{2}$$

T_2 is the observed relaxation time, P_D is the probability that a solvent molecule is in the diamagnetic environment (bulk), and P_M is the probability that a proton is in the paramagnetic environment (solvation shell). T_{2D} and T_{2M} are the relaxation times characteristic of the two environments, respectively. In a solution dilute in paramagnetic solute, $P_D \simeq 1$ and the term $1/T_{2D}$ may be measured from study of solvents free of paramagnetic solute. Therefore, P_M/T_{2M} is accessible experimentally. It is simply related to the excess width at half-height in the nmr absorption signal

$$\pi\Delta\nu = \frac{P_M}{T_{2M}} \tag{3}$$

where $\Delta\nu$ is the excess width of the signal produced by the paramagnetic solute. T_{2M} is difficult to evaluate accurately. If we may hope that $T_{2M} = T_{2M0}$ where T_{2M} is the relaxation time for protons on a particular component (*e.g.*, the methyl protons of CH_3CN) in a mixed solvent and T_{2M0} is the value for the same protons in the pure solvent (*e.g.*, pure acetonitrile), we may write

$$\frac{\Delta\nu}{\Delta\nu_0} = \frac{P_M}{T_{2M}}\frac{T_{2M0}}{P_{M0}} = \frac{P_M}{P_{M0}} \tag{4}$$

where the subscript 0 designates excess width, probability of solvation shell occupancy, or relaxation time in solvation shell for the *pure solvent*, and the unsubscripted quantities refer to the *mixture*. From a knowledge of the bulk composition of the solvent, it is straightforward to convert P_M/P_{M0} data into the fraction of the particular solvent (*e.g.*, CH_3CN) remaining in the solvation shell of the complex in the mixed solvent. The "hope" that $T_{2M} = T_{2M0}$ is drawn from the earlier successes of this approximation.[5,6,9] That the hope is warranted is verified semiquantitatively by study of the small solvent dependence of the energies of the ligand field bands of $Cr(NCS)_6{}^{3-}$.

Experimental Section

Materials. The complex $K_3Cr(NCS)_6$ was obtained from Alfa Inorganics, Inc. and recrystallized from ethanol. Reagent grade acetonitrile from Fisher Scientific and distilled water were used in solution preparation.

Kinetics. The rate of solvolysis was estimated by measurement of free SCN^- spectrophotometrically as the $FeNCS^{2+}$ complex in aqueous perchloric acid following the recipe of Adamson.[10] The spectrophotometer was a Gilford Model 240. Aliquot portions of the reacting solution were withdrawn and diluted by a factor of 12.5 with the analytical solution. The analytical system was calibrated in each of the solvent mixtures with standard thiocyanate solutions. The thermal reactions were run at 29.0° in completely blackened flasks. All transfers were carried out by the light of red "photographic" bulbs only. As has been previously noted,[11] the loss of a second SCN^- interferes with study of the loss of the first from $Cr(NCS)_6{}^{3-}$. In agreement with Poulson, Bjerrum, and Poulson, we find that there is no detectable deviation from first-order kinetics for loss of one SCN^- to well beyond 25% reaction. Reactions in all systems were followed to 25% reaction. Normally, the complex concentration was 5×10^{-3} *M*. In several mixtures, doubling this value does not change the rate.

The solvent dependence of photochemical solvolysis was studied by simultaneous illumination of solutions of three different solvent compositions by sunlight filtered through double plate-glass windows and a Pyrex test tube. We presume that the illumination was principally in the ligand field bands of the complex.

Spectra and Preferential Solvation. Preferential solvation data were derived from the proton resonance of CH_3CN recorded at 29° on a Varian A-60. In highly aqueous solution the measured line widths were extrapolated to zero time to correct for solvolysis. Water line widths add little to the data since they are quite narrow when CH_3CN is strongly preferred. As a solvation parameter independent of T_2, the small solvent shift of the ligand field bands were recorded on a Cary 14 spectrophotometer.

Results

Table I gives solvolysis rates in various solvents at 29° according to eq 5. They are correlated with the

$$Cr(NCS)_6{}^{3-} + S \longrightarrow Cr(NCS)_5S^{2-} + NCS^- \tag{5}$$

solvent ionizing power parameter **Z**.[12] The table also records solvolytic rates in mixtures of CH_3CN and water. Only the water appears to be reactive. Table II records paramagnetic broadening of the CH_3CN proton resonance in CH_3CN–water mixtures containing 0.043 *M* $Cr(NCS)_6{}^{3-}$ and values of n/n_0, the number of solvent molecules in the outer coordination sphere of

Table I. Rate Constants for Solvolytic Reactions of $Cr(NCS)_6{}^{3-}$ at 29.0°

	I. Pure Solvent Data					
Solvent	H_2O	CH_3OH	C_5H_5N	D_2O		
k, sec^{-1} × 10^5	5.25	3.47	1.89	7.08		
Z value[12]	94.6	79.6	71.3			
	II. Mixed Solvent Data					
Mole fraction of CH_3CN	0.01	0.03	0.04	0.05	0.07	0.10
k, sec^{-1} × 10^5	4.27	2.68	2.38	2.06	1.49	1.07
Mole fraction of CH_3CN	0.15	0.20	0.30	0.40	1.00	
k, sec^{-1} × 10^5	0.66	0.50	0.38	0.17	Very slow[a]	

[a] In a solvent no more than 0.1% by weight water, 12.4% of the first thiocyanate was released in 31 hr.

Table II. Excess Line Broadening of ^1H Nmr Signal of CH_3CN in CH_3CN–H_2O Mixtures and Values of the Preferential Solvation Parameter n/n_0[a]

Mole fraction of CH_3CN	$\Delta\nu$, Hz	n/n_0[b]
1.000	5.2	1.00
0.757	5.6	0.96
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] In CH_3CN. $[K_3Cr(NCS)_6]$ = 0.0426 *M*. [b] n/n_0 for H_2O is taken in what follows as $1.00 - (n/n_0)(CH_3CN)$. This may introduce error if substitution is not one for one, but the error will certainly be small compared to present precision.

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

(9) L. S. Frankel, Ph.D. Thesis, University of Massachusetts, Amherst, 1966.

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

(11) K. G. Poulson, J. Bjerrum, and I. Poulson, *Acta Chem. Scand.*, **8**, 921 (1954).

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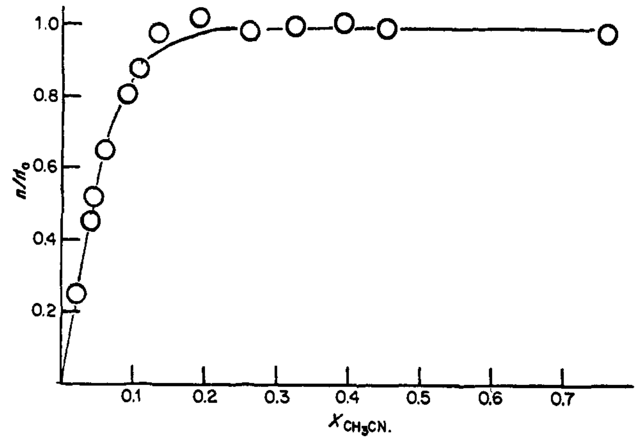

Figure 1. Values of the solvation parameter n/n_0 for CH_3CN as a function of the mole fraction of CH_3CN.

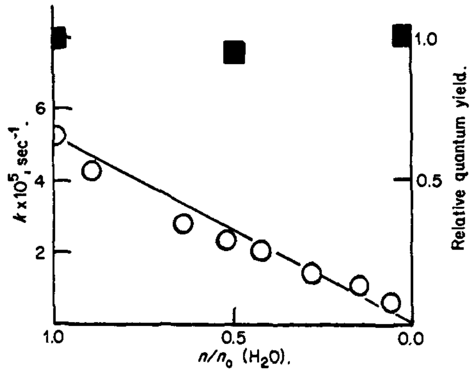

Figure 2. Open circles show the rate constant for hydrolysis as a function of the solvation parameter n/n_0 for water. Squares show the relative (to water) quantum yield for photohydrolysis measured by the thiocyanate released for constant illumination (about 20% of the first thiocyanate) as a function of the solvation parameter n/n_0 for water.

the solute in the mixed solvent compared to the number in a solution in pure solvent. It is derived from P_M/P_{M0} since this ratio equals n/n_0 times N_0/N where N_0 represents the number of CH_3CN molecules/ml in pure CH_3CN and N the number/ml in the mixed solvent.

The "preferential solvation curve," a plot of n/n_0 for CH_3CN *vs.* the mole fraction of CH_3CN, is shown in Figure 1. Figure 2 shows the rate of hydrolysis of $Cr(NCS)_6{}^{3-}$ as a function of n/n_0 for water. A straight line is drawn from the pure water rate to zero. Considering the precision of the measurements in the narrow range of solvent compositions which are relevant and the inevitable incursion of second-order solvent effects, the experimental points fit remarkably closely to the line. The figure omits rates in solutions where n/n_0 is too small to measure accurately (points that would cluster near the origin). Square points also show the relative thiocyanate released photochemically for three solvent compositions.

Figure 3 shows the shift of the two ligand field bands of $Cr(NCS)_6{}^{3-}$ as a function of the mole fraction of CH_3CN. This independent physical parameter lends important qualitative support to Figure 1 and the assumptions of the relaxation time analysis.

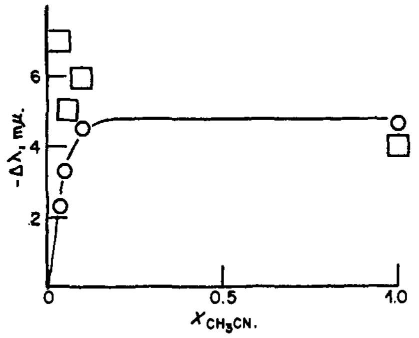

Figure 3. Open circles show the position of the 421-mμ (in water) band of $Cr(NCS)_6{}^{3-}$ as a function of mole fraction of CH_3CN. Squares show the position of the 565-mμ (in water) band.

Discussion

The first point to consider is whether the role of water is to be associated with a nucleophilic attack or whether the solvolytic reactions follow the normal dissociative mode of activation which seems quite general for octahedral complexes. Unfortunately, there is little reason to associate the dependence of the solvolytic rate on water with a water attack. This is strongly suggested by the nonselectivity of the solvolytic rate in reactive solvents. The reaction proceeds at *about the same rate* in several solvents (H_2O, methanol, pyridine) of different nucleophilicities. The rate differences that are observed parallel Kosower's solvent ionizing power parameter, **Z**.[12] This parallelism may follow from the solvation requirements of NCS^- or from negative catalysis following increased ion pairing with K^+, but both explanations emphasize the role of thiocyanate dissociation in activation. A dissociative mode of activation is quite consistent with the available evidence concerning the behavior of Cr(III) complexes.[13] We are therefore required to consider the significance of the close parallel of solvolysis rate to water encounter probability in the context of the presumption in favor of dissociative activation. This is closely related to earlier discussions of reactions in ion pairs[14] and speculation on mixed solvent situations.[15]

Since we presume that a nucleophilic attack by the entering solvent molecule does not significantly stabilize the transition state, we must explain why the solvolysis rate is so nearly proportional to n/n_0 (H_2O). Proportionality implies, in the absence of secondary solvent effects, that one site in the solvation shell must be occupied by H_2O, not CH_3CN, for the reaction to proceed, or that the encounter complex for the reaction involves $Cr(NCS)_6{}^{3-}$ and one water molecule. The problem is the role that water can play that CH_3CN cannot. One possibility would be specific hydrogen bonding, but the very small solvent deuterium isotope effect persuasively excludes this idea.

Consider now the structure of a dissociative transition state. It may reasonably be presumed to resemble a five-coordinated complex with some interactions with its second sphere ligands. If the geometry is approximately square pyramidal, there might be special interactions with the leaving group and an adjacent solvent

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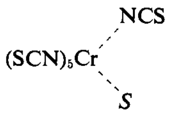
(13) C. H. Langford and T. R. Stengle, *Ann. Rev. Phys. Chem.*, **19**, 193 (1968).

(14) M. Tobe, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 7.

(15) A. W. Adamson, *J. Inorg. Nucl. Chem.*, **28**, 1955 (1964).

molecule (which is a candidate for entry). We sketch



$$(SCN)_5Cr\begin{matrix}\diagup NCS \\ \diagdown S\end{matrix}$$

where *S* is a solvent molecule. The operational meaning of dissociative activation is that the role of *S* is *nonspecific* as we see from choosing $S = H_2O$, CH_3OH, or C_5H_5N without great rate change. The trouble with CH_3CN appears to be that it cannot form a stable bond to Cr(III) in the octahedral ground state.

Now, if the five-coordinate state had sufficient stability to exchange *S* with the bulk before the system returned to the six-coordinate state, the reaction would be characterized as going through an "intermediate" because the reaction would not correlate with n/n_0 (H_2O); the reactive intermediate could "seek" the reactive solvent and would not require its prior presence. However, if the activated five-coordinate state has so short a life that it may only choose SCN^- or the *S* that was in the encounter complex before "dissociation," SCN^- loss can occur only if *S* was a reactive solvent (H_2O), and the rate should parallel n/n_0 (H_2O). Such a process has been called *dissociative interchange* between the inner and outer coordination spheres. It provides a felicitous model for interpretation of the present results.

The photochemical solvolysis stands in significant contrast to the thermal reaction. The photoexcited state of a Cr(III) complex might be expected to have a lifetime near 10^{-8} sec if the quartet state is involved, or considerably longer if there is efficient crossover to the doublet. These excited-state lifetimes exceed the expected lifetime of a particular solvation shell and, as a result, the excited state may "seek" a reactive solvent molecule. The rate (quantum yield) is independent of n/n_0 (H_2O). The photoexcited state may be an operationally identifiable intermediate in the reaction. Alternately, a metastable $Cr(NCS)NCCH_3{}^{2-}$ may be accessible along the high-energy photochemical pathway.

Finally, it would be interesting to inquire after the reasons for the strong preference of $Cr(NCS)_6{}^{3-}$ for CH_3CN. The thermodynamics of CH_3CN–H_2O mixtures show why any preference appears strong. Figure 4 records the partial vapor pressures relative to that over pure solvent for CH_3CN and H_2O as a function of the mole fraction of CH_3CN. The data are from de Landsberg.[16] Note the very large deviation from Raoult's law. At comparatively low mole fraction of either component, the activity of that component will approach its pure solvent value. A small preference for one solvent in the solvation shell will be expressed extensively in concentration equilibria at low mole fraction of that solvent. This point is of general significance for the understanding of reactions in mixed solvents which deviate from Raoult's law. Crude estimates based on an independent site model of the solvation shell suggest that the solvation shell preference in this case is less than 1 kcal/mole. This small preference has rather spectacular kinetic consequences.

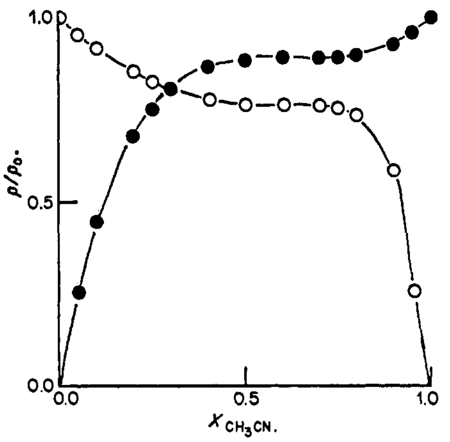


Figure 4. Partial vapor pressure relative to the vapor pressure over the pure solvent as a function of mole fraction of CH_3CN: open circles, water; Closed circles, CH_3CN. The data were obtained at 20°.

All that we can yet say about the origins of this preference for CH_3CN is that it does not occur (quite the reverse) in the solvation shell around $Cr(C_2O_4)_3{}^{3-}$.[17] Possibly the hydrogen-bond acceptor sites on the oxalate complex are important to its solvation.

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[16] V. de Landsberg, *Bull. Soc. Chim. Belges*, **49**, 59 (1940).

[17] D. Fairbairn and C. H. Langford, unpublished observation.