Tris(2,2′-bipyridine)ruthenium(II) Sensitized Reactions of Some Oxalato Complexes

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Abstract: Aqueous $K_3Fe(C_2O_4)_3$, $K_3Cr(C_2O_4)_3$, and $K_3Co(C_2O_4)_3$ are efficient quenchers of the emission from triplet state $Ru(bipy)_3{}^{2+}$. In the $Cr(C_2O_4)_3{}^{3-}$ and $Co(C_2O_4)_3{}^{3-}$ cases, the quenching is shown to proceed *via* an encounter mechanism and at about the diffusion controlled rate; the same is probably true for $Fe(C_2O_4)_2{}^{-}$, the principal species present in the $K_3Fe(C_2O_4)_3$ solutions. $Ru(bipy)_3{}^{2+}$ sensitizes the redox decomposition of $Co(C_2O_4)_3{}^{3-}$ in 0.1 N H_2SO_4, with a limiting yield of ~0.85; in 1.0 N H_2SO_4, $Ru(bipy)_3{}^{3+}$ is produced with a yield of ~0.7. It is suggested that ${}^3Ru(bipy)_3{}^{2+}$ is acting as a one-electron reducing agent in both cases. In the case of $Cr(C_2O_4)_3{}^{3-}$, sensitized racemization occurs, probably through conventional excitation energy transfer, with a limiting yield of ~0.03, or 30–40% of the direct photolysis yield. Redox decomposition of $Fe(C_2O_4)_2{}^{-}$ is not appreciably sensitized. Possible explanations of this last finding are discussed and also some general aspects of the sensitized photochemistry of Co(III) complexes.

We reported recently[1] on the use of a new sensitizer, $Ru(bipy)_3{}^{2+}$ (where bipy denotes 2,2′-bipyridine), in the study of the sensitized photochemistry of certain transition metal complex ions. The principal application described was to the sensitized aquation of aqueous $PtCl_4{}^{2-}$. Additional studies with various Co(III) complexes have since been reported.[2-4]

This sensitizer has several useful attributes. (1) It is water soluble and thus well suited for studies in aqueous media. (2) It absorbs strongly in the visible (ϵ ~14,000 M^{-1} cm^{-1} at 450 nm) so that quite dilute solutions can be used. As a consequence, it is easy to determine whether any appreciable amount of decomposition of the sensitizer occurs, relative to the amount of sensitized reaction. (3) The $Ru(bipy)_3{}^{2+}$ donor is reasonably photostable toward light in the visible and near-uv wavelength region so that direct photolysis presents no complication.[5] (4) The donor excited state is a low-lying triplet charge transfer (^{3}CT) state having the convenient energy of 17.8 kK or 51 kcal mol^{-1} above the ground state.[6] (6) The donor state shows a strong yellow-orange luminescence in room temperature aqueous solution, with a lifetime of ~0.7 μsec.[1] The emission is noticeably but not strongly quenched by dissolved oxygen. The presence of this emission makes it possible to determine qualitatively whether sensitization may be occurring in a given system by observing whether there is any emission quenching. The quantitative comparison of the quenching and sensitization yield dependencies on the acceptor and on oxygen concentrations provides a diagnostic test of whether the emitting and the sensitizing state are the same. Knowledge of the emission lifetime makes possible calculation of the bimolecular quenching rate constant as a means of characterizing a given quencher.

The above combination of properties seems to make $Ru(bipy)_3{}^{2+}$ and related complexes[5b,c] very useful in sensitization studies involving coordination compounds. Organic sensitizers, the only present alternative, often suffer in lack of water solubility, lack of strong absorption bands in the visible or near-uv, or lack of phosphorescence emission in room temperature solution. Their use in sensitization studies can therefore be difficult.[7,8]

The present paper details our study of $Ru(bipy)_3{}^{2+}$ as a sensitizer for various transition metal oxalato complexes. We conclude, in brief, that sensitized racemization of d-$Cr(C_2O_4)_3{}^{3-}$ occurs *via* excitation energy transfer, while the sensitized redox decomposition of $Co(C_2O_4)_3{}^{3-}$ probably takes place through the action of the donor as a one-electron reductant. The labile iron(III) oxalato complexes exhibit a yet different behavior in that the net reaction is one of quenching only.

Experimental Section

Materials and Equipment. $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ was prepared by the method of Hatchard and Parker.[9] $K_3Co(C_2O_4)_3 \cdot 3H_2O$ and $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ were prepared by standard procedures;[10] also, a commercial sample of the former complex (Alfa Inorganics) recrystallized from water by the addition of methanol exhibited the same sensitized quantum yields as did our material. The d isomer of $Cr(C_2O_4)_3{}^{3-}$ was obtained with the use of strychnine sulfate.[11] Finally, $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$ was purchased from the G. Frederick Smith Chemical Co. and was used without further purification. The visible absorption spectra of all samples agreed well with the published ones.

Solutions containing $Ru(bipy)_3{}^{3+}$ were prepared by the oxidation of $Ru(bipy)_3{}^{2+}$ in 1 N H_2SO_4 by excess PbO_2. The solutions were filtered after a few minutes, and the filtrate was used in making up the desired mixtures.

The light sources comprised a PEK 200-W high-pressure mercury arc lamp, a 1000-W Hanovia Xe arc lamp, a G.E. G8T5 lamp, and

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[1] J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 1800 (1971).

[2] P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 3635 (1972).

[3] H. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

[4] A. W. Adamson, Abstracts of the XIV International Conference on Coordination Chemistry, Toronto, June, 1972.

[5] (a) H. Gafney and A. W. Adamson, unpublished observations. (b) J. W. Addington and J. N. Demas, manuscript in preparation. (c) J. N. Demas, Abstracts for the Eighth MARM Symposia Program, Washington, D. C., Jan 1973.

[6] J. N. Demas and C. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 2841 (1971).

[7] See H. Gafney and A. W. Adamson, *J. Phys. Chem.*, **76**, 1105 (1972).

[8] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[9] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., London*, **235**, 518 (1956).

[10] H. W. Booth, Ed., "Inorganic Synthesis," Vol. 1, McGraw-Hill, New York, N. Y., 1939, p 37.

[11] S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).

an ionized argon laser equipped with an intracavity prism wavelength selector and light intensity stabilizer (Coherent Radiation Laboratories, Model 52B). The first source was used to supply 450-nm radiation; this wavelength region was isolated with the use of a narrow band-pass Bausch and Lomb interference filter (10-nm width at 50% of maximum transmission). A Corning CS 3-72 glass filter was used to eliminate uv light; a 5-cm path length of water was interposed between the lamp and the filters to minimize possible thermal damage to the latter. The second lamp was used to supply 436-nm radiation, this line being isolated by means of a monochromator set to a 9-nm band pass. The purity of the 253.7-nm line from the G.E. lamp was improved by passing the radiation through a Corning CS 7-54 uv filter. The 457.9-nm laser line was selected when this source was used. A 2-in. focal length lens was placed in the laser beam to increase the beam's size from ~2 to ~1 cm diameter, almost retaining collimation. No filters were necessary. Unless otherwise specified, the sensitization experiments were made with the use of 450-, 436-, or 457.9-nm radiation.

The incident light intensities were generally as follows, in einsteins $\sec^{-1}$. The values for the 450- and the 436-nm irradiations were $\sim 5 \times 10^{-8}$; the intensity of the 253.7-nm radiation was $\sim 2 \times 10^{-8}$. The laser was set at $\sim 5 \times 10^{-8}$ for the experiments with $Co(C_2O_4)_3{}^{3-}$ and at $\sim 2 \times 10^{-7}$ for the direct photolyses of $Ru(bipy)_3{}^{2+}$.

Quenching studies based on emission intensity were carried out with the use of an Aminco spectrofluorimeter equipped with a 200-W Hg-Xe arc lamp and a 1P28 phototube or on specially assembled equipment to be described elsewhere.[5b] Excitation was at 436 or at 450 nm and the emission was monitored at 585 or at 650 nm. Excitation and emission band passes were 3–20 nm. Right angle viewing was employed. All measurements were carried out on deoxygenated samples, in 1-cm² Pyrex cells, unless otherwise specified. In the case of samples containing $Co(C_2O_4)_3{}^{3-}$, photoinduced decomposition was rapid enough that some correction for it was necessary. The emission intensity was, in these cases, followed with time, and extrapolated to the beginning of the measurement. Oxygen concentrations were estimated from Henry's Law.

All intensity quenching data are corrected by means of the equation

$$\left(\frac{\theta_0}{\theta}\right)_{\mathrm{corr}} = \left(\frac{\theta_0}{\theta}\right)_{\mathrm{app}}\left[\frac{1 - 10^{-(A_{\mathrm{D}}+A_{\mathrm{Q}})l}}{1 - 10^{-A_{\mathrm{D}}l}}\right]\frac{A_{\mathrm{D}}10^{-A_{\mathrm{Q}}'l'}}{A_{\mathrm{D}} + A_{\mathrm{Q}}} \qquad (1)$$

where $(\theta_0/\theta)_{\mathrm{app}}$ is the observed ratio of luminescence intensity in an unquenched sample to that in a quenched one, and $(\theta_0/\theta)_{\mathrm{corr}}$ is the ratio corrected for trivial absorption of the incident light by the quencher and for trivial absorption of the emitted light by the solution. A_{D} and A_{Q} are the absorbances per centimeter at the exciting wavelength for the donor and the quencher, respectively; A_{Q}' is the absorbance per centimeter of the quencher at the emission wavelength monitored, l is the excitation path length within the cell (1 cm), and l' is the effective path length for reabsorption of the emitted radiation, estimated to be 0.5 cm. These corrections amounted to 10–20% at the higher quencher concentrations in the case of $Co(C_2O_4)_3{}^{3-}$, somewhat less in the case of $Cr(C_2O_4)_3{}^{3-}$, and were negligible in the case of the iron(III) oxalate systems. Errors in this correction and errors arising from the finite band pass of the excitation and emission monochromators may make our Stern–Volmer quenching constants uncertain by 10–20% at the most.

Quenching studies by lifetime measurements were carried out by means of a 100-kW peak power N_2 laser of ~5 nsec pulse duration as the excitation source. The emitted radiation was passed through a Bausch and Lomb 0.50-m grating monochromator set at 580 nm (the apparent emission maximum) and allowed to fall on an RCA 931 photomultiplier. The phototube signal, monitored through a 50 ohm load resistor, was displayed on a high-speed oscilloscope, and the decay curves, photographed on Polaroid film, were fitted to a single exponential curve by replotting the data in semilogarithmic form. Mean lifetimes, τ, are reported. Agreement between results for a single sample was usually better than 10%, and we estimate our Stern–Volmer constants to be precise to about this degree.

The photosensitized racemization of d-$Cr(C_2O_4)_3{}^{3-}$ was monitored in 10-cm cells by means of a Perkin-Elmer 141 spectropolarimeter using the Hg 578-nm line as the analyzing wavelength. A 10-cm photolysis path was used. Samples were thermostated at 20.0°. Because of the rapid thermal racemization at this temperature, a blank of unirradiated ("dark") solution was necessary; the procedure for calculating quantum yields is that reported previously.[11]

All absorption measurements were made on a Cary Model 14 or a Beckman DU spectrophotometer. The photolysis cells were of either 2- or 5-cm path length (~15-ml capacity except 254 nm which were ~6-ml capacity) and could be thermostated by means of water circulated through an outer jacket. During all photolyses, a vigorous stream of N_2 or of Ar was bubbled through the solution, to effect thorough mixing and to keep out oxygen. In the case of the sensitization experiments the bubbling was begun at least 5 min before photolysis, to remove most of the dissolved oxygen.

Procedures. Reineckate actinometry[12] was used for all visible intensity measurements except when laser power levels greater than 50 mW were used. In this case, the internal power reading system of the laser unit was used. Its output was found to be linear with actinometrically measured intensities to within 1%, over at least a tenfold range at lower power levels (and has since been found to be linear at the higher power levels, using a beam splitting technique[5a]). The procedure consisted of measuring the beam intensity actinometrically at a low power level (where secondary photolysis was not important) and determining the actual intensity used from the ratio of the power outputs, as read by means of a high-resolution voltmeter. Aqueous $K_3Co(C_2O_4)_3$ was used as the actinometer for 253.7-nm irradiations; the disappearance yield was taken as 0.8.

Analytical procedures were as follows. The sensitized production of Fe^{2+} from aqueous $K_3Fe(C_2O_4)_3$ in 0.1 N H_2SO_4 was determined by means of the usual 1,10-phenanthroline spectrophotometric method, taking the extinction coefficient of the produced Fe(II) complex to be 1.11×10^4 M^{-1} cm^{-1} at 510 nm.[9] A dark solution was used in the reference beam of the spectrophotometer. $Co(C_2O_4)_3{}^{3-}$ concentrations were determined spectrophotometrically from the absorbance at 605 nm, a region where Co^{2+} absorbs negligibly (even in the presence of small concentrations of free oxalate ion). Photodecompositions were allowed to go to 20–75% completion for good accuracy since no complications due to secondary photolysis or to sensitizer quenching by Co^{2+} were present. However, since the transmission of the sample changed significantly during the photolysis, in the case of the unsensitized photolyses, the procedure of Spees and Adamson[11] was used in evaluating the direct photolysis yields. The solutions were generally 0.1 N in H_2SO_4, to prevent precipitation of CoC_2O_4; a small correction was necessary for the dark, acid-catalyzed decomposition, which amounted to about 1% in the apparent yield, ϕ_{app}.

The photosensitivity study of $Ru(bipy)_3{}^{2+}$ was carried out fluorimetrically using 457.9-nm laser irradiation. The luminescence intensity of an optically dilute (absorbance ~0.01) solution was monitored by means of an RCA 931 photomultiplier tube which viewed the photolysis cell at right angles to the irradiating beam. Corning CS 3-68 and CS 3-67 filters and a Bausch and Lomb 580 nm, 10 nm band-pass interference filter were used to reduce the intensity of light scattered from the laser beam and also to reduce intensity of the emitted light which reached the photomultiplier. The data were corrected for the scattered light intensity, about 1% of that of the initial emission intensity.

Under the conditions of the above experiments the luminescence intensity should decay exponentially with time since all probable photolysis products are not expected to emit. The rate constant for this decay is given by $k = 2.303I_0\phi\epsilon l/V$ where I_0 is the excitation intensity, ϵ is the extinction coefficient of $Ru(bipy)_3{}^{2+}$ at 457.9 nm, V is the photolyzed volume, and l is the optical path length of the photolysis cell. Linear plots of $\ln \theta$ *vs.* time were in fact obtained, where θ is the relative emission intensity.

In certain experiments $Ru(bipy)_3{}^{3+}$ was formed, and its concentration was determined from absorbance measurements at 450 nm, at which wavelength $\epsilon_{(\mathrm{RuII})}$ is 14,000 M^{-1} cm^{-1} and $\epsilon_{\mathrm{Ru(III)}}$ is only ~500 M^{-1} cm^{-1}, where Ru(II) and Ru(III) denote the 2,2′-bipyridine complexes. $Ru(bipy)_3{}^{3+}$ is somewhat unstable toward reduction to $Ru(bipy)_3{}^{2+}$ in the media in which the former was photoproduced. The halftime is about 1 hr in 1 N H_2SO_4, for example. The absorbance of irradiated solutions was therefore followed for sufficient time to allow accurate extrapolation to the midpoint of the photolysis; we assume this to be the composite absorbance, A_{irr}, due to $Ru(bipy)_3{}^{3+}$ and $Ru(bipy)_3{}^{2+}$ at the end of the photolysis were there no thermal reaction. The total ruthenium complex concentration was known, of course, but as a check the absorbance of irradiated solutions was also determined after the addition of a small amount of solid $K_2C_2O_4 \cdot H_2O$ to the cuvette, which greatly accelerated the reduction back to $Ru(bipy)_3{}^{2+}$, to give A_0, the absorbance with all ruthenium present as the divalent complex. The quotient $(A_0 - A_{\mathrm{irr}})/(\epsilon_{\mathrm{Ru(II)}} - \epsilon_{\mathrm{Ru(III)}})$ gives the concentration of $Ru(bipy)_3{}^{3+}$ present.

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(12) E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).

Table I

Complex	Quantum yield: Direct (wavelength, nm)	Quantum yield: Sensitized ϕ_0	Quenching constant K_{SV}, M^{-1}: Eq 11	Quenching constant K_{SV}, M^{-1}: Eq 9	Quenching constant K_{SV}, M^{-1}: Eq 10	$k_2 \times 10^{-9}$, M^{-1} sec^{-1}: Obsd[a]	$k_2 \times 10^{-9}$, M^{-1} sec^{-1}: Calcd
$Ru(bipy)_3Cl_2$	$<10^{-4}$ (457.9)[c] $<10^{-5}$ (457.9)[d]	0.68[b] ± 0.02		2130 (O_2 quenching of $Ru(bipy)_3{}^{2+}$)		3.2	6
$K_3Cr(C_2O_4)_3$	~0.09 (360–605)[e] ~0.07 (697)[f]	0.033 ± 0.05[g]		5780	5420	8.5	50
$K_3Fe(C_2O_4)_3$	1.11 (436)[h] 0.93 (468)[h] 0.94 (480)[h] 0.86 (509)[h] 0.15 (546)[h] 0.013 (577–579)[h]	$<10^{-3}$		2370		3.6	10
$K_2Co(C_2O_4)_3$	0.10 (457.9) 0.002 (>530)[e]	0.855[c,i]	4080[c]	4880[c] 2460[j]	4280[c]	6.7	50

[a] From K_{SV} using $\lambda_0 = 0.66$ μsec. [b] Yield for appearance of $Ru(bipy)_3{}^{3+}$ in the presence of $Co(C_2O_4)_3{}^{3-}$ in 1.0 N H_2SO_4; see Results section. [c] In 0.1 N H_2SO_4. [d] In water. [e] Reference 11. [f] In 30% ethanol–water. [g] From eq 11 using $K_{SV} = 5600$ M^{-1} and $\beta = 1$. [h] Reference 9 values for $\lambda \leq 436$ are for 0.006 F complex; all others are for 0.15 F complex. [i] From eq 11; see Figure 3. [j] In 1.0 M H_2SO_4.

The acceptors sometimes absorbed a significant fraction of the incident light and, where necessary, sensitization yields were corrected for this trivial absorption and consequent direct photolysis of the acceptor by means of the equation

$$\phi_{corr} = \frac{\phi_{app} - (1 - \bar{f}_D)\phi_Q}{\bar{f}_D} \tag{2}$$

where ϕ_{app} is the apparent yield, ϕ_Q is the yield or direct photolysis of the quencher at the excitation wavelength, and $\bar{f}_D$ is the average fraction of exciting light absorbed by the donor during the photolysis. This last is given by

$$f_D = A_D/(A_D + \bar{A}_Q) \tag{3}$$

where $\bar{A}_Q$ is the average of the absorbances due to the quencher before and after the irradiation.

Results

A general summary of our results is given in Table I, including relevant literature values for direct photolysis yields. The theoretical values for the bimolecular quenching constants, k_2, corrected for the attraction between unlike charged ions, were estimated by means of an equation due to Debye,[13] taking both ionic radii to be 5 Å and ignoring ionic strength effects.

Photobehavior of $Ru(bipy_3)^{2+}$. We find $Ru(bipy)_3{}^{2+}$ to be only slightly photosensitive at 457.9 nm, using the fluorimetric method of analysis. The yield for disappearance of the complex is $<10^{-5}$ in water and $<10^{-4}$ in 0.1 N H_2SO_4. Other observations are that the insensitivity is not due to a rapidly reversible photoelectron production[3] and that no transients of appreciable yield are produced in flash photolysis.[3,14] Our results confirm that direct photodecomposition was negligible both in the present studies and in the earlier ones.

The emission from $Ru(bipy)_3{}^{2+}$ is slightly sensitive to oxygen quenching. Air saturated solutions exhibit about two-thirds of the emission intensity of those deaerated by N_2 bubbling. An intensity Stern–Volmer plot for oxygen quenching is included in Figure 1. It gives a bimolecular quenching constant of 3.2×10^9 M^{-1} sec^{-1}, using our observed unquenched lifetime of the complex, of 6.6×10^{-7} sec. The effect is small enough that simple bubbling of N_2 or of Ar through solutions to be irradiated is sufficient to reduce oxygen quenching to less than 1%.

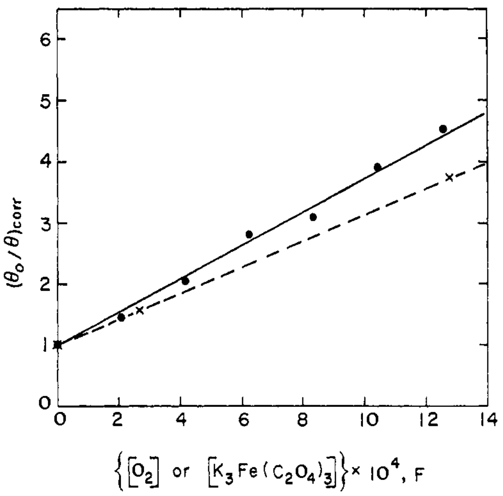

Figure 1. Intensity Stern–Volmer quenching plot for $Ru(bipy)_3{}^{2+}$ by $K_3Fe(C_2O_4)_3$ (●—●) in 0.1 N H_2SO_4 and by oxygen (×— —×) in water.

Results with $Cr(C_2O_4)_3{}^{3-}$. The emission of $Ru(bipy)_3{}^{2+}$ is quenched by the $Cr(C_2O_4)_3{}^{3-}$ ion. The lifetime and the intensity quenching results are plotted in Figure 2. The two sets of data agree to within experimental error, and give a Stern–Volmer constant, K_{SV}, of 5600 M^{-1}, corresponding to a bimolecular quenching constant of 8.5×10^9 M^{-1} sec^{-1}.

No net chemical change was observed but sensitized racemization did occur. For example, ϕ_{corr} was 0.024 for a solution 7×10^{-5} M in $Ru(bipy)_3{}^{2+}$ and 1.4×10^{-3} M in $Cr(C_2O_4)_3{}^{3-}$. No determination of the concentration dependence of this yield was attempted, but the limiting yield, at infinite quencher concentration, ϕ_0 of eq 11, is 0.033 if K_{SV} is the same as for quenching.

Results with $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ Solutions. Aqueous solutions of this complex in 0.1 N H_2SO_4, or pH 1.3, were effective in quenching emission from $Ru(bipy)_3{}^{2+}$. The Stern–Volmer intensity plot is shown in Figure 1; it is linear and its slope gives a bimolecular quenching constant of ~4×10^9 M^{-1} sec^{-1}. Solutions of the complex are virtually insensitive to 578-nm light, that

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(13) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(14) P. Natarajan and J. Endicott, *J. Amer. Chem. Soc.*, **94**, 5909 (1972).

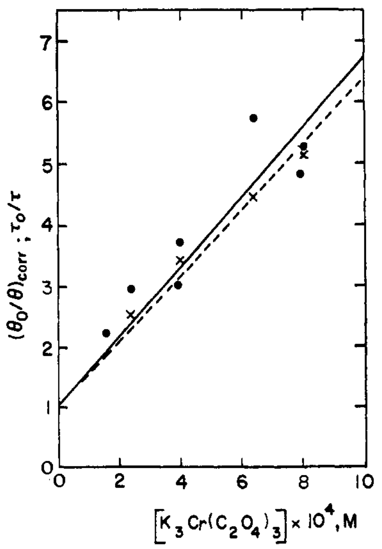

Figure 2. Intensity (●—●) and lifetime (X— —X) Stern–Volmer quenching plots for $Ru(bipy)_3^{2+}$ by $K_3Cr(C_2O_4)_3$ in water.

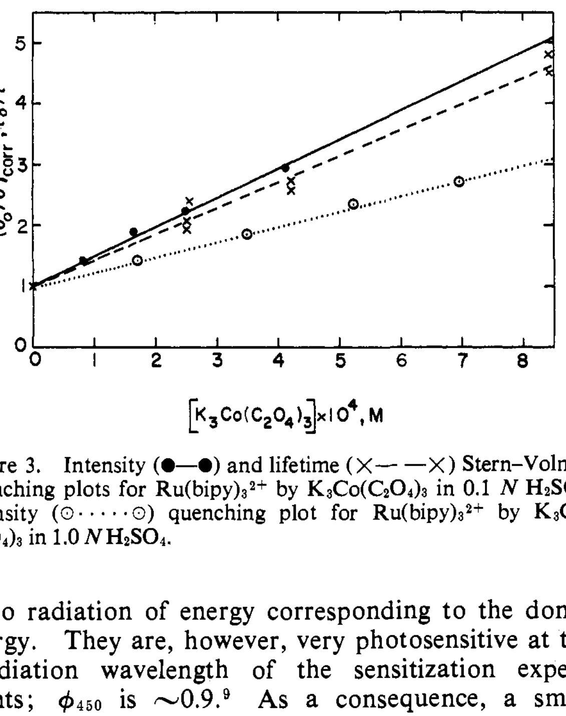

Figure 3. Intensity (●—●) and lifetime (X— —X) Stern–Volmer quenching plots for $Ru(bipy)_3^{2+}$ by $K_3Co(C_2O_4)_3$ in 0.1 *N* H_2SO_4. Intensity (⊙·····⊙) quenching plot for $Ru(bipy)_3^{2+}$ by $K_3Co(C_2O_4)_3$ in 1.0 *N* H_2SO_4.

is, to radiation of energy corresponding to the donor energy. They are, however, very photosensitive at the irradiation wavelength of the sensitization experiments; ϕ_{450} is ~0.9.[9] As a consequence, a small amount of direct or trivial photolysis occurred in the sensitization experiments, for which correction had to be made.

Two experiments gave the following results. Irradiation at 457.8 nm of a solution 1.3×10^{-3} *F* in complex and 5×10^{-4} *M* in sensitizer (and 0.1 *N* in H_2SO_4) gave an observed yield for Fe^{2+}, ϕ_{obsd}, of 0.0024. That due to trivial photolysis is estimated to be 0.0022, however. A less accurate experiment using the arc source and 450-nm excitation gave $\phi_{obsd} \simeq 0.004$, as compared to a calculated trivial yield of ~0.005. We infer that the yield of any sensitized net redox decomposition is less than 10^{-3}, or at least three orders of magnitude below that for direct photolysis at 450 nm.

Results with $Co(C_2O_4)_3^{3-}$. Three types of experiments were performed: direct photolyses, sensitized photolyses, and certain corollary experiments.

1. Direct Photolysis Experiments. It is known that photolysis of $Co(C_2O_4)_3^{3-}$ yields Co(II) and CO_2 (al-

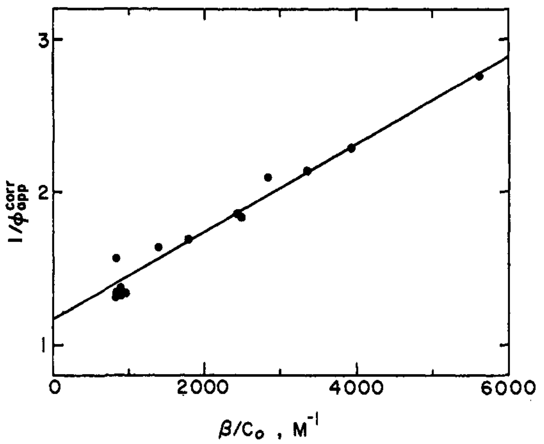

Figure 4. Photochemical Stern–Volmer quenching plot for the decomposition of $Co(C_2O_4)_3^{3-}$ sensitized by $Ru(bipy)_3^{2+}$ in 0.1 *N* H_2SO_4.

though traces of other products may be present) and transient radicals such as CO_2^- or $C_2O_4^-$ are postulated.[8,15] We find ϕ to be 0.10 at 457.9 nm for solutions 0.1 *N* in H_2SO_4, and to be 0.11 with no acid present; these values are in reasonable agreement with the reported one of 0.13 at 450 nm.[11]

2. Sensitization Experiments. $Ru(bipy)_3^{2+}$ strongly sensitizes the redox decomposition of $Co(C_2O_4)_3^{3-}$. Solutions containing this sensitizer are extremely photosensitive; noticeable decomposition occurs within minutes under ordinary fluorescent lighting where days would be required in the absence of the sensitizer. Consistent with this observation, the complex strongly quenches the $Ru(bipy)_3^{2+}$ emission. Figure 3 shows our intensity and lifetime quenching data. For solutions 0.1 *N* in H_2SO_4, the two plots are in good agreement, and give a Stern–Volmer quenching constant of 4.4×10^3 M^{-1}. The corresponding intensity quenching data for solutions 1 *N* in H_2SO_4 give $K_{SV} = 2.6 \times 10^3$ M^{-1}, but complications are now present—see below. Figure 4 shows the variation of the sensitized yield for Co(II) with complex concentration, plotted as $1/\phi_{corr}$ *vs.* β/C_0, where β is a function allowing for the decrease in complex concentration during photolysis from its initial value, C_0.[16] As detailed in the Discussion, the ratio of the intercept to slope should also give K_{SV}; we thus find $K_{SV} = 4.08 \times 10^3$ M^{-1}, in reasonable agreement with the value for the quenching data. The limiting sensitization yield, ϕ_0, is given by the intercept at 0.85. Further, the values of ϕ_0 calculated from various isolated experiments, using $K_{SV} = 4.4 \times 10^{-3}$ M^{-1}, were invariant within experimental error for C_0's ranging from 4×10^{-4} to 2×10^{-3} *M* and for fractional decompositions ranging from 20 to 80%.

The temperature dependence of the sensitization yield was tested using solutions 0.1 *N* in H_2SO_4, 1.6×10^{-3} *M* in $Co(C_2O_4)_3^{3-}$ and 1×10^{-4} *M* in $Ru(bipy)_3^{2+}$, over the range 18–35°. The results were corrected for trivial effects by means of eq 1 and gave approximately the same yields. The concentrations of $Co(C_2O_4)_3^{3-}$ varied somewhat, however, and as an alternative procedure, a ϕ_0 was calculated for each value using eq 11

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(15) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(16) A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 5943 (1968).

and an assumed K_{SV} of 4.4 × 10^{-3} M^{-1}. The ϕ_0's so obtained agreed within 3% and without any systematic drift. We conclude that the sensitization is negligibly temperature dependent.

There is a solvent effect. Solutions 3 × 10^{-3} M in $Co(C_2O_4)_3{}^{3-}$, 4 × 10^{-4} M in $Ru(bipy)_3{}^{2+}$, and 0.1 N in H_2SO_4 were diluted to double their initial volume with USP ethanol. A considerable acceleration of the thermal or dark decomposition of the complex occurs in this medium. The rate is conveniently measurable at 45° and at this temperature the rate of the thermal decomposition in the alcohol–water medium was found to be about four times greater than the rate in an aqueous solution of the same formal acidity. This dark rate, incidentally, is acid dependent, increasing with increasing acidity.

Sensitization is less efficient in the mixed solvent medium. The value of ϕ_{app} for a solution 8 × 10^{-4} M in complex was found to be 0.15 at 22° as compared to 0.56 for the corresponding aqueous solution, both 0.05 N in H_2SO_4. Sufficient quenching data were obtained to establish semiquantitative Stern–Volmer plots, and K_{SV}'s of ~5 × 10^3 M^{-1} resulted. The solvent effect on the sensitization yield is thus not a reflection of a reduced quenching efficiency.

The results for 0.1 N aqueous H_2SO_4 media are entirely consistent with an ordinary sensitization process involving excitation energy transfer from excited state $Ru(bipy)_3{}^{2+}$ to the cobalt complex. A dramatic indication that the situation was probably rather different was found on carrying out sensitizations in 1.0 N H_2SO_4. Under this acidity condition, $Ru(bipy)_3{}^{3+}$ is relatively stable, and we observe this species to be a major product of the "sensitization" process. $Ru(bipy)_3{}^{2+}$ disappears during the irradiation, as signaled by a change in the color of the solution from yellowish to greenish, and a decrease almost to zero of the $Ru(bipy)_3{}^{2+}$ emission intensity. On long (several hours) standing in the dark, the $Ru(bipy)_3{}^{2+}$ completely regenerates. This return could be accelerated by the addition of a small amount of $K_2C_2O_4$. Both the spectral changes during irradiation and the nature of the subsequent dark return are fully consistent with the production of the strong oxidizing agent, $Ru(bipy)_3{}^{3+}$.

In 1.0 N H_2SO_4 sensitized production of $Ru(bipy)_3{}^{3+}$ is highly efficient. $\phi_0 = 0.68 \pm 0.02$ (calculated by eq 11 and $K_{SV} = 2460$ M^{-1}) for initial concentrations of $[Co(C_2O_4)_3{}^{3-}] = 3.4 \times 10^{-4}$ M and $[Ru(bipy)_3{}^{2+}] = 8 \times 10^{-5}$ M under conditions where ~40% oxidation occurs. Because ϕ_0 is an indirectly calculated quantity, we estimate its accuracy to be ±10–20%.

The production of $Ru(bipy)_3{}^{3+}$ is not readily noticeable in 0.1 N H_2SO_4 because the rate of reduction back to $Ru(bipy)_3{}^{2+}$ by the medium is now quite rapid; however, reexamination of the behavior of 0.1 N H_2SO_4 systems showed clearly that some transient oxidation of the ruthenium complex does occur. The experiment consisted of monitoring the emission intensity from the front portion of the photolysis cell while the solution was being irradiated. For the case of 7 × 10^{-5} M $Ru(bipy)_3{}^{2+}$ and 1.4 × 10^{-4} M $Co(C_2O_4)_3{}^{3-}$, the intensity of the emission from excited state $Ru(bipy)_3{}^{2+}$ began to decrease immediately on turning on the lamp and dropped to about 80% of its original value. It rose again on longer irradiation, as the cobalt complex was consumed. In the case of solutions containing lower concentrations of $Ru(bipy)_3{}^{2+}$, the decrease in intensity was even larger; the effect would be relatively unimportant, however, for the solutions used in the sensitization yield experiments, since a higher concentration, ~1.4 × 10^{-4} M, of the $Ru(bipy)_3{}^{2+}$ was used.

3. Corollary Experiments. Several experiments were carried out which were designed to clarify or to eliminate certain possibilities. First, it appears that ion pairing between $Ru(bipy)_3{}^{2+}$ and $Co(C_2O_4)_3{}^{3-}$ is not important. The absorption spectrum of mixed solutions is accurately additive with respect to the separate component spectra. We conclude that the ion pairing constant is less than 300 M^{-1}, assuming that its extinction coefficient differs from the sum of those of the components by at least 5% in the sensitive charge transfer region of 430–470 nm. This means that at most a few per cent of ion pairing could be present in our systems.

It is noted above that $Ru(bipy)_3{}^{3+}$ is produced in the "sensitized" reaction, but is reduced by the medium back to $Ru(bipy)_3{}^{2+}$. A quantitative test, *experiment A*, for any irreversible destruction of the ruthenium complex was made using a solution 6 × 10^{-5} M in $Ru(bipy)_3{}^{2+}$, 1.6 × 10^{-3} M in $Co(C_2O_4)_3{}^{3-}$, and 0.1 N H_2SO_4, which was exhaustively photolyzed at 457.9 nm. Assuming that the extinction coefficient of any decomposition products differed by at least a factor of 2 from that of $Ru(bipy)_3{}^{2+}$ in the region of the CT band of the latter, the loss of $Ru(bipy)_3{}^{2+}$ was less than 3 × 10^{-7} M. We thus estimate that at least 5 × 10^3 molecules of $Co(C_2O_4)^{3-}$ were consumed per molecule of $Ru(bipy)_3{}^{2+}$ decomposed permanently. Also, as mentioned, several observations were made that in 1 N H_2SO_4 solutions $Ru(bipy)_3{}^{2+}$ was regenerated in the dark following a "sensitization" photolysis, such regeneration being complete, within experimental error, as judged by the return of the absorption at 450 nm, the band maximum for $Ru(bipy)_3{}^{2+}$.

It was next of interest to determine whether radicals produced by the direct photolysis of $Co(C_2O_4)_3{}^{3-}$ are reactive toward $Ru(bipy)_3{}^{3+}$. In *experiment B*, a solution 1.0 N in H_2SO_4, 3.2 × 10^{-4} M in $Co(C_2O_4)_3{}^{3-}$, and 3.5 × 10^{-5} M in $Ru(bipy)_3{}^{3+}$ was irradiated at 254 nm; at this wavelength 85% of the exciting light was absorbed by the cobalt complex. The concentration of $Ru(bipy)_3{}^{2+}$ was determined spectrophotometrically at 450 nm, and, in a 1-min irradiation, a concentration of ~2.3 × 10^{-5} M was produced. The yield for the photodecomposition of $Co(C_2O_4)_3{}^{3-}$ to give oxalate radicals (or $CO_2{}^-$) may be taken to be half of that of the Co(III) decomposed.[8,15,17] So from the incident intensity and the fraction of light absorbed by $Co(C_2O_4)_3{}^{3+}$ the production of radicals was estimated at ~1.5 × 10^{-5} M in this case. It thus appears that in 1 N H_2SO_4, oxalate radical production leads to an efficient reduction of $Ru(bipy)_3{}^{3+}$ to $Ru(bipy)_3{}^{2+}$; the rate constant for this process must be significantly greater than that for loss of oxalate radical by reaction with $Co(C_2O_4)_3{}^{3-}$ or by other processes. The minimally interpretive

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(17) (a) T. B. Copestake and N. Uri, *Proc. Roy. Soc., Ser. A*, **228**, 252 (1955); (b) N. S. Rowan, R. M. Milburn, and M. Z. Hoffman, *Inorg. Chem.*, **11**, 2272 (1972); (c) A. F. Vaudo, E. R. Kantrowitz, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 6655 (1972).

conclusion is that photolysis of $Co(C_2O_4)_3^{3-}$ produces species which are reducing toward $Ru(bipy)_3^{3+}$.

A related experiment, *experiment C*, is the following. A solution 1.3×10^{-3} *M* in $Ru(bipy)_3^{3+}$, 2.1×10^{-3} *M* in $Co(C_2O_4)_3^{3-}$, and 1.0 *N* in H_2SO_4 was made additionally 5.2×10^{-3} *F* in $K_2C_2O_4$. The $Ru(bipy)_3^{3+}$ was thereby reduced rapidly to $Ru(bipy)_3^{2+}$ (in the absence of the added oxalate, reduction by the medium is relatively slow) and completely, as verified by measuring the increased absorbance at 450 nm. Less than 1% of the cobalt complex was reduced during this reaction. We assume here that oxidation of $C_2O_4^{2-}$ by $Ru(bipy)_3^{3+}$ yields $C_2O_4^-$ or CO_2 and CO_2^-. We conclude that these radicals are not very reactive toward $Co(C_2O_4)_3^{3-}$ under these conditions and are lost by other pathways. Experiment A suggests that the radicals reduce $Ru(bipy)_3^{3+}$ and do so at least 100 times faster than with the cobalt complex.

Finally, *experiment D* consisted of photolysis of 3.2×10^{-4} *M* $Co(C_2O_4)_3^{3-}$ in the presence of 3.4×10^{-5} *M* $Ru(bipy)_3^{2+}$ in 1.0 *N* H_2SO_4 medium. The photolysis was for 1 min at 253.7 nm, at which wavelength ~90% of the exciting light was absorbed by the cobalt complex. The concentration of $Ru(bipy)_3^{2+}$ was determined immediately after the photolysis (30 sec elapsed time), from the absorbance at 450 nm. We expect the primary photolysis of $Co(C_2O_4)_3^{3-}$ to have produced 2.3×10^{-5} *M* Co(II) along with 2.3×10^{-5} *M* oxalate radical. Only ~10^{-6} *M* $Ru(bipy)_3^{2+}$ was oxidized, or 30–50% of the amount expected as a result of trivial direct light absorption by $Ru(bipy)_3^{2+}$ followed by the "sensitized" production of $Ru(bipy)_3^{3+}$. Thus no significant amount of $Ru(bipy)_3^{3+}$ was formed from reaction with radical or with other products from the direct photolysis of $Co(C_2O_4)_3^{3-}$. The same solution, however, does form considerable quantities of $Ru(bipy)_3^{3+}$ when exposed for 1 min to fluorescent room lights, that is, to light of wavelength such that absorption by $Ru(bipy)_3^{2+}$ is important.

Discussion

Sensitization Kinetics. We adopt the usual bimolecular encounter model as the kinetic basis for treating our data, including the possibility, however, of either excitation energy transfer or chemical reaction between the donor and the acceptor. The emitting state of excited $Ru(bipy)_3^{2+}$ has been identified as a triplet charge transfer state,[6] here labeled D*, and we assume that it is the only state implicated either as donor or as reactant. The postulated processes are as follows.

$$\mathrm{D} \xrightarrow{h\nu,\ \phi_{\mathrm{isc}}'} \mathrm{D}^* \tag{4}$$

$$\mathrm{D}^* \xrightarrow{k_1} \mathrm{D} \text{ or } \mathrm{D} + h\nu \tag{5}$$

$$\mathrm{D}^* + \mathrm{C} \xrightarrow{k_2} \mathrm{D} + \mathrm{C}^* \text{ (excitation energy transfer) or } \mathrm{D} + \mathrm{C} \text{ (catalyzed deactivation)} \tag{6}$$

$$\mathrm{C}^* \xrightarrow{\phi_{\mathrm{d}}} \text{products} \tag{7}$$

or in place of eq 6 and 7

$$\mathrm{D}^* + \mathrm{C} \xrightarrow{k_2} \text{products of chemical reaction} \tag{8}$$

where C denotes the acceptor complex, ϕ_{isc}' is the efficiency of population of the donor's emitting level following optical excitation, and ϕ_{d} is the fraction of C* which decomposes. In the absence of significant donor decomposition or quenching by products, the use of either scheme leads to the usual relationships

$$\theta_0/\theta = 1 + K_{\mathrm{SV}}(\mathrm{C}) = 1 + k_2\tau_0(\mathrm{C}) \tag{9}$$

$$\tau_0/\tau_0 = 1 + K_{\mathrm{SV}}(\mathrm{C}) = 1 + k_2\tau_0(\mathrm{C}) \tag{10}$$

$$1/\phi = 1/\phi_0 + (1/\phi_0 K_{\mathrm{SV}})(\beta/C_0)$$
$$\beta = \ln (C/C_0)/(C - C_0) \tag{11}$$

Here, θ is the donor emission intensity, and θ_0 is the value in the absence of quencher; τ is the lifetime of the donor state while τ_0 is the lifetime in the absence of quencher. The rate constant $k_1 = 1/\tau_0$ is the sum of all rate constants for all processes depleting the donor state in the absence of quencher, and k_2 is the rate constant for the bimolecular quenching process, whether one of excitation energy transfer, induced radiationless deactivation, or chemical reaction between D* and C. The limiting quantum yield for decomposition of acceptor at infinite concentration is a product of several terms. In the energy transfer scheme, it is the product $\phi_{\mathrm{isc}}'\phi_{\mathrm{et}}\phi_{\mathrm{d}}$, where ϕ_{et} is the fraction of quenching encounters which result in an energy transfer event. The yield ϕ_{isc}' is believed to be unity[6] and will be so assumed here.

The use of the above kinetic scheme anticipates our conclusion that quenching is a dynamic rather than a static process in our systems. It should be noted that an accurate description of the observed sensitized photochemical and intensity quenching data by eq 9 and 11 does not prove that the quenching occurs by the kinetic mechanism. If the acceptor concentration is always much greater than that of the donor (the usual situation in our experiments) and a nonluminescent donor–acceptor association pair is formed which has an absorption spectrum similar to that of the sum of the two components, then the above two equations will still be obeyed.[18] Under these conditions, the amount of donor tied up increases in proportion to the acceptor concentration. Thus the fraction of emitting light going into the emitting form is reduced and so is the luminescence intensity. Similarly, in the photochemical experiment, if association is occurring, one could just be photolyzing the association pair, a new chemical entity which could well have its own characteristic photochemistry.

In the lifetime experiment, however, one is probing directly the free emitting form, and any shortening of the lifetime must be due to encounter phenomena. Because of the weak absorbances of our acceptor and the short donor lifetime, we can safely neglect any energy transfer mechanism with a range much beyond that of the encounter distance. Consequently, if eq 10 is obeyed, the inescapable implication is that some quenching occurs by the kinetic rather than the static mechanism. Furthermore, if the K_{SV} value obtained from eq 11 agrees with those from eq 9 and 10, the kinetic scheme is almost certainly the major mechanism operating for the luminescent quenching and the photochemistry. Conversely, disagreement between the various K_{SV}'s indicates the presence of a more complex or of a mixed scheme.

[18] C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968.

We find that the luminescence intensity and lifetime quenching plots are indistinguishable in the cases of $Cr(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_3^{3-}$ as acceptor molecules and, in the earlier study, found the analogous result for $PtCl_4^{2-}$.[1] The identity of the K_{SV} values obtained by the two types of quenching experiments assures us that the contribution of any ion pairing path is small. While we do not have the lifetime quenching data for the iron oxalate system, the principal species present is $Fe(C_2O_4)_2^-$ (see below), and it seems unlikely, on electrostatic grounds, that the static mechanism could apply in this case if it does not in the other two.

The $Co(C_2O_4)_3^{3-}$ System. This is perhaps the more interesting and certainly appears to be the more complex of the three. $Co(C_2O_4)_3^{3-}$ has two visible ligand field bands, at 605 and 436 nm. The lower energy band is essentially photoinactive ($\phi \simeq 0.002$ for redox decomposition).[11] The higher energy band exhibits a relatively uniform yield of approximately 0.1 from 450 to 480 nm.[19] At higher energies the yield rises and levels out in the region of the uv charge transfer band at a value of 0.76.[17,20] Thus the direct photolysis yield is negligible in the wavelength region corresponding to the energy of $^3Ru(bipy)_3^{2+}$ and is small for light of the 450-nm region of wavelength used in the sensitization studies.

We first note that K_{SV} as obtained from eq 11 is the same as that from eq 9 and 10, which we take to establish that the same donor state is both emitting and sensitizing. It seems highly improbable that the K_{SV}'s would be the same for two different excited states of the donor, especially since there is no emission evidence of any other long-lived excited state.[6] We take this state to be the ^3CT state to which the phosphorescence emission has been assigned.[6]

The finding that $Ru(bipy)_3^{3+}$ is produced in the sensitization reaction appears to limit us to two types of detailed mechanism. In the first, excitation energy transfer occurs, to produce C*, which then undergoes redox decomposition to produce a radical (or radicals) capable of oxidizing $Ru(bipy)_3^{2+}$. If the radical is taken to be $C_2O_4^-$, the processes become

$$^3Ru(bipy)_3^{2+} + Co(C_2O_4)_3^{3-} \longrightarrow Ru(bipy)_3^{2+} + [Co(C_2O_4)_3^{3-}]^* \quad (12)$$

$$[Co(C_2O_4)_3^{3-}]^* \longrightarrow Co^{2+} + 2C_2O_4^{2-} + C_2O_4^- \quad (13)$$

$$C_2O_4^- + Ru(bipy)_3^{2+} \longrightarrow C_2O_4^{2-} + Ru(bipy)_3^{3+} \quad (14)$$

$$C_2O_4^- + Co(C_2O_4)_3^{3-} \longrightarrow Co^{2+} + 3C_2O_4^{2-} + 2CO_2 \quad (15)$$

$$2C_2O_4^- \longrightarrow C_2O_4^{2-} + 2CO_2 \quad (16)$$

(Analogous processes to 13 and 16 would be written if it is assumed that $C_2O_4^-$ promptly decomposes to CO_2 and CO_2^-, the latter now playing the role of $C_2O_4^-$.) The observed yield of $Ru(bipy)_3^{3+}$ of $\sim$0.7 in 1.0 *N* aqueous H_2SO_4 requires that at least 70% of the quenching events produce the sequence 12–14.

We believe that certain arguments against the above mechanism are persuasive. The $C_2O_4^-$ radical is a good reducing agent. The radical can probably reduce $Co(C_2O_4)_3^{3-}$ to Co(II)[17b] and certainly can reduce $Fe(C_2O_4)_3^{3-}$ to Fe(II).[8,15] It seems unlikely that such a reducing agent could oxidize $Ru(bipy)_3^{2+}$; it is possible but a delicate balance of free energies must exist between the radical and its oxidized and reduced forms. Our photolysis of $Co(C_2O_4)_3^{3-}$ in the presence of $Ru(bipy)_3^{3+}$, experiment B, confirms that $C_2O_4^-$ is reducing toward the latter ion. Experiment D, photolysis of $Co(C_2O_4)_3^{3-}$ in the presence of $Ru(bipy)_3^{2+}$, confirms that $C_2O_4^-$ is not oxidizing. Were this radical a very fast, good oxidizer, we would expect up to about 70% of the total ruthenium present to have been converted to $Ru(bipy)_3^{3+}$; only a trace was found. The radical postulated to result from the decomposition of excited state $Co(C_2O_4)_3^{3+}$ formed in reaction 12 is presumably the same as that formed in the direct photolysis of the oxalato complex. We therefore conclude that the production of $Ru(bipy)_3^{3+}$ in the sensitization experiments is not due to a radical derived from the redox decomposition of $Co(C_2O_4)_3^{3-}$.

Nor can the sensitization behavior be assigned to radicals produced in a photolytic decomposition of $Ru(bipy)_3^{2+}$. The complex is not significantly decomposed by light in the wavelength region used here. The remaining possibility is that photoelectron production occurs, with $e^-(aq)$ recombining with the produced $Ru(bipy)_3^{3+}$ in the absence of other scavengers, but reacting with $Co(C_2O_4)_3^{3-}$ in the sensitization experiments. Photoelectron production has been ruled out, however, by other studies (see ref 3 and 4). In brief, $Ru(bipy)_3^{3+}$ production does not occur in the presence of a good $e^-(aq)$ scavenger such as N_2O and, furthermore, the capture of $e^-(aq)$ by $Ru(bipy)_3^{3+}$ produces $^3Ru(bipy)_3^{2+}$ in high efficiency, so that the latter is not likely to be a photoelectron producer.[21]

The mechanism which does account for our results invokes $^3Ru(bipy)_3^{2+}$ as a one-electron reducing agent. This type of mechanism has been proposed for systems involving $Co(NH_3)_5X^{2+}$ complexes[3,4] and takes the following form in the present case.

$$^3Ru(bipy)_3^{2+} + Co(C_2O_4)_3^{3-} \longrightarrow Ru(bipy)_3^{3+} + Co^{2+} + 3C_2O_4^{2-} \quad (17)$$

$$Ru(bipy)_3^{3+} + \text{solvent} \longrightarrow Ru(bipy)_3^{2+} + \text{oxidation products} \quad (18)$$

$$Ru(bipy)_3^{3+} + C_2O_4^{2-} \longrightarrow Ru(bipy)_3^{2+} + C_2O_4^- \quad (19)$$

$$Ru(bipy)_3^{3+} + C_2O_4^- \longrightarrow Ru(bipy)_3^{2+} + 2CO_2 \quad (20)$$

$$Ru(bipy)_3^{2+} + C_2O_4^- \longrightarrow Ru(bipy)_3^{3+} + C_2O_4^{2-} \quad (21)$$

Reaction 17 accounts for the production of $Ru(bipy)_3^{3+}$, and reactions 18–20 for the regeneration of $Ru(bipy)_3^{2+}$. If these are fast, the overall process takes on the appearance of being a sensitized decomposition of $Co(C_2O_4)_3^{3-}$ obeying the usual sensitization kinetics (eq 9–11). Experiment C demonstrates that reaction 19 occurs and experiment B is certainly consistent with reaction 20 being fast. It is next necessary to consider the detailed pH effects. We find that 1.3×10^{-4} *F* oxalate reduces dilute $Ru(bipy)_3^{3+}$ with apparent first order rate constants of $\sim$1 and 0.02 min^{-1} in 0.1 *N* and 1.0 *N* H_2SO_4, respectively. In the photolysis experiments in 0.1 *N* H_2SO_4 at least 4×10^{-4} *F* oxalate would have been generated through reaction 17 at complete oxidation to $Ru(bipy)_3^{3+}$. The lifetime of the latter species should be only several seconds, however, because of the speed of reaction 19. The photolysis

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[19] J. N. Demas, H. Gafney, and A. W. Adamson, unpublished results.

[20] G. B. Porter, J. G. W. Doering, and S. Karanka, *J. Amer. Chem. Soc.*, **84**, 4027 (1962).

[21] J. E. Martin, E. J. Hart, A. W. Adamson, H. Gafney, and J. Halpern, *J. Amer. Chem. Soc.*, **94**, 9238 (1972).

times were 1–10 min, so that the ruthenium should always be largely present as $Ru(bipy)_3^{2+}$, as observed. The effective termination of the photolyses in 1.0 *N* H_2SO_4, as $Ru(bipy)_3^{2+}$ was converted to $Ru(bipy)_3^{3+}$, simply reflects the inability of either solvent or $C_2O_4^{2-}$ ion to reduce significant amounts of $Ru(bipy)_3^{3+}$ during the time scale of the experiment. Although not central to the present analysis, we assume that $C_2O_4^{2-}$ rather than some protonated form is the reactant in eq 19 because of the strong inverse acid dependence of the observed rate in a given formality of oxalate. We conclude from the results of experiment C that $C_2O_4^-$ disappears primarily through reaction 20 or by radical recombination, rather than by reaction with $Co(C_2O_4)_3^{3-}$. Reaction 21 is included for completeness, but we have no experimental evidence for it.

It would be desirable to confirm that the stoichiometry of the primary reaction is indeed that of eq 17; we have done this approximately and indirectly. The yield for "sensitized" Co(II) production in 0.1 *N* H_2SO_4 is *ca.* 25% higher than the yield of $Ru(bipy)_3^{3+}$ in 1.0 *N* H_2SO_4, but the discrepancy is barely outside of our estimated uncertainties and could be due to a small systematic error. It is also possible that in 0.1 *N* H_2SO_4 medium the concentration of $Ru(bipy)_3^{3+}$ which develops during the photolysis is small enough so that some $Co(C_2O_4)_3^{3-}$ is reduced by the $C_2O_4^-$ formed.

The Ferrioxalate System. The oxalato complexes of Fe(III) are labile, and it is necessary to consider what species are actually present in our systems. The stepwise dissociation constants of $Fe(C_2O_4)_3^{3-}$ are known[22–24] and we conclude that in the range 0.1 to 1.6×10^{-3} *F* $K_3Fe_3(C_2O_4)_3$ about 98% of the Fe(III) is present as $Fe(C_2O_4)_2^-$. At 10^{-4} *F* the remaining 2% is largely $Fe(C_2O_4)^+$ and at 1.6×10^{-3} *F* the principal secondary species is $Fe(C_2O_4)_3^{3-}$. At 6×10^{-3} *F* oxalate, the composition is ~93% $Fe(C_2O_4)_2^-$ and ~7% $Fe(C_2O_4)_3^{3-}$. These conclusions are sensitive to the accuracy of our pH measurements (and, of course, to that of the reported equilibrium constants), but it seems reasonable to conclude that the predominate species in our solutions is $Fe(C_2O_4)_2^-$. The composition of the usual actinometric solution, which is 0.15 *F* in $K_3Fe(C_2O_4)_3$, is known with less certainty, but the solution surely contains a large amount of $Fe(C_2O_4)_2^-$ as well as of $Fe(C_2O_4)_3^{3-}$. Since the direct photolysis yield for such a solution is very low at 578 nm, we conclude that $Fe(C_2O_4)_2^-$ has available very low lying but photoredox inactive excited states.

The failure to find significant Fe^{2+} production on sensitization would tend to rule out efficient energy transfer to redox active excited states. Quenching by an electron transfer mechanism can not be discounted, however (see below).

The $Cr(C_2O_4)_3^{3-}$ System. Our results appear to rule out a process analogous to eq 17; were reduction of the chromium complex to have occurred, either Cr(II) would have been found, or its oxidation product $Cr(H_2O)_6^{3+}$ contrary to observation. We infer that an ordinary sensitization, that is, excitation energy transfer, occurs to produce an excited state of $Cr(C_2O_4)_3^{3-}$ which racemizes.

It is known that in the double salt of $Ru(bipy)_3^{2+}$ and $Cr(C_2O_4)_3^{3-}$ energy is efficiently transferred from the former to the latter, following excitation of the $Ru(bipy)_3^{2+}$.[25] While such solid-state data do not prove that energy transfer is also involved in our fluid solution systems, they do strongly suggest that such a process is the likely one.

The visible absorption spectrum of $Cr(C_2O_4)_3^{3-}$ contains two relatively intense bands centered at 571 and 417 nm, assigned to the first two spin-allowed d–d transitions. In addition, a very sharp feature at 697 nm is assigned to the first spin forbidden d–d transition, ${}^4A_{2g} \rightarrow {}^2E_g$ in O_h symmetry.[26] Direct photolysis studies[11] have shown that the spin-allowed absorptions are approximately uniformly sensitive toward photoracemization, with $\phi = 0.09$, while absorption in the region of the doublet band gives a ϕ of 0.07. In view of the experimental difficulty of directly pumping the weak 697 nm feature (an undetermined fraction of the exciting light is going into the quartet state), this last ϕ value can be regarded as a maximum ϕ for racemization due to photolysis *via* the doublet excited state.

The energies of the thermally equilibrated quartet states corresponding to the first two spin-allowed transitions are estimated to be 61 and 45 kcal mol^{-1}, while that of the first doublet state is about 41 kcal mol^{-1}.[27] The last two values are below the energy of ${}^3Ru(bipy)_3^{2+}$, 51 kcal mol^{-1}, and it is therefore not possible to determine on energetic grounds which state is being populated directly by the donor. Nor are there any strong theoretical reasons for making a choice on the basis of spin multiplicity change. Further, any propensity for such selective transfer is almost certainly weakened by the fact that our donor contains the high atomic number atom, Ru, so that its singlet and triplet states are probably strongly mixed.[6]

Our limiting sensitization yield of 0.03 is about one-third of that found for direct photolysis in the region of the spin-allowed bands, and perhaps one-half of that found on irradiation in the region of the doublet feature. The yield of 0.03 may, however, be close to that which would be found if the doublet band could be irradiated more cleanly. Several interpretations of our results are thus possible. The sensitizer may be populating the lowest lying states of the chromium complex, but doing so inefficiently so that ϕ_{et} is small. It may be populating the first doublet state, whose racemization efficiency is actually about 0.03. Finally, since oppositely charged ions are involved, the donor–acceptor complex may have a lifetime exceeding that of excited state $Cr(C_2O_4)_3^{3-}$ toward racemization. The presence of the donor as a neighbor to the racemizing complex might then perturb the racemization efficiency relative to that for the same excited state formed in direct photolysis. Further experiments (by J. N. Demas)

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(22) For all computations the pH is assumed to be 1.3 and $\beta_1 = 4 \times 10^7$, $\beta_2 = 1.6 \times 10^{16}$, $\beta_3 = 1.6 \times 10^{20}$, $K_1 = 4.3 \times 10^{-2}$, and $K_2 = 1.5 \times 10^{-4}$ where the β's are the stability constants and the *K*'s are the first and second proton dissociation constants.[23] Calculations were carried out by conventional methods.[24]

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using sensitized luminescence are in progress to attempt to clarify these possibilities.

General Discussion

Gafney and Adamson[3,4] have suggested that ^{3}Ru(bipy)$_3^{2+}$ is capable of acting as a one-electron reducing agent toward a number of acidopentaammine cobalt(III) complexes. They concluded on the basis of four systems studied that reduction would not occur efficiently if the standard reduction potential of the quencher was more negative than about 0.0 V. The issue is not yet clear cut, however, as radical oxidations rather than excited-state electron transfers may have accounted for the observed reactions. The standard reduction potential of $Co(C_2O_4)_3^{3-}$ if 0.6 V.[8] On this basis, our proposed reaction (17) should indeed occur readily (see below also).

The sensitized redox decomposition of Co(III) ammines has been reported for various organic sensitizers, and it has been assumed that a low-lying ^{3}CT state of the complex is populated.[8,16] We suggest that the electron transfer mechanism should be considered as a serious alternative possibility. As an example, Scandola and Scandola[28] found an efficient ($\phi = 0.8$) sensitized decomposition of $Co(NH_3)_6^{3+}$ by triplet state biphenyl. No net decomposition of the donor was observed, and it was postulated that a ^{3}CT state of energy lying below that of the biphenyl triplet state was populated. A similar observation and postulation was made in the case of quinoline as donor.[7] (Biacetyl, also a sensitizer, may function *via* a chemical mechanism involving hydrogen atom abstraction,[7] and the same may be true for benzophenone.)

Perhaps the chief difficulty with the ^{3}CT hypothesis as applied in the above cases resides in the fact that the onset of ^{1}CT absorption, about 38 kK, suggests that the thermally equilibrated ^{1}CT state lies at about 110 kcal mol^{-1} above the ground state. A 45 kcal mol^{-1} singlet–triplet splitting is implied if the ^{3}CT state lies below 65 kcal mol^{-1}. This seems unreasonable in view of the much smaller values found in cases where they can be observed directly.[6] The electron transfer mechanism seems more plausible. Biphenyl has a standard oxidation potential of -2.2 V[29] and the potential corresponding to the singlet–triplet separation of 23 kK is 2.8 V so that it seems entirely possible that the reaction

$$^3C_{12}H_{10} + Co(NH_3)_6^{3+} \longrightarrow C_{12}H_{10}^+ + Co^{2+} + 6NH_3 \quad (22)$$

is a favorable one. A back electron transfer from one of the escaping products of reaction 22 or a subsequent bulk reaction could account for the lack of appreciable net donor decomposition. The same qualitative justification can be made in the case of quinoline as sensitizer. A search for organic cations by flash photolysis may prove fruitful.

The Ru(bipy)$_3^{2+}$ sensitized decompositions of Co(EDTA)$^-$ and Co(HEDTA)X$^-$ (X = Cl, Br, NO$_2$)[2] may fall into a different class. The standard reduction potential for Co(EDTA)$^-$ is $+0.60$ V[30] so that according to the Gafney–Adamson rule, reduction by ^{3}Ru(bipy)$_3^{2+}$ is feasible. Similarly for the Co(HEDTA)X$^-$ series, the reduction potentials are probably more positive than that for Co(EDTA)$^-$, judging from the corresponding acidopentaammine series. Thus, electron transfer is quite possibly feasible in all of these cases. Natarajan and Endicott have, however, obtained flash photolysis evidence that suggests an energy transfer rather than an electron transfer pathway.[31]

The lack of any appreciable sensitized redox decomposition in the ferrioxalate system, even though the emission quenching is efficient, again suggests a violation of the rule. The standard reduction potential of $Fe(C_2O_4)_2^-$ should not be very negative, and the analog of reaction 15 should therefore occur. It is possible, however, that the back electron transfer from the reduced iron to Ru(bipy)$_3^{3+}$ may occur, either before the encounter pair disengages, or as subsequent bulk reactions. Alternative possibilities, of course, are that an excitation energy transfer to produce a photoinactive or substitution labile excited state of $Fe(C_2O_4)_2^-$ occurs, or, simply, that this particular complex is especially efficient at catalyzing the radiationless deactivation of the donor.

We wish to point out that excited-state electron transfer reactions are not new. This pathway for luminescence quenching and sensitized photochemistry has been well established in organic systems.[32,33] Rehm and Weller have even presented a theoretical equation for predicting when electron-transfer reactions can occur.[33] By means of this criterion, however, we would predict that ^{3}Ru(bipy)$_3^{2+}$ should rapidly reduce $Co(NH_3)_6^{3+}$ and $CoF(NH_3)_5^{2+}$. The failure of Gafney and Adamson[3] to see a facile reduction in these cases suggests that the Weller criterion can not be transferred to inorganic systems without careful reconsideration of its basic assumption and further evaluation of its applicability. For this reason in the preceding discussion we have selected the Gafney–Adamson criterion for judging when reactions should occur in spite of its very limited experimental support and the objections which have been raised to it. As a concluding point, it should be noted that the Weller criterion predicts that reaction 22 can occur.

We return to the $Co(C_2O_4)_3^{3-}$ system for a comment on solvent effects. The contrasting observations are that the thermal redox decomposition rate is increased about fourfold in 50% ethanol–water as compared to water medium, the direct photolysis yield is unaffected, as is the quenching constant, K_{SV}, and the yield for the sensitized decomposition is decreased about fourfold. The constancy and high value of K_{SV} suggests that the encounter rate is not much different in the two solvent media and that nearly every encounter is effective at quenching; if this is true, the different solvent effect on the direct *vs.* the sensitized decomposition yield is at least consistent with our postulation that "sensitization" occurs *via* reaction 17. That is, if the direct and the sensitized photolyses pass through quite different transition states of the cobalt complex, quite different solvent medium effects are not expected. Alterna-

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tively, variations in the solvent may be changing the nature of the encounter which could in turn yield different probabilities for the catalyzed deactivation, energy transfer, and electron transfer processes.

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Relative Insertion Rates of Silylene and Evidence for Silylsilylene Insertion into Silicon–Hydrogen and Silicon–Silicon Bonds

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Abstract: The relative rates of SiH_2 insertions into several methylsilanes and methylgermane in competition with disilane were measured in our recirculating flow system. When the results are expressed in terms of relative rate per E–H (E = Si, Ge) bond available for insertion, the order was as follows: $(CH_3)_3SiH > Si_2H_6 > (CH_3)_2SiH_2 > CH_3SiH_3 > SiH_4 > CH_3GeH_3$. No insertion products were found with CH_3PH_2 or $ClSiH_3$ in competition with disilane. The above rates have been explained in terms of the hydridic character of the E–H bond. Trisilane was pyrolyzed at 330° and the primary products were SiH_4, SiH_2, Si_2H_6, and Si_2H_4. The diradicals, SiH_2 and Si_2H_4, have been chemically trapped by $(CH_3)_3SiD$ and Si_3H_8, and the structure of Si_2H_4 is discussed. The relative ratios of normal to isotetrasilane and normal to isopentasilane produced from the neat pyrolysis of Si_3H_8 provide the strongest evidence to date for SiH_2 and Si_2H_4 insertions into both silicon–hydrogen and silicon–silicon bonds.

Although the chemistry of divalent carbon has been exhaustively investigated and reviewed,[1] studies with divalent silicon have been concentrated mainly on SiF_2[2] and other disubstituted silylenes.[3] Silylene, the silicon analog of methylene, has recently been shown to be an intermediate in the homogeneous thermal decomposition of disilane.[4,5] The insertion of SiH_2

$$Si_2H_6 \longrightarrow SiH_2 + SiH_4 \qquad (1)$$

into silicon–hydrogen bonds has been conclusively demonstrated[4,5] and insertion into silicon–silicon bonds has been suggested to account for product ratios in the static pyrolysis of Si_2H_6 ($n\text{-}Si_4H_{10}/i\text{-}Si_4H_{10} \simeq 4.8$)[5] and the higher per bond insertion into Si_2H_6 compared with SiH_4.[6]

Qualitative results from the SiH_2 insertions into $(CH_3)_2SiH_2$ and $ClSiH_3$[4] suggested that silylene acts as an electrophile during insertions into silicon–hydrogen bonds and that substituents do significantly affect the insertion rates into the remaining Si–H bonds. In an effort to better understand these nonstatistical insertion rates, we have investigated the relative insertion rates of SiH_2 into various silanes, CH_3GeH_3, and CH_3PH_2 in competition with Si_2H_6. Particular attention has been paid to the change in relative insertion rates per Si–H bond of silane due to the successive replacement of hydrogen atoms by methyl groups.

An investigation of the primary products in the pyrolysis of Si_3H_8 has produced evidence for (i) a new diradical species, Si_2H_4, which has been chemically trapped and (ii) the insertions of SiH_2 and Si_2H_4 into silicon–silicon bonds.

Results and Discussion

The pyrolysis of silicon hydrides lead to the formation of slightly more stable lighter hydrides and to more catenated less stable hydrides.[7] Therefore, only initial rates of a static silicon hydride decomposition are valid. An alternate approach to avoid secondary decompositions is to carry out the pyrolysis in a flow system containing a low-temperature trap which removes the less volatile (and less stable) products from the reaction stream. Further, the decompositions should be carried out for a very short time so that the partial pressure of any lighter product is still low. The problem of secondary reactions can occur in studying reactions of SiH_2 generated from Si_2H_6. Silane is the other product from the Si_2H_6 decomposition and it

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