

wavelength CTML bands (436 nm) of these complexes dissolved in inert solvents is followed by an emission from CTML excited states. In CHCl_3 this emission was quenched with simultaneous oxidation of the complexes. A further example of this type is apparently the photooxidation of (2,2'-bipyridine)(3,4-toluenedithiolato)platinum(II) in CHCl_3 following charge-transfer ligand-to-ligand (CTLL) excitation at long wavelength (577 nm).^{10c} It is interesting to note that the similar complex $\text{Ni}^{\text{II}}(\text{phen})[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]$ (phen = 1,10-phenanthroline) is photooxidized in CHCl_3 only by short-wavelength irradiation ($\lambda < 350$ nm), while the CTLL band at longer wavelength is not photoactive.^{10d} Compared to the Pt complex, the Ni compound should have LF excited states

at much lower energies which can quench the CTLL state. In distinction, the CTLL excited states at higher energies react so rapidly that other lower excited states apparently do not interfere.

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Registry No. $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$, 14876-79-0; $[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$, 19555-33-0; $[\text{Pt}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$, 15152-99-5; $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$, 46761-25-5; $[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$, 19570-29-7; $[\text{Pt}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$, 14977-45-8; $\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2$, 28984-20-5; $\text{Pt}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2$, 15607-55-3; $[\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2]^-$, 14879-11-9.

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High-Pressure Mechanistic Studies of the Photochemical Reactions of Transition-Metal Complexes. 3. Medium Effects on the Photoaquation of Some Co(III) and Cr(III) Complexes in Solution

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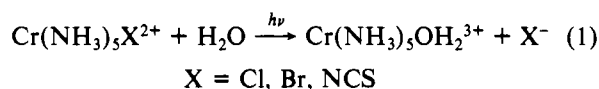
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The viscosity dependence of the photoaquation reactions of $\text{Co}(\text{CN})_6^{3-}$, $\text{Cr}(\text{CN})_6^{3-}$, $\text{Cr}(\text{NCS})_6^{3-}$, $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$, and $\text{Cr}(\text{NH}_3)_6^{3+}$ was studied in glycerol/water mixtures (≤ 65 wt %) at normal pressure. The results indicate that significant cage recombination occurs during the photosubstitution of NH_3 in $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ and $\text{Cr}(\text{NH}_3)_6^{3+}$ in pure water. However, no significant cage effect was observed in the photosubstitution of CN^- and NCS^- in the studied systems. In addition, the combined medium-pressure dependence of the photoaquation of NCS^- in $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ was studied over the ranges $1 \leq p \leq 1500$ bar and $1 < \eta < 30$ cP. A rather unexpected pressure dependence of the quantum yield is reported for this reaction in highly viscous media. The results are discussed in reference to data reported in the literature.

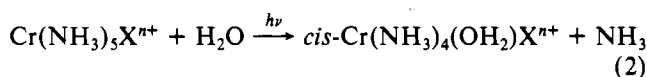
Introduction

The earlier papers in this series^{2,3} concerned high-pressure mechanistic studies of the ligand field photolysis of some cationic Cr(III) ammine and some anionic pseudohalogeno Co(III) and Cr(III) complexes in aqueous solution. From the pressure dependence of the observed quantum yields for the photoaquation processes, apparent volumes of activation were calculated. These data permitted a detailed discussion of the molecular nature of the intimate mechanism involved in such photoaquation reactions.

It was concluded² that reactions of the type

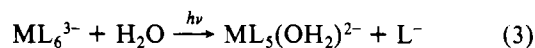


proceed according to an I_a mechanism, during which substantial Cr-X bond cleavage occurs in the transition state. Furthermore, reactions of the type



$n = 2$ for $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$; $n = 3$ for $\text{X} = \text{NH}_3$

also follow such a mechanism but with significantly less Cr-NH₃ bond cleavage in the transition state. In contrast, it was found³ that reactions of the type



$\text{M} = \text{Co(III)}$ for $\text{L} = \text{CN}$

$\text{M} = \text{Cr(III)}$ for $\text{L} = \text{NCS}, \text{CN}$

proceed according to an I_d mechanism in which some M-OH₂ bond formation occurs in the transition state.

Scandola et al.^{4,5} followed a different approach. They studied medium effects on the photoaquation of $\text{Co}(\text{CN})_6^{3-}$ and presented evidence for the occurrence of cage recombination in such photosubstitution reactions. The viscosity of the solvent had a meaningful influence on the quantum yield of the aquation reaction, and a good correlation between these variables was reported. The cage effect seemed to be quite efficient in more viscous solvents but relatively unimportant in pure aqueous solution for the studied system. Scandola et al. concluded that these tendencies may not hold for other photosubstitution reactions and are expected to depend on the nature of the leaving group.⁵

Wong and Kirk⁶ observed similar viscosity effects for the photoaquation of $\text{Co}(\text{CN})_6^{3-}$ in water/glycerol, water/ethylene glycol, and water/ethanol mixtures. In contrast, however, they⁶ argued that cage recombination is not established by their data since they do not find such an effect in water/acetonitrile and water/poly(vinylpyrrolidone) mixtures. Alternative explanations such as changes in the extent of solvent structure⁷

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and preferential or mixed solvation with consequent alteration of the effective water activity in the solution shell of the ion were offered. Although such effects may play a significant role, the reported data^{5,6} seem to indicate that viscosity has a meaningful influence on the photochemical quantum yield as long as the study is limited to a series of chemically similar solvents, for example, alcohols. This may not be true in the case of water/acetonitrile mixtures and aqueous solutions of viscous polymers.⁸

In our earlier studies,^{2,3} variations in pressure had no meaningful influence on the viscosity of the medium (pure water) such that no cage effect could be observed. However, for water/glycerol mixtures variations in pressure will significantly influence the viscosity of the medium and as such should demonstrate the possible role played by cage effects in these reactions. We have accordingly studied first the medium dependence of the photoaquation reactions of $\text{Co}(\text{CN})_6^{3-}$, $\text{Cr}(\text{CN})_6^{3-}$, $\text{Cr}(\text{NCS})_6^{3-}$, $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$, and $\text{Cr}(\text{NH}_3)_6^{3+}$ at normal pressure and then the combined medium–pressure dependence of the photoaquation of $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$.

Experimental Section

Materials. The complexes $\text{K}_3\text{Co}(\text{CN})_6$, $\text{K}_3\text{Cr}(\text{CN})_6$, $\text{K}_3\text{Cr}(\text{NCS})_6 \cdot 4\text{H}_2\text{O}$, $[\text{Cr}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$, and $[\text{Cr}(\text{NH}_3)_6](\text{ClO}_4)_3$ were prepared in the way outlined before.^{2,3,9} A series of reaction media of varying viscosity was obtained from glycerol/water mixtures (ranging from 0 to 65 wt % glycerol) at 5 and 15 °C. Analytical reagent grade chemicals and doubly distilled water were used in the preparation of all solutions.

Measurements. The instrumentation is similar to that described in part I of this series.² The different photoaquation reactions were followed in the manner outlined before.^{2,3} With the exception of the photoaquation of $\text{Co}(\text{CN})_6^{3-}$, all reactions were followed by measuring the concentration of the released ligand after irradiation. In the former case, the reaction was followed spectrophotometrically.⁵ The addition of glycerol to the reaction medium had no detectable influence on the concentration determination of the photochemically released ligand.^{5,9} Appropriate background titrations and extinction coefficient determinations were performed⁹ in the various reaction media for the analysis of released NH_3 and NCS^- , respectively.

Results and Discussion

The investigated Co(III) and Cr(III) complexes undergo photoaquation according to reactions 1–3 in aqueous media.^{2,3,10–17} Preliminary studies indicated that in reaction media containing up to 65 wt % (i.e., 27 mol %) glycerol, no observable ligand exchange involving glycerol occurred. This is in agreement with similar findings reported in the literature.^{5,18} It must be noted, however, that such observations are based on UV–visible spectral analyses of various irradiated reaction mixtures. The discrimination ability of such analyses is not very good since small photochemical conversions are involved, so that possible partial substitution by glycerol especially at high glycerol concentrations cannot be ruled out completely.⁶ Furthermore, at 27 mol % glycerol the effective water concentration has decreased substantially and secondary

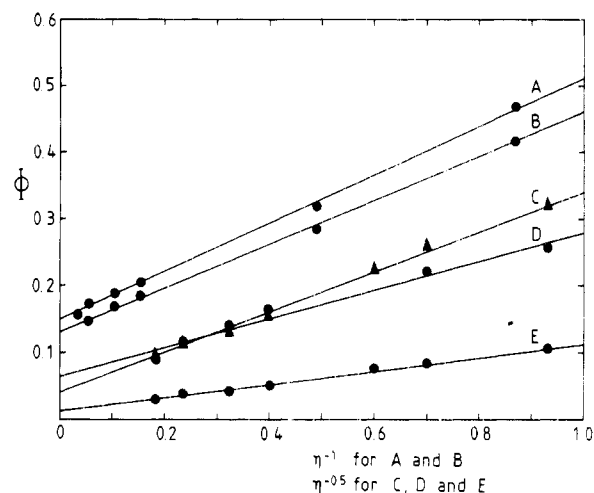


Figure 1. Plots of Φ vs. η^{-1} or $\eta^{-0.5}$ for various photoaquation reactions: A, $\text{Cr}(\text{NH}_3)_6^{3+}$; B, $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ (substitution of NH_3); C, $\text{Co}(\text{CN})_6^{3-}$; D, $\text{Cr}(\text{NCS})_6^{3-}$; E, $\text{Cr}(\text{CN})_6^{3-}$.

effects are bound to occur in reactions that involve the entrance of water molecules.

a. Viscosity Dependence at Normal Pressure. The viscosity dependence of the quantum yield for the photoaquation reactions of the different complexes is summarized in Table I. In all cases, the quantum yield (Φ) decreases significantly with increasing viscosity (η) of the reaction medium. This general trend is in agreement with findings reported^{5,6} for the viscosity dependence of the photoaquation of $\text{Co}(\text{CN})_6^{3-}$. In general, the temperature dependence of Φ is small in contrast to the significant temperature dependence of the viscosity of glycerol/water mixtures. It is, therefore, remarkable that Φ measured at two different temperatures, viz., 5 and 15 °C, correlate so well on the basis of the viscosity dependence of Φ . The overall decrease in Φ is approximately 70% over the viscosity range concerned and independent of the complex involved. This contrasts with the findings of Wong and Kirk,⁶ who reported that the viscosity dependence of Φ for the aquation of a cationic Cr(III) complex differs completely from that of anionic Co(III) and Cr(III) complexes.

The curvature and initial slope of the Φ vs. η or $1/\Phi$ vs. η plots for the data in Table I differ significantly for the various reactions studied. The quantum yield at zero viscosity, Φ_0 , was determined from plots of Φ vs. η by extrapolating graphically to $\eta \rightarrow 0$. This extrapolation was previously shown⁵ to be in good agreement with data obtained in a completely different way.⁴ The values of Φ_0 along with those obtained from literature data are summarized in Table II. The determination of Φ_0 in the case of the photosubstitution of NH_3 in $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ and $\text{Cr}(\text{NH}_3)_6^{3+}$ is complicated by the fact that Φ changes considerably in the low-viscosity range. However, one must keep in mind that Φ_0 cannot exceed unity, and the absolute values of Φ_0 in Table II should therefore be treated as crude extrapolated values. This rather unsatisfactory fit of the data does not influence our further interpretation since this is based on the relative magnitude of these values.

The viscosity dependence of Φ is generally interpreted¹⁹ as evidence for a cage effect, although the exact correlation between this effect and η remains controversial^{19–23} despite numerous studies especially in the field of organic photo-

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Table I. Viscosity Dependence of the Quantum Yield for the Photoaquation of Some Co(III) and Cr(III) Complexes^a

complex	departing ligand	irradiation wavelength, nm	[H ⁺], M	ionic strength, M	viscosity, cP	quantum yield, ^b mol/einstein
Co(CN) ₆ ³⁻	CN ⁻	316.5	0	0	1.15 ^c	0.321 ± 0.011
					2.05 ^c	0.261 ± 0.011
					2.77 ^d	0.213 ± 0.014
					6.55 ^c	0.156 ± 0.008
					9.59 ^d	0.132 ± 0.006
					18.08 ^c	0.116 ± 0.005
Cr(CN) ₆ ³⁻	CN ⁻	364.5	0	0.3	1.15 ^c	0.106 ± 0.003
					2.05 ^c	0.085 ± 0.005
					2.77 ^d	0.076 ± 0.003
					6.55 ^c	0.050 ± 0.003
					9.59 ^d	0.043 ± 0.003
					18.08 ^c	0.038 ± 0.004
Cr(NCS) ₆ ³⁻	NCS ⁻	546	0.1	0.15	1.15 ^c	0.256 ± 0.009
					2.05 ^c	0.219 ± 0.005
					6.55 ^c	0.158 ± 0.006
					9.59 ^d	0.138 ± 0.003
					18.08 ^c	0.116 ± 0.004
					29.37 ^d	0.087 ± 0.004
Cr(NH ₃) ₅ NCS ²⁺	NCS ⁻	488	0.01	0.015	1.15 ^c	(1.98 ± 0.08) × 10 ⁻²
					2.05 ^c	(1.70 ± 0.06) × 10 ⁻²
					6.55 ^c	(1.23 ± 0.06) × 10 ⁻²
					9.59 ^d	(1.07 ± 0.05) × 10 ⁻²
					18.08 ^c	(0.90 ± 0.04) × 10 ⁻²
					29.37 ^d	(0.68 ± 0.05) × 10 ⁻²
Cr(NH ₃) ₅ NCS ²⁺	NH ₃	488	0.01	0.015	1.15 ^c	0.420 ± 0.004
					2.05 ^c	0.284 ± 0.012
					6.55 ^c	0.184 ± 0.007
					9.59 ^d	0.169 ± 0.005
					18.08 ^c	0.146 ± 0.003
					29.37 ^d	0.146 ± 0.003
Cr(NH ₃) ₆ ³⁺	NH ₃	436	0.01	0.015	1.15 ^c	0.470 ± 0.010
					2.05 ^c	0.309 ± 0.011
					6.55 ^c	0.204 ± 0.011
					9.59 ^d	0.187 ± 0.007
					18.08 ^c	0.172 ± 0.006
					29.37 ^d	0.155 ± 0.006

^a Reaction volume = 3.4–3.5 cm³. ^b Mean value of five determinations. ^c Temperature = 15 °C. ^d Temperature = 5 °C.

Table II. Values of Φ_0 , $\Phi_{\text{water}}/\Phi_0$, and k_7/A for Various Photoaquation Reactions

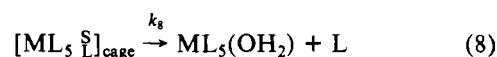
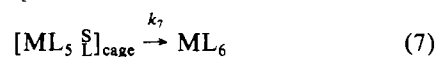
complex	departing ligand	Φ_0 , mol/einstein	$\Phi_{\text{water}}/\Phi_0^c$	k_7/A^d
Co(CN) ₆ ³⁻	CN ⁻	0.40	0.80	0.38
Cr(CN) ₆ ³⁻	CN ⁻	0.39 ^a	0.82	0.31
		0.14 ^b		
Cr(NCS) ₆ ³⁻	NCS ⁻	0.30	0.85	0.22
Cr(NH ₃) ₅ NCS ²⁺	NCS ⁻	0.023	0.86	0.22
		NH ₃	>0.60	<0.70
Cr(NH ₃) ₆ ³⁺	NH ₃	>0.68	<0.69	0.83

^a Calculated from data reported in ref 5. ^b Calculated from data reported in ref 30. ^c Φ_{water} = quantum yield for pure water, where $\eta = 1.15$ cP. ^d $k_7/A \sim k_7/k_8$ for pure water, since $\eta \sim 1$.

chemistry. For this reason various data processing procedures were investigated. Zink et al.²⁴ applied the Noyes theory,^{25,26} originally developed to treat the scavenging of photoproduct radical pairs in solution, to the charge-transfer photoreaction of tris(dibenzylthiocarbamate)iron(III) with halogenated hydrocarbons. According to this treatment Φ should depend linearly on $\eta^{-0.5}$, which was indeed found to be the case for some of the studied photoaquation reactions as illustrated in Figure 1. Cusumano and Langford²⁷ reported a linear de-

pendence of Φ on η^{-1} for the photoaquation of Cr(NH₃)₂(NCS)₄⁻ in glycerol/water mixtures. We found a similar relationship (see Figure 1) for the photoaquation of NH₃ ligands in Cr(NH₃)₆³⁺ and Cr(NH₃)₅NCS²⁺. Both procedures illustrate that the quantum yield parallels the fluidity of the medium and reaches a limiting value at high viscosity, which is in agreement with earlier findings.^{5,6,28} These trends emphasize the significant role played by cage effects even if their detailed understanding remains uncertain.^{24,27}

Notwithstanding other opinions,⁶ we at present prefer to consider the viscosity dependence of Φ for the experimental conditions concerned as a strong indication of a cage-recombination mechanism,^{5,19} which is presented in eq 4–8. In



reactions 6–8 S represents a solvent (water) molecule, which competes with L for the sixth coordination site on M within

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the solvent cage. The bonding modes of S and L will depend on the associative/dissociative nature^{2,3} of reaction 6. The observed quantum/yield for such a mechanism is

$$\Phi = \left(\frac{k_6}{k_5 + k_6} \right) \left(\frac{k_8}{k_7 + k_8} \right) = \Phi_0 \left(\frac{k_8}{k_7 + k_8} \right) \quad (9)$$

where Φ_0 is the primary quantum yield of bond cleavage and as a first approximation is assumed to be independent of η . The viscosity dependence of Φ is ascribed to the competition between reactions 7 and 8, where k_8 is expected to decrease with increasing viscosity and k_7 is expected to be essentially independent of η .^{5,24} In the case of an associative mechanism, k_6 may also show an indirect viscosity dependence, since k_6 depends on the water concentration of the solvent, which decreases with increasing glycerol content. Under such conditions Φ_0 may show some apparent viscosity dependence.

The ratio $\Phi_{\text{water}}/\Phi_0$ was estimated from the values of Φ for pure water ($\eta = 1.15$ cP) in Table I and Φ_0 in Table II. A value close to unity indicates that $\Phi_{\text{water}} \sim \Phi_0$ and that no cage effect is present in pure water. Strong deviations from unity indicate that significant cage recombination occurs in pure water.

Equation 9 can be rewritten as

$$\Phi^{-1} = \Phi_0^{-1} + (k_7\eta/A\Phi_0) \quad (10)$$

if we assume that $k_8 = A/\eta$, where A is a constant.⁵ Plots of Φ^{-1} vs. η for the data in Table I are only linear over a limited viscosity range ($\eta \leq 4$ cP). The observed deviations at higher viscosities are probably due to secondary reactions with glycerol and/or a more complex relation between k_8 and η .^{5,20-23} as mentioned before. This is illustrated in Figure 2, where plots of Φ^{-1} vs. $\eta^{0.5}$ are linear for some of the studied reactions. With use of the above estimated values of Φ_0 , k_7/A was determined from the initial slope of the Φ^{-1} vs. η plots, and its values are included in Table II. For pure water, $\eta \sim 1$ and $k_8 \sim A$, such that $k_7/A \sim k_7/k_8$.

The values of $\Phi_{\text{water}}/\Phi_0$ and k_7/A in Table II fall into three groups, which cannot be correlated on the basis of the charge on the complex ion or the nature of the central metal ion. $\Phi_{\text{water}}/\Phi_0$ and k_7/A seem to correlate well with the nature of the departing ligand, notwithstanding the fact that completely different values of Φ are observed in each case (see Table I). The only reasonable explanation for this correlation must originate in the varying degree of cage recombination, combined with specific solvation of the leaving ligand, in the different systems.

The photoaquation reactions that involve the substitution of CN^- and NCS^- do not exhibit a strong cage-recombination effect in water, since $\Phi_{\text{water}}/\Phi_0$ lies between 0.80 and 0.86. This implies that $k_7 \ll k_8$, such that $\Phi_{\text{water}} \sim \Phi_0$. In addition, the extent of bond breakage that occurs in reaction 6 largely depends on the nature of the complex species involved. Our earlier studies^{2,3} presented arguments in favor of an I_a type of aquation mechanism for $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ and an I_d type of mechanism for the anionic $\text{Co}(\text{III})$ and $\text{Cr}(\text{III})$ complexes, as concluded from the pressure dependence of the quantum yields in water. However, a significant contribution from bond breakage to the observed ΔV^\ddagger was estimated in all cases.

The values of k_7/k_8 (Table II) are constant for the photo-substitution of NCS^- in $\text{Cr}(\text{NCS})_6^{3-}$ and $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$. This is rather surprising since k_8 is expected to be considerably larger for the departure of NCS^- from $[\text{Cr}(\text{NCS})_5^{2-}\cdot\text{NCS}^-]_{\text{cage}}$ (repulsion of charges) than from $[\text{Cr}(\text{NH}_3)_5^{3+}\cdot\text{NCS}^-]_{\text{cage}}$ (attraction of charges). Consequently k_7 should be considerably larger for the recombination reaction to produce $\text{Cr}(\text{NCS})_6^{3-}$ than to produce $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$. This can only be the case when reaction 6 is dissociative in nature for $\text{Cr}(\text{NCS})_6^{3-}$ such that a vacant coordination site is available for

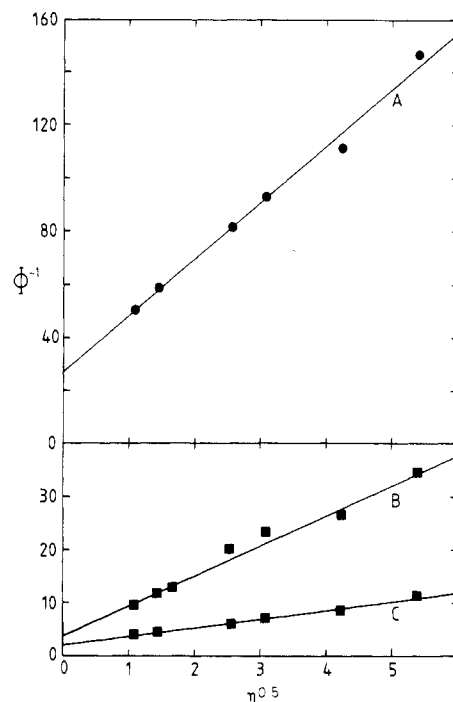
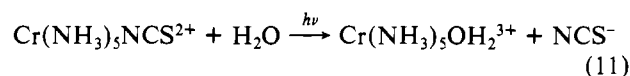


Figure 2. Plots of Φ^{-1} vs. $\eta^{0.5}$ for various photoaquation reactions: A, $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ (substitution of NCS^-); B, $\text{Cr}(\text{CN})_6^{3-}$; C, $\text{Cr}(\text{NCS})_6^{3-}$.

the reentrance of NCS^- in reaction 7. In comparison, reaction 6 should be associative in nature for $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$, such that NCS^- reacts with $\text{Cr}(\text{NH}_3)_5^{3+}\cdots\text{OH}_2$ in the cage-recombination step (7). These conclusions are in good agreement with those obtained from the activation volume measurements mentioned above.^{2,3}

Significant cage recombination is observed for the photoaquation of NH_3 in pure water, since $\Phi_{\text{water}}/\Phi_0 < 0.7$ (Table II). This implies that $k_7 \sim k_8$, as seen in the values for k_7/k_8 reported in Table II. The pressure dependence of Φ resulted² in $\Delta V_{\text{app}}^\ddagger$ values of -6.4 ± 0.3 cm^3 mol^{-1} . It was suggested² that the mechanism is of the I_a type and is basically more associative (less dissociative) in nature than that suggested for the photosubstitution of X^- in $\text{Cr}(\text{NH}_3)_5\text{X}^{2+}$ complexes. This tendency can now be ascribed to the additional pressure-accelerating effect of the cage-recombination term in eq 9, i.e., reactions 7 and 8 for such photoaquation reactions in pure water, and illustrates the associative nature of these processes.²⁷

b. Viscosity Dependence at Elevated Pressures. For the reaction



a combined viscosity-pressure-dependence study was performed, and the results are summarized in Table III. Values for Φ_0 , $\Phi_{\text{water}}/\Phi_0$, and k_7/A (i.e., k_7/k_8 in pure water) were determined in the way outlined above and are summarized in Table IV. The linear pressure dependence of $\ln \Phi_0$ results in $\Delta V^\ddagger = -9.5 \pm 0.5$ cm^3 mol^{-1} , which is indeed close to the value of -9.8 ± 0.2 cm^3 mol^{-1} reported² for this reaction in pure water, and can be interpreted as the volume of activation for reaction 6. This correlation is not surprising since the viscosity of water is essentially independent of pressure in the temperature and pressure ranges concerned. This leads to the suggestion that the above reaction at $\eta \rightarrow 0$ proceeds according to an I_a mechanism in which substantial Cr-NCS bond cleavage occurs in the transition state. In addition, the values of $\Phi_{\text{water}}/\Phi_0$ and k_7/A (i.e., k_7/k_8 in pure water) in Table IV are, within experimental error limits, independent of pressure and close to unity or small, respectively, such that $\Phi_{\text{water}} \sim$

Table III. Viscosity-Pressure Dependence of the Quantum Yield for the Reaction^a

$$\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+} + \text{H}_2\text{O} \xrightarrow{h\nu} \text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+} + \text{NCS}^-$$

viscosity, ^b cP	10 ² Φ, ^c mol/einstein			
	1 bar	500 bar	1000 bar	1500 bar
1.15 ^d	1.98 ± 0.08	2.40 ± 0.04	2.95 ± 0.07	3.68 ± 0.07
2.05 ^d	1.70 ± 0.06	2.13 ± 0.08	2.62 ± 0.05	3.25 ± 0.09
6.55 ^d	1.23 ± 0.06	1.57 ± 0.05	1.93 ± 0.04	2.12 ± 0.05
9.59 ^e	1.07 ± 0.05	1.43 ± 0.06	1.88 ± 0.06	1.81 ± 0.09
18.08 ^d	0.90 ± 0.05	1.30 ± 0.06	1.70 ± 0.06	1.48 ± 0.05
29.37 ^e	0.68 ± 0.05	1.17 ± 0.05	1.60 ± 0.06	1.35 ± 0.05

^a Irradiation wavelength = 488 nm, reaction volume = 3.5 cm³, [H⁺] = 0.01 M, ionic strength = 0.015 M. ^b Data at normal pressure. ^c Mean value of five determinations. ^d Temperature = 15 °C. ^e Temperature = 5 °C.

Table IV. Values of Φ₀, Φ_{water}/Φ₀, and k₇/A as Function of Pressure^a for the Photoaquation of Cr(NH₃)₅NCS²⁺

pressure, bar	Φ ₀ , mol/einstein	Φ _{water} /Φ ₀ ^b	k ₇ /A ^c
1	0.023	0.86	0.22
500	0.027	0.89	0.16
1000	0.034	0.87	0.16
1500	0.042	0.88	0.17

^a See Table III for experimental conditions. ^b Φ_{water} = quantum yield for pure water, where η = 1.15 cP. ^c k₇/A = k₇/k₈ for pure water, since η ~ 1.

Φ₀. These tendencies further illustrate that no significant cage recombination occurs during this reaction in pure water. k₈ is expected to be independent of pressure in pure water since η does not change significantly over the temperature and pressure ranges concerned. From the observation that k₇/k₈ is pressure independent, it follows that k₇ is also independent of pressure under these conditions.

However, significant effects are observed at higher viscosities. Plots of ln Φ vs. p at various viscosities change from linear to significantly curved with increasing viscosity. Furthermore, the initial slope of such plots increases with increasing viscosity; i.e., ΔV[‡] becomes more negative. This may point toward an additional contribution of the solvational component,² ΔV[‡]_{solv}, to the overall ΔV[‡] value under such conditions. In the extreme case, η ≥ 9.6 cP (Table III), these plots show maxima around 1000 bar, after which ln Φ decreases on further increasing the pressure. This was originally interpreted⁹ as resulting from a combination of two opposing effects. In the one, Φ increases with increasing pressure as illustrated by the values of Φ₀ (in water or at low η) in Table III. In the other, Φ decreases with increasing pressure due to the increase in viscosity (see normal-pressure data in Tables I and III) with increasing pressure. The viscosities of 21, 48, and 65 wt % glycerol/water mixtures were measured²⁹ for pressures up to 1700 bar. For the 65 wt % mixture at 15 °C, η increases from 18.58 to 25.66 cP over the pressure range 1–1500 bar. The associated decrease in Φ cannot, however, account for the maximum in the ln Φ vs. p plot. If Φ at high η is corrected for the decrease due to the increase in η with increasing pressure, the resulting ln Φ vs. p plot remains curved

with a maximum around 1000 bar. An alternative explanation must therefore be sought.

A number of possibilities can be visualized to partially account for the observed phenomenon. These are, however, rather speculative in nature due to lack of supporting evidence. The pressure dependence of the glycerol/water equilibrium in the solvent cage may constitute a possible explanation. If this equilibrium shifts under pressure in such a way that the concentration of water in the immediate vicinity of the reaction center decreases with increasing pressure, Φ will also decrease due to a decrease in k₆. On the other hand, the associative nature of reaction 6 causes k₆ to increase with increasing pressure, such that a maximum in k₆ (i.e., in Φ) is observed. In addition, cage recombination will decrease with increasing pressure for these solvent mixtures due to the pressure dependence of the viscosity.²⁹ An alternative explanation is that secondary reactions involving substitution by glycerol⁶ may play an important role under such extreme high-viscosity-high-pressure conditions. Such a reaction will proceed with a completely different ΔV[‡] and may explain the larger initial slope of the ln Φ vs. p plot, i.e., more negative ΔV[‡], observed at higher viscosities. In addition, k₈ for diffusion out of the solvent cage (reaction 8) is significantly smaller at high viscosity than in pure water (where k₈ >> k₇), such that eq 9 simplifies to

$$\Phi = \Phi_0(k_8/k_7) \quad (12)$$

According to the data in Table IV, k₈/k₇ does not vary significantly with pressure for pure water, i.e., where k₈/k₇ = A/k₇. In highly viscous medium, however, k₈ is expected to decrease with increasing pressure as discussed before. In addition, k₇ could increase with increasing pressure under conditions where glycerol substitutes a solvent molecule in the cage species. The overall effect of increasing pressure on the magnitude of k₈/k₇ could then be so large that it overrules the increase in Φ₀, and a net decrease in Φ is observed. Whatever the real explanation for the curvature and maximum in the ln Φ vs. p plot at high η may be, the observation itself is unique and motivates further investigation into this phenomenon.

In conclusion we emphasize the usefulness of measuring the viscosity dependence of the quantum yield of photosubstitution reactions. Such measurements should in general be restricted to limited viscosity ranges, to exclude possible secondary reactions with the medium,⁶ and to simplify the interpretation of such data.

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(29) Measurements performed by Professor E. Kuss, Institut für Erdölforschung, 3000 Hannover, West Germany.

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