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Notes

Solvent Cage Effects on the Ligand Field Photochemistry of the Cyanoferrate(II) Complexes

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Introduction

Studies analyzing the role of solvent cage in photosubstitution reactions are rare in inorganic chemistry literature, although attempts to relate reactivity trends to selected empirical solvent parameters for mechanism diagnosis continue to challenge photochemists. Except for a few systems discussed later, the great majority of the reported studies is concerned with charge-transfer processes.[1−8]

The pentacyanoferrate(II) complexes, $[Fe(CN)_5L]^{n-}$, have been an interesting system to exploit photosubstitution reaction mechanisms. They exhibit the photolabilization of either CN^- or L, depending on the experimental conditions. We have been investigating the photosubstitution of a cyanide ligand using bidentate diamine ligands (N⌒N), which favor a ring closure process,[9,10] yielding the corresponding chelated tetracyanoferrate(II) complex. The cyanide photolabilization is strongly wavelength dependent,[11] and the solvent plays an important role for this process.[12] Competition between one end of the N⌒N ligand and the solvent is also invoked. This seemingly unusual behavior raised the question of the role of the solvent in the ligand field photochemistry. Is the change in the quantum yield magnitude due to the stabilization of the transition state or the variation in the kinetic parameter that governs excited-state deactivation?

The reported data in the literature reveal that the photosubstitution of L for the $[Fe(CN)_5L]^{3-}$ complexes is wavelength dependent for species that present charge-transfer bands in the visible region. For these cases, efficient interconversion between LF and MLCT is observed with the magnitude of the quantum yield, dependent on whether the LF or MLCT excited state is lowest in energy.[13]

On the other hand, for those complexes that do not display metal-to-ligand charge-transfer bands, the photosubstitution of L is essentially wavelength independent over the range of 313 to 365 nm irradiation energy.[14−16] The thermally inert $[Fe(CN)_5PPh_3]^{3-}$ and $[Fe(CN)_5CO]^{3-}$ complexes are some of those mentioned in this case, for which the photoexcitation leads to a direct access of ligand field excited states which present the labilization of L as the reactive deactivation pathway, as shown in eq 1.

$$[Fe(CN)_5L]^{3-} + H_2O \xrightarrow{h\nu} [Fe(CN)_5H_2O]^{3-} + L \qquad (1)$$

Here, our previous work is extended to analyze solvent effects in the photoreactivity of $[Fe(CN)_5PPh_3]^{3-}$ and $[Fe(CN)_5CO]^{3-}$ in an attempt to develop models to explain their behavior.

Experimental Section

Materials. The $Na_3[Fe(CN)_5CO]\cdot 3H_2O$ complex was synthesized and characterized according to the procedure previously described.[17] The $Na_3[Fe(CN)_5PPh_3]\cdot 3H_2O$ complex was prepared according to Nast and Kruger.[18] Reagent grade water and/or aqueous mixtures of glycerol 99.9% (Merck) were used.

The potassium tris(oxalate)ferrate(III) salt was prepared and purified with slight modifications of the literature procedure.[19] Iron(III) chloride (15 g, 0.060 mol) was added in the dark to an aqueous solution containing potassium oxalate (32 g, 0.20 mol) (Merck) at 40 °C under stirring for 30 min. After cooling, the green crystals were collected and washed with cold water. The crude product was recrystallized three times from water at 65 °C (10 g per 15 mL of water) and stored under vacuum.

N-Methylpyrazinium iodide was synthesized and purified according to the procedure adapted from that described by Bahner and Norton.[20] To the solution of pyrazine (5.0 g, 62 mmol) (Aldrich) in 12 mL of benzene (Merck), previously distilled methyl iodide (8.0 g, 56 mmol) (Merck) was added dropwise. The resulting mixture was kept in the dark for 48 h at room temperature. The hygroscopic yellow Mpz^+I^- crystals were collected and washed with chloroform (Merck). The crude product was recrystallized from ethanol at 45 °C (1.3 g per 100 mL of ethanol) and stored under vacuum. Yield 5.6 g (41%). Anal. Calcd For $C_5N_2H_7I$: C, 27.03; N, 12.61; H, 3.15. Found: C, 27.10; N, 12.72; H, 3.36.

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Table 1. Quantum Yields for the L Photolabilization of the $[Fe(CN)_5L]^{3-}$ Complexes at the 313 and 334 nm Excitations at Various Glycerol Contents

glycerol (wt %)	η/Cp[a]	ϵ[a]	$[Fe(CN)_5CO]^{3-}$		$[Fe(CN)_5PPh_3]^{3-}$	
			313 nm	334 nm	313 nm	334 nm
0.00	0.89	78.54	0.44 ± 0.01	0.42 ± 0.01	0.14 ± 0.01	0.14 ± 0.01
10.75	1.18	75.80	0.39 ± 0.01	0.35 ± 0.01	0.13 ± 0.01	0.12 ± 0.01
19.30	1.51	74.05	0.34 ± 0.01	0.33 ± 0.01	0.11 ± 0.01	0.11 ± 0.01
38.25	2.97	69.32	0.26 ± 0.01	0.26 ± 0.01	0.097 ± 0.002	0.095 ± 0.002
57.34	7.45	63.37	0.18 ± 0.01	0.16 ± 0.01	0.049 ± 0.002	0.048 ± 0.002
61.85	9.90	61.75	0.12 ± 0.01	0.14 ± 0.01	0.035 ± 0.002	0.032 ± 0.002
79.52	43.40	54.34	0.067 ± 0.003	0.062 ± 0.003	0.010 ± 0.001	0.010 ± 0.001

[a] Reference 41. $[[Fe(CN)_5L]^{3-}] \sim 3.0$ mM; $T = (25.0 \pm 0.2)$ °C.

Physical Measurements and Procedures. Continuous photolyses were performed using an Oriel 200 W Hg(Xe) arc lamp model 6291. Excitation wavelength was selected by using an adequate Oriel interference filter to isolate the selected irradiation energy. The photolysis system and the analytical procedure were described in detail elsewhere.[10] Freshly prepared solutions of the complexes were irradiated to less than 3% conversion to avoid secondary photoreactions. The Mpz^+ ion, employed in analyses, was kept around 10-fold excess to the maximum amount of the photolyzed $[Fe(CN)_5L]^{3-}$.

The light intensity at each wavelength was determined by tris(oxalate)ferrate(III) actinometry carried out before and after each photolysis run. The actinometries for water−glycerol systems had the same light intensity values as those for aqueous solution. All absorption spectra were recorded on a Beckman DU 70 or HP 8453 spectrophotometers at 25.0 °C.

Results

Electronic Spectra. The $[Fe(CN)_5CO]^{3-}$ complex exhibits a low-intensity absorption band ($\lambda_0 = 304$ nm, $\epsilon_0 = 3.7 \times 10^2$ M^{-1} cm^{-1}) which is assigned to the ligand field transition $^1A_1 \rightarrow {}^1E(1)$ under C_{4v} symmetry.[17] For the $[Fe(CN)_5PPh_3]^{3-}$ complex this band appears around 365 nm ($\epsilon_0 = 4 \times 10^2$ M^{-1} cm^{-1}).[15] The low lying LF band is well separated from the charge-transfer $d\pi \rightarrow \pi*$ (CN) band, whose maximum absorption is around 250 nm, allowing a selective access to the d−d excited states upon excitation. The presence of glycerol in the employed concentration range does not have any detectable influence either on the maximum wavelength or on the extinction coefficient of the absorption spectra, which are indistinguishable regardless of the solvent composition.

Solvent Effect. The quantum yield determinations for the photosubstitution of CO or PPh_3 were carried out by adding the *N*-methylpyrazinium ion in order to trap efficiently the photoproduct, $[Fe(CN)_5H_2O]^{3-}$, via the fast thermal reaction 2, yielding a highly detectable species.[10,15]

$$[Fe(CN)_5H_2O]^{3-} + Mpz^+ \rightarrow [Fe(CN)_5Mpz]^{2-} + H_2O \quad (2)$$

Quantum yield determinations for CO photolabilization in aqueous solutions were found to be wavelength independent for the 313, 334, or 365 nm irradiation. For $[Fe(CN)_5PPh_3]^{3-}$, the same behavior was observed for the 313, 334, 365, or 404 nm irradiation. Quantum yields for the CO or PPh_3 release at the 313 or 334 nm excitation wavelengths and glycerol contents in the mixed solvent are shown in Table 1. These values resulted from several quantum yield determinations made for each set of conditions, and at least six values with comparable data were collected, within experimental error, in independent photolysis runs.

The quantum yields in Table 1 present a strong dependence on the solvent viscosity, exhibiting a continuous decrease as the solvent viscosity is increased.

Discussion

The continuous photolysis of aqueous or mixed aqueous solutions of $[Fe(CN)_5CO]^{3-}$ or $[Fe(CN)_5PPh_3]^{3-}$ yields the aquapentacyanoferrate(II) ion as the only observed photoproduct. The results of this investigation show a relation between the glycerol content and the quantum yield magnitude. The role of solvent viscosity is very clear; its decrease favors a more efficient escape of the L ligand from the solvent cage.

According to the literature,[21] the back reaction for $[Fe(CN)_5CO]^{3-}$ was not expected to be as important as for $[Fe(CN)_6]^{4-}$ due to the more efficient escape of CO from the solvent cage when compared to that of the CN^- one. By working only in aqueous solutions, the previous investigation was not able to detect the importance of geminate recombination. In addition, the analytical method employed here allows a very efficient detection with low net conversion of the starting material, in contrast to the high conversion required for measurement of $[Fe(CN)_5H_2O]^{3-}$. The present data show that the recombination occurs in a high level, ruling out the hypothesis that the CO ligand diffuses with high efficiency due to its low solubility in water.[21]

Correlations of quantum yields with viscosity of bulk solutions have been mainly considered for evaluating the role of the solvent. Most of these studies have been performed in water−glycerol or water−ethylene glycol solutions,[22−26] for which the properties of cosolvents are similar, exhibiting a strong tendency to form intermolecular hydrogen bonds.[27] Therefore, in this case, it is not likely that the solvent structure changes significantly in the mixture due to the weak hydrophobicity of the cosolvent.[27]

It is interesting to note here that viscosity has not been the only solvent parameter which influences the quantum yields, but it should be the most significant factor.[12] A higher dielectric constant in a lower viscosity solution may stabilize the charge separated species yielding an efficient photoconversion into the products. Nakamaru et al.[28] employed a wide variety of solvents to measure the cyanide photosubstitution in $[Co(CN)_6]^{3-}$. It was found out that the variation in quantum yields for different solvents is modest when compared with the large difference in dielectric constant. Our previous work,[12] analyzing the CN^-

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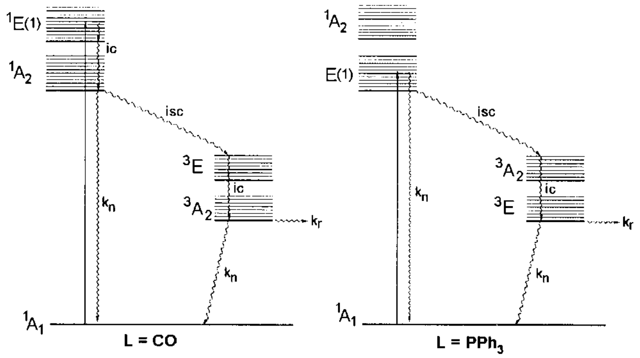

Figure 1. Simplified energy diagram and the excited-state decay pathways for the $[Fe(CN)_5CO]^{3-}$ and $[Fe(CN)_5PPh_3]^{3-}$ complexes. k_n, nonradiative decay; k_r, chemical reaction; ic, internal conversion; isc, intersystem crossing.

photosubstitution in $[Fe(CN)_5(tn)]^{3-}$ using various water−acetonitrile mixtures, in comparison with the water-glycerol one, came to the similar conclusion. Also, for other systems reported, the quantum yield variation was dominated by the change in viscosity, despite the significant change in dielectric constant.[12,22,29]

Yet the solvent can also play an important role on the deactivation process,[24] the major source of the quantum yield dependence on its composition can be ascribed to the cage recombination, as for $[Co(CN)_6]^{3-}$.[23]

For a given solvent composition, the quantum yield magnitude for $[Fe(CN)_5CO]^{3-}$ and $[Fe(CN)_5PPh_3]^{3-}$ reported in Table 1 has previously been related to the nature of the lowest excited state, which depends on the tetragonal distortion parameter.[30] For $[Fe(CN)_5PPh_3]^{3-}$, in which the ligand field strength of L is weaker than that of the cyanide ion, the photoreactive state is the ^3E one as in the schematic energy levels represented in Figure 1. For the carbonylpentacyanoferrate(II) complex, the lowest excited state is the $^3A_2$, since CO has a ligand field strength stronger than that of CN^-. As a consequence, the energy of the d−d band for these species differs significantly. Calculations also show that a high reactivity is expected for $[Fe(CN)_5CO]^{3-}$ upon decreasing the electron density in the iron center.[31,32]

A parallel of our results with mechanisms of cage recombination of Fe−CO investigated in iron(II) porphyrin complexes is not straightforward. In contrast to the system discussed here, the reactions in porphyrin complexes require the conversion of high-spin iron(II) to the diamagnetic state.[33−35]

For the $[Co(CN)_6]^{3-}$ ion, a wavelength-independent quantum yield for the photoaquation is reported.[36] On the other hand, wavelength-dependent quantum yields were measured for a cyanide release in $[Co(CN)_5OH]^{3-}$ and $[Co(CN)_5OH_2]^{2-}$, leading to *trans*-diaquatetracyanocobaltate(III).[37] Quantitative determinations can be affected by the presence of the released cyanide, which quickly reverts the photoproduct to the monoaqua species.[38] When compared to aqua and hydroxopentacyanocobaltate(III), a much higher quantum yield is reported for $[Fe(CN)_5N^{\frown}N]^{3-}$. In the latter system the cyanide recombination is precluded by formation of the inert tetracyanoferrate(II) species due to the neighboring effect. For instance, at the 313 nm irradiation, the cyanide photosubstitution is respectively 0.060 and 0.24 for $[Co(CN)_5OH]^{3-}$ and $[Fe(CN)_5(en)]^{3-}$.[11,37]

Another interesting feature is related to the fact that the cyanide release for $[Fe(CN)_5N^{\frown}N]^{3-}$ shows remarkable wavelength dependence,[11] while the photosubstitution of L does not. The results reported here show that the solvent dependence is essentially wavelength independent. Usually, the competitive decay pathways would be expected to possess very different solvent dependencies, leading to a complex dependence pattern with many solvent parameters. A strong correlation with one single parameter represents an unusual occurrence and indicates that one single decay pathway is likely to dominate. Moreover, this interpretation is reinforced by the wavelength independent L photolabilization.

For most of the systems presented in the literature, the excited-state responsible for the photoreactivity and the decay processes have been analyzed through direct measurements of the intermediates in a fast time domain.[33−35,39] However, the use of a proper analytical method for efficient detection of the photoproduct used in our studies permitted to obtain dependable information that usually is only available by employing fast techniques.

Despite its simplicity, the solvent cage mechanism can explain the photochemical behavior presented by pentacyanoferrate(II). These complexes present substantial photosubstitution quantum yields, even higher when compared to isostructural and isoelectronic Co(III) complexes. For both Fe(II)[9−11,40] and Co(III)[23−26] systems, evidences were found in order to postulate a dissociative process involving a solvent-caged species. Our study underlines the importance of solute−solvent interactions in mediating or tuning the excited-state dynamics of the $[Fe(CN)_5L]^{3-}$ complexes. It represents a significant contribution to the field by tracing some general lines observed in the photochemistry of $3d^6$ metal complexes.

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Supporting Information Available: Figures showing electronic spectra of $[Fe(CN)_5CO]^{3-}$ and $[Fe(CN)_5PPh_3]^{3-}$, plots of quantum yield variation versus viscosity or the dielectric constant (and its reciprocal) of the water−glycerol mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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