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Mechanistic Information from Medium and High-Pressure Effects on the Photooxidation of Nitrosylpentacyanoferrate(II)

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Photooxidation of the title compound (reaction 3) was studied in CH_3CN, CH_3OH, DMF, Me_2SO, C_5H_5N, H_2O, and H_2O–glycerol as solvents. The quantum yields correlate with solvent fluidity, suggesting a cage recombination mechanism. The effect of pressure on the quantum yields was used to determine the apparent volumes of activation, which vary between +5.5 and +8.4 $cm^3\ mol^{-1}$ depending on the solvent employed. These suggest that the rate-determining step in the photooxidation mechanism is of the D type. In highly nucleophilic solvents a photosubstitution step (reaction 4) competes with the photooxidation reaction.

Introduction

Increased interest in the photochemistry of transition-metal complexes in nonaqueous media induced a revived interest in the photochemical reactions of nitrosylpentacyanoferrate(II).[2-9] A rather complex behavior was encountered in these investigations, wherein photoreduction 1, followed by rapid loss of one cyanide

$$[Fe(CN)_5NO]^{2-} \xrightarrow[S]{h\nu} [Fe(CN)_5NO]^{3-} + {}^{\bullet}S^{+} \tag{1}$$

$$[Fe(CN)_5NO]^{3-} \rightarrow [Fe(CN)_4NO]^{2-} + CN^{-} \tag{2}$$

$$[Fe(CN)_5NO]^{2-} \xrightarrow[S]{h\nu} [Fe^{III}(CN)_5S]^{2-} + NO \tag{3}$$

ligand (2), was the major route recorded in the glassy state,[3,4] whereas photooxidation of the metal center and solvation of the NO ligand (3) was recently reported to be the major mode not only in aqueous[5,10] but also in nonaqueous[6-8] liquid phases.[11] Generation of $[Fe(CN)_5S]^{2-}$ in reaction 3 was mainly followed spectrophotometrically,[6-8,10] whereas NO was detected in the gas phase by using gas chromatography, mass spectrometry, and isotopic-labeling techniques.[3,10] In the presence of oxygen, NO is transformed to nitrite and nitrate ions.[10] A minor photosubstitution path (4) was also found to occur[5] in aqueous solution.

$$[Fe(CN)_5NO]^{2-} \xrightarrow[H_2O]{h\nu} [Fe^{II}(CN)_5H_2O]^{3-} + NO^{+} \tag{4}$$

As yet, few efforts have been made to study the intimate molecular nature of the photooxidation reaction (3). Two isotope-labeling studies with $H_2{}^{18}O$ were performed but, unfortunately, led to divergent conclusions: an associative[3] compared to a more likely dissociative mechanism.[10] Recent studies of medium and pressure effects on some photoreactions of transition-metal complexes[12-25] revealed interesting mechanistic information. These methods were therefore adopted in this work to study the photooxidation reaction (3) in aqueous and nonaqueous solutions.

Experimental Section

Materials. $Na_2[Fe(CN)_5NO]$ was prepared from a commercially available dihydrate as described elsewhere.[7] Analytical reagent grade solvents and doubly distilled water were used in the preparation of all solutions.

Instrumentation and Procedure. Quantum yields for photooxidation were measured at 298 ± 0.2 K according to the method described elsewhere.[19] The reaction progress was followed by differential spectral measurements using a Perkin-Elmer 551 spectrophotometer. Spectral parameters of the photooxidation products were those published earlier.[7,26] The concentration of the $[Fe(CN)_5NO]^{2-}$ complex was varied within the range 10^{-3}–5×10^{-2} M. Radiation of 436 and 313 nm was selected from a high-pressure mercury lamp (Osram, HBO 100/2) using Oriel interference filters. The photochemical conversion was kept very small (<5%) throughout the investigation in order to suppress the inner filter effects and to minimize the influence of secondary reactions.[8,27]

High-pressure experiments were performed in a thermostated (298.0 ± 0.2 K) high-pressure cell described elsewhere[19]. Solutions were irradiated in a "pill-box" cell[28] and vigorously stirred during exposure. Quantum yield measurements were performed at five different pressures over the range 1 - 200 MPa in H_2O or CH_3OH, and over the range 1 - 100 MPa in DMSO as solvent. Partial molar volumes were determined from density measurements at 298.000 ± 0.002 K using an Anton Paar DMA 02/C digital precision densimeter. Apparent molar volumes were measured over the concentration range 5×10^{-4} to 5×10^{-3} M, and extrapolated to infinite dilution to obtain the partial molar volume.

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Table I. UV-Vis Spectral Data for the $[Fe(CN)_5NO]^{2-}$ Ion in Different Solvents

	$10^{-3}\nu_{max}$, cm^{-1}				solvent params		
solvent	ν_1	ν_2	ν_3	ν_4	AN[a]	Z,[a] kcal mol^{-1}	E_T,[a] kcal mol^{-1}
H_2O	20.0	25.4	30.5	36.9	54.8	94.6	63.1
CH_3OH	18.9	24.8	30.0	36.6	41.3	83.6	55.5
Me_2SO	18.4	24.7	30.1	35.8	19.3	71.1	45.0
CH_3CN	~18.9	~25	~30	~37	18.9	71.3	46.0
DMF	18.6	24.6	29.7	35.8	16.0	68.4	43.8
C_5H_5N	~19	~25	~29		14.2	64.0	40.2

[a] Values from ref 31 and 32.

Table II. Quantum Yields for the Formation of $[Fe(CN)_5S]^{2-}$ in Various Solvents at 298 K

	Φ, mol $einstein^{-1}$		solvent params	
solvent	λ = 436 nm	λ = 313 nm	$\eta^a \times 10$, cP	DN[b]
CH_3CN	0.44 ± 0.01	0.84 ± 0.02	3.41	14.1
CH_3OH	0.39 ± 0.01	0.63 ± 0.01	5.43	19.0
DMF	0.40 ± 0.02	0.46 ± 0.01	7.96	26.6
Me_2SO	0.33 ± 0.02	0.42 ± 0.02	19.6	29.8
H_2O^c	0.17 ± 0.01	0.37 ± 0.02	8.90	33
C_5H_5N	~0.05	~0.15	8.83	33.1

[a] Values from ref 36. [b] Values from ref 31 and 32. [c] According to ref 10, Φ_{436} = 0.18.

Results

Spectra of the $[Fe(CN)_5NO]^{2-}$ Complex in Different Solvents. The electronic spectrum of the complex is only slightly affected by the solvent[27,29,30] (Table I). The small shifts in the bands seem to correlate with the solvent polarity factors Z and E_T, as well as with the Gutmann acceptor numbers.[31,32] This would be in line with an interaction between solvent molecules and lone electron pairs on the nitrogen atoms of the CN^- ligands, something that was also observed in the case of other cyanide complexes.[33] The effect was alternatively interpreted as resulting from the interaction between a solvent molecule and the NO^+ ligand.[29] These interactions have no appreciable influence on the partial molar volume of $Na_2[Fe(CN)_5NO]$, which was found to be 122.0 ± 1.4 and 125.4 ± 1.8 cm^3 mol^{-1} in H_2O and Me_2SO, respectively.

Medium Effects. Solutions of nitrosylpentacyanoferrate(II) in CH_3CN, CH_3OH, DMF, Me_2SO, C_5H_5N, or H_2O were irradiated at 313 and 436 nm up to less than 5% conversion. In all cases the major photolysis product was the iron(III) complex $[Fe^{III}(CN)_5S]^{2-}$ (S = solvent molecule), generated according to reaction 3. Photoreduction to Fe(I) species (reactions 1 and 2) was detected, but its quantum yield was about 2 orders of magnitude lower than for the photooxidation.[8] The formation of iron(II) complexes, viz. $[Fe^{II}(CN)_5S]^{3-}$ (reaction 4), were only detected in the case of aqueous and pyridine solutions.

Quantum yields for the production of $[Fe^{III}(CN)_5S]^{2-}$ (Table II) were found to depend on the irradiation energy and the nature of the solvent. High irradiation energies lead to higher photooxidation yields. The dependence on the nature of the solvent is not so simple; among the various solvent parameters only Gutmann donor numbers and viscosity seem to play a significant role. The photooxidation quantum yield decreases with increasing donor number and viscosity of the medium. To obtain more information on the latter trend, the relationship between the photooxidation quantum yield at 313 nm and viscosity was measured for water-glycerol mixtures. The data presented in Table III indicate that the quantum yield parallels the fluidity of the medium. The plot of Φ^{-1} vs. η (Figure 1) is linear within the range for which no observable ligand-exchange involving glycerol occurred (i.e. up to 50% glycerol).

Table III. Quantum Yields for the Formation of $[Fe(CN)_5H_2O]^{2-}$ in Water-Glycerol Mixtures at 298 K

% glycerol[a]	Φ_{313}, nm	η,[b] cP	% glycerol[a]	Φ_{313}, nm	η,[b] cP
60	0.14	9.48	30	0.25	2.16
50	0.16	5.34	20	0.30	1.54
45	0.18	4.16	10	0.31	1.15
40	0.23	3.24	0	0.37	0.89

[a] In weight percent. [b] Values from ref 37.

Pressure Effects. Elevated pressures were found to have no observable influence on the overall photochemical reaction. For all the investigated systems an increase in pressure was accompanied by a significant decrease in the photooxidation quantum yield (Table IV). The plots of ln Φ vs. p were linear within the experimental error limits over the pressure range investigated. The apparent volumes of activation, $\Delta V^{\#}_{app}$, were calculated from the slopes of such plots according to the equation[16]

$$\Delta V^{\#}_{app} = -RT(\partial \ln \phi/\partial p)_T \qquad (5)$$

The values of $\Delta V^{\#}_{app}$ are all positive and range from 5.5 to 8.4 cm^3 mol^{-1}, with the highest value found for Me_2SO as solvent.

Discussion

The results of this investigation clearly indicate that in all studied solvents $[Fe(CN)_5NO]^{2-}$ undergoes mainly photooxidation according to reaction 3 upon irradiation at both 313 and 436 nm, the quantum yield for the latter wavelength being considerably lower for all the investigated solvents (Table II). The reported quantum yields are in good agreement with those found before[8,26,27] or published by other investigators.[10] The wavelength dependence of the quantum yield can be interpreted in different ways depending on the assignment of the electronic absorption spectrum of $[Fe(CN)_5NO]^{2-}$. Unfortunately, contradictory assignments have been reported in the literature based on SCCC MO[30,34] and SINDO[9] methods. Application of the SCCC MO calculations[30,34] led to the assignment that bands I (497 nm) and II (394 nm) originate from d→π*(NO) transitions, whereas bands III (330), IV (265), and V (238 nm) are due to d→d transitions, with the possibility of a σ(CN)→π*(NO) transition for band V.[34] According to this assignment irradiation at 436 nm (within band II) should favor photooxidation whereas that at 313 nm (within bands III and IV) is expected to initiate photosubstitution. The results obtained by the SINDO method[9] seem to be more reliable due to the separate calculation of all excited states and the lack of empirical parameters for fitting the electronic spectra. According to this method bands I–III originate from transitions being partly d→d and partly within the NO ligand (the latter contributing considerably only in the case of bands II and III), whereas band IV is due to $Fe(CN)_5$→NO charge transfer. All transitions were found to be accompanied by considerable weakening of the π-bond between the metal center and the NO ligand. These calculations clearly substantiate the photooxidation and solvation of the NO ligand upon irradiation at 313 nm and photosubstitution of the NO ligand induced by irradiation at 436 nm. The photooxidation proceeding with lower yield at 436 nm could be a consequence of weakening of the Fe–NO bond and of the charge shift within the NO ligand. Recently, Zink et al.[35] investigated the excited-

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Table IV. Pressure Dependence of the Quantum Yield and Apparent Volumes of Activation for the Formation of $[Fe(CN)_5S]^{2-}$ at 298 K

λ_{irr}, nm	solvent	P, MPa	Φ, mol einstein^{-1}	$\Delta V^\#_{app}$, cm^3 mol^{-1}	$\Delta V^\#(k_7)$, cm^3 mol^{-1}
436	H_2O	0.1	0.17 ± 0.01	7.7 ± 0.4	8.8 ± 0.4
		50	0.15 ± 0.01		
		100	0.13 ± 0.01		
		150	0.11 ± 0.01		
		200	0.09 ± 0.01		
	CH_3OH	0.1	0.39 ± 0.01	7.2 ± 0.5	10.3 ± 0.6
		50	0.36 ± 0.02		
		100	0.30 ± 0.01		
		150	0.26 ± 0.01		
		200	0.22 ± 0.01		
	Me_2SO	0.1	0.33 ± 0.02	7.9 ± 0.3	11.1 ± 0.4
		25	0.31 ± 0.02		
		50	0.28 ± 0.03		
		75	0.26 ± 0.03		
		100	0.24 ± 0.02		
405	Me_2SO	0.1	0.39 ± 0.02	7.5 ± 1.1	11.4 ± 1.6
		25	0.37 ± 0.03		
		50	0.36 ± 0.02		
		75	0.31 ± 0.01		
		100	0.29 ± 0.02		
313	H_2O	0.1	0.37 ± 0.02	5.5 ± 0.7	7.8 ± 1.0
		50	0.30 ± 0.01		
		100	0.28 ± 0.01		
		150	0.25 ± 0.03		
		200	0.23 ± 0.01		
	CH_3OH	0.1	0.63 ± 0.01	6.5 ± 0.8	13.0 ± 1.9
		50	0.54 ± 0.02		
		100	0.45 ± 0.02		
		150	0.39 ± 0.01		
		200	0.38 ± 0.02		
	Me_2SO	0.1	0.42 ± 0.02	8.4 ± 1.3	14.1 ± 1.0
		25	0.35 ± 0.01		
		50	0.34 ± 0.01		
		75	0.31 ± 0.01		
		100	0.29 ± 0.01		

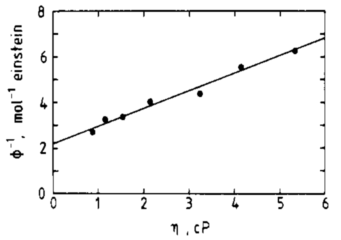

Figure 1. Plot of Φ^{-1} vs. η for the photooxidation of $[Fe(CN)_5NO]^{2-}$ in water–glycerol mixtures at 313 nm and 298 K.

state character of $[Fe(CN)_5NO]^{2-}$ by using excited-state Raman spectroscopy. They conclude that excitation at 406 nm leads to a change in the FeNO geometry from linear to bend and a concomitant large increase in the positive charge on the metal. These findings are in general agreement with the assignments referred to above.

The process leading to the generation of $[Fe^{III}(CN)_5S]^{2-}$ seems to proceed similarly at both irradiation wavelengths: the volumes of activation differ only insignificantly (Table IV) and the quantum yields exhibit a very similar dependence on the fluidity of the medium (Table II). We will therefore only consider the simplified mechanism, involving the decay of a reactive excited state, in the remainder of this report. The viscosity dependence of the data reported in Tables II and III is a strong indication of a cage recombination mechanism, which has been found to occur in a number of photoreactions of coordination compounds.[12-16,38] The decay of the LF or CT excited state may then be presented by reactions 6–9, where S = solvent molecule. In this mechanism

$$[Fe(CN)_5NO]^{2-*} \xrightarrow{k_6} [Fe(CN)_5NO]^{2-} \quad (6)$$

$$[Fe(CN)_5NO]^{2-*} \xrightarrow{k_7} [Fe^{III}(CN)_5{}^{2-}\text{---}NO]_{cage} \quad (7)$$

$$[Fe^{III}(CN)_5{}^{2-}\text{---}NO]_{cage} \xrightarrow{k_8} [Fe(CN)_5NO]^{2-} \quad (8)$$

$$[Fe^{III}(CN)_5{}^{2-}\text{---}NO]_{cage} \xrightarrow[S]{k_9} [Fe^{III}(CN)_5S]^{2-} + NO \quad (9)$$

reaction (7) is visualized as a radical pair formation step in the case of a CT excited state and as an oxidative denitrosylation step in the case of a LF excited state.

The observed photooxidation yield for such a mechanism is given by eq 10, where ϕ_0 presents the primary quantum yield for radical

$$\Phi = \left(\frac{k_7}{k_6 + k_7}\right)\left(\frac{k_9}{k_8 + k_9}\right) = \Phi_0\left(\frac{k_9}{k_8 + k_9}\right) \quad (10)$$

pair formation/bond cleavage.[13,14,18,38] Φ_0 and k_8 are expected to be independent of viscosity η, whereas k_9 is expected to decrease with increasing viscosity, i.e. $k_9 = A/\eta$ where A is a constant. Substitution and rearrangement of (10) results in (11).[13,14,38,39]

$$\Phi^{-1} = \Phi_0^{-1} + (k_8\eta/A\Phi_0) \quad (11)$$

It follows that a plot of Φ^{-1} vs. η should be linear, which is indeed the case for the data in Table III, as demonstrated by the plot in Figure 1 (slope 0.77 ± 0.05, intercept 2.2 ± 0.2). It follows from this plot that $\Phi_0 = 0.45$ mol einstein^{-1}, such that $\Phi_{H_2O}/\Phi_0 = 0.82$, from which we conclude that no significant cage effects are present in pure water. Strong deviations from unity would indicate that significant cage recombination occurs.[18] With this

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value of Φ_0 and the slope of the line in Figure 1, k_8/A was calculated to be 0.35. Since $\eta \sim 1$ for pure water, $k_8/A \sim k_8/k_9 = 0.35$, such that $k_9 > k_8$ and cage recombination plays a minor role in the overall process.

The solvent dependence data in Table II can be treated in a similar way. Plots of Φ^{-1} vs. η for CH_3CN, CH_3OH, DMF, and Me_2SO as solvents exhibit a fairly good correlation, from which $\Phi_0 = 0.45$ and 0.79 and $k_8/A = 0.19$ and 0.50 at 436- and 313-nm irradiation, respectively. These values are such that Φ_{H_2O}/Φ_0 deviates significantly from unity, and we conclude that cage effects do play a significant role in these solvents. The data for water as solvent do not fit these correlations, presumably due to other solvent effects not accounted for by viscosity only.[18] In this respect it is important to note that Φ decreases with increasing Gutmann donor number (see Table II). The observed trends do allow us to draw some qualitative conclusions. In solvents with the highest donor numbers, such as water and pyridine, interaction between a nucleophilic solvent molecule and the positively charged nitrogen atom of the NO^+ ligand should be stronger than in the other cases.[40-42] Although this interaction is not strong enough to influence the absorption spectrum of the $[Fe(CN)_5NO]^{2-}$ complex (see Table I), it could provide a correct orientation of solvent molecules for nucleophilic attack in the excited state, leading to the photosubstitution reaction (4) and generation of the solventopentacyanoferrate(II) complex. The quantum yields for its formation are rather difficult to determine, but it seems likely that this contribution from photosubstitution parallels the solvent donor number and its mechanism could be an associative one.[18] This competing effect probably accounts for the observed decrease in the quantum yield for photooxidation with increasing donor number. Formation of iron(I) products in the photochemistry of $[Fe(CN)_5NO]^{2-}$ is not included in the suggested mechanism since their yields in the liquid phase are too low to influence the present results.

We now turn to a discussion of the data measured at elevated pressure. It is well-known that the viscosity of water exhibits no meaningful pressure dependence over the range investigated,[18] such that the observed pressure dependence of Φ must originate from the dependencies of k_6–k_9. From the above analysis for the reaction in water we concluded that $k_9 > k_8$, such that $k_9/(k_8 + k_9) \sim 1$ and eq 10 simplifies to $\Phi \approx \Phi_0$. Furthermore, we have good reasons to believe that nonradiative deactivation (k_6) will exhibit a minor pressure dependence[20,22,24] with the result that the apparent volume of activation mainly presents the contribution from k_7, i.e. the formation of the caged radical pair. In the case of a CT excited-state reaction, even smaller volume changes are expected during deactivation (6) than for LF excited-state deactivation.[20,22,24] The significantly positive value of $\Delta V^{\#}_{app}$ strongly supports the dissociative nature of reaction 7. Similar arguments can be applied to the reaction in other solvents. For these the pressure dependencies of k_8 and k_9 and the solvent viscosity may contribute toward $\Delta V^{\#}_{app}$, but according to the data in Table IV these effects seem to be small and $\Delta V^{\#}_{app}$ has a fairly constant value. It follows that it is mainly reaction 7 that is responsible for the observed pressure effects. The volume of activation for reaction 7, $\Delta V^{\#}(k_7)$ in Table IV, can be obtained from a plot of $\ln(\Phi/(1 - \Phi))$ vs. pressure.[20-22] The corresponding values are larger than those of $\Delta V^{\#}_{app}$ since the quantum yields are fairly large, but the overall trends remain very similar to those described above. Some solvent dependence of $\Delta V^{\#}(k_7)$ is obvious from the data in Table IV. A part of this trend can be ascribed to the pressure dependence of the viscosity of the solvents employed.[18] The expected increase in viscosity with increasing pressure, especially for Me_2SO, will result in a decrease in Φ (see Figure 1) and a more positive volume of activation.

A comparison with related systems reveals that the presently obtained value for $\Delta V^{\#}_{app}$ of between +5.5 and +8.4 cm^3 mol^{-1} is in close agreement with that found for the CT photochemistry of *trans*-$[Pt(CN)_4(N_3)_2]^{2-}$[43] and of $[Co(en)_2(SO_2CH_2CH_2NH_2)]^{2+}$.[44] In all these cases bond cleavage involves the dissociation of a neutral species, i.e. no charge creation accompanied by major solvational effects.[20] In addition, these results are also in excellent agreement with those reported for the LF photochemistry of Rh(III) amine complexes in which NH_3 is the leaving group.[20,22]

Finally, the results of this investigation reveal the intimate character of the excited-state species and underline the dissociative reaction mode. Wolfe and Swinehart,[10] on the basis of their measurements at ambient pressure, could not rule out the possibility of an associative reaction with the solvent to produce the major photolysis product. We can now definitely rule this out on the basis of our $\Delta V^{\#}_{app}$ data.

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Registry No. DMF, 68-12-2; $[Fe(CN)_5NO]^{2-}$, 15078-28-1; $[Fe(CN)_5H_2O]^{2-}$, 19413-97-9; $[Fe(CN)_5CH_3OH]^{2-}$, 53230-77-6; $[Fe(CN)_5Me_2SO]^{2-}$, 61348-42-3; H_2O, 7732-18-5; CH_3OH, 67-56-1; Me_2SO, 67-68-5; CH_3CN, 75-05-8; C_5H_5N, 110-86-1; glycerol, 56-81-5.

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