

one-electron energies for the planar (linear) geometries to those of the bent models shows a slightly larger difference for SO₂ than for NO. It has been pointed out that substitution of a π acceptor in the equatorial positions of square pyramids containing the NO ligand at the axial position tends to stabilize the linear M–NO geometry.^{2b} This is also true for the tetrahedral models and those with L = CO predict linear M–NO and planar M–SO₂ moieties. It is indeed interesting, then, that with the one notable exception [Ni(NO)(N₃)(PPh)₂], all of the four-coordinate transition metal nitrosyls exhibit a nearly linear M–NO geometry^{2a,11–16} and tetrahedral environment about the metal atom. In contrast, the one known structure of a pseudotetrahedral mono(sulfur dioxide) complex (Ph₃P)₃PtSO₂⁸ has recently been reexamined⁹ and can be interpreted in terms of a bent M–SO₂. Further, the monomeric complex (Ph₃P)₂Pt(SO₂)₂ has recently been determined by single-crystal x-ray techniques¹⁷ and clearly contains two strongly bent M–SO₂ moieties, while all of the known bisnitrosyl–transition metal complexes exhibit linear or nearly linear M–NO geometries. In general it appears that the tendency to bend is greater for M–SO₂ complexes than for nitrosyls, a consequence of the smaller energy separation between π^* and σ^* orbitals in SO₂.

In conclusion, the SO₂ ligand promises to be at least as useful a probe to the bonding of transition metal complexes as NO has been and no doubt this ligand deserves considerably more attention than it has received in the past.

Acknowledgment. The authors are indebted to Dr. P. J. Hay for helpful discussions and for assistance in making some of the calculations.

Registry No. SO₂, 7446-09-5.

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Received June 3, 1975

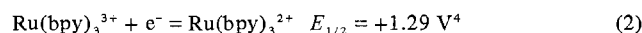
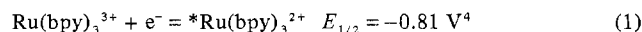
Electron-Transfer Reactions of Excited States. Reductive Quenching of the Tris(2,2'-bipyridine)ruthenium(II) Luminescence

AIC50522H

Sir:

Recently reported quenching^{1,2} and flash photolysis^{3,4} experiments have demonstrated the operation of electron-

transfer processes in the photochemistry of the charge-transfer excited state of tris(2,2'-bipyridine)ruthenium(II), *Ru(bpy)₃²⁺. To date these studies have dealt with reactions in which this excited state, which is a very strong reducing agent, gives up an electron to yield Ru(bpy)₃³⁺ and reduced quencher. The reduction potential for the couple Ru(bpy)₃³⁺–*Ru(bpy)₃²⁺ (eq 1) implicated in these processes has recently been

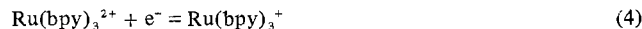


evaluated using rate comparisons.⁴ From eq 1 and 2 (where both $E_{1/2}$ values were determined in acetonitrile vs. SCE) the excited-state free energy of *Ru(bpy)₃²⁺ (eq 3) is calculated Ru(bpy)₃³⁺ = *Ru(bpy)₃²⁺



to be 2.10 V in acetonitrile. If the free energy content of the excited state is the same in water and acetonitrile, the above value may be combined with the E° value for the Ru(bpy)₃³⁺–Ru(bpy)₃²⁺ couple (1.27 V⁵) in water to give $E^\circ_{\text{III,II}} = -0.83$ V for the couple Ru(bpy)₃³⁺–*Ru(bpy)₃²⁺ in water. The latter is in excellent agreement with the value –0.84 V calculated from spectroscopic considerations.^{2,6}

The above processes involve loss of an electron from Ru(bpy)₃²⁺ or *Ru(bpy)₃²⁺ to give Ru(bpy)₃³⁺. The ion Ru(bpy)₃²⁺ may also take on an electron to give Ru(bpy)₃⁺. This reduction (eq 4) occurs electrochemically in *N,N*-dimethyl-



formamide at $E_{1/2} = -1.25$ V vs. SCE⁷ and in acetonitrile at $E_{1/2} = -1.33$ V⁸ vs. SCE. The reduction product (in which the added electron probably resides in ligand-centered π^* orbitals^{7–9}) has been observed in pulse radiolysis studies of aqueous Ru(bpy)₃²⁺ solutions as well.⁹ As is the one-electron oxidation product, the one-electron reduction product of Ru(bpy)₃²⁺ is, in principle, more readily attained from *Ru(bpy)₃²⁺ by the excited-state free energy.¹⁰ Combining the values from ref 4 and ref 8 for reactions 3 and 4, respectively, the $E_{1/2}$ for reduction of the excited state (eq 5)



is estimated to be +0.77 V vs. SCE in acetonitrile. Upon correction for the liquid junction potential,¹¹ the value +0.84 V relative to hydrogen is obtained as $E^\circ_{\text{III,I}}$ for the couple. Thus the charge-transfer excited state *Ru(bpy)₃²⁺ is expected to be a moderately strong oxidizing agent in addition to exhibiting the reducing properties already elucidated. In this paper, which describes the results of studies of the quenching of *Ru(bpy)₃²⁺ emission by several reducing agents, some observations which support this point of view are reported.

Emission intensity measurements were made on a Perkin-Elmer Model MPF4 spectrofluorimeter using exciting wavelengths between 452 and 530 nm with emission monitored at 608 nm and 10–20-nm slit widths. With the exception of Co(phen)₃²⁺, all of the quenchers had negligible absorbance at 608 nm and at the excitation wavelength used. For Co(phen)₃²⁺, absorption corrections were made according to published methods.¹² Solutions of Co(phen)₃²⁺ were prepared in situ with 1,10-phenanthroline in 25% excess. Hexammineruthenium(III) chloride (Matthey-Bishop, Inc.) was recrystallized according to published procedures.¹³ Hexammineruthenium(II) solutions were generated by reduction of hexammineruthenium(III) with europium(II).^{13,14} Europium(II) solutions were prepared by amalgamated zinc reduction of europium(III). Sodium dithionite (Fisher) was standardized using ferricyanide.¹⁵ All intensity measurements were made at 25.0 ± 0.1° using deaerated solutions except where noted.

Stern–Volmer plots for the quenchers used are shown in Figure 1. From these plots, K_{SV} , the Stern–Volmer constant,

Table I. Stern-Volmer and Rate Constants Obtained at 25.0° and 0.50 M Ionic Strength for the Quenching of Emission from *Ru(bpy)₃²⁺ ^a

Quencher	E°_Q, V	$k_{11}, M^{-1} \text{ sec}^{-1}$	$\bar{\nu}_{\text{min}}, \text{kK}$	K_{SV}, M^{-1}	$k_q, M^{-1} \text{ sec}^{-1}$	
					Obsd	Calcd ^y
Fe ²⁺	0.73 ^b	4.0 ^h	10.4, ^l 8.3	1.65	2.8×10^6 ^s	5.0×10^7
Fe ³⁺	0.73 ^b	4.0 ^h			2.3×10^9 ^t	1.8×10^9
Fe(CN) ₆ ⁴⁻	0.45 ^c	9.6×10^3 ⁱ	31.3, ^m 23.7	2070 ± 100	3.5×10^9 ^u	1.6×10^9
Fe(CN) ₆ ³⁻	0.45 ^c	9.6×10^3 ⁱ			6.5×10^9 ^t	3.8×10^{10}
Co(phen) ₃ ²⁺	0.42 ^d	5.0 ^j	18.7, 16.0, 11.3 ⁿ	490 ± 25	8.9×10^8 ^s	8.0×10^7
Co(phen) ₃ ³⁺	0.42 ^d	5.0 ^j			3.0×10^9 ^t	3.4×10^9
Ru(NH ₃) ₆ ²⁺	0.10 ^e	8.2×10^2 ^e	25.6, ^o 19.6	1410 ± 68	2.4×10^9 ^v	2.5×10^9
Ru(NH ₃) ₆ ³⁺	0.10 ^e	8.2×10^2 ^e		1860 ± 80	3.1×10^9 ^v	1.2×10^9
Eu(II)	-0.43 ^f	2.3×10^{-4} ^h	31.3, ^p 24.9	17.0 ± 1.0	2.8×10^7 ^w	2.5×10^9
Eu(III)	-0.43 ^f	2.3×10^{-4} ^h			1.3×10^5 ^t	5.3×10^5
S ₂ O ₄ ²⁻	-0.18 ^g		28.6 ^q	1450 ± 98	2.4×10^9 ^u	
Mo(CN) ₈ ⁴⁻	0.54 ^f		19.6 ^r		$(9 \pm 2) \times 10^9$ ^x	

^a Sodium chloride supporting electrolyte unless otherwise stated. E°_Q is for the half-reaction $Q^+ + e^- = Q$ (see text), while k_{11} is for the $Q^+ - Q$ electron exchange; $\bar{\nu}_{\text{min}}$ refers to the lowest energy transitions observed (or predicted) in the absorption spectrum of the quencher. ^b E. H. Swift, "A System of Chemical Analysis", Prentice-Hall, New York, N.Y., 1949, p 542. ^c I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945 (1935). ^d E. Paglia and C. Sironi, *Gazz. Chim. Ital.*, **87**, 1125 (1957). ^e T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968). ^f W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, Englewood Cliffs, N.J., 1964. ^g Reference 15. ^h J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). ⁱ R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *Inorg. Chem.*, **6**, 672 (1967). ^j R. Farina and R. G. Wilkins, *ibid.*, **7**, 514 (1968). ^k D. J. Meier and C. S. Garner, *J. Phys. Chem.*, **56**, 853 (1952). ^l F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960). ^m Assigned to the $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^3T_{1g}$ transitions: V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970, p 146. ⁿ By analogy with the spectrum of Co(bpy)₃²⁺ reported by R. A. Palmer and S. T. Piper, *Inorg. Chem.*, **5**, 864 (1966). ^o This work; tentatively assigned to the $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^3T_{1g}$ transitions by analogy with the spectra of other ruthenium(II) complexes reported by A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, N.Y., 1968, p 302. ^p F. D. Butement, *Trans. Faraday Soc.*, **44**, 617 (1948). The 24.9-kK band is for fluorescence observed from solids only. ^q This work. ^r J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963). ^s D. W. Marshall and N. Sutin, unpublished results (1975); $\mu = 0.64 M$, 0.5 M perchloric acid (sodium perchlorate). ^t From ref 6. ^u This work; 0.02 M acetate buffer, pH 5. ^v This work; 0.2 M acetate buffer, pH 5. ^w This work; 0.05 M hydrochloric acid. ^x F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Phys. Chem.*, **78**, 1374 (1974); $\mu = 0.01 M$. ^y The k_q values in this column were calculated from $k_{\text{calcd}} = k_{\text{act}} k_{\text{diff}} / (k_{\text{act}} + k_{\text{diff}})$ where k_{act} was obtained from the Marcus equation $k_{\text{act}} = (k_{11} k_{22} K_{12} f_{12})^{1/2}$ and k_{diff} from the Smoluchowski equation corrected for electrostatic effects. Values of K_{12} , the equilibrium constant for $Q^+ + *Ru(bpy)_3^{2+} = Q + Ru(bpy)_3^{3+}$ (oxidative quenching, k_{Ox}) or $Q + *Ru(bpy)_3^{2+} = Q^+ + Ru(bpy)_3^+$ (reductive quenching, k_{Red}), were calculated from the E°_Q values in Table I for the quenchers and $E^{\circ}_{\text{III}, *II} = -0.83 V$ for the $Ru(bpy)_3^{3+} - *Ru(bpy)_3^{2+}$ couple and $E^{\circ}_{*II, I} = +0.84 V$ for the $*Ru(bpy)_3^{2+} - Ru(bpy)_3^+$ couple. For both the above couples involving the excited state k_{22} (the electron exchange rate constant at 25°) was assumed to be $10^9 M^{-1} \text{ sec}^{-1}$.

is calculated from the slope, and k_q , the quenching rate constant, is calculated from $K_{\text{SV}} = k_q \tau_0^{-1}$, using τ_0 (excited-state lifetime in the absence of quencher) = $6.0 \times 10^{-7} \text{ sec}$.² From the linearity of the Stern-Volmer plots it is evident that contributions from static quenching are negligible for these quenchers in the region studied. For ferrocyanide ion this conclusion is further supported by the results obtained for air-saturated solutions. The ratio $K_{\text{SV,air}}/K_{\text{SV,Ar}}$ (Stern-Volmer constants measured for air- and argon-saturated solutions, respectively) is 0.68 in good agreement with the value 0.65 obtained for $I_{0,\text{air}}/I_{0,\text{Ar}}$ under these conditions. The K_{SV} values determined in this study were independent of both exciting wavelength and light intensity. The Eu(II)-Ru(bpy)₃²⁺ solutions were moderately photosensitive, the luminescence intensity decaying ~10% over 1-2 min in the spectrofluorimeter. The spectrum of a solution subjected to prolonged photolysis ($\lambda \geq 450 \text{ nm}$) with a 450-W xenon lamp had a maximum at 466 nm (rather than at 452 nm before photolysis).

In Table I are summarized K_{SV} and k_q values obtained for Fe(CN)₆⁴⁻, Co(phen)₃²⁺, Ru(NH₃)₆²⁺, Eu(II), and S₂O₄²⁻, the reducing agents (Q) used in this study. Values obtained by other workers for Fe²⁺ and Mo(CN)₈⁴⁻ are included in the table as these two ions are also reducing agents. Included for comparison are k_q values for the quenching agents in their oxidized forms (Q⁺). The pairs of quenchers are arranged by decreasing E°_Q (second column) for the $Q^+ + e^- = Q$ half-reaction, with the entry for Q preceding that for Q⁺. Values of k_{11} , the electron self-exchange rate constant at 25°, are included for the $Q^+ - Q$ couples (third column). Finally, spectral data concerning the position(s) of the lowest energy excited states ($\bar{\nu}_{\text{min}}$, fourth column) available to the reducing agent quenchers are tabulated.

Neglecting exciplex formation and static quenching (for which there is no evidence under the conditions used in these

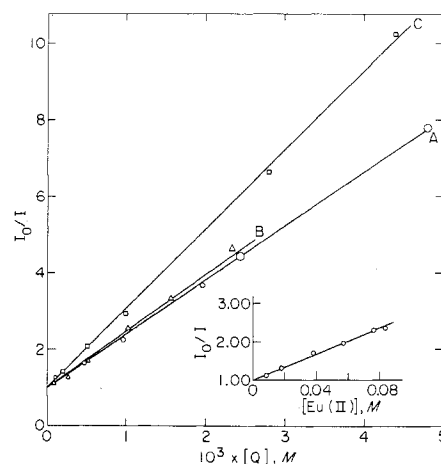
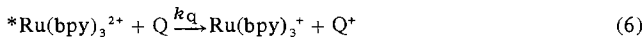


Figure 1. Stern-Volmer plots for quenching of the *Ru(bpy)₃²⁺ emission at 25° and 0.5 M ionic strength (sodium chloride) by the quencher Q: (A) Q = Ru(NH₃)₆²⁺; (B) Q = S₂O₄²⁻; (C) Q = Fe(CN)₆⁴⁻. Inset shows the results for Eu(II).

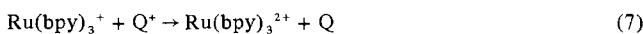
studies), energy-transfer and electron-transfer processes are the most likely mechanisms by which the emission of *Ru(bpy)₃²⁺ may be quenched.¹⁶ We first consider to what extent energy transfer by the collisional electron-exchange mechanism described by Dexter¹⁷ could be responsible for the quenching observed in this study. In Dexter's treatment the quenching probability is determined by the extent of overlap of the donor emission and the (spin-forbidden) absorption bands of the acceptor. It thus becomes necessary to consider quencher transitions overlapping the *Ru(bpy)₃²⁺ emission which is maximal at 630 nm (15.8 kK, water, 25°).¹⁸ Transitions to the ²T₁ and ²T₂ states are found in the absorption spectrum of Co(bpy)₃²⁺ (see Table I) at ~16 kK. The spectrum of

Co(phen) $_3^{2+}$ is not expected to differ substantially; thus this complex is likely to provide a rather good energy acceptor for $^*Ru(bpy)_3^{2+}$. The other reducing agents used as quenchers in this study were chosen because they were not expected to quench very efficiently by energy-transfer mechanisms. None absorbs detectably at 630 nm and so "vertical" energy transfer would have to occur to unobserved states of the quencher. Such states are normally accessible only via intersystem crossing from those produced directly by light absorption. For $Fe(CN)_6^{4-}$ and $Ru(NH_3)_6^{2+}$ no such unobserved states should exist if the spectra (Table I) have been correctly assigned. Therefore, for these two, with acceptor transition energies of 23.7 and 19.6 kK, respectively, energy transfer should be very inefficient. The same conclusion applies for Eu(II) if the lowest energy transition available is that at 31.3 kK (Table I). The band observed at 28.6 kK in the spectrum of dithionite ion is probably associated with a singlet-to-singlet charge-transfer transition. The position of the corresponding triplet transition is unknown, but a singlet-triplet energy separation of ~ 13 kK required for overlap of the dithionite singlet-to-triplet charge transfer transition with the emission of $^*Ru(bpy)_3^{2+}$ seems unreasonably large; efficient energy transfer from $^*Ru(bpy)_3^{2+}$ to $S_2O_4^{2-}$ also therefore seems quite unlikely. For $Fe(H_2O)_6^{2+}$ no transitions occur in the spectral range relevant to Dexter's model, but transitions at much lower energy (Table I) could be involved if the spectral overlap requirement is relaxed for exothermic energy transfers.¹⁸ For octacyanomolybdate(IV), the lowest energy transition (19.6 kK) observed is again rather high in energy for highly efficient energy-transfer quenching. It thus appears that, with the exception of Co(phen) $_3^{2+}$, the absorption spectra of the reducing agents considered in this study do not overlap the emission spectrum of $^*Ru(bpy)_3^{2+}$; consequently an energy-transfer mechanism of the kind described by Dexter is precluded for these systems.

It is proposed that the dominant quenching mechanism for at least some of the reducing agent quenchers in Table I involves the electron-transfer reaction



which yields oxidized quencher and $Ru(bpy)_3^+$. No net reaction is likely to be observed in these systems since the back-reaction



should occur with a very high rate constant as a consequence of its large equilibrium constant; $Ru(bpy)_3^+$ is a very strong reducing agent.^{7,8} Support for the proposed reductive electron-transfer quenching mechanism comes from the relative magnitudes of the quenching rate constants in Table I. The k_q values obtained for $Ru(NH_3)_6^{2+}$, $S_2O_4^{2-}$, and $Fe(CN)_6^{4-}$ are very similar ($(2.4-3.5) \times 10^9 M^{-1} sec^{-1}$) while that for Eu(II) is about 100 times smaller. The same rate pattern has been observed for outer-sphere reduction of horse heart ferricytochrome *c*: at 0.1–0.2 *M* ionic strength and neutral pH the rate constants k for reduction by $Ru(NH_3)_6^{2+}$, $S_2O_4^{2-}$, and $Fe(CN)_6^{4-}$ lie in the range $(2.6-3.8) \times 10^4 M^{-1} sec^{-1}$.²⁰ At 1.0 *M* ionic strength and acid pH the rate constant for reduction by $Ru(NH_3)_6^{2+}$ is 100 times greater than that for Eu(II).²¹ Furthermore the k_q patterns follow those observed for reduction of tris(2,2'-bipyridine)osmium(III) for which the E° value of 0.878 V²² is similar to that predicted for the $^*Ru(bpy)_3^{2+}$ – $Ru(bpy)_3^+$ couple: for reduction by $Ru(NH_3)_6^{2+}$ in 0.5 *M* sodium chloride $k > 1 \times 10^9 M^{-1} sec^{-1}$;⁶ for reduction by $Fe(CN)_6^{4-}$ in 0.5 *M* perchloric acid $k > 10^8 M^{-1} sec^{-1}$;²³ for reduction by Fe^{2+} in 0.5 *M* HClO₄ $k = 1.4 \times 10^3 M^{-1} sec^{-1}$;²³ and for reduction by $Mo(CN)_8^{4-}$ in 0.5 *M* sodium nitrate at 10° $k = 4 \times 10^9 M^{-1} sec^{-1}$.²⁴ Although detailed discussion of k_q patterns is somewhat premature, it

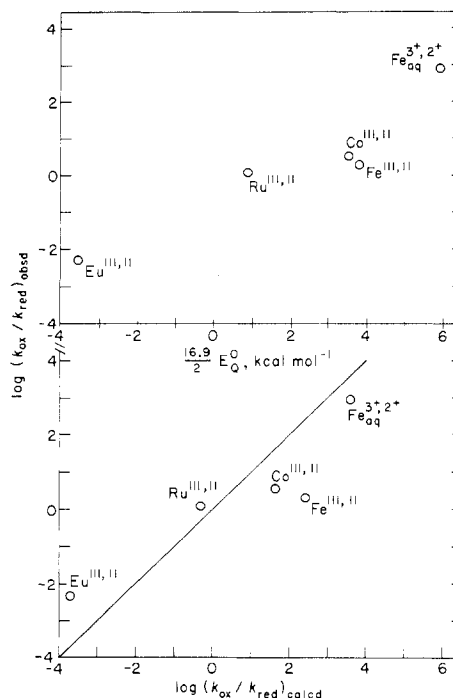


Figure 2. Top: plot of $\log(k_{Ox}/k_{Red})_{obsd}$ vs. $8.45E^\circ_Q$, where k_{Ox} is k_q for the oxidized form of the quencher (Q^+) and k_{Red} is k_q for the reduced form of the quencher (Q). All values were taken from Table I. Bottom: plot of observed values of $\log(k_{Ox}/k_{Red})$ vs. those calculated on the basis of electron-transfer quenching as described in Table I, footnote y.

seems a rather striking coincidence that the patterns in k_q observed here should parallel so faithfully the patterns found for outer-sphere reduction reactions if the quenching mechanism for these systems does not involve electron transfer.

It is interesting to compare the rate constants for oxidative (k_{Ox}) and reductive (k_{Red}) quenching by a given couple with reduction potential E°_Q . If the driving force for the electron-transfer quenching by both oxidized and reduced quencher is not too large and the reactions are not diffusion controlled, it can be shown that

$$\log \left[\frac{k_{Ox}}{k_{Red}} \right] \propto 2E^\circ_Q - E^\circ_{III,*II} - E^\circ_{*II,I} \quad (8)$$

which is a limiting form of the Marcus equation when the exchange rates for the $Ru(bpy)_3^{3+}$ – $^*Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_3^{2+}$ – $Ru(bpy)_3^+$ couples are identical. This approximation suggests the plot shown at the top of Figure 2. It will be seen that the rate ratios do indeed correlate with E°_Q . Further, as expected from eq 8 and the E° values -0.83 and $+0.84$ V for $E^\circ_{III,*II}$ (eq 1) and $E^\circ_{*II,I}$ (eq 5) calculated in the introductory paragraphs, $\log(k_{Ox}/k_{Red})$ approaches zero near $E^\circ_Q = 0$. Equation 8 neglects the Marcus f factors (which do not cancel when the ratio of quenching constants is taken) and does not allow for the possibility that the quenching reactions may be diffusion controlled. These factors are taken into account in calculating the last column of Table I and in constructing the lower portion of Figure 2. The line drawn there is for the theoretical slope of unity and the observed and calculated rate ratios are seen to be in good agreement. An exception is the rate of quenching by Co(phen) $_3^{2+}$ which appears to be higher than predicted; this may be due to a contribution from an energy-transfer path as discussed above.

In summary, the charge-transfer excited state $^*Ru(bpy)_3^{2+}$ appears to be more reactive toward both oxidation and reduction reactions than the ground-state molecule. The zinc uroporphyrin triplet excited state has also been shown to

undergo both oxidation and reduction reactions.²⁵ Thus the behavior of $^*Ru(bpy)_3^{2+}$ is not without precedent, but the reductive quenching mechanism reported here has not been previously proposed for systems of this kind.

Acknowledgment. This research was supported by the U.S. Energy Research and Development Administration.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Fe(CN)_6^{4-}$, 13408-63-4; $Co(phen)_3^{2+}$, 16788-34-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Eu(II)$, 16910-54-6; $S_2O_4^{2-}$, 14844-07-6.

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Received July 22, 1975

Stereoselectivity in Electron-Transfer Reactions

AIC506071

Sir:

Despite the vast amount of information available on electron-transfer reactions involving transition metal systems, relatively little is known about possible stereoselectivity in such reactions between pairs of chiral complexes. The use of

optically active reagents has generally been restricted to self-exchange reactions, where racemization serves as a convenient monitor of the redox process.^{1,2} For example, racemization accompanies self-exchange in aqueous solution between optically inert (+)-D-[Co(phen)₃]³⁺ and labile [Co(phen)₃]²⁺ (phen = 1,10-phenanthroline) and has been implicitly attributed to a lack of stereopreference.³ Paradoxically (+)-D-[Co(phen)₃]³⁺ was recently reported by Sutter and Hunt⁴ to react with labile [Cr(phen)₃]²⁺ to yield (-)-D-[Cr(phen)₃]³⁺. We note that it is possible to rationalize these apparently contradictory results if stereoselectivity is a rather general phenomenon, requiring electron transfer to occur preferentially between reactants of opposite absolute configuration. Although operative, this preference would go undetected in self-exchange reactions—since inversion occurs in both the forward and reverse steps. The model is also consistent with the ΔC_3 and ΔC_3 absolute configurations assigned (+)-D-[Co(phen)₃]³⁺ and (-)-D-[Cr(phen)₃]³⁺ from circular dichroism studies.⁵ However, in a kinetic study of several redox systems involving non-self-exchange situations, Grossman and Wilkins⁶ found no evidence for stereopreference. Inspection of the reactions examined suggests that stereoselectivity may require systems containing π -acceptor ligands (e.g., phen) and/or reductants involving strongly reducing metals (e.g., Cr²⁺). This model would not specify a particular isomeric preference, although recent NMR studies by La Mar and co-workers^{7,8} suggest electron transfer might then be most facile between reactants with the same chirality.

Our research objectives have been to resolve these anomalies and delineate the extent and nature of redox stereospecificity. The initial experiments involved repeating the work of Sutter and Hunt⁴ on the (+)-D-[Co(phen)₃]³⁺ + [Cr(phen)₃]²⁺ reaction. Despite numerous attempts, following the experimental procedure outlined by the authors, we have been unable to observe any induction of optical activity in the [Cr(phen)₃]³⁺ product. Rotation measurements were recorded at 546 nm immediately after reaction using a Bendix Model 1144 automatic polarimeter with digital readout to $\pm 0.0002^\circ$. A small positive rotation was initially observed after reaction, consistent with the slight excess of (+)-D-[Co(phen)₃]³⁺ employed in each instance. This activity was subsequently lost at a rate consonant with expected [Co(phen)₃]²⁺-[Co(phen)₃]³⁺ self-exchange. It was verified that [Cr(phen)₃]³⁺ is optically stable in the presence of [Co(phen)₃]²⁺, using a genuine sample of (+)-D-[Cr(phen)₃]³⁺.⁹ As noted by Sutter and Hunt, the presence of redox stereoselectivity is not a sufficient condition for the experimental observation of the phenomenon. It is also essential that [Cr(phen)₃]²⁺ inversion proceed more rapidly than electron transfer. To enhance the probability of this latter condition being met, the reaction was also followed at substantially lower reagent concentrations than those reported. Even when solutions 10^{-4} M in (+)-D-[Co(phen)₃]³⁺ and [Cr(phen)₃]²⁺ were mixed, no resultant induction was observed. Assuming the reported formation of 92% (-)-D-[Cr(phen)₃]³⁺, a final rotation of -0.067° (5-cm cell 546 nm) was anticipated, a value well within the capabilities of the instrument available. Furthermore, the reaction has been repeated without success at elevated temperatures (up to 70 °C) to take advantage of a probable activation enthalpy difference for the redox and racemization processes. Identical runs carried out at room temperature in 50% ethanol and 50% DMSO met with a similar lack of success. We conclude that the previous communication on this system is most probably in error.¹⁰

We have extended our present investigation to other outer-sphere redox reactions of the type described. The systems examined are collated in Table I. In no instance was a successful optical induction achieved. Reactions 5-7 provide