Direct Determinations of the Ion Pairing Equilibrium Constant and First-Order Rate Constant for Outer Sphere Electron Transfer Reactions

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Abstract: The kinetics of the outer sphere electron transfer reactions between the ions $Fe(CN)_5L^{3-}$ and $Co(NH_3)_5L'^{3+}$ (where L and L' are conjugated and unconjugated derivatives of 4,4'-bipyridine and 4-phenylpyridine, respectively) have been investigated. The observed pseudo-first-order rate constants (at pH 7.0, ionic strength 0.0769, temperature 25.0 °C, and in the presence of 6.0×10^{-4} M EDTA) were plotted as a function of the cobalt concentration, and, in two out of four cases, these plots were found to deviate from linearity, as expected from the full form of the rate law for outer sphere electron transfer reactions. Nonlinear least-squares fitting of the rate constant vs. cobalt concentration data to the equation $k_{obsd} = k_{et}K_{os}[Co]/1 + K_{os}[Co]$ allowed a direct determination of the ion pairing equilibrium constant, K_{os}, and of the first-order rate constant, k_{et}, for unimolecular electron transfer within the ion pair. The values are as follows: L = 4,4'-bipyridine and L' = 4-phenylpyridine, $K_{os} = 1047 \pm 20$ M^{-1}, $k_{et} = 3.12 \pm 0.03 \times 10^{-3}$ s^{-1}; L = 1,2-bis(4-pyridyl)ethane and L' = 4-phenylpyridine, $K_{os} = 761 \pm 13$ M^{-1}, $k_{et} = 8.99 \pm 0.02 \times 10^{-3}$ s^{-1}. The average of the above two values for K_{os} was used to calculate that $k_{et} = 11.5 \times 10^{-3}$ s^{-1} when L = 4,4'-bipyridine and L' = 4-benzoylpyridine while $k_{et} = 27.5 \times 10^{-3}$ s^{-1} when L = 1,2-bis(4-pyridyl)ethane and L' = 4-benzoylpyridine. Direct, experimental determinations of the equilibrium constants, K_{os}, have allowed a calculation of the distance of closest approach of the two reactant ions within the ion-pair intermediate. Variations in the values for both K_{os} and k_{et}, as the nature of the ligands L and L' are changed, are discussed.

Introduction

The generally accepted mechanism for outer sphere electron transfer reactions between two transition-metal complexes[1] is shown in the equations

$$\mathrm{Ox} + \mathrm{Red} \rightleftharpoons \mathrm{Ox;Red} \qquad K_{os} \tag{1}$$

$$\mathrm{Ox;Red} \rightarrow \mathrm{Ox}^- + \mathrm{Red}^+ \qquad k_{et} \tag{2}$$

This mechanism, involving a preequilibrium ion pairing (eq 1) characterized by equilibrium constant K_{os} and an electron-transfer step (eq 2) characterized by the first-order rate constant k_{et}, has been substantiated by numerous studies[2] since its proposal[3] in 1953. There have been only some cases,[4] however, where it proved possible to resolve experimentally the ion pairing equilibrium constant K_{os} from the first-order rate constant for electron transfer, k_{et}. While theoretical estimates[5] of the value of K_{os} have been useful in evaluations of k_{et},[6] it clearly would be more desirable if a series of reactions could be studied where direct, experimental determinations of both K_{os} and k_{et} were possible.

The difficulty in measuring K_{os} and k_{et} separately arises because of the form of the rate law for the outer sphere electron transfer mechanism. The rate law for eq 1 and 2 is shown in eq 3. For experiments performed with the oxidant concentration in pseudo-first-order excess, one measures a pseudo-first-order rate constant, k_{obsd}, which depends on the oxidant concentration according to eq 4. While the dependence of the

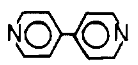
$$\text{rate} = \frac{k_{et}K_{os}[\mathrm{Ox}][\mathrm{Red}]}{1 + K_{os}[\mathrm{Ox}]} \tag{3}$$

$$k_{obsd} = \frac{k_{et}K_{os}[\mathrm{Ox}]}{1 + K_{os}[\mathrm{Ox}]} \tag{4}$$

rate constant k_{obsd} on the oxidant concentration should be less than linear, the limiting form of eq 4 (at low oxidant concentrations) is a straight line with a slope equal to the product $K_{os}k_{et}$. Most reports of outer sphere electron transfer reactions have involved the limiting form of eq 4, and only in the cases previously mentioned[4] has the full form of eq 4 been verified by experimental observation of curvature in the plot of pseudo-first-order rate constant k_{obsd} as a function of a reactant concentration. All other studies have been constrained to the region where the pseudo-first-order rate constant is equal to the unresolvable product $K_{os}k_{et}$.

We have begun work on a series of outer-sphere reductions by the ions $Fe(CN)_5L^{3-}$ of the ions $Co(NH_3)_5L'^{3+}$, where

L =



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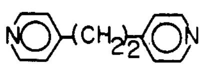
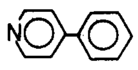


and

L' =



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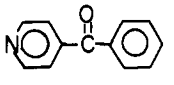

The system was chosen because of the high charge type of the reactants and because of the expected slowness of the electron-transfer step, k_{et}, both of which should enhance the effective concentration of the ion-pair intermediate, and allow the best chance for observation of the full form of the rate law as in eq 4. The ligands L were chosen to be conjugated or unconjugated derivatives of 4,4'-bipyridine (L) or of 4-phenylpyridine (L') in order to test the suggestions[4,7] that these types of ligands can become involved in the orbital path of the electron during an outer sphere redox process. In two out of four systems, we have been able to resolve the equilibrium constant K_{os} and the first-order rate constant k_{et}. The direct determination of the ion pairing equilibrium constant has allowed a calculation[5] of the distance of closest approach of the metal complexes in the ion pair. This, together with a comparison of first-order rate constants for electron transfer, has allowed us to conclude that the orientation of the metal complexes within the ion pair involves approach of the ammonia side of the cobalt complex to the cyano side of the iron complex in each ion pair. We conclude that the orbital pathway for redox does not involve the π system of the ligands L, but direct overlap of primarily d orbitals on the two metal centers.

Experimental Section

Materials. House distilled water was purified by passing it through a Continental Deionized Water ion exchanger. Pyridine and dimethyl sulfoxide (Fischer) were distilled under vacuum and stored under nitrogen atmosphere until used. $LiClO_4$ (G. F. Smith) was multiply

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Table I. Pseudo-First-Order Rate Constants[a] for the Reduction of $Co(NH_3)_5L'^{3+}$ by $Fe(CN)_5L^{3-}$

L′	L	$[Co(NH_3)_5$-$L'^{3+}]$, M × 10^4	k_{obsd},[a] s^{-1} × 10^4
4-phenylpyridine	4,4′-bipyridine	0.351	4.88 ± 0.90
		3.53	10.52 ± 0.23
		6.34	15.28 ± 0.13
		10.56	20.29 ± 0.84
		13.26	21.71 ± 0.74
		17.93	22.77 ± 0.95
4-phenylpyridine	1,2-bis(4-pyridyl)-ethane	0.365	4.43 ± 1.04
		3.65	19.82 ± 0.15
		6.01	29.72 ± 1.48
		10.56	42.32 ± 0.82
		17.50	52.54 ± 1.26
4-benzoylpyridine	4,4′-bipyridine	0.424	5.97 ± 0.36
		1.27	12.49 ± 0.60
		2.12	23.40 ± 0.80
4-benzoylpyridine	1,2-bis(4-pyridyl)-ethane	0.348	9.00 ± 0.03
		0.580	17.24 ± 0.60
		1.74	44.46 ± 1.20

[a] Observed pseudo-first-order rate constants at ca. $[Fe]_0 = 10^{-5}$ or 10^{-6} M, temperature = 25.0 °C, total ionic strength = 0.0769 M, pH 7.0, $[L] = 10^{-3}$ or 10^{-4} M, and $[EDTA] = 6.0 \times 10^{-4}$ M.

recrystallized from water, as were Na_2H_2EDTA (MCB), and 4,4′-bipyridine (Aldrich). 4-Phenylpyridine (Aldrich) was sublimed under vacuum. $Na_3[Fe(CN)_5NH_3]\cdot 2H_2O$ was prepared by the method of Brauer[8] and multiply recrystallized from ethanol-water. All other materials were reagent grade and were used without further purification.

Stock solutions of Na_2H_2EDTA and phosphate buffer were prepared gravimetrically. The stock solution of $LiClO_4$ was standardized by passing an aliquot through a cation exchange resin and titrating the eluted hydrogen ion with standardized base.

Preparation of Compounds. The cobalt complexes $Co(NH_3)_5NC_5H_4\text{-}C_6H_5^{3+}$ and $Co(NH_3)_5NC_5H_4\text{-}CO\text{-}C_6H_5^{3+}$ were both prepared as dithionate salts by reaction of the appropriate pyridine derivative with $[Co(NH_3)_5Me_2SO](ClO_4)_3\cdot 2H_2O$[9] in anhydrous dimethyl sulfoxide, under a nitrogen atmosphere. A typical synthesis was as follows. $[Co(NH_3)_5Me_2SO](ClO_4)_3\cdot 2H_2O$, 1.0 g ($1.7 \times 10^{-3}$ mol), was dissolved in 2.5 mL of anhydrous dimethyl sulfoxide. The resulting purple solution was stored over 4 Å molecular sieves and under an atmosphere of dry nitrogen gas for 24 h. A solution of 4-phenylpyridine, 0.5 g (3.2×10^{-3} mol), in 2.5 mL of dimethyl sulfoxide was similarly prepared and dried. The two dimethyl sulfoxide solutions were mixed using syringe techniques and the reaction solution was stirred in the dark at 50 °C for 4 h. This resulted in a gradual change in color from purple to orange. Longer reaction times are recommended for other ligands. The reaction was quenched with 200 mL of 0.1 M HCl and the aqueous solution (now orange and acidic) was eluted onto a column of cation exchange resin, Dowex 50W-X2. The column was washed with water, 0.1 M HCl, 1.0 M HCl, 2.0 M HCl, and 4.0 M HCl, the desired compound being eluted from the column by the latter. The 4.0 M HCl washings were reduced to dryness by rotoevaporation to give orange crystals of the chloride salt of the desired compound. These crystals were dissolved in a minimum of hot water, and a saturated aqueous solution of $Na_2S_2O_6$ was added dropwise until slightly less than a stoichiometric amount had been added. The resulting crystals were recrystallized five times from warm water by cooling, and the product was washed with water, ethanol, and ether and air dried, yield 1.8 g (90%). The infrared spectrum confirmed the presence of water of crystallization. Anal.[10] Calcd for $[Co(NH_3)_5NC_5H_4C_6H_5]_2(S_2O_6)_3\cdot 4H_2O$: C, 22.95; H, 4.96; N, 14.60; Co, 10.24. Found: C, 23.01; H, 5.10; N, 14.50; Co, 10.23. Calcd for $[Co(NH_3)_5NC_5H_4COC_6H_5]_2(S_2O_6)_3\cdot 2H_2O$: C, 24.61; H, 4.48; N, 14.36; Co, 10.06. Found: C, 24.23; H, 4.86; N, 13.98; Co, 10.20.

The iron compounds were prepared in situ for kinetic studies by aquation[12] of the compound $Na_3[Fe(CN)_5NH_3]\cdot 2H_2O$ at pH 7.0, in the presence of a 100-fold excess of the desired ligand. Appropriate aliquots of this solution, protected from light, were then diluted to make the stock solutions on which the kinetics experiments were performed.

Kinetic Experiments. All kinetic experiments were performed at pH 7.0 (phosphate buffer), ionic strength 0.0769 M (adjusted with $LiClO_4$), and in the presence of 6.0×10^{-4} M disodium ethylenediaminetetraacetate.[13] The temperature in each case was maintained by a Lauda-Brinkman Model K-2R constant temperature bath at 25.0 ± 0.1 °C, as measured by a calibrated thermistor at the reaction site. The solutions, mixing bottle, and reaction cell were all prethermostated at 25.0 °C prior to mixing. The experiments were performed under pseudo-first-order conditions, with the cobalt compound in excess. The absorbance of the reaction solution was monitored at the wavelength of maximum absorbance of the iron compound (369 or 432 nm) using a Cary Model 14 spectrophotometer. Plots of ln $(A_t - A_\infty)$ vs. time were linear for 4-5 half-lives, and pseudo-first-order rate constants were evaluated by linear least-squares analysis of ln $(A_t - A_\infty)$ vs. time. The stoichiometries of the reactions were determined by reduction of the iron(III) product with ascorbic acid[14] and comparing the absorbance changes to those expected based on the known molar absorptivities of the compounds. The starting concentrations of the iron compounds were checked by aquation of the ammonia derivative in the presence of pyridine and measuring the absorbance of the complex $Fe(CN)_5py^{3-}$, whose molar absorptivity is also known.[12] All determinations of a pseudo-first-order rate constant at a particular cobalt concentration were performed in triplicate, and the rate constants reported represent averages, the error limits indicated being average deviations from the mean.

Results

The stoichiometry of the reactions is given in the equation

$$Fe(CN)_5L^{3-} + Co(NH_3)_5L'^{3+} + HEDTA^{3-} + 4H^+ \rightarrow Fe(CN)_5L^{2-} + Co(EDTA)^{2-} + 5NH_4^+ + L' \quad (5)$$

where the ligand at iron, L, is 4,4′-bipyridine or its unconjugated derivative 1,2-bis(4-pyridyl)ethane, and the ligand at cobalt, L′, is 4-phenylpyridine or its unconjugated derivative 4-benzoylpyridine. Four sets of kinetics experiments were performed, reacting the two iron derivatives with each of the two cobalt derivatives. All of the experiments were performed under identical conditions of temperature, ionic strength, pH, and EDTA concentration. Only the concentration of the cobalt complex was changed, being careful to maintain pseudo-first-order excess concentrations at all times. The results of these experiments are presented in Table I. These data are plotted in Figure 1 as the observed pseudo-first-order rate constant as a function of cobalt concentration. The two slower reactions of Figure 1 gave slight nonzero intercepts owing to a slow oxidation of the iron solutions by molecular oxygen, as no precautions were taken to establish rigorously anaerobic conditions during the kinetic experiments. The rate constants listed in Table I were found to be independent of added dithionate ion in the range 2.0×10^{-4} to 1.6×10^{-3} M added dithionate.

For two of the plots, where the ligand at cobalt, L′, is 4-benzoylpyridine, the limited solubility of the cobalt compound prevented the use of high concentrations of the cobalt compound. For the case where the ligand at cobalt, L′, is 4-phenylpyridine, however, experiments were possible at increasingly high cobalt concentrations, and the corresponding curves in Figure 1 show the saturation effect expected by the full form of eq 4. The data of these latter plots were fit, by a nonlinear least-squares analysis, to eq 4. This allowed the separate determination of both K_{os} and k_{et}, and these values are listed in Table II. The curved lines in Figure 1 represent the computer-generated values obtained from this nonlinear least-squares analysis, and the fit of the data is seen to be excellent. For the two plots of Figure 1 that did not show deviations from linearity, the slopes of the two plots were taken to be the unresolved product $K_{os}k_{et}$, and these are also listed in Table II.

Table II. Calculated Values of K_{os} and k_{et} for the Reaction $Fe(CN)_5L^{3-} + Co(NH_3)_5L'^{3+}$

L′	L	$K_{os}k_{et}$, $M^{-1}\,s^{-1}$	K_{os}, M^{-1}	$k_{et} \times 10^3$, s^{-1}
4-phenylpyridine	4,4′-bipyridine	3.27 ± 0.04[a]	1047 ± 20[a]	3.12 ± 0.03[a]
4-phenylpyridine	1,2-bis(4-pyridyl)ethane	6.84 ± 0.04[a]	761 ± 13[a]	8.99 ± 0.02[a]
4-benzoylpyridine	4,4′-bipyridine	10.38 ± 0.03[b]	904[c]	11.5
4-benzoylpyridine	1,2-bis(4-pyridyl)ethane	24.83 ± 0.06[b]	904[c]	27.5

[a] Calculated by nonlinear least-squares analysis, as described in the Results. [b] Calculated by linear least-squares analysis, as described in the Results. [c] Assumed to be the average of the first two values, as described in the Results.

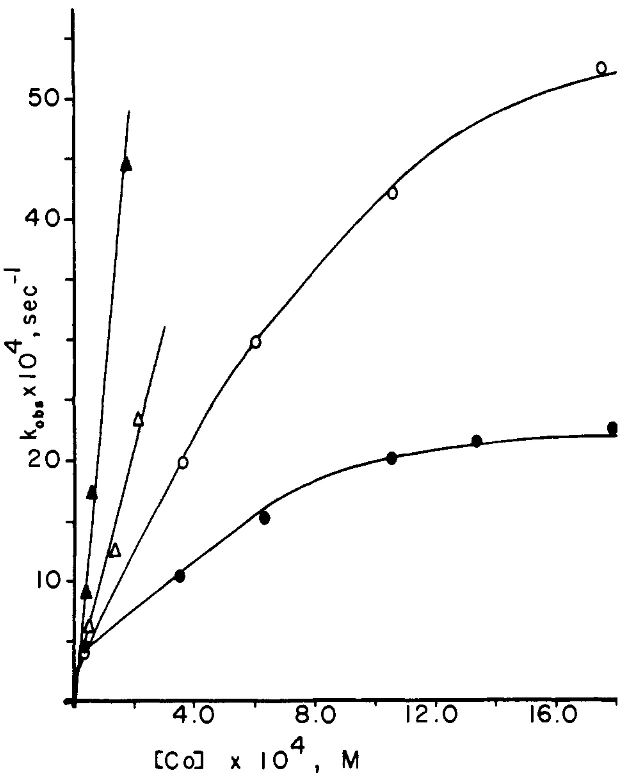

Figure 1. Observed pseudo-first-order rate constant as a function of the cobalt concentration for the reaction $Fe(CN)_5L^{3-} + Co(NH_3)_5L'^{3+}$ where L = 4,4′-bipyridine and L′ = 4-phenylpyridine, ●; L = 1,2-bis(4-pyridyl)ethane and L′ = 4-phenylpyridine, ○; L = 4,4′-bipyridine and L′ = 4-benzoylpyridine, △; L = 1,2-bis(4-pyridyl)ethane and L′ = 4-benzoylpyridine, ▲.

Here the straight lines on Figure 1 represent computer-generated values from linear least-squares treatment of the data.

Although the product $K_{os}k_{et}$ is not directly resolvable for two of the four studies, it is reasonable to assume that the value of K_{os} will not be much different if one compares values for systems where only the ligand at cobalt is changed. Consequently, the average of the values 1047 and 761 M^{-1} was used as the estimate of K_{os} in determining the last two values of k_{et} reported in Table II, where the ligand at cobalt is 4-benzoylpyridine and the ligands at iron are 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethane.

Discussion

The ligands L and L′ were chosen to test the suggestions that have been made[4,7] for a number of different systems that π-conjugated ligands at a metal center can provide an orbital pathway for the reducing electron in outer sphere electron transfer reactions. If a ligand such as 4,4′-bipyridine or 4-phenylpyridine were to provide such a pathway for redox, interruption of the π conjugation of the ligand should reduce the value of k_{et}. This has been observed in the studies[7a] of the redox quenching of the luminescence excited state of $Ru(bpy)_3{}^{2+}$, where substantial evidence for a ligand bound radical intermediate lent validity to the arguments.

The data reported in Table II, however, indicate the opposite trend. The first-order electron transfer rate constant, k_{et}, is highest where both the ligands at iron and at cobalt are unconjugated, the lowest where the ligands are conjugated. We take this to indicate that the redox process within the outer-sphere ion pair does not involve the chemical mechanism of prior reduction of the ligands L and L′, but an electron transfer involving direct overlap of primarily d orbitals of the two metal centers. The trends in the values of k_{et} are then explained as follows.

For a given ligand at cobalt, the value of k_{et} is highest when the ligand at iron, L, is the unconjugated 1,2-bis(4-pyridyl)ethane and lowest when the ligand at iron, L, is 4,4′-bipyridine. The latter ligand is more extensively involved in metal-to-ligand π back-bonding,[12] and the oxidation potential of the iron complex is consequently more negative. This produces a corresponding decrease in the value of k_{et}, as the complex is more difficult to oxidize.

For a given ligand at iron, the value of k_{et} is highest when the ligand at cobalt is the unconjugated 4-benzoylpyridine and lowest when the ligand at cobalt is 4-phenylpyridine. This can be explained by (in addition to the expected differences in reduction potentials of the two cobalt complexes) the orbital symmetry requirements in the orbital overlap along the path of the reducing electron. The electron originates in an orbital on iron of π symmetry (one of the d_{xy}, d_{xz}, or d_{yz} orbitals of the low-spin d^6 configuration). The acceptor orbital on cobalt must also be a d orbital of π symmetry.[15] As the cobalt reactant is in the low-spin d^6 configuration, promotion of electron density to the e_g set is required prior to electron transfer. Indeed, this is thought[17] to be the main reason why the reductions of cobalt(III) complexes are so much slower than the reductions of the corresponding ruthenium complexes, where this spin change is not necessary. The trends in the present data can then be explained by the size of the spin promotional activation energies at cobalt, the rate of first-order electron transfer, k_{et}, being slowest for the strong field ligand 4-phenylpyridine ($\sigma_p = 0.009$)[18] and fastest for the weaker field ligand 4-benzoylpyridine ($\sigma_p = 0.459$).[18] We note that this situation is opposite to that reported by Endicott et al.,[19] where spin changes were not involved in a redox reaction at cobalt.

If, as argued above, the redox process involves d-orbital overlap within the ion pair, then the ion pair must be oriented in such a way that the ligands L and L′ are pointed away from each other. Further evidence for this particular orientation comes from an analysis of the values for K_{os} listed in Table II. For the case where the ligand at cobalt is 4-phenylpyridine, the directly determined experimental values for K_{os} are 1047 ± 20 and 761 ± 13 M^{-1}, for the ligands at iron being 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethane, respectively. These values can be used in the Fuoss equation

$$K_{os} = \frac{4\pi N a^3}{3000} \exp\left(\frac{-U_{(a)}}{kT}\right) \qquad (6)$$

where

$$U_{(a)} = \frac{Z_1 Z_2 e^2}{aD} \frac{-Z_1 Z_2 e^2 \kappa}{D(1 + \kappa a)}$$

and

$$\kappa^2 = \frac{8Ne^2I\pi}{1000DkT}$$

to calculate a, the distance of closest approach of the two metal ions within the ion-pair intermediate. Definitions: N, Avogadro's number; a, distance of closest approach; k, Boltzmann's constant; T, absolute temperature; Z_1 and Z_2, charges on the ions 1 and 2, respectively; e, electronic charge in esu units; D, bulk dielectric constant at the prevailing temperature; I, ionic strength. The above two experimental values of K_{os} were used in eq 6 to determine the value of a, the distance of closest approach of the two metal ions. These values proved to be $5.54 \pm 0.01 \times 10^{-8}$ and $5.80 \pm 0.01 \times 10^{-8}$ cm for the ligands at iron being 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethane, respectively. In each case the ligand at cobalt is 4-phenylpyridine. Two points about these distances are troubling. In the first place, if, as argued above, the ion pair in each case is oriented in the same way (ammonia side of the cobalt complex against the cyano side of the iron complex), then one would expect the distance of closest approach to be the same in each of the above two cases. Secondly, the distance of closest approach should be more on the order of $6–7 \times 10^{-8}$ cm.[6a] The values of a obtained using eq 6 are, therefore, too small. We have also used the modified Fuoss equation of Sutin and Haim,[20] with the result that even shorter distances of closest approach were obtained.

The Fuoss[5] equation is of questionable utility in calculations of ion pairing equilibrium constants because spherical ions are treated with a purely electrostatic approach. The ions used in this study are definitely not spherical, and the association of the reactant ions can be influenced by effects other than electrostatic ones. Interactions of pyridine-type ligands[4c] and hydrogen bonding[20] have both been invoked to explain the observation of values of K_{os} larger than expected by the Fuoss equation. If, as argued above, the orientation of the ion pair involves approach of the ammonia side of the cobalt complex to the cyano side of the iron complex, then hydrogen bonding would appear to be the better explanation for our results.

The most important conclusion to be drawn from the present study may be that the π-conjugated ligands are uninvolved in the orbital pathway for an outer sphere electron transfer reaction. While few would dispute the important role of such ligands in inner-sphere reactions[21] or in outer-sphere reactions where evidence for ligand-bound radicals is available,[7a,b] it may be incorrect to invoke ligand π conjugation in general as the orbital pathway for outer-sphere reactions where direct overlap of d orbitals is possible.

We wish to point out the very interesting comparison between the outer sphere redox rate constants reported here and the values for a series of similar unimolecular inner sphere redox reactions reported by Haim et al.[22] The latter involved the direct determinations of the first-order rate constants for unimolecular inner sphere redox reactions of the binuclear zwitterions $Co(NH_3)_5$-LB-$Fe(CN)_5$. For two of the reactions studied by Haim et al.,[22] for the cases where the ligand bridges, LB, were 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene, the directly determined values for inner-sphere electron transfer through the ligand bridges were 2.6×10^{-3} and 1.4×10^{-3} s^{-1}, respectively. These values are comparable to that reported here of 3.12×10^{-3} s^{-1}, for the outer-sphere reaction of Table II where L = 4,4′-bipyridine and L′ = 4-phenylpyridine. The latter represents an outer-sphere reaction that is as close as possible in terms of the identity of the ligands involved to the inner-sphere reactions of Haim et al.,[22] and we therefore feel that the comparison is especially meaningful. The important conclusion to be drawn from this comparison is that the inner-sphere path provides no apparent advantage in terms of rate, if one compares true values for the first-order rate constants of unimolecular redox reactions, as we have been able to do. The same observation has been made recently by Weighardt et al.[4c]

A further comparison with the reactions of Haim et al.[22] is possible. In two of the reactions studied by Haim et al., the binuclear zwitterion contained the ligand bridge LB = 1,2-bis(4-pyridyl)ethane and 1,3-bis(4-pyridyl)propane. While a net redox process was observed for these two systems ($k = 2.0 \times 10^{-3}$ and 4.8×10^{-3} s^{-1}, respectively), it was shown that the redox step was consummated not through the unconjugated bridging ligands LB, but by an "outer-sphere" electron transfer, "the bridging ligands serving to keep the two metal ions together."[22] This system then represents a case where a strictly outer-sphere process obtains, but also represents a case where the contact ion pairing between the two metal centers is fixed in orientation by the ligand bridge. Thus the equatorial ammonias of the cobalt half are constrained to approach the equatorial cyano groups of the iron half of the precursor binuclear zwitterion. Because this is an orientation opposite to the one which we have argued exists in the true outer-sphere reactions on which we here report, a comparison should be intriguing, especially since we have argued above that a special orientation of ions within an outer-sphere ion pair is important for electron transfer. The proper rate constant for comparison is the first-order rate constant for outer-sphere electron transfer, $k_{et} = 2.75 \times 10^{-2}$ s^{-1}, listed in Table II for the case where the ligand at cobalt, L′, is 4-benzoylpyridine and the ligand at iron, L, is 1,2-bis(4-pyridyl)ethane. This set of ligands most closely matches the unconjugated situation within the binuclear intermediates of Haim which undergo "outer-sphere" electron transfer. The true outer sphere electron transfer rate constant from Table II is a full order of magnitude greater than the binuclear "outer sphere" electron transfer rate constants where the approach of the iron and cobalt centers is constrained to one particular orientation by the bridging ligand. This supports our contention that the nonspherical geometries of the ions $Fe(CN)_5L^{3-}$ and $Co(NH_3)_5L'^{3+}$ place orientational requirements on the ion-pair intermediate.

We are presently extending our studies to include other cases where it will be possible to obtain experimental resolutions of the constants K_{os} and k_{et}. We intend looking especially at the dependence of these constants on ionic strength and temperature.

Note Added in Proof. Haim and Phillips have recently studied[23] the kinetics and mechanism of the reactions of the complexes $Fe(CN)_5L^{2-}$ with $CoEDTA^{2-}$. These are the final products of the reactions reported here, and we have observed the subsequent reaction of these products, as described by Haim. The rate of these subsequent reactions is sufficiently slow, under the conditions of our experiments, so as not to interfere with our rate measurements.

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Intramicellar Electron Transfer Quenching of Excited States. Determination of the Binding Constant and Exchange Rates for Dimethylviologen[1]

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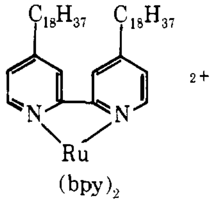
Abstract: The quenching of a water-insoluble surfactant analogue of $Ru(bpy)_3^{2+}$ by the dimethylviologen cation, DMV^{2+}, has been investigated in anionic (SDS) and cationic (CTAB) micelles. Quenching by DMV^{2+} in the former is much more effective than in homogeneous solutions; the converse is true for the latter. The quenching event in anionic micelles is dynamic and totally intramicellar. Analysis of the quenching data obtained for the SDS micelles provides an estimate for the binding constant of DMV^{2+} on the micellar surface as well as values for the rates of binding and dissociation. The rate of diffusion of the cationic DMV^{2+} on the surface of the anionic micelles has been determined to be similar to apparent intramicellar diffusional rates for quite different probes studied in several other systems.

Introduction

There has been much recent interest in excited-state phenomena occurring within organized assemblies such as micelles, vesicles, and monolayers in interfacial processes. In a number of cases recently, there has been emphasis on bimolecular processes where one or both of the substrates participating in a photoprocess is sequestered in a micelle.[2-7] In this paper a luminescent surfactant ruthenium complex is used to examine the exchange of a divalent cation with a monovalent cation on the surface of sodium dodecyl sulfate micelles by examining quenching of the luminescent probe by the divalent ion. In the present case, exchange of the dication is much faster than the rate of luminescence decay of the excited probe.

A number of kinetic expressions have been developed to describe excited state quenching processes in which both the excited species and the quencher are at least partially associated with the micelle.[8-11] In cases where both the excited complex and quencher are exclusively bound to the micelle (and the quencher is nonionic), a Poisson distribution of the quenching species results.[12] The luminescence decay observed in such cases is multiexponential and consists of components of emission from excited states in micelles containing varying numbers of quenchers. The decay at long times becomes a single exponential and corresponds to emission of the unquenched complex. A second case occurs where the quencher is partially water solubilized. In this case, multiexponential decay is also observed but the decay at long times corresponds to the emission of the complex partially quenched by the water-solubilized quencher. The kinetic analyses of these cases have been examined in detail by several groups.[8,9,13] In cases where the quenching species is ionic and the luminescent probe is micelle solubilized, results similar to those obtained for nonionic quenchers are obtained when the rate of exchange of quenchers in the Stern layer is slow on the time scale of the experiment. Several groups have examined the quenching of pyrene fluorescence by ionic quenchers in both cationic and anionic micelles.[14,15] In the present paper we examine the quenching of the surfactant ruthenium complex **1** with the dimethylviologen dication, DMV^{2+}, in both cationic and anionic micelles. Of particular interest is our finding that the exchange of DMV^{2+} is very rapid relative to the rate of decay of the excited state of **1**. A comparison of our results with those of others allows an estimation of the exchange rate of the dication with the monocationic sodium ion. We have also estimated an equilibrium constant for the exchange of DMV^{2+} with Na^+ on the micelle surface. Further, the Stern-Volmer quenching constant obtained provides a picture of the diffusional rate over the micelle surface and is compared to values obtained by others for intramicellar diffusional rates.



1

Experimental Section

The sodium dodecyl sulfate used (Aldrich) was purified by Soxhlet extraction with hexane for 25 h to remove dodecanol followed by crystallization from acetone/water (95/5). Cetyltrimethylammonium bromide (Aldrich) was twice recrystallized from acetone. The

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