

Contribution from the Instituto de Química, University of São Paulo, São Paulo, Brazil, and the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

Pentacyanoferrate(II) Complexes: Evaluation of Their Formal Potentials and Mechanism of Their Quenching of Tris(2,2'-bipyridine)ruthenium(II) Luminescence

HENRIQUE E. TOMA^{1a} and CAROL CREUTZ^{1b}

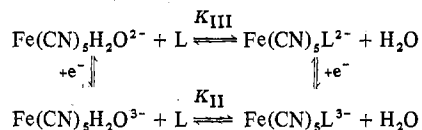
Received August 9, 1976

AIC60559H

Formal reduction potentials (E°) for complexes of the pentacyanoferrate ion with a number of unsaturated ligands have been measured by cyclic voltammetry and potentiometry. From the association constants for the complexes in the iron(II) form (K_{II}) and the E° values, the corresponding constants for the iron(III) complexes (K_{III}) have been calculated. The K_{III} values are found to increase with the basicity of the ligand, while the opposite trend is found for the K_{II} values. These opposing trends are discussed in terms of the bonding properties of the pentacyanoferrate ion. The quenching of the luminescence of the excited state of tris(2,2'-bipyridine)ruthenium(II) by pentacyanoferrate(II) complexes has also been investigated. For most of the complexes, including several previously reported hexacyanometalates, the quenching rate constants parallel their reduction potentials as is expected for a quenching mechanism involving reduction of the ruthenium excited state by iron(II).

Introduction

Although the dependence of the redox properties of transition metal complexes on the nature of the donor atom and the ligand is now well understood,² there are only a few systems displaying a range of potentials great enough for systematic studies. The immine complexes of transition metal ions, in particular those of the 1,10-phenanthroline and 2,2'-bipyridine derivatives, form one such series. The strong affinity of the pentacyanoferrate(II) ion for unsaturated ligands can be used to make another very interesting series of complexes with imidazole,^{3a} pyridine, pyrazine,^{3b} sulfoxides,^{3c} CO, or NO as the sixth ligand. In this series, the σ -donor and π -acceptor powers of the ligands are expected to vary considerably thus providing large differences in the stability constants for the complexes in their oxidized and reduced forms. This should result in large differences in redox potentials, as predicted from the cycle



where

$$E^\circ_{(\text{Fe}(\text{CN})_5\text{L})^{2-/3-}} = E^\circ_{(\text{Fe}(\text{CN})_5\text{H}_2\text{O})^{2-/3-}} + \frac{RT}{F} \ln \frac{K_{II}}{K_{III}} \quad (1)$$

Since the equilibrium constants K_{II} are known for many of the pentacyanoferrate(II) complexes,⁴ measurement of the reduction potentials makes it possible to calculate K_{III} and, from this information, the relationships between K_{II} and K_{III} and the properties of the ligand may be evaluated.

The use of the pentacyanoferrate(II) complexes in the quenching of the luminescence of the excited state ($^* \text{Ru}(\text{bpy})_3^{2+}$) of tris(2,2'-bipyridine)ruthenium(II) was suggested by the recent observation that ferrocyanide^{5,6} and other transition metal hexacyanides⁶ are efficient quenchers via energy-transfer or electron-transfer mechanisms. If the quenching occurs by an electron-transfer mechanism, the regularities in the redox properties of the pentacyanoferrates are expected to be reflected in the rate constants for the quenching process. In fact, such correlations were observed for most of the cyano complexes reported here, but with some interesting exceptions. For some of these cases, other mechanisms, including electron-transfer reactions of the coordinated ligands, are considered.

Experimental Section

Materials. The pentacyanoferrate(II) complexes were prepared from sodium amminepentacyanoferrate(II) trihydrate, as previously

described.³ Solutions of the carbonylpentacyanoferrate(II) complex (10^{-2} M) were prepared as follows: in a flask provided with bubblers, pure carbon monoxide was passed through the yellow solution of the amminepentacyanoferrate(II) complex for ca. 2 h. During the reaction, the free ammonia released in the substitution process was carefully neutralized with dilute sulfuric acid containing traces of ascorbic acid⁷ to reduce eventual oxidizing impurities. When the reaction was complete, a colorless solution was obtained. Bluish impurities are formed in the absence of ascorbic acid. The presence of the residual aquopentacyanoferrate(II) ion was tested by adding *N*-methylpyrazinium ion ($\epsilon_{\text{max}} 1.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 658 nm for the pentacyano(*N*-methylpyrazinium)ferrate(II) complex).

Cyclic Voltammetry Measurements. A Princeton Applied Research Corp. system consisting of a Model 173 potentiostat and a Model 175 universal programmer was employed in the cyclic voltammetry measurements. Reversible cyclic voltammograms were obtained at sweep rates varying from 20 to 200 mV/s, using platinum wires as auxiliary and working electrodes vs. saturated calomel electrode.

All of the measurements were carried out under argon, with millimolar solutions of the pentacyanoferrate(II) complexes at 25 °C, $\mu = 1.00$ M (NaCl), pH 4.5 (acetate buffer, 10^{-2} M). For the imidazole and pyridine complexes, the ligand buffers (rather than acetate) were employed in order to prevent the dissociation of the coordinated ligand.

Absorption and Emission Spectra. A Cary 17 spectrophotometer was used for the absorption measurements in the visible and UV region. The emission spectrum and emission intensity of tris(2,2'-bipyridine)ruthenium(II) complex, in the presence or absence of quenchers, were determined with a Perkin-Elmer Model MPF4 spectrofluorimeter, equipped with a 150-W xenon lamp. The measurements were carried out at 25 °C, with samples always freshly prepared under an argon atmosphere. With the exception of the pyrazinecarboxylate and *N*-methylpyrazinium complexes, all of the quenchers have no appreciable absorption at the excitation (450 nm) and emission (607 nm) wavelengths. Only minor corrections⁸ have been applied, when necessary.

Lifetime Measurements. Solutions of tris(2,2'-bipyridine)ruthenium(II) containing strongly absorbing quenchers such as the pentacyano(*N*-methylpyrazinium)ferrate(II) complex could not be readily studied by intensity measurements. For these systems, the quenching rate constants were obtained by directly determining the excited-state lifetime τ as a function of quencher concentration. The lifetimes were determined by monitoring the decay in emission intensity after excitation by a ~ 30 -ns pulse of 530-nm light. A neodymium laser (Korad Model K1500) which lases at 1060 nm was employed as the excitation source.⁹ Frequency doubling was accomplished by a potassium deuterated dihydrogen phosphate crystal. Excitation intensities at 530 nm were typically $10 \text{ einsteins cm}^{-2} \text{ s}^{-1}$. The emitted light passed through a Bausch and Lomb high-intensity grating monochromator (605 nm, 10 nm band-pass) and was detected with a photomultiplier (Hitachi R446) and a preamplifier having a combined bandwidth in excess of 30 MHz. The signals from the preamplifier were displayed and photographed on a Tektronix 7633 oscilloscope equipped with a Tektronix 7B71 time base and 7A13

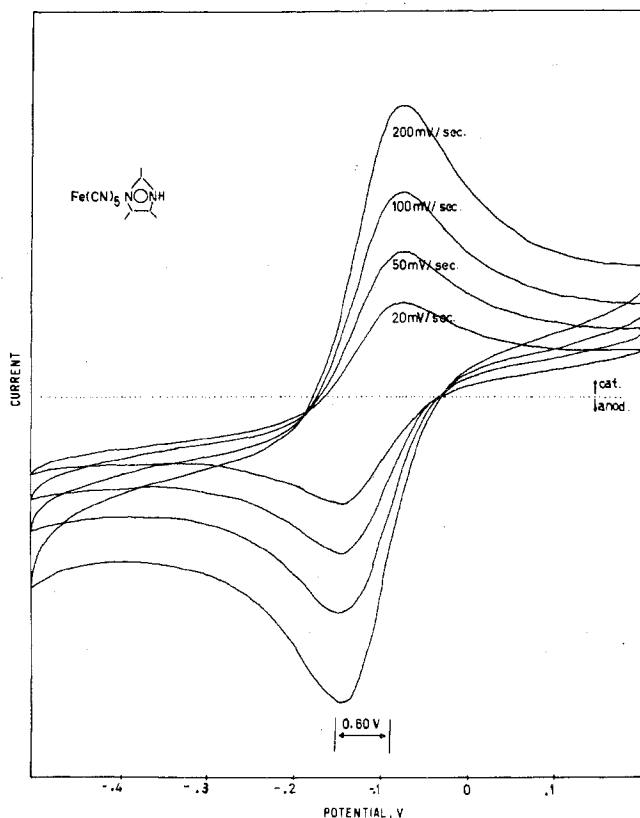


Figure 1. Cyclic voltammograms for the pentacyano(imidazole)ferrate complex at several scan rates at $\mu = 1.0$ M (sodium chloride) and 25 °C with imidazole buffer (10^{-2} M).

amplifier. Values of I_t , the emission intensity at time t , were read from the photographs and plots of $\log I_t$ vs. time were constructed. The lifetimes were obtained from the slopes of the semilog plots. The measurements were made at 25 °C on deaerated solutions 10^{-5} to 10^{-3} M in $\text{Ru}(\text{bpy})_3^{2+}$. Neutral density filters were used to attenuate the emission intensity at low quencher concentrations.

Results and Discussion

Formal Potentials and Cyclic Voltammetry Measurements.

Formal reduction potentials (E°') for a number of substituted pentacyanoferrate complexes were evaluated by direct potentiometry or by cyclic voltammetry. Most of the complexes, e.g., those derived from pyridine and pyrazine, are sufficiently stable and inert in both the iron(II) and iron(III) forms to permit the application of direct potentiometry to equimolar solutions in order to evaluate E°' . The junction potentials in these cases were estimated to be in the range of ± 5 mV by checking the quinhydrone electrode against SCE. The oxidized form of the *N*-methylpyrazinium complex aquates slowly in aqueous solution¹⁰ but without any appreciable changes in the potentials measured. For the dimethyl sulfoxide and carbon monoxide complexes, decomposition takes place rapidly, and cyclic voltammetry was employed instead of direct potentiometry.

For all the complexes, well-behaved and reversible cyclic voltammograms have been obtained, as shown in Figures 1 and 2. The cathodic and anodic peak separation was typically 60–65 mV, as expected for a one-electron, reversible process. Since the diffusion coefficients for the oxidized and reduced pentacyanides are very similar,¹¹ the $E_{1/2}$ values can be regarded as good estimates of E°' .

The values of the formal reduction potentials of the pentacyanoferrates are collected in Table I. Also included are the values of the association constants for the complexes (K_{II} and K_{III}) and, for comparison purposes, the basicity constants for the heterocyclic ligands and $K_{\text{II}}/K_{\text{III}}$ ratios. Except for that of the imidazole complex, the values of K_{II} have been previously reported.⁴ The K_{III} values tabulated were calculated from eq 1 using the K_{II} and $E^\circ'_{\text{III,II}}$ values given in Table I and +0.39 V as the potential for reduction of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{2-}$ to $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$. This approach neglects (a) the medium change from 0.5 M perchlorate (in which most of the K_{II} values were determined) to 1.0 M chloride (in which most of the E°' values were measured) and (b) differences in the activity coefficients of the $\text{Fe}(\text{CN})_5\text{H}_2\text{O}$ and $\text{Fe}(\text{CN})_5\text{L}$ complexes. Although the resulting K_{III} values are consequently only es-

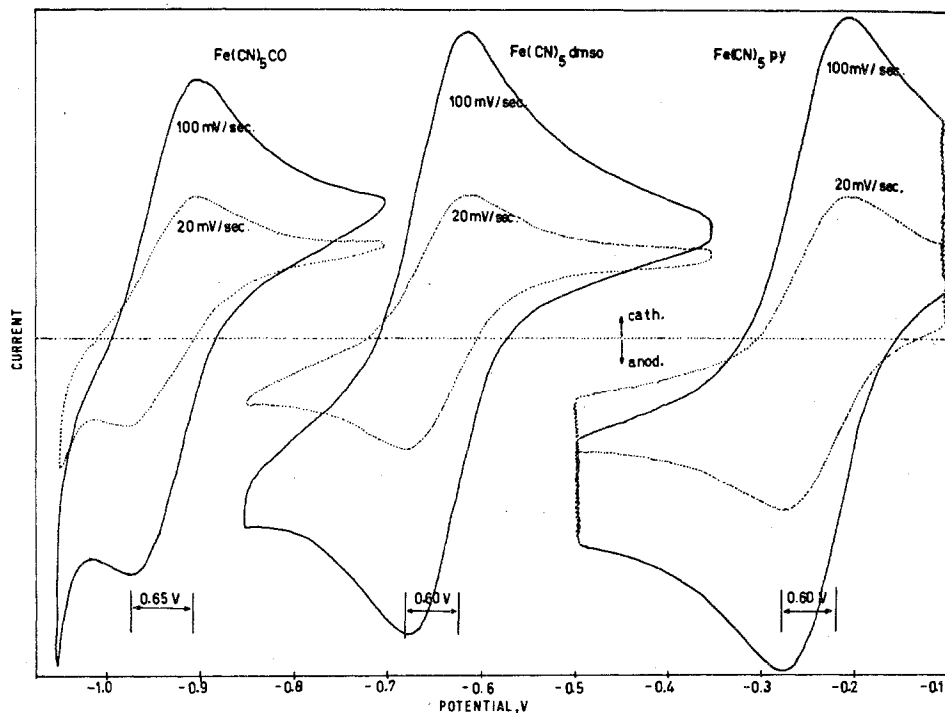


Figure 2. Cyclic voltammograms for the pyridine, dimethyl sulfoxide, and carbonyl complexes of pentacyanoferrate ion at $\mu = 1.0$ M (sodium chloride) and 25 °C showing the shifts in $E_{1/2}$ as a function of the nature of the ligands.

Table I. Formal Potentials and Association Constants for Pentacyanoferrate(II) and -(III) Complexes at 25 °C

L in Fe(CN) ₅ L	E ^o _{III/II} , ^a V	K _{II} , ^b M ⁻¹	K _{III} , M ⁻¹	pK _a ^c	K _{II} /K _{III}
H ₂ O	0.39 (pot.) 0.409 ^d	1	1		1
Imidazole (imid)	0.35 (CV)	1.8 × 10 ⁵ ^e	8.3 × 10 ⁵	7.0	2 × 10 ⁻¹
γ-Picoline	0.45 (pot.)	3.1 × 10 ⁵	2.9 × 10 ⁴	6.11	1.1 × 10
Pyridine (py)	0.47 (pot.) ^f 0.48 (CV)	3.3 × 10 ⁵	9.4 × 10 ³	5.30	3.5 × 10
Isonicotinamide	0.50 (pot.) ^f	4.0 × 10 ⁵	5.2 × 10 ³	3.65	7.7 × 10
Pyrazine (pz)	0.55 (pot.) ^f	9.0 × 10 ⁵	1.7 × 10 ³	0.65	5.3 × 10 ²
N-Methylpyrazinium (NMPz)	0.78 (pot.) ^f 0.79 (CV)	2.0 × 10 ⁶ ^g	4.7 × 10 ⁻¹	-5.8	4.3 × 10 ⁶
Dimethyl sulfoxide (Me ₂ SO)	0.89 (CV)	3.3 × 10 ⁶ ^g	1.1 × 10 ⁻²		3 × 10 ⁸
Carbonyl	1.18 (CV)	>10 ⁷	<10 ⁻⁷		>10 ¹⁴

^a CV = cyclic voltammetry; pot. = potentiometry. $\mu = 1.0$ M (NaCl) for CV studies (this work). ^b $\mu = 0.5$ M (LiClO₄) unless otherwise stated; from ref 3 and 4. ^c From K. Schofield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, N.Y. 1967; R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds", Interscience, New York, N.Y., 1960. ^d At 0 °C, $\mu = 1.0$ M; A. D. James, R. S. Murray, and W. C. E. Higginson, *J. Chem. Soc., Dalton Trans.*, 1274 (1974). ^e $K_{II} = 2.1 \times 10^5$ M⁻¹ at $\mu = 0.1$ M; ref 3a. ^f Reference 3b; $\mu = 0.1$ M. ^g $\mu = 1.0$ M LiClO₄.

timates, as contributions from the above factors are expected to be small, they should be rather good estimates.

The values obtained for K_{III} show a good correlation with the pK_a values of the free ligands; a decrease in the basicity of the unsaturated nitrogen ligands from +7 to -5 pK_a units is paralleled by a reduction in the association constants for Fe(CN)₅²⁻ complexes of ~6 orders of magnitude. Thus the σ -donating power of the ligand (reflected in the ligand affinity for H⁺) seems to be the major factor in determining the affinity of the Fe(CN)₅²⁻ moiety for the unsaturated nitrogen bases. In sharp contrast the association constants for the iron(II) complexes with these nitrogen bases span only 2 orders of magnitude, increasing in value as the pK_a of the free ligand decreases. This pattern indicates that the loss in σ -donor strength is more than compensated by an increase in the π -acceptor abilities of the ligands and that the back-bonding ability of the ligand is evidently the major factor in determining the affinity of the Fe(CN)₅³⁻ moiety for these ligands (although a synergistic mechanism should also be important in complexes of this type¹²). Thus the opposite trends observed for K_{III} and K_{II} are quite informative since they reflect the relative contributions of the ligand σ -donor and π -acceptor interactions to the stabilities of the complexes in their oxidized and reduced forms. The same kinds of affinity comparisons have been made for the Ru(NH₃)₅³⁺ and Ru(NH₃)₅²⁺ moieties with a number of saturated and unsaturated ligands.^{13a} Comparison of the present results with data for the ruthenium system leads to the conclusion that the two pairs of parent ions are rather similar in their properties. Over a wide range of ligand basicity the ratio K_{II}/K_{III} is similar for the two series: for Ru(NH₃)₅ complexes the ratio is 1.5, 4 × 10³, and 8 × 10⁶ for imidazole,^{13b} pyridine,^{13c} and dinitrogen,^{13c} respectively, as the sixth ligand while for the Fe(CN)₅ series the ratio is 0.2, 35, and >10¹⁴ for imidazole, pyridine, and carbonyl, respectively, as the sixth ligand. Direct comparison for the two series is possible only for imidazole and pyridine. For these two ligands the data indicate that, while the Ru(III) and Fe(III) affinities are quite similar ($K_{III} = 19 \times 10^5$ ^{13b} and 8.3×10^5 M⁻¹ for imidazole; $K_{III} = 6.0 \times 10^3$ ^{13c,d} and 9.4×10^3 M⁻¹ for pyridine, for Ru(III) and Fe(III), respectively), Ru(II) has a somewhat greater affinity for imidazole and pyridine than Fe(II) ($K_{II} = 28 \times 10^5$ ^{13b} and 1.8×10^5 M⁻¹^{3a} for imidazole; $K_{II} = 240 \times 10^5$ ^{13d} and 3.3×10^5 M⁻¹ for pyridine,⁴ for Ru(II) and Fe(II), respectively). Thus Ru(NH₃)₅²⁺ appears to exhibit a somewhat greater capacity for back-bonding than Fe(CN)₅³⁻.

Quenching of the Luminescence of the Excited State of Tris(2,2'-bipyridine)ruthenium(II). Stern-Volmer plots obtained from intensity or lifetime measurements for several pentacyanoferrate(II) complexes are shown in Figure 3. In

Table II. Quenching of Ru(bpy)₃²⁺ Luminescence by Some Cyanide Complexes of Transition Metal Ions^a

Quencher Q	$\bar{\nu}_{\min}$, μm^{-1}	E ^o _{Q⁺/Q} , V	k _q , M ⁻¹ s ⁻¹
Pt(CN) ₄ ²⁻	2.30 ^b		<10 ⁶ ^b
Pd(CN) ₄ ²⁻	2.27 ^b	>1 ^b	<10 ⁶ ^b
Fe(CN) ₅ CO ³⁻	3.27 ^c	1.18	6 × 10 ⁶
Fe(CN) ₅ (Me ₂ SO)	2.84 ^c	0.89	5.6 × 10 ⁷ ^j
Mo(CN) ₆ ⁴⁻	1.96 ^b	0.79 ^g	3.4 × 10 ⁸ ^b
Os(CN) ₆ ⁴⁻	4.7 ^b	0.65 ^h	1.2 × 10 ⁹ ^b
Fe(CN) ₅ (pzCO ₂) ⁴⁻	2.12 ^d	0.61	1.9 × 10 ⁹
Fe(CN) ₆ ⁴⁻	2.37 ^e	0.45 ⁱ	3.5 × 10 ⁹ ^k
Fe(CN) ₅ (imid) ³⁻	2.58 ^c	0.35	3.8 × 10 ⁹ ^j
Fe(CN) ₅ py ²⁻	2.76 ^d	0.48	4.2 × 10 ⁹ ^j
Fe(CN) ₅ (NMPz) ²⁻	1.52 ^d	0.79	5.3 × 10 ⁹
Ni(CN) ₄ ²⁻	2.3 ^b	>1 ^b	5.6 × 10 ⁹ ^b
Fe(CN) ₅ NO ²⁻	2.00 ^f	l	6.0 × 10 ⁹

^a $\mu = 0.50$ M (sodium chloride), pH 4-5 unless otherwise stated; $\bar{\nu}_{\min}$ is the position of the lowest energy observable transition in the spectrum of Q; E^o is for the half-reaction Q⁺ + e⁻ = Q. ^b Taken from Table I in ref 6. ^c ¹A_{1g} → ¹E(1) ligand field transition. ^d Charge-transfer bands. ^e ¹A_{1g} → ¹T_{1g} transition. ^f Charge-transfer, ¹A_{1g} → ¹E transition: P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3340 (1965). ^g I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **40**, 247 (1936); extrapolated to $\mu = 1.0$ M NaCl. ^h F. Opekar and P. Beran, *J. Electroanal. Chem.*, **71**, 120 (1976). ⁱ Formal potential at $\mu = 0.5$ M. ^j I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945 (1935). ^k In the presence of a small excess (10⁻⁴ M) of Me₂SO, imidazole buffer (10⁻³ M), or pyridine buffer (10⁻³ M). Quenching by the ligands is negligible under the conditions employed. ^l Reference 5. ^l For the Fe(CN)₅NO⁻/Fe(CN)₅NO²⁻ couple E^o should exceed that for the carbonyl complex, i.e., E^o > 1.2 V; however, the potential for this couple has not been determined.

Table III. Quenching of Ru(bpy)₃²⁺ Luminescence by Free Ligands at 25 °C and 0.5 M Ionic Strength

Ligand	k _q , M ⁻¹ s ⁻¹	Ligand	k _q , M ⁻¹ s ⁻¹
Dimethyl sulfoxide	<10 ⁶	N-Methylpyrazinium	2.1 × 10 ⁹
Imidazole/imidazole H ⁺	<10 ⁵	Pyrazinecarboxylic acid	1.8 × 10 ⁹
Pyridine/pyridine H ⁺	<10 ⁷		

Table II, the quenching rate constants calculated from eq 2

$$I_0/I = 1 + k_q \tau_0 [Q] \quad \tau_0/\tau = 1 + k_q \tau_0 [Q] \quad (2)$$

are collected for comparison purposes. Here I_0 and I are the emission intensities of a solution of Ru(bpy)₃²⁺ in the absence and presence of quencher, respectively; τ_0 and τ are the lifetimes of *Ru(bpy)₃²⁺ in the absence and presence of quencher, respectively; and k_q is the quenching rate constant. Data from ref 5 and 6 for other cyano complexes are also

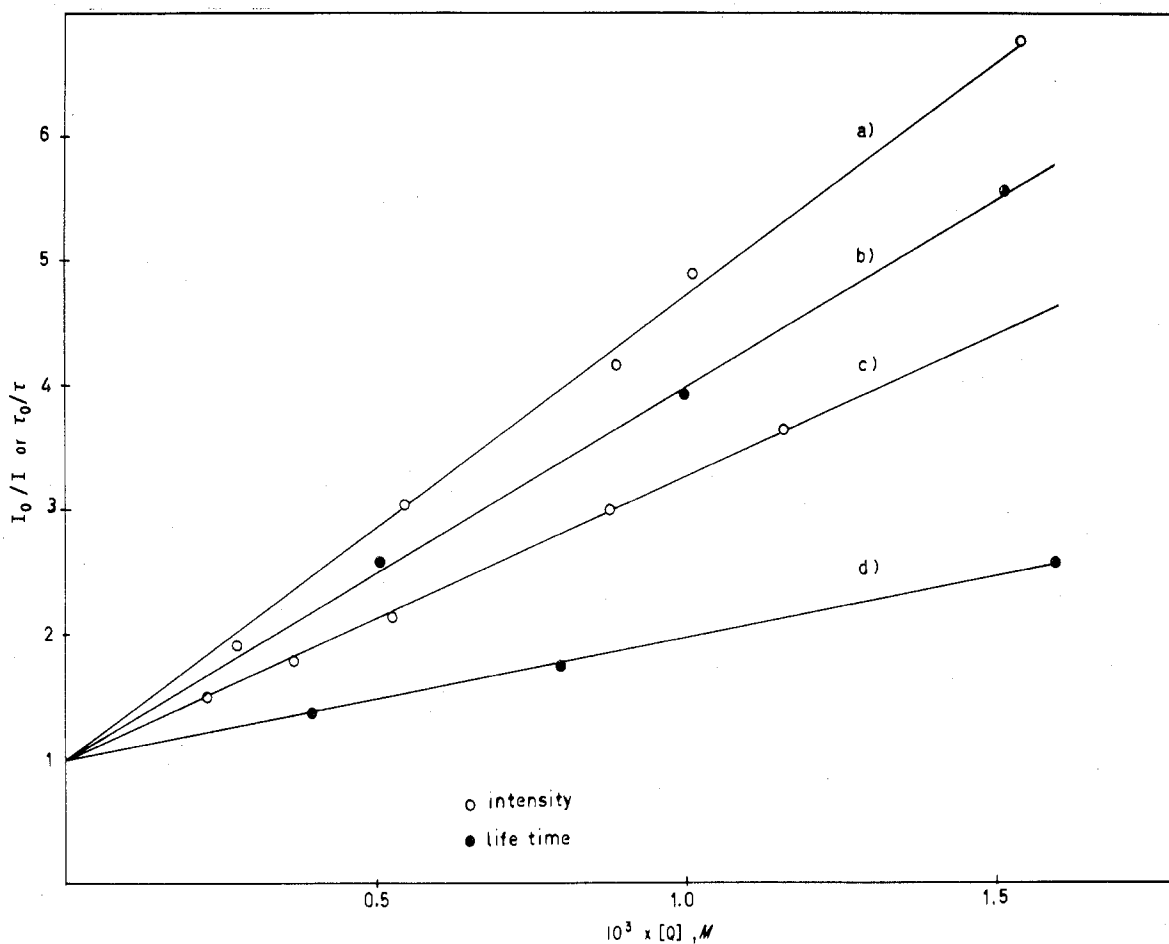
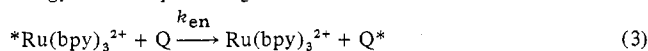


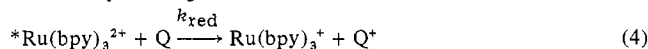
Figure 3. Stern-Volmer plots for the complexes: (a) $\text{Fe}(\text{CN})_5\text{NO}^{2-}$, $K_{\text{SV}} = 3.65 \times 10^3 \text{ M}^{-1}$; (b) $\text{Fe}(\text{CN})_5(\text{NMPz})^{2-}$, $K_{\text{SV}} = 2.95 \times 10^3 \text{ M}^{-1}$; (c) $\text{Fe}(\text{CN})_5(\text{imid})^{3-}$, $K_{\text{SV}} = 2.28 \times 10^3 \text{ M}^{-1}$; (d) $\text{Fe}(\text{CN})_5(\text{pzCO}_2)^{4-}$, $K_{\text{SV}} = 9.6 \times 10^2 \text{ M}^{-1}$; at 25 °C and $\mu = 0.50 \text{ M NaCl}$. τ_0 values used: for intensity measurements, 10^{-6} – $10^{-5} \text{ M Ru}(\text{bpy})_3^{2+}$, 0.5 M NaCl , $\tau_0 = 0.60 \mu\text{s}$; for lifetime measurements, $5 \times 10^{-4} \text{ M Ru}(\text{bpy})_3^{2+}$, 0.5 M NaCl , $\tau_0 = 0.56 \mu\text{s}$; $10^{-3} \text{ M Ru}(\text{bpy})_3^{2+}$, 0.5 M NaCl , $\mu_0 = 0.50 \mu\text{s}$.

included in Table II. The table is organized in order of increasing k_q . Quenching rate constants for a number of the free ligands were also determined in the course of this study. These results are presented in Table III.

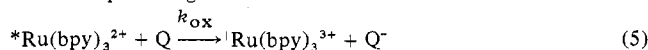
The quenching of the luminescence of tris(2,2'-bipyridine)ruthenium(II) by cyanide complexes of transition metal ions has recently been reported by Juris et al.⁶ and by Creutz and Sutin.⁵ In these systems, if one neglects the possibility of exciplex formation and static quenching,¹⁴ the possible quenching mechanisms are energy transfer (eq 3),¹⁴ in which energy-transfer quenching



reductive quenching

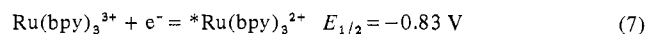
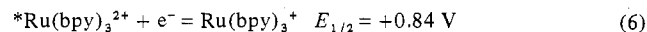


oxidative quenching

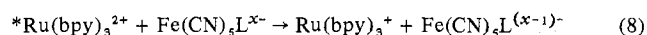


deexcitation of the $\text{Ru}(\text{bpy})_3^{2+}$ excited state ($*\text{Ru}(\text{bpy})_3^{2+}$) to the ground state is accompanied by excitation of the quencher Q to an excited state Q^* ,¹⁴ or oxidation-reduction reactions in which the excited state takes on (eq 4)^{5,6,15} or gives up (eq 5) an electron.¹⁶ Which of the quenching mechanisms predominates should depend on characteristics related to the electronic structures and redox properties of the quenchers and $*\text{Ru}(\text{bpy})_3^{2+}$. While a requisite for energy transfer seems to be the existence of (spin-forbidden) quencher absorption bands which overlap the emission spectrum of the $\text{Ru}(\text{bpy})_3^{2+}$, the

operation of an oxidative or reductive mechanism will be determined by the oxidizing or reducing properties of the quencher and the excited state. The excited-state energy of $*\text{Ru}(\text{bpy})_3^{2+}$ relevant to energy-transfer processes is generally taken to be $1.71 \mu\text{m}^{-1}$.⁶ The $E_{1/2}$ values for reduction and oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ in the excited state have recently been estimated as 0.84⁵ and 0.83 V,^{16,17} respectively, i.e.



For the first 10 entries in Table II, the quenching rate constants parallel the increasing reducing power of the complexes and approach the diffusion-controlled limit when $E^{\circ'}$ becomes smaller than $\sim 0.5 \text{ V}$. This rate dependence suggests that a reductive quenching mechanism (eq 8) is the



dominant one for the pentacyanoferrate(II) complexes. The dependence of quenching rate constant on the reducing power of the quencher is shown more clearly in Figure 4. Although the $\log k_q$ vs. $E^{\circ'}$ plot is rather nicely linear, there is probably no fundamental significance to the linearity or to the slope of the line because of the varying properties of the different reducing agents; the quenchers are of two charge types (3- and 4-) and, furthermore, are expected to differ in their inherent barriers to electron transfer (different self-exchange rates). It is, however, of considerable interest to compare the observed quenching rate constants with those expected for the proposed electron-transfer mechanism. The quenching rate

$M^{-1} s^{-1}$ reported for the $Co(CN)_6^{3-}$ ion.⁶ Since the complex does not absorb below $2.80 \mu m^{-1}$, an electron-transfer mechanism involving reduction of the pyrazine carboxylate ligand seems implicated.

For the $Ni(CN)_4^{2-}$, an energy-transfer mechanism has been proposed.⁸ The pentacyano(nitrosyl)ferrate complex presents the same difficulties reported for the *N*-methylpyrazinium ion case; energy transfer to the triplet of the charge-transfer excited state whose singlet-singlet transition is centered at $2.0 \mu m^{-1}$ may be possible. In addition, reduction of coordinated nitrosyl is also feasible; for the $Fe(CN)_5NO^{2-}$ couple $E_{1/2}$ is $-0.61 V^{27}$ so that oxidation of $*Ru(bpy)_3^{2+}$ is energetically favorable. Furthermore, there is evidence that the reorganization barrier for the bound NO^+/NO couple is small.²⁸ Thus in this system, as well, quenching may occur by parallel energy-transfer and oxidative pathways involving the ligand.

Acknowledgment. A fellowship (H.E.T.) from the Cons. Nacional de Desenv. Científico e Tecnológico (Brazil) and the invaluable assistance of Dr. William Clark (BNL) in the cyclic voltammetry experiments are gratefully acknowledged. This research was supported in part by the U.S. Energy Research and Development Administration. We thank Dr. Norman Sutin for helpful discussions.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Fe(CN)_5H_2O^{2-}$, 19413-97-9; $Fe(CN)_5(imid)^{2-}$, 61332-60-3; $Fe(CN)_5(\gamma\text{-picoline})^{2-}$, 61332-61-4; $Fe(CN)_5(py)^{2-}$, 61332-63-6; $Fe(CN)_5(isonicotinamide)^{2-}$, 61332-64-7; $Fe(CN)_5(pz)^{2-}$, 61332-65-8; $Fe(CN)_5(NMPz)^{-}$, 61363-44-8; $Fe(CN)_5(Me_2SO)^{2-}$, 61348-42-3; $Fe(CN)_5CO^{2-}$, 61332-62-5; $Fe(CN)_5CO^{3-}$, 17455-62-8; $Fe(CN)_5(Me_2SO)^{3-}$, 59422-09-2; $Fe(CN)_5(pzCO_2)^{4-}$, 59422-16-1; $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_5(imid)^{3-}$, 60105-88-6; $Fe(CN)_5py^{3-}$, 37475-75-5; $Fe(CN)_5(NMPz)^{2-}$, 40299-79-4; $Fe(CN)_5NO^{2-}$, 15078-28-1; Me_2SO , 67-68-5; imid, 288-32-4; py, 110-86-1; NMPz, 17066-96-5; $pzCO_2$, 61288-78-6; $Mo(CN)_8^{4-}$, 17923-49-8.

References and Notes

- (1) (a) University of São Paulo. (b) Brookhaven National Laboratory.
- (2) D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N.Y., 1964, p 237.
- (3) (a) J. M. Martins, work in progress; (b) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973); (c) H. E. Toma, J. M. Malin, and E. Giesbrecht, *ibid.*, **12**, 2084 (1973).
- (4) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 2080 (1973).
- (5) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 496 (1976).
- (6) A. Juris, M. T. Gandolfi, M. F. Manfrin, and V. Balzani, *J. Am. Chem. Soc.*, **98**, 1047 (1976).
- (7) The contribution of the ascorbic acid to the quenching of $Ru(bpy)_3^{2+}$ luminescence was found to be negligible under the conditions employed for the pentacyano(carbonyl)ferrate(II) complex.
- (8) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).
- (9) (a) D. H. Turner, G. W. Flynn, N. Sutin, and J. V. Beitz, *J. Am. Chem. Soc.*, **94**, 1554 (1972); (b) C.-T. Lin, W. Botzcher, M. Chou, C. Creutz, and N. Sutin, *ibid.*, **98**, 6536 (1976).
- (10) H. E. Toma and J. M. Malin, *J. Am. Chem. Soc.*, **97**, 288 (1975).
- (11) K. D. Schleinitz and G. von Lowis of Menar, *Z. Chem.*, **15**, 493 (1975).
- (12) H. Taube, *Surv. Prog. Chem.*, **6**, 1 (1973).
- (13) (a) The affinity comparisons are developed extensively in C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, **98**, 689 (1976), but the original data come from ref 13b-d. (b) R. J. Sundberg, R. F. Bryan, I. F. Taylor, Jr., and H. Taube, *J. Am. Chem. Soc.*, **96**, 381 (1974). (c) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972). (d) R. E. Shepherd and H. Taube, *ibid.*, **12**, 1392 (1973).
- (14) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
- (15) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6384 (1976).
- (16) (a) See C.-T. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976), and references cited therein and R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 286 (1976), and references cited therein. (b) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974).
- (17) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 2909 (1975).
- (18) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975).
- (19) A. Haim and N. Sutin, *Inorg. Chem.*, **15**, 476 (1976).
- (20) R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964).
- (21) The value used for the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ exchange was obtained by the extrapolation to $0.5 M K^+$ and $25^\circ C$ of data given by R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *Inorg. Chem.*, **6**, 672 (1967).
- (22) This value was obtained from a Marcus calculation from the $Fe(CN)_6^{4-}/Fe(CN)_5py^{2-}$ cross reaction: H. E. Toma and J. M. Malin, *J. Am. Chem. Soc.*, **97**, 288 (1975).
- (23) M. Chan, Ph.D. Thesis, Washington University, 1974.
- (24) K. B. Wiberg and T. P. Lewis, *J. Am. Chem. Soc.*, **92**, 7154 (1970).
- (25) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).
- (26) The reactions of $*Ru(bpy)_3^{2+}$ with the free ligands *N*-methylpyrazinium ion and pyrazinecarboxylic acid were investigated in 1 N sulfuric acid by flash photolysis using the frequency-doubled neodymium laser as excitation source. The only absorbance changes observed at 450 nm (λ_{max} for $Ru(bpy)_3^{2+}$) were the initial bleaching which accompanies excitation of $Ru(bpy)_3^{2+}$ to $*Ru(bpy)_3^{2+}$ and the subsequent restoration of 450-nm absorbance accompanying the return of the excited state to the ground state. Thus if $Ru(bpy)_3^{2+}$ and reduced free ligand are formed in the quenching process, "back-reaction" between the quenching products to make ground-state $Ru(bpy)_3^{2+}$ and the original quencher molecule must occur with a diffusion-controlled rate constant. This is a reasonable result as Bock, Meyer, and Whitten found the corresponding back-reactions with the radicals of *trans*-1,2-bis(*N*-methyl-4-pyridyl)ethylene and 1,1'-dimethyl-4,4'-bipyridine to be $(5-8) \times 10^9 M^{-1} s^{-1}$ in acetonitrile at 0.1 M ionic strength.²⁵
- (27) J. Masek, *Inorg. Chim. Acta, Rev.*, **3**, 99 (1969).
- (28) R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 894 (1975).

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

Charge-Transfer Photochemistry of Thiocyanatopentaamminecobalt(III)

MATO ORHANOVIĆ¹ and NORMAN SUTIN²

Received August 11, 1976

AIC60585F

The continuous photolysis of $Co(NH_3)_5SCN^{2+}$ has been studied as a function of excitation wavelength, temperature, and the composition of the medium. The major photolysis products are $Co(NH_3)_5NCS^{2+}$ and Co^{2+} with $Co(NH_3)_5H_2O^{3+}$ being formed in low yield. The relative yields of the major products are constant throughout the 550–250-nm spectral region suggesting that both are derived from the thiocyanate-to-cobalt charge-transfer excited state. The results are discussed in terms of a model in which photoisomerization of the sulfur-bonded thiocyanate results from kinetic factors in the electron-transfer collapse of the $Co(NH_3)_5^{2+} \cdot SCN$ radical pair while the retention of configuration results from the deactivation of the LMCT excited state without its net dissociation into radicals.

Introduction

Linkage isomerization of the "wrong-bonded" isomers of octahedral coordination complexes in aqueous solution generally occurs more rapidly than their aquation.²⁻⁴ The linkage isomerization reactions are generally dissociative: during the isomerization-aquation process a metal-ligand bond is broken,

an intermediate of reduced coordination number is formed, and effects associated with the solvent cage appear to be of primary importance in determining the products. In a recent study of the mercury(II)-catalyzed isomerization-aquation of the unstable sulfur-bonded isomer $Co(NH_3)_5SCN^{2+}$, the available data were surveyed and the cage effects discussed.⁴