

- (16) T. W. Newton, "The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions", ERDA Critical Review Series, Technical Information Service, TID-26506, 1975.
- (17) M. Choi, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977).
- (18) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).
- (19) A. Adegite, H. Egboh, J. F. Ojo, and R. Olich, *J. Chem. Soc., Dalton Trans.*, 833 (1977).
- (20) J. D. White and T. W. Newton, *J. Phys. Chem.*, **75**, 2117 (1971).
- (21) T. K. Keenan, *J. Phys. Chem.*, **61**, 1117 (1957).

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Photosolvolysis of *trans*-Tetrathiocyanatodiamminechromium(III) and *trans*-Dithiocyanatobis(ethylenediamine)chromium(III) Ions: Nucleophilicity and Solvent Orientation¹

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Received January 18, 1978

Photorelease of thiocyanate from two similar complexes which differ with respect to sign of charge, *trans*-[Cr(NCS)₄(NH₃)₂]⁻ and *trans*-[Cr(en)₂(NCS)₂]⁺, has been studied in several solvents: H₂O, Me₂SO, DMF, CH₃CN, CH₃NO₂, and H₂O-glycerol. The quantum yield for reaction of the cation is a linear function of the Guttmann donor number of the solvent, supporting the associative mechanism for photosubstitution at Cr(III) which has been suggested on the basis of stereochemistry. But attack on a very short-lived species is indicated by the fact that reaction of the otherwise similar anion correlates only with solvent fluidity (inverse viscosity). This suggests that only solvent molecules which are correctly oriented toward the center can achieve nucleophilic attack. In this context, the lack of temperature dependence in a reaction of the cation is significant. This photonucleophilic attack is not an activated process analogous to thermal nucleophilic attack. The role of a good nucleophile appears to be to select the reactive relaxation channel.

Introduction

The suggestion has been made, primarily on the basis of stereochemistry, that the well-known³ photosubstitution reactions of six-coordinate Cr(III) complexes are *associative*.⁴ Only one publication so far has reported measurements of the relative reactivity of different nucleophiles toward a Cr(III) center.⁵ This question, photonucleophilicity, is interesting because important differences from nucleophilicity in thermal reactions may arise. A nucleophile in a thermal reaction lowers the barrier for substitution by stabilization of the transition state through new bond formation. A nucleophile in a photoreaction may be involved with an excited state which is at an energy well above the thermal substitution barrier. In that case, it may play a role in selection of a relaxation channel rather than in lowering a barrier.

In this paper, we examined two compounds similar to two examined in several solvent mixtures by Wong and Kirk.⁴ In their studies, quantitative comparison of solvent nucleophilicities could not be accomplished because of complications with preferential solvation and steric effects. The complexities of preferential solvation in CH₃CN-H₂O mixtures and alcohol-water mixtures are known with respect to Cr(III) complexes.⁶ We have chosen single solvent systems for most of these studies and sought a wide range of probable solvent nucleophilicity. The limit on the range was finally imposed by complex salt solubilities. The reaction monitored is thiocyanate release which has been observed as a consequence of irradiation of the first quartet ligand field band of the complexes.^{7,8}

Experimental Section

Materials. K[Cr(NH₃)₂(NCS)₄] was obtained from the ammonium salt by reprecipitation with potassium nitrate⁹ and twice recrystallized from warm water. *trans*-[Cr(en)₂(NCS)₂]Cl was prepared from Cr(en)₃(NCS)₃ according to the method reported in the literature.¹⁰ *trans*-[Cr(en)₂(NCS)₂]ClO₄ for use in CH₃CN and *trans*-[Cr(en)₂(NCS)₂]BPh₄ for use in CH₃NO₂ were obtained with HClO₄ and sodium tetraphenylboride, respectively. The solvents were all reagent grade and were used without further purification.

Table I. Extinction Coefficient Values of the Iron(III) Thiocyanate Species in Different Water-Solvent Mixtures

solvent	ϵ , M ⁻¹ cm ⁻¹	λ , nm
H ₂ O ^a	4.3×10^3	450
20% CH ₃ CN/80% H ₂ O	4.1×10^3	450
20% CH ₃ NO/30% CH ₃ OH	3.1×10^3	510
20% DMF/80% H ₂ O	2.3×10^3	510
20% Me ₂ SO/80% H ₂ O	2.1×10^3	510

^a This value also applies to water-glycerol mixtures.

Table II. Quantum Yields for Photosolvolysis of [Cr(NH₃)₂(NCS)₄]⁻ and *trans*-[Cr(en)₂(NCS)₂]⁺

solvent	[Cr(NH ₃) ₂ (NCS) ₄] ⁻ ϕ	[Cr(en) ₂ (NCS) ₂] ⁺ ϕ	η , ^b cP	DN ^c
H ₂ O	0.311 ± 0.003^a	0.152 ± 0.002	8.93	33
Me ₂ SO	0.135 ± 0.002	0.141 ± 0.001	19.8	29.8
DMF	0.184 ± 0.002	0.120 ± 0.006	7.96	26.6
CH ₃ CN	0.257 ± 0.001	0.061 ± 0.003	3.45	14.1
CH ₃ NO ₂	0.216 ± 0.002	0.021 ± 0.003	6.08	2.7

^a Value from ref 9. ^b Value from ref 12. ^c DN = donor number. Value from ref 11.

Photolyses. The solutions to be photolyzed were made up just prior to use and were irradiated for 15–40 min in a 5-cm quartz vessel. The light source was a xenon lamp; the irradiation wavelength was 465 nm and was selected by means of a Jarrel-Ash 1/4-m grating monochromator. The intensity of the light before and after irradiation was measured by Reineckate actinometry.⁹ In order to avoid interference by the products, the extent of the photosolvolysis never exceeded 4%. The quantum yields were determined by spectrophotometric analysis of the released SCN⁻ as the complex "Fe(SCN)²⁺" in aqueous perchloric acid. Aliquots of the reacting solution were withdrawn and diluted by a factor of 5 with the analytical solution. A value of 4.3×10^3 M⁻¹ for the extinction coefficient of Fe(SCN)²⁺ in water at 450 nm was used. The analytical system was calibrated in each of the nonaqueous solvents with standard thiocyanate solutions at 510 nm. At this wavelength the complex Fe(SCN)²⁺ was the only absorbing species in the mixture and the calibration curve was linear. When the solvent was nitromethane, the aliquot of solution to be examined had to be made 30% in methanol in order to make

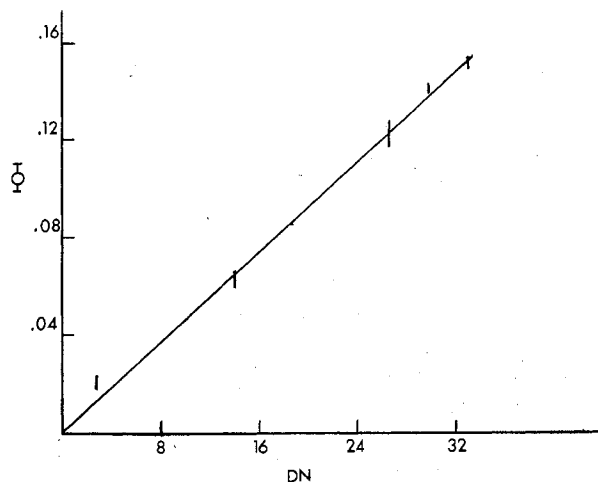
Table III. Quantum Yields for Photosolvolytic of $[Cr(NH_3)_2(NCS)_4]^-$ in Water-Glycerol Mixture

% of glycerol	ϕ	$1/\eta,^a [1/cP]^{25^\circ} \times 10$
	0.181 ± 0.002	1.98
45	0.195 ± 0.003	2.52
40	0.202 ± 0.003	3.14
30	0.216 ± 0.002	4.64
20	0.239 ± 0.006	6.48
10	0.280 ± 0.006	8.67
0	0.311 ± 0.003^b	11.20

^a Values from ref 13. ^b Values from ref 9.

Table IV. Quantum Yields for Photosolvolytic of $[Cr(NH_3)_2(NCS)_4]^-$ and $[Cr(en)_2(NCS)_2]^+$ in Me_2SO at Different Temperatures

temp, °C	$[Cr(en)_2(NCS)_2]^+$		$[Cr(NH_3)_2(NCS)_4]^-$	
	ϕ	$E_a, kcal/mol$	ϕ	$E_a, kcal/mol$
21	0.141 ± 0.02	~0	0.134 ± 0.002	2.2
25			0.151 ± 0.004	
35	0.135 ± 0.05		0.169 ± 0.005	
45	0.141 ± 0.04			


Figure 1. Relationship between the quantum yields for photosolvolytic of $trans-[Cr(en)_2(NCS)_2]^+$ in different solvents and solvent donor number.

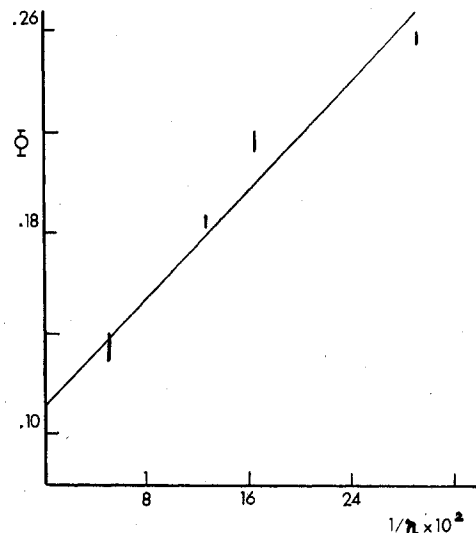
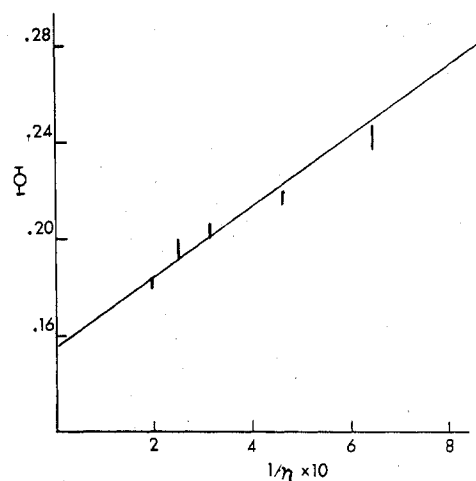
it compatible with the aqueous analytical solution. Either a Gilford 240 or a Coleman 124 spectrophotometer was used to record the values of absorbances. Parameters for various solvents appear in Table I. A dark run was conducted in each case for thermal correction of the photochemical solvolysis result.

Results

The quantum yields for the reactions studied are collected in Tables II and III. Each quantum yield is the average of five values. The values of quantum yield for the reactions in dimethyl sulfoxide at three different temperatures and the apparent activation energies are reported in Table IV.

The results clearly show that the quantum yields for both the reactions are solvent dependent; however, the trend of solvent dependence is very different for the two complexes. An additional feature is that the cationic complex is more sensitive than the anionic one to the change in the nature of the solvent. If we focus our attention on the values of quantum yield for the photosolvolytic of $trans-Cr(en)_2(NCS)_2^+$ we note that they increase with increasing nucleophilicity of the solvent. A satisfactory linear relation (see Figure 1) is observed between the quantum yields of the reaction and the donor numbers¹¹ of the solvents. These numbers are taken to be a quantitative index of Lewis basicity.

By way of contrast, the dependence of the quantum yield on the solvent nature for the photosolvolytic of $[Cr(N-$


Figure 2. Relationship between the quantum yields for the photosolvolytic of $[Cr(NH_3)_2(NCS)_4]^-$ in different solvents and solvent fluidity.

Figure 3. Relationship between the quantum yields for the photosolvolytic of $[Cr(NH_3)_2(NCS)_2]^-$ in a water-glycerol mixture and fluidity of the medium.

$H_3)_2(NCS)_4]^-$ is not straightforward; no simple relation can be found between the values of quantum yield and solvation parameters of the solvents related with their interaction with either the metal center or the leaving ligand SCN^- . Parameters considered included the donor numbers and the various solvation parameters from kinetics and spectra, Y and Z , as well as dielectric constant. However, it is interesting to note that for all the solvents except water there is relationship between the quantum yields and the viscosity of the medium: the more fluid the medium, the higher the quantum yield. This relation is represented in Figure 2 where the quantum yields for the reactions in the various solvents, except water, are plotted against the reciprocal of solvent viscosity (i.e., their fluidity). Although water does not fit on this plot, there is a relationship between the quantum yield in aqueous glycerol solutions and the medium viscosity. Figure 3 shows the relation between the quantum yield for the photolysis of $[Cr(NH_3)_2(NCS)_2]^-$ in water-glycerol mixtures and the medium viscosity. Obviously the departure of the water behavior from the pattern followed by the other solvents is a clear indication that viscosity is not the only property of solvent which influences the quantum yield of the $[Cr(NH_3)_2(NCS)_4]^-$ complex photosolvolytic, but it does seem to be a significant factor.

Discussion

Let us turn first to the more complex correlation observed. The anionic complex is no doubt solvated by solvent molecules oriented approximately with the positive end of the molecular dipole directed toward the complex.⁶ The consequences of such solvent orientation were considered by Wong and Kirk.⁴ The molecule would need to rotate in order to act as a nucleophile at Cr(III). Since there is much evidence that the ⁴T state of the Cr(III) complex is both very short-lived (picoseconds) and is the precursor to the solvolysis product,^{14,15} it seems reasonable that equilibration of an encounter species with respect to solvent reorientation cannot take place prior to the primary photophysical and, probably, photochemical events. Two models may be advanced, tentatively, which would lead to a solvent fluidity dependence.

The first model would envision a primary photodissociation to an ion pair between a five-coordinate $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_3]^0$ and NCS^- which can either separate or undergo geminate recombination. The rate of diffusional separation will depend on fluidity. The alternative model would envision relaxation to a relatively long-lived thermally equilibrated excited state with a lifetime $\geq 10^{-10}$ s. On this time scale, radiationless deactivation could be in competition with solvent rotation and nucleophilic attack. In this model, reaction could be occurring from the equilibrated ⁴T state with a rate comparable to solvent reorientation or it could be occurring from a hot ground state with decay to that state occurring in competition with rotational reorientation. The observation of an apparent activation energy comparable to the activation barrier to viscous flow is consistent with either model as long as one does not postulate, in the second case, a significant barrier to the nucleophilic attack.

It is not clear that either of these models predicts the detailed features of Figures 2 and 3. But, it must be acknowledged that other factors besides viscosity are important since H_2O does not fit the viscosity correlation for nonaqueous solvents.

Let us turn now to the simpler correlation, that of cation reactivity with Guttmann donor number. It is from this correlation (contrasted to anion behavior) that the main conclusion and interpretation of this study emerges. The correlation suggests solvent participation by forming a new bond to Cr(III) in a way related to Lewis basicity.¹⁶ In the cation case, this may occur immediately following excitation

since the solvent molecules are oriented at the negative end of the dipole (basic center) toward the Cr(III). That immediate participation by the nucleophile in selecting a reactive channel for relaxation of the excited state is the best description of photonucleophilicity is supported by the observation of a zero apparent activation energy for one case.

The study emphasizes two differences from behavior in thermal nucleophilic substitution. First, nucleophilic orders can be *masked* by excited state relaxation which occurs on a time scale shorter than solvent reorientation time. Second, differential reactivity may be accompanied by zero *apparent* thermal barriers. This may arise because the critical events occur exothermally during relaxation of excited states. We see here some limitations on imagining the excited state as simply an altered version of a ground-state molecule. Despite this, photonucleophilicity can be operationally defined as the dependence of the rate constant for the reactive relaxation channel on donor properties of an entering ligand.

Registry No. *trans*- $[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]^-$, 16248-93-4; *trans*- $[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$, 29845-02-1.

References and Notes

- (1) This work was supported by the National Research Council of Canada.
- (2) Visiting from Istituto di Chimica Fisica, Messina, Italy.
- (3) E. Zinato in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, Chapter 4.
- (4) C. F. C. Wong and A. D. Kirk, *Can. J. Chem.*, **54**, 3794 (1976), and earlier references cited therein.
- (5) C. H. Langford and J. P. K. Tong, *J. Chem. Soc., Chem. Commun.*, 138 (1977).
- (6) C. H. Langford and J. P. K. Tong, *Acc. Chem. Res.*, **10**, 258 (1977).
- (7) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).
- (8) C. Bifano and R. G. Linck, *Inorg. Chem.*, **13**, 3 (1974).
- (9) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
- (10) G. G. Schlessinger "Inorganic Laboratory Preparations", Chemical Publishing Co., New York, N.Y., 1962, p 224.
- (11) V. Guttmann, *Electrochim. Acta*, **21**, 661 (1976).
- (12) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, N.Y., 1972, pp 4-18.
- (13) M. L. Sheely, *Ind. Eng. Chem.*, **24**, 1060 (1932).
- (14) A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley, and M. Windsor, *Chem. Phys. Lett.*, **37**, 199 (1976). See also N. A. P. Kane-Maguire, J. E. Phifer, and G. D. Toney, *Inorg. Chem.*, **15**, 593 (1976).
- (15) S. Chen and G. B. Porter, *J. Am. Chem. Soc.*, **92**, 3196 (1970); *Chem. Phys. Lett.*, **6**, 41 (1970).
- (16) It must be made clear that this is a correlation with basicity. Since basicity is a thermodynamic parameter, the correlation no doubt arises in a subtle way and no causal connection is suggested between basicity and photonucleophilicity. Indeed, photonucleophilicity is a new phenomenon whose features are only dimly perceived at present.