

Supramolecular Adducts between the Hexacyanocobaltate(III) Anion and Poly(ethyleneimines): Influence on the Photoaquation Efficiency of the Complex

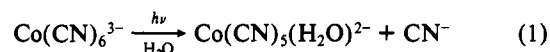
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Addition of open-chain branched poly(ethyleneimines) (PEIs) to aqueous solutions of $\text{Co}(\text{CN})_6^{3-}$ causes a decrease of the quantum yield for the photoaquation reaction of the complex. This quenching effect is analogous to that caused by cyclic poly(ethyleneimines), and it is attributed to the formation of adducts between the complex ion and the polymer, in which some CN^- ligands are hydrogen-bonded to protonated N atoms of the PEI and thus are prevented from definitely leaving the first coordination sphere of the metal ion. The analysis of the quantum yield as a function of pH, PEI molecular weight, and PEI concentration shows that a very high fraction of the N atoms of the polymer may be involved in the hydrogen bonds and that adducts with very large complex:polymer stoichiometric ratios are formed under the most appropriate experimental conditions. In these adducts, as well as in the 1:1 adducts with cyclic polyimines, no more than approximately four CN^- ligands per complex ion are bound to the polymer, which indicates that PEIs and cyclic polyimines offer the same protection against $\text{Co}(\text{CN})_6^{3-}$ photoaquation; however, PEIs exhibit this protection in a larger pH range than the cyclic compounds.

Introduction

Cyclic polyimines are known^{1,2} to form 1:1 "supramolecular" adducts with anionic cyano complexes, via hydrogen bonds between protonated ammonium groups of the imine and CN^- ligands of the complex. In the case of the hexacyanocobaltate(III) ion, $\text{Co}(\text{CN})_6^{3-}$, we have found³ that the formation of such adducts does not affect the nature of the photoreaction of the complex



but strongly decreases its quantum yield. The influence of the ionic charge and of the dimension of the cyclic polyimine on the quantum yield suggested^{3c} that the observed decrease of Φ is due to the hydrogen bonds, which prevent the bound CN^- ligands from leaving the first coordination sphere of the metal ion; as a consequence, the ratio of the photoaquation quantum yields for "free" $\text{Co}(\text{CN})_6^{3-}$ and its adducts is related to the fraction of ligands which are involved in hydrogen bonds with the polyimine. In the light of this interpretation, it also appeared that no more than four ligands per complex ion can be involved in the hydrogen bonds, even in the case of the adduct with the largest and most charged polyimine.

In order to obtain additional information on this "supramolecular" protection of coordination compounds against photoaquation, we have studied the photochemical behavior of aqueous solutions of $\text{Co}(\text{CN})_6^{3-}$ in the presence of open-chain poly(ethyleneimines) (polyaziridines, $(\text{C}_2\text{H}_5\text{N})_n$), and the results obtained are reported in this paper. The selected polymers have average molecular weights $\bar{M} = 600, 1800, 10\,000$, and $>40\,000$, which correspond to 14, 42, 230, and >900 monomeric units per molecule, respectively. These compounds, which will be hereafter called PEI-6, PEI-18, PEI-100, and PEI-400, are highly branched polymers; for $\bar{M} \geq 1800$, it has been found^{4,5} that they contain primary, secondary, and tertiary amino groups in a ratio of about 25:50:25, which leads to tridimensional structures⁶ similar to that

shown in Figure 1. PEIs are polybasic species, since the N atoms may be protonated to form ammonium groups; their degree of protonation in aqueous solutions was found⁷⁻⁹ to increase monotonically on going from basic (pH 10-11) to acidic (pH 2-3) solutions, but a complete protonation seems to be impossible.⁸ Changes in the degree of protonation do not appear to cause large changes in the conformation of the polymers.⁸ The formation of adducts between PEIs and $\text{Co}(\text{CN})_6^{3-}$ has been investigated in the case of PEI-400: by means of potentiometric titrations and ⁵⁹Co-NMR spectroscopy, it has been demonstrated⁹ that the formation of an adduct occurs at pH < 11. The basic strength of PEI-400, like that of cyclic polyimines,² increases when the polymer is bound to $\text{Co}(\text{CN})_6^{3-}$.

Experimental Section

Materials. Potassium hexacyanocobaltate(III), $\text{K}_3\text{Co}(\text{CN})_6$, was prepared according to Bigelow.¹⁰ The poly(ethyleneimines) PEI-6, PEI-18, and PEI-100 are commercial products (Polysciences Inc.). PEI-400 is available from Fluka as a 50% aqueous solution (Polyimin P).

All the other chemicals used were commercial products of reagent grade.

Apparatus. Electronic absorption spectra were recorded on an Ovikon 860 spectrophotometer. The excitation of the complex was performed with 313-nm light, isolated from a Hanau Q-400 medium-pressure Hg lamp by means of a Balzer interference filter. The intensity of the exciting light falling on the reaction cell, measured by means of a ferrioxalate actinometer,¹¹ was of the order of 10^{-7} N $h\nu$ /min.

Procedure. The examined solutions were prepared by dissolving $\text{K}_3\text{Co}(\text{CN})_6$ (2×10^{-3} M) and the polymer (up to 0.2 mol of monomer units/L) in bidistilled water; the pH of the solution (~ 10) was then adjusted by adding HClO_4 . Three-milliliter samples of these solutions were irradiated in a spectrophotometric quartz cell of 1-cm optical path length and were magnetically stirred during the irradiation. After appropriate irradiation periods, the absorption spectrum of the solution was recorded in the 250-450-nm spectral range. The amount of $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$ formed (reaction 1), evaluated from the increase in absorbance at 380 nm (which corresponds to the absorption maximum of $\text{Co}(\text{CN})_5(\text{H}_2\text{O})^{2-}$), was found to be a linear function of the number of 313-nm photons absorbed by the reactant. The quantum yield of reaction 1 was then calculated from these spectral changes, using the photo-reaction of "free" $\text{Co}(\text{CN})_6^{3-}$ ($\Phi = 0.30$ at pH 2)¹² as an internal reference; the uncertainty is ± 0.01 . The same procedure was used for studying the photochemistry of aqueous solutions of $\text{K}_3\text{Co}(\text{CN})_6$ at pH 10.

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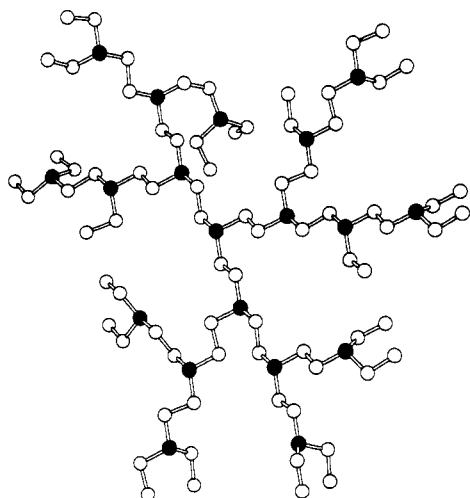


Figure 1. Schematic representation of the structure of branched poly(ethyleneimines). Open circles are primary or secondary amino groups, solid circles are tertiary amino groups, and bars represent $-\text{CH}_2\text{CH}_2-$ groups.

All the experiments were carried out at room temperature ($\sim 22^\circ\text{C}$).

Results

The photochemistry of aqueous solutions of $\text{Co}(\text{CN})_6^{3-}$ has already been studied in the pH range 1–7.^{3c,12} We have extended these studies to pH 10 and obtained the same spectral changes and the same quantum yield (0.30) as those already observed in solutions at $\text{pH} \geq 2$.

The addition of a PEI to a 2×10^{-3} M solution of $\text{Co}(\text{CN})_6^{3-}$ does not cause any change to the absorption spectrum of the complex at $\lambda > 310$ nm, i.e., in the region of the lowest-energy metal-centered absorption band; at lower wavelengths, the spectrum is equal to the sum of the spectra of the two components.

Irradiation at 313 nm of solutions containing PEI and $\text{Co}(\text{CN})_6^{3-}$ causes, above 310 nm, the same spectral variations already observed in the photochemistry of $\text{Co}(\text{CN})_6^{3-}$ alone¹² or $\text{Co}(\text{CN})_6^{3-}$ in the presence of cyclic polyimines,³ which are characteristic of the photoaquation reaction (1). The quantum yield of this reaction, Φ , has been systematically measured as a function of PEI concentration at pH 1, i.e. when almost all the N atoms of the

Table I. Photochemical Properties of the Adducts between PEIs and $\text{Co}(\text{CN})_6^{3-}$ at pH 1

	PEI-6	PEI-18	PEI-100	PEI-400
Φ_{lim}	0.14	0.10	0.10	0.10
$[\text{m}]_{\text{lim}}$, mM	~ 30	~ 20	~ 15	~ 10
β_{lim}	3.5	4.2	4.2	4.2
γ_{lim}^a	~ 0.23	~ 0.42	~ 0.56	~ 0.83
γ^b	~ 0.71	~ 1.0	~ 1.0	~ 1.0
δ_{lim}^c	~ 1	~ 4	~ 30	> 190

^a Calculated at $[\text{m}]_{\text{lim}}$. ^b Calculated at $[\text{m}] = [\text{Co}(\text{CN})_6^{3-}] = 2 \times 10^{-3}$ M. ^c Calculated at $[\text{m}]_{\text{lim}}$, assuming $\alpha = 1$.

polymer are protonated;^{7,8} the results are summarized in Figure 2, where the molar concentration of the polymer, $[\text{m}]$, is expressed in terms of monomer units. Starting from the lowest concentration used, $[\text{m}] = 2 \times 10^{-3}$ M = $[\text{Co}(\text{CN})_6^{3-}]$, Φ decreases at first with increasing $[\text{m}]$ and then reaches a low limiting value, Φ_{lim} . The values of Φ_{lim} are reported in Table I, as well as the lowest value of $[\text{m}]$, $[\text{m}]_{\text{lim}}$, at which $\Phi = \Phi_{\text{lim}}$.

At pH 6 and 10, the dependence of Φ on $[\text{m}]$ has been investigated with PEI-6, PEI-18, and PEI-100, and the results are again collected in Figure 2. At pH 6, Φ , Φ_{lim} , and $[\text{m}]_{\text{lim}}$ have practically the same values as at pH 1, while, at pH 10, Φ is higher than that at pH 1. For PEI-18 and PEI-100, no limiting values of Φ were obtained even in saturated solutions of the polymers, but the trend of Φ vs $[\text{m}]$ suggests that a limiting value of Φ , equal to Φ_{lim} at pH 1, could be reached at higher concentrations. A more systematic investigation of the influence of pH on the quantum yield has been done with PEI-18 at $[\text{m}] = 0.1$ M: Φ slowly decreases with an increase in pH from 1 ($\Phi = 0.10$) to 6 ($\Phi = 0.08$), while it progressively increases in basic solutions ($\Phi = 0.14$ at pH 10). The variation of Φ in the pH range 1–2 practically reflects the analogous variation of the quantum yield Φ^0 for "free" $\text{Co}(\text{CN})_6^{3-}$; ^{3c} the variations observed at $\text{pH} > 2$, on the contrary, are characteristic of the adduct between $\text{Co}(\text{CN})_6^{3-}$ and the PEI, since Φ^0 is constant above $\text{pH} 2$.^{3c}

Discussion

The data in Figure 2 clearly show that the quantum yield of reaction 1 is quenched by PEIs and, in the light of the results obtained with cyclic polyimines,³ provide evidence for the formation of adducts between these compounds and $\text{Co}(\text{CN})_6^{3-}$. Since receptor sites similar to the rings of cyclic polyimines are

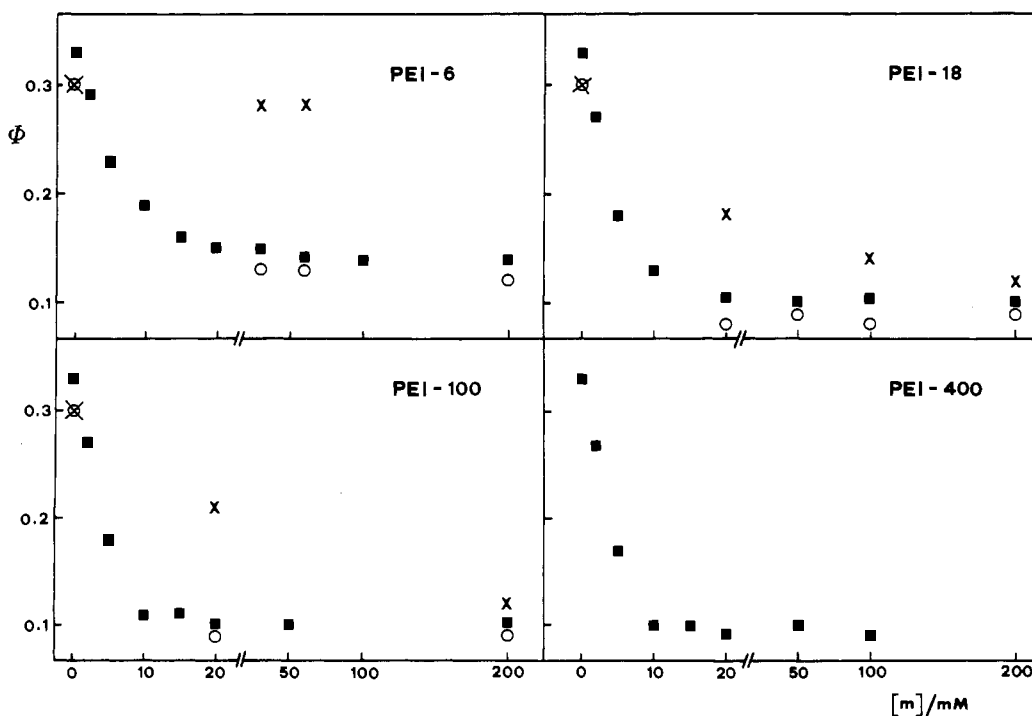


Figure 2. Dependence of the photoaquation quantum yield for $\text{Co}(\text{CN})_6^{3-}$ -PEI systems on polymer concentration, at pH 1 (■), 6 (○), or 10 (×).

Table II. Photochemical Properties of Adducts between $\text{Co}(\text{CN})_6^{3-}$ and Cyclic Poly(ethyleneimines)

imine ^a	Φ_{lim}^b	β_{lim}	γ_{lim}^c
[24]ane-N ₈	0.15 ^d	3.0	0.37
[30]ane-N ₁₀	0.14 ^d	3.2	0.31
[33]ane-N ₁₁	0.10 ^e	4.0	0.36
[36]ane-N ₁₂	0.10 ^e	4.0	0.33

^a [24]ane-N₈ = 1,4,7,10,13,16,19,22-octazaacyclotetracosane; [30]ane-N₁₀ = 1,4,7,10,13,16,19,22,25,28-decaazaacyclotriacontane; [33]aza-N₁₁ = 1,4,7,10,13,16,19,22,25,28,31-undecaazaacyclotriatriacontane; [36]ane-N₁₂ = 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazaacyclohexatriacontane. ^b At [imine] = $[\text{Co}(\text{CN})_6^{3-}] = 2 \times 10^{-3}$ M; pH 2.0–2.5. ^c $[m]_{\text{lim}}$ calculated from $[\text{Co}(\text{CN})_6^{3-}]$, considering the 1:1 stoichiometric ratio of the adducts. ^d From ref 3c. ^e M. F. Manfrin and E. Di Martino, unpublished results.

present in the branched structures of PEIs (Figure 1), the adducts of the branched polymers are expected to be analogous to those of the cyclic compounds^{3c} and their quantum yield of $\text{Co}(\text{CN})_6^{3-}$ photoaquation should therefore depend on the number of "blocked" CN^- ligands, i.e., the ligands that are hydrogen-bound to the polymer and precluded from diffusing far from the metal ion once the metal–ligand bond is temporarily broken by light excitation. From a quantitative point of view, this dependence is expressed by the equation

$$\Phi = (1 - \alpha)\Phi^{\circ} + \alpha\Phi^{\circ}\frac{6 - \beta}{6}$$

where Φ° is the quantum yield of "free" $\text{Co}(\text{CN})_6^{3-}$ photoaquation, α is the fraction of $\text{Co}(\text{CN})_6^{3-}$ ions which are actually bound to the polymer, and β is the average number of CN^- ligands per bound complex ion which are involved in the hydrogen bonds. This equation can be rearranged to

$$\alpha\beta = 6\frac{\Phi^{\circ} - \Phi}{\Phi^{\circ}} \quad (2)$$

The fraction of amino groups involved in the hydrogen bonds, γ , and the number of $\text{Co}(\text{CN})_6^{3-}$ ions bound to one polymer molecule, δ , can also be evaluated by means of the following equations:

$$\gamma = \alpha\beta[\text{Co}(\text{CN})_6^{3-}]/[m] \quad \delta = n\alpha[\text{Co}(\text{CN})_6^{3-}]/[m]$$

where n is the average number of monomeric units per polymer molecule. Values of γ and δ are summarized in Table I; for a comparison, values of Φ_{lim} , β_{lim} , and γ evaluated for adducts between $\text{Co}(\text{CN})_6^{3-}$ and cyclic poly(ethyleneimines) are collected in Table II.

It is important to note that, unlike the adducts between cyclic polyimines and $\text{Co}(\text{CN})_6^{3-}$, which have definite 1:1 structures, the systems studied in this work are variable, since each polymer comprises a mixture of molecules having different masses¹³ and each polymer molecule is capable of forming adducts with different complex:polymer ratios; moreover, the complex ions may be bound to the polymer in receptor sites having different bonding abilities. Therefore, all the data obtained in our experiments must be considered as *average* quantities for the particular system examined.

At polymer concentrations higher than $[m]_{\text{lim}}$, the constancy of Φ (Figure 2) implies that all the $\text{Co}(\text{CN})_6^{3-}$ ions are bound to the polymer ($\alpha = 1$) and that β has reached an upper-limit constant value, β_{lim} . The values of β_{lim} at pH 1, calculated by means of eq 2 with $\Phi = \Phi_{\text{lim}}$, $\alpha = 1$, and $\Phi^{\circ} = 0.33$ ^{3c} and summarized in Table I, are clear evidence that, for the three large polymers PEI-18, PEI-100, and PEI-400, the adducts form the same average number of bonds with one complex ion. This result can be explained by considering that these polymers have the same degree of branching^{4,5} and thus form quite similar receptor sites. Only "less favorable" receptor sites (i.e., sites that can only form a smaller number of hydrogen bonds) must be present in PEI-6,

since this polymer exhibits a smaller value of β_{lim} .

The three major polymers are also able to form adducts having $\text{Co}(\text{CN})_6^{3-}$:polymer stoichiometric ratios (δ_{lim} in Table I) larger than 1. Since the largest cyclic polyimines in Table II have β_{lim} values almost equal to those of these PEIs, but $\delta = 1$, the main difference between branched and cyclic compounds seems to lie more in the number of $\text{Co}(\text{CN})_6^{3-}$ ions bound to each polymer molecule than in the number of bonds formed by each complex ion.

The values of γ in Table I clearly show that, at pH 1, the open-chain branched polymers with $\bar{M} \geq 1800$ may utilize a very large fraction of their N atoms (practically, the totality at $[m] = 2 \times 10^{-3}$ M) for the hydrogen bonds; cyclic polyimines, on the contrary, may only utilize a small fraction of them (Table II). For these last compounds, steric limitations prevent both the formation of adducts having complex:imine ratios higher than 1 and the bonding of two consecutive N atoms of an imine molecule with two adjacent ligands of the same complex ion. In the case of PEIs, on the contrary, steric limitations are reduced, since three out of four N atoms of a branched segment of the polymer can easily be bound to the same complex ion and the presence of two or more $\text{Co}(\text{CN})_6^{3-}$ ions enclosed in adjacent receptor sites of a polymer molecule allows two consecutive N atoms be bound to CN^- ligands of different complex ions.

For all the PEIs examined, the γ values at $[m]_{\text{lim}}$ are smaller than those at the lowest polymer concentration. This can be explained by considering that receptor sites having different sizes or geometries (and thus capable of forming different numbers of hydrogen bonds) may be present in molecules of different masses, or even in the same molecule. At high polymer concentrations, the $\text{Co}(\text{CN})_6^{3-}$ ions are preferentially enclosed in "more favorable" receptor sites (i.e., those that form the highest number of bonds), because the overall bonding energy is higher; at low values of $[m]$, on the contrary, the relative excess of $\text{Co}(\text{CN})_6^{3-}$ forces "less favorable" receptor sites to be used for bonds, in order to accommodate the largest number of complex ions in the adducts. The trends of both γ_{lim} and $[m]_{\text{lim}}$ as a function of \bar{M} (Table I) are in agreement with this hypothesis, since an increase in \bar{M} is expected to cause a decrease in the fraction of small polymer molecules which, like PEI-6, are only able to form adducts with a relatively low number of hydrogen bonds.

An increase in pH is expected to cause a decrease in the degree of protonation of the polymer and, as a consequence, a decrease in α and/or β and an increase in Φ . Actually, such an expected increase in Φ has been experimentally observed only at pH > 6; in addition, for PEI-18 and PEI-100 the increase in pH from 6 to 10 affects the values of Φ and $[m]_{\text{lim}}$, but not those of Φ_{lim} and β_{lim} .¹⁴ All these effects of pH could be explained by assuming that the observed⁹ enhancement of the basic strength of the polymer caused by $\text{Co}(\text{CN})_6^{3-}$ is mainly a local effect, so that, at relatively high pH values, the protonated N atoms of the polymer are mainly concentrated around the receptor sites which enclose $\text{Co}(\text{CN})_6^{3-}$ ions. According to this hypothesis, in fact, the deprotonation of fully protonated polymers should involve at first the N atoms of the receptor sites which do not interact with complex ions, leaving Φ unchanged; at relatively low degrees of protonation, a further deprotonation is expected to cause a decrease in the number of protonated receptor sites involved in the formation of an adduct (i.e., a decrease of α), but not a decrease in the number of hydrogen bonds formed by each of them (i.e., not a decrease in β).

The behavior of the adduct between PEI-6 and $\text{Co}(\text{CN})_6^{3-}$ at pH 10 is quite different from that of the other polymers: a relatively high value of Φ (0.28) was obtained for $[m] = 30$ mM, which does not change on doubling the concentration of the polymer. Since very few N atoms are expected to be protonated at pH 10 and their distribution along the polymer is probably scarcely affected by the presence of $\text{Co}(\text{CN})_6^{3-}$, such a value of Φ (very close to Φ°) may be explained by assuming that a large

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(14) Note that the adduct between $\text{Co}(\text{CN})_6^{3-}$ and the cyclic polyimine [24]ane-N₈ exhibits similar properties in the pH range 2–4.^{3c}

fraction of the adducts involve only one hydrogen bond per complex ion. Experiments carried out in the presence of Et_2NH_2^+ have in fact demonstrated^{3b} that the quantum yield of photoaquation for the adducts with only one hydrogen bond is equal to that of "free" $\text{Co}(\text{CN})_6^{3-}$.

In conclusion, in acidic solutions the $\text{Co}(\text{CN})_6^{3-}$ -PEI interaction is very similar to the $\text{Co}(\text{CN})_6^{3-}$ -cyclic polyimine interaction, so that the two classes of organic compounds practically offer analogous protections against the photoaquation of the complex; unlike cyclic polyimines, however, PEIs offer the same protection in a relatively large pH range (from 1 to 6). Another important property of the branched polymers is the high number of $\text{Co}(\text{CN})_6^{3-}$ ions which can be bound to a polymer molecule (about 200 for PEI-400); the local concentration of $\text{Co}(\text{CN})_6^{3-}$ in the adducts so obtained is extremely large, since two adjacent complex ions are separated only by a $-\text{CH}_2\text{CH}_2\text{NH}-$ chain. Similar adducts may represent a useful alternative to other types of su-

pramolecular structures like polymer-pendant coordination compounds and micelle aggregates. The importance of similar very large supramolecular compounds in the future development of chemistry and photochemistry was recently demonstrated.¹⁵

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Registry No. [24]ane- N_8 , 297-11-0; [30]ane- N_{10} , 862-28-2; [33]ane- N_{11} , 60464-68-8; [36]ane- N_{12} , 24904-24-3; $\text{Co}(\text{CN})_6^{3-}$, 14897-04-2; $(\text{C}_2\text{H}_5\text{N})_n$, 9002-98-6.

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Activation-Controlled Outer-Sphere Oxidation of Thiosulfate: Reaction with Bis(1,4,7-triazacyclononane)nickel(III)

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Oxidation of $\text{S}_2\text{O}_3^{2-}$ by $[\text{Ni}(\text{tacn})_2]^{3+}$ has been studied in aqueous medium at 25.0 °C and 0.10 M ionic strength. The reaction produces $[\text{Ni}(\text{tacn})_2]^{2+}$ and $\text{S}_4\text{O}_6^{2-}$. It is catalyzed by trace levels of Cu(II), but the catalysis can be eliminated by using $\text{C}_2\text{O}_4^{2-}$ as a copper scavenger. A stopped-flow kinetic study of the uncatalyzed reaction with excess $[\text{S}_2\text{O}_3^{2-}]$ showed that the rate law is $-\text{d}[\text{Ni}(\text{III})]/\text{d}t = 2k_1[\text{Ni}(\text{III})][\text{S}_2\text{O}_3^{2-}]$ with $k_1 = 1.40 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The reactions of $[\text{Fe}(\text{bpy})_3]^{3+}$, $[\text{IrCl}_6]^{2-}$, and $[\text{IrBr}_6]^{2-}$ with $\text{S}_2\text{O}_3^{2-}$ are also copper catalyzed. A reinvestigation of these reactions in the presence of copper scavengers shows that the reactions of $[\text{Fe}(\text{bpy})_3]^{3+}$ and $[\text{IrCl}_6]^{2-}$ have the same rate laws as that of $[\text{Ni}(\text{tacn})_2]^{3+}$, with k_1 values of 2.05×10^5 and $1.38 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. For the reaction of $[\text{IrBr}_6]^{2-}$, the rate law is $-\text{d}[\text{IrBr}_6^{2-}]/\text{d}t = (k_0 + 2k_1[\text{S}_2\text{O}_3^{2-}])([\text{IrBr}_6^{2-}])$ with $k_1 = 1.23 \times 10^3$ and $k_0 = 1.46 \times 10^{-2} \text{ s}^{-1}$. It is inferred that for all four reactions the k_1 term represents a mechanism involving rate-limiting formation of S_2O_3^- and the reduced complex. Analysis of a plot of k_1 vs E_f for oxidations of $\text{S}_2\text{O}_3^{2-}$ indicates that the reactions of $[\text{Ni}(\text{tacn})_2]^{3+}$ and $[\text{Fe}(\text{bpy})_3]^{3+}$ are activation controlled, whereas those of $[\text{IrCl}_6]^{2-}$ and $[\text{IrBr}_6]^{2-}$ are limited by diffusion apart of the products. Values of $E_f = 1.30 \text{ V}$ and k_{11} for the $\text{S}_2\text{O}_3^-/\text{S}_2\text{O}_3^{2-}$ redox couple are deduced from this analysis.

Introduction

Over the last several years we have been investigating the rates and mechanisms of electron-transfer reactions of simple main-group compounds in aqueous solution. In many cases the reactions have low rate constants that can be traced to significant internal Franck-Condon barriers. One such example is the reaction of NO_2^- with $[\text{Ni}(\text{tacn})_2]^{3+}$, for which the rate-limiting step is formation of NO_2 and $[\text{Ni}(\text{tacn})_2]^{2+}$; the change in bond angle between NO_2^- and NO_2 (19°) leads to a major component of the activation barrier.¹ Another example is the oxidation of SO_3^{2-} by $[\text{Os}(\text{bpy})_3]^{3+}$, where a significant portion of the barrier arises from the pyramidalization mode that relates SO_3^{2-} and SO_3^- .² Quite a different problem is presented in reactions where there is insignificant structural reorganization. Oxidations of monatomic species such as I^- are extreme cases, because there is no internal structure, but certain molecular species also possess this property, as exemplified by reactions in which N_3^- is oxidized to N_3 .³ There is virtually no structural difference between N_3^- and N_3 , and so the only barrier to their outer-sphere self-exchange reaction is imposed by solvent reorganization. Consistent with this idea is the result that the effective self-exchange rate constant (derived from the Marcus cross relationship) is $4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which is

much greater than the value deduced for the $\text{NO}_2/\text{NO}_2^-$ system ($0.3 \text{ M}^{-1} \text{ s}^{-1}$).

An interesting question is whether reactions can be found in which nonlinear main-group molecules undergo outer-sphere electron transfer with no structural reorganization. Reactions of $\text{S}_2\text{O}_3^{2-}$ are expected to be pertinent to this question, because ESR measurements and MO calculations on S_2O_3^- indicate that the unpaired electron resides in an a_1 orbital localized on the terminal sulfur atom.⁴⁻⁸ It is therefore expected that the structural differences between $\text{S}_2\text{O}_3^{2-}$ and S_2O_3^- are minimal.

A preliminary survey of the reactions of $\text{S}_2\text{O}_3^{2-}$ with $[\text{IrBr}_6]^{2-}$, $[\text{IrCl}_6]^{2-}$, and $[\text{Fe}(\text{bpy})_3]^{3+}$ revealed that electron transfer does occur on a convenient time scale and that the general degree of reactivity is consistent with a small structural barrier.⁹ Very recently we reported a detailed study of the oxidation of $\text{S}_2\text{O}_3^{2-}$ by $[\text{Os}(\text{phen})_3]^{3+}$ and related Os(III) species;¹⁰ this paper demonstrated that electron-transfer reactions of $\text{S}_2\text{O}_3^{2-}$ are generally

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