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Quenching of the Doublet Excited State of Tris(polypyridine)chromium(III) Ions by Oxalate Ions: An Example of Irreversible Electron Transfer

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The kinetics and mechanism of the reductive quenching of ^{2}E CrL_3^{3+} (L = 2,2′-bipyridine, 1,10-phenanthroline, and their substituted analogues) by oxalate were studied. Quenching rate constants vary from 85.4×10^5 M^{-1} s^{-1} for the 5-chloro-1,10-phenanthroline complex to 0.21×10^5 M^{-1} s^{-1} for the 4,4′-dimethyl-2,2′-bipyridine complex and depend on the $E^\circ_{3*/2}$ value. The mechanism involves an ion-pairing preequilibrium followed by rate-limiting electron transfer. The $CO_2^{\bullet-}$ produced in the quenching step reacts with ground state CrL_3^{3+} to produce another mole of CrL_3^{2+} in the case of the 2,2′-bipyridine complex and its substituted analogues, while in the case of the 1,10-phenanthroline complex and its analogues a secondary transient is produced that decays to CrL_3^{2+}.

Introduction

The ^{2}E excited states of $Cr(bpy)_3^{3+}$, $Cr(phen)_3^{3+}$, and their substituted analogues have been well characterized.[1] The excited states are powerful one-electron oxidizing agents[2] that have a lifetime long enough to permit bimolecular quenching events. In the case of $Cr(phen)_3^{3+}$, for example, $E^\circ_{3*/2}$ is 1.42 V[2], and the lifetime is in the range 250–420 μs in aqueous solutions of various electrolytes.[3-5]

If the quenching occurs by electron transfer, it can be represented by the equation

$$*CrL_3^{3+} + D \rightarrow CrL_3^{2+} + D^+ \qquad (1)$$

In general, this will be followed by a back-electron-transfer reaction

$$CrL_3^{2+} + D^+ \rightarrow CrL_3^{3+} + D \qquad (2)$$

This work concerns the quenching of five $*CrL_3^{3+}$ excited states by oxalate ions at neutral pH. Oxalate ions are of particular interest[6] because a one-electron oxidation presumably proceeds by way of $C_2O_4^{\bullet-}$, a species that generates CO_2 and $CO_2^{\bullet-}$

$$*CrL_3^{3+} + C_2O_4^{2-} \rightarrow CrL_3^{2+} + [C_2O_4^{\bullet-}] \qquad (3)$$

$$[C_2O_4^{\bullet-}] \rightarrow CO_2 + CO_2^{\bullet-} \qquad (4)$$

This sequence of events prevents any back electron transfer, unless it were to occur within the caged radical pair, because the lifetime of $C_2O_4^{\bullet-}$ is (evidently) extremely short. (Indeed, it is conceivable that the products of eq 3 are directly CO_2 and $CO_2^{\bullet-}$.) The quenching process is akin to that between $*Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$, where electron transfer in the opposite direction is also irreversible. Events are more complicated, however, than the single quenching step of eq 3. The objective of this study is to characterize all aspects of the process by which $C_2O_4^{2-}$ quenches $*CrL_3^{3+}$.

Experimental Section

The salt $[Cr(2,2'\text{-}bpy)_3](ClO_4)_3\cdot{}^1/_2H_2O$ was made by the literature procedure.[2] The remaining CrL_3^{3+} complexes were available from other studies.[6] The electronic spectra[7,8] and luminescence lifetimes[9] agreed with the literature values.

A stock solution of titanium(III) was prepared by dissolving titanium sponge in 3.3 M HCl under anaerobic conditions.[10] The concentration of Ti^{3+} was determined spectrophotometrically, $\epsilon_{520} = 3.9$ L mol^{-1} cm^{-1}. The stock solution of Fe^{2+} was made by dissolving ferrous ammonium sulfate in 1 M H_2SO_4 and by treating the solution with zinc amalgam to reduce any trace of Fe^{3+} possibly present.

All other materials were the best grade commercially available. Some experiments were also performed by using sodium oxalate that had been recrystallized from water. This made no difference in the results.

The kinetics of the quenching reaction were studied by use of the laser flash photolysis system described earlier.[11,12] The excitation of CrL_3^{3+} was provided by a single 0.6-μs pulse from a Phase-R Model DL-1100 dye laser with excitation wavelengths of 423 and 460 nm.

The kinetics of the quenching process were followed by monitoring the decay in the emission signal at 727 nm. All quenching reactions were evaluated with oxalate ions present in large excess over the excited-state concentration.

The kinetics of the decay of the intermediate that was formed in several reactions was followed by monitoring the decrease in absorbance at 605 nm, starting at the point at which quenching was complete (some 7 to 12 μs, depending on the complex and the oxalate concentrations). In these experiments high oxalate concentrations were used to increase the rate of the quenching step.

The spectrum of the intermediate was determined for the complex $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$, whose quenching by oxalate ions is the fastest. The absorbance readings were made point-by-point over the desired wavelength range. The spectrum of $Cr(5\text{-}Cl\text{-}phen)_3^{2+}$ was then substracted from this composite spectrum.

The quantum yields for formation of CrL_3^{2+} were determined by measuring both the final $[CrL_3^{2+}]$ and the initial $[*CrL_3^{3+}]$. For $Cr(bpy)_3^{3+}$ the excited-state concentration was determined in the absence of $C_2O_4^{2-}$ from the absorbance at 445 nm, $\epsilon_{3*} = 3.0 \times 10^3$ M^{-1} cm^{-1}. The concentration of chromium(II) was determined at 560 nm in experiments containing $C_2O_4^{2-}$ with $\epsilon_2 = 4.85 \times 10^3$ M^{-1} cm^{-1}.[7] For $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$ and $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$ the situation was different because ϵ_{3*} values were unknown. They were determined in this work by employing the one-electron quenchers[6,13,14] Fe^{2+}, Ti^{3+}, and $Co([14]aneN_4)^{2+}$. The initial excited-state concentration was taken to be equal to the concentrations of chromium(II) formed under conditions of complete quenching. (ϵ_2 values are 3.0×10^3 M^{-1} cm^{-1} for $Cr(5\text{-}Cl\text{-}phen)_3^{2+}$ at 480 nm and 4.5×10^3 for $Cr(4,4'\text{-}Me_2bpy)_3^{2+}$ at 560 nm.[8]) All three one-electron reagents were used for $*Cr(5\text{-}Cl\text{-}phen)_3^{3+}$, but only Ti^{3+} was used for $*Cr(4,4'\text{-}Me_2bpy)_3^{3+}$, since the other quenchers featured too rapid back electron transfer. The values of ϵ_{3*} for $*Cr(5\text{-}Cl\text{-}phen)_3^{3+}$ are 2.4×10^3 M^{-1} (at 490 nm (sh)), 2.6×10^3 (510 nm), and 2.5×10^3 (545 nm); for $*Cr(Me_2bpy)_3^{3+}$ ϵ_{3*} is 4.7×10^3 M^{-1} cm^{-1} at 445 nm.

Results

Kinetics of Quenching by Oxalate Ions. The rates of quenching were determined by monitoring the exponential decrease in intensity of the emission from $*CrL_3^{3+}$ with time. All the preliminary experiments were done for L = bpy. In the first set of experiments the ground-state concentration was fairly high, 3.3

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[1] (a) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Lawrence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321. (b) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

[2] Brunschwig, B.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.

[3] Jamieson, M. A.; Serpone, N.; Hoffman, M. Z.; Bolletta, F. *Inorg. Chim. Acta* **1983**, *72*, 247.

[4] Bolletta, F.; Maestri, M.; Moggi, L.; Jamieson, M. A.; Serpone, N.; Henry, M. S.; Hoffman, M. Z. *Inorg. Chem.* **1983**, *22*, 2502.

[5] Serpone, N.; Jamieson, M. A.; Sriram, R.; Hoffman, M. Z. *Inorg. Chem.* **1981**, *20*, 3983.

[6] Bakac, A.; Zahir, K.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 5059.

[7] Konig, E.; Herzog, S. *J. Inorg. Nucl. Chem.* **1970**, *32*, 585.

[8] Serpone, N.; Jamieson, M. A.; Emmi, S. S.; Fuochi, P. G.; Mulazzani, Q. G.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1981**, *103*, 1091.

[9] Serpone, N.; Jamieson, M. A.; Henry, M. S.; Hoffman, M. Z.; Bolletta, F.; Maestri, M. *J. Am. Chem. Soc.* **1979**, *101*, 2907.

[10] Bakac, A.; Espenson, J. H.; Lovric, J.; Orhanovic, M. *Inorg. Chem.* **1987**, *26*, 4096.

[11] Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4104.

[12] Hoselton, M. A.; Lin, C.-T.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 2383.

[13] Bakac, A.; Zahir, K.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 315.

[14] (a) Simmons, C. A.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 581. (b) Huston, P. L.; Bakac, A.; Espenson, J. H. Submitted for publication in *Inorg. Chem.*

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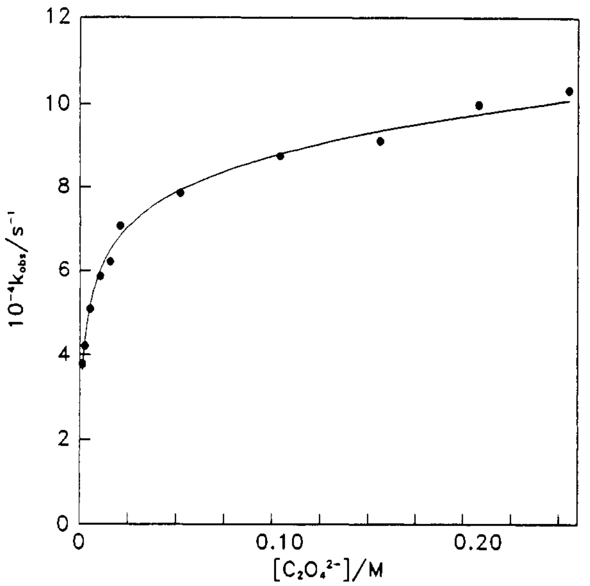

Figure 1. Plot of observed rate constants versus the oxalate ion concentration for the quenching of $^*Cr(bpy)_3^{3+}$ at nonconstant ionic strength. Experiments were done at low initial ground-state concentrations (1.6×10^{-5} M). The solid line shows the best-fit line according to eq 6.

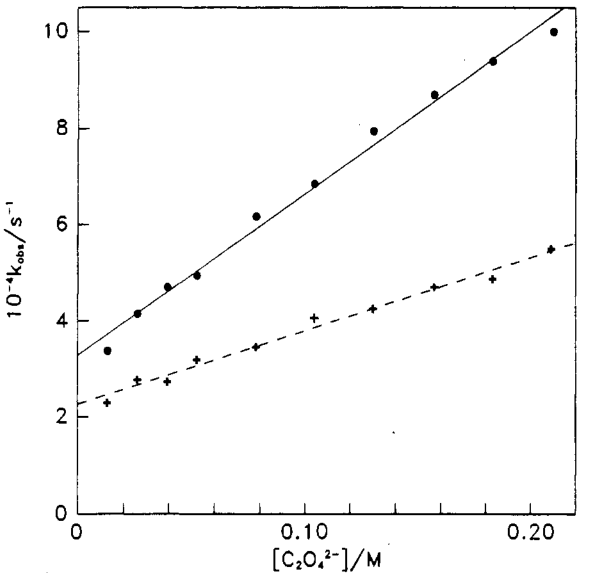

Figure 2. Variation of k_{obsd} with $[C_2O_4^{2-}]$ for quenching of $^*Cr(bpy)_3^{3+}$ at 1.6×10^{-5} M $Cr(bpy)_3^{3+}$. Data were taken at constant ionic strengths of 0.75 (upper) and 2.00 M (lower). The lines represent the least-squares fits to eq 10.

$\times 10^{-4}$ M $Cr(bpy)_3^{3+}$, and the concentration of oxalate ions was varied from 2.5 mM up to about 0.24 M. These trials consisted of one series in which the ionic strength varied with the concentrations of oxalate and others in which ionic strength was maintained at 1.0 and 2.0 M with sodium sulfate.

The system containing only oxalate ions yields a nonlinear dependence of k_{obsd} upon $[C_2O_4^{2-}]$, whereas there was but mild curvature in the same plot when μ was constant. There are two causes of the curvature: (a) the effect of variable ionic strength on the bimolecular quenching rate constant, which is due to the ionic strength effect on the ion-pairing constant between 3+ and 2− ions, and (b) the effect of an additional quenching pathway[13] between $Cr(bpy)_3^{2+}$ (the product of reductive quenching) and $^*Cr(bpy)_3^{3+}$ (eq 5; $k_5 = 5 \times 10^9$ M^{-1} s^{-1}). Both factors influence

$$^*Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+} \rightarrow Cr(bpy)_3^{2+} + Cr(bpy)_3^{3+} \qquad (5)$$

the situation when ionic strength is variable, but only factor b applies at constant ionic strength.

Table I. Summary of Rate Constants for the Quenching of $^*CrL_3^{3+}$ by Oxalate Ions[a]

L	$E°_{3^*/2}$[b]	$10^{-4}k_0/s^{-1}$	$10^{-5}k_q/M^{-1}\ s^{-1}$	$10^{-5}k_{ox}/s^{-1}$
5-Cl-phen	1.53	4.4	85.4	34.1
bpy	1.44	3.1	3.59	1.43
bpy	1.44	2.2[c]	1.57[c]	1.41
phen	1.42	0.8	4.14	1.65
5-Mephen	1.39	0.9	3.18	1.27
4,4′-Me_2bpy	1.25	0.8	0.21	0.084

[a] At 25.0 °C and (except as noted) $\mu = 0.75$ M. [b] Reference 2. [c] $\mu = 2.00$ M.

The quenching step represented by eq 5 is regarded in the context of this work as an undesirable side reaction that partially obscures the quenching by oxalate. To render reaction 5 harmless, additional experiments were done at a much lower concentration of the ground-state complex, 1.6×10^{-5} M. This results in a correspondingly lower concentration of $Cr(bpy)_3^{2+}$ such that the Cr(II) quenching pathway of eq 5 becomes negligible. Again, the rate constants were determined as a function of oxalate concentration, at both variable and constant ionic strengths of 0.75 and 2.00 M. In the case of nonconstant ionic strength, curvature is again observed (Figure 1), whereas at constant ionic strength, the variation of k_{obsd} with $[C_2O_4^{2-}]$ is linear (Figure 2).

Consider first the data at nonconstant ionic strength. We postulate an ion-pairing mechanism and arrive at the equation

$$k_{obsd} = \frac{k_0 + (k_0' + k_{ox})K_1[C_2O_4^{2-}]}{1 + K_1[C_2O_4^{2-}]} \qquad (6)$$

where K_1 is the ion-pairing constant, k_{ox} is the unimolecular rate constant for quenching within the ion pair, and k_0 and k_0' are the sums of rate constants for oxalate-independent decay of the excited state and ion pair, respectively. The ion-pairing constant is a function of the ionic strength. The value of K_1 was calculated at each ionic strength by using the Fuoss equation:[15,16]

$$K_1 = \frac{4\pi N\sigma^3}{3000} \exp[-(w(\sigma))/kT] \qquad (7)$$

$$w(\sigma) = \frac{Z_1Z_2e^2}{D_s\sigma(1 + \beta\sigma\mu^{1/2})} \qquad (8)$$

$$\beta = \left(\frac{8\pi Ne^2}{1000D_skT}\right)^{1/2} \qquad (9)$$

where D_s is the solvent dielectric constant, μ is the ionic strength, Z_1 and Z_2 are the charges of the ions, and σ is the distance of closest approach. Other symbols have their standard meanings. The distance of closest approach was taken to be the sum of the radii for $Cr(bpy)_3^{3+}$ (6.8 Å)[16,17] and $C_2O_4^{2-}$ (2.0 Å).[18] With these values of K_1, the data were fitted to eq 6 to yield the parameters $k_0 = 2.14\ (\pm 0.02) \times 10^4\ s^{-1}$ and $(k_0' + k_{ox}) = 1.46\ (\pm 0.03) \times 10^5\ s^{-1}$.

In the case of the experiments at constant ionic strength the rate law for excited-state quenching takes the form

$$-d \ln [^*Cr(bpy)_3^{3+}]/dt = a + k_q[C_2O_4^{2-}] \qquad (10)$$

The least-squares fits of the data, which are shown in Figure 2, resulted in values of $k_q = 3.59 \times 10^5$ M^{-1} s^{-1} ($\mu = 0.75$ M) and 1.57×10^5 M^{-1} s^{-1} ($\mu = 2.00$ M).

Equation 10 applies as well to the quenching of other tris(polypyridine)chromium(III) ions by oxalate ions at constant ionic strength. The complexes studied were $Cr(5\text{-Cl-phen})_3^{3+}$, $Cr(5\text{-Mephen})_3^{3+}$, $Cr(phen)_3^{3+}$, and $Cr(4,4'\text{-Me}_2bpy)_3^{3+}$. Quenching rate constants were determined as a function of $[C_2O_4^{2-}]$ at a constant ionic strength of 0.75 M. Values of k_q are listed in Table

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(15) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.
(16) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.
(17) Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777.
(18) Pederson, B. F.; Pederson, B. *Acta Chem. Scand.* **1964**, *18*, 1454.

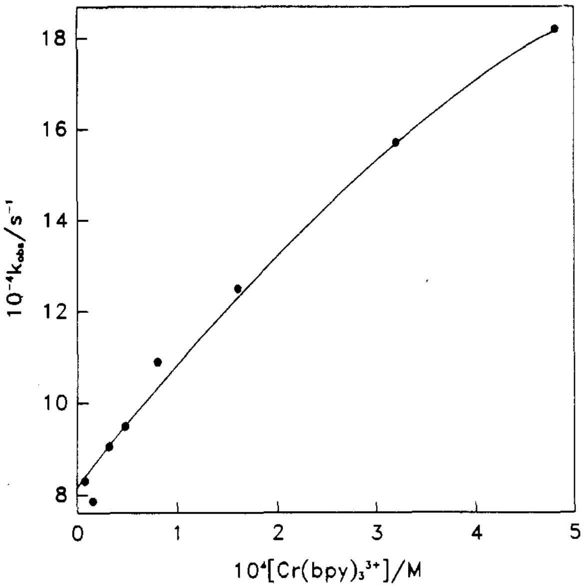

Figure 3. Variation of the first-order quenching rate constant with the ground-state concentration of $Cr(bpy)_3^{3+}$ at a constant oxalate ion concentration of 0.0522 M.

I. The values span a considerable range; a factor of 160 separates the fastest and slowest members.

Quantum Yields. In the case of $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$ the quantum yield, defined as $[Cr^{II}L_3^{2+}]_\infty/[{*}CrL_3^{3+}]_0$, is 2.1 ± 0.2. The value for this one complex, which has the highest quenching rate constant, is independent of the ground-state concentration over the range $(2.4\text{–}14.4) \times 10^{-5}$ M. The sequence of events represented by eq 3, 4, and 11 shows how the value $\Phi = 2$ arises.

$$CO_2^{\bullet -} + CrL_3^{3+} \rightarrow CO_2 + CrL_3^{2+} \text{ (or } CrL_2L'^{2+}\text{)} \quad (11)$$

For $Cr(bpy)_3^{3+}$ the quantum yield decreases systematically with increasing ground-state concentration, ranging from $\Phi = 1.7$ to 0.89. The limit of 1.7 at low $[Cr(bpy)_3^{3+}]$ again represents the idealized sequence of eq 3, 4, and 11, for which a value of 2.0 is expected. At higher ground-state concentration, however, a higher concentration of $Cr(bpy)_3^{2+}$ is formed and reaction 5 takes effect. That process is catalytic in chromium(II) and thus serves to reduce the quantum yield below the limiting value of 2.0. Also, simulations were performed in which a scheme consisting of eq 3, 4, and 11 was used, and the family of differential equations were solved by numerical methods by use of the program KINSIM.[19] Experimental results and the simulation agree qualitatively and stand in support of the model presented.

The effect of the CrL_3^{2+} quenching is also manifest in the kinetic data. Figure 3 shows the plot of k_{obsd} against $[Cr(bpy)_3^{3+}]$ at constant oxalate concentration. As $[Cr(bpy)_3^{3+}]$ increases, quenching by $Cr(bpy)_3^{2+}$, eq 5, becomes more important and the overall rate constant for the loss of ${*}Cr(bpy)_3^{3+}$ increases.

The excited state that is least reactive with oxalate ions is ${*}Cr(4,4'\text{-}Me_2bpy)_3^{3+}$. In this case, eq 5 becomes relatively much more important, and the quantum yield of the chromium(II) complex stays low, ca. 0.4–0.6, even at the lowest concentrations of CrL_3^{3+} employed. The relative contribution of the k_0 term is therefore greater, reducing the yield of CrL_3^{2+}.

Secondary Transient. In addition to the primary transients $C_2O_4^{\bullet -}$ and $CO_2^{\bullet -}$, quenching of the excited state of the 1,10-phen and substituted phen complexes by $C_2O_4^{2-}$ and H_2edta^{2-} produces a secondary transient characterized by a broad absorption in the range 500–660 nm (Figure 4). A transient is not seen when the 2,2'-bpy or 4,4'-Me_2bpy complexes are quenched by oxalate ions, although it is observed even in these cases when the quencher is H_2edta^{2-}. (The H_2edta^{2-} quenching was studied to elucidate the mechanism of quenching by oxalate ions, since similarities between the two cases had been noted.[6a]) The spectra of the secondary transient and of the final product for L = 5-Cl-phen are recorded in Figure 4. The spectrum of the final product matches that reported for $Cr(5\text{-}Cl\text{-}phen)_3^{2+}$.[8]

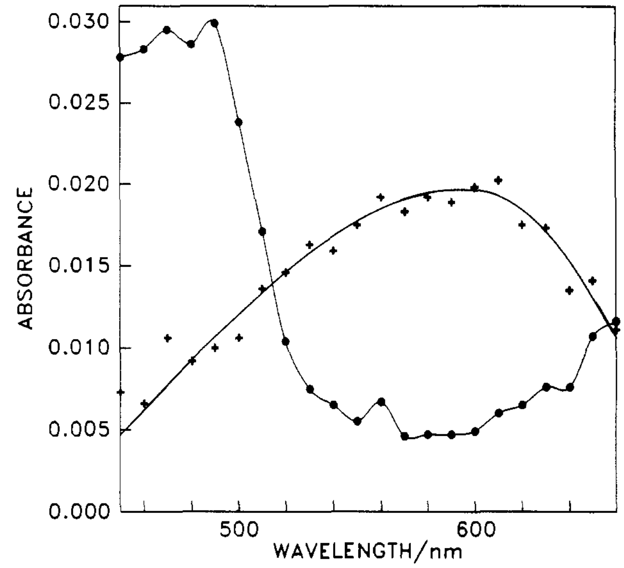

Figure 4. Spectra of the secondary transient (+) and of the final CrL_3^{2+} product (•) formed by the quenching of ${*}Cr(5\text{-}Cl\text{-}phen)_3^{3+}$ by oxalate ions. The absorbances of the secondary transient were evaluated 8 μs after the flash.

The rate constants for loss of the transient were determined at 605 nm at various ground-state concentrations. Experiments were done for $Cr(5\text{-}Cl\text{-}phen)_3^{3+}$ and $Cr(phen)_3^{3+}$ with both H_2edta^{2-} and $C_2O_4^{2-}$ as quenchers and for $Cr(bpy)_3^{3+}$ with H_2edta^{2-} as quencher only. The observed rate constants proved independent of the monitoring wavelength, 530–640 nm, and gave pseudo-first-order rate constants that are directly proportional to the ground-state concentration. Thus, the secondary transient (T) decays with a rate law $-d[T]/dt = k_T[T][CrL_3^{3+}]$. The values of the second-order rate constants ($10^{-9}k_T$, M^{-1} s^{-1}) are as follows:

L	quencher = $C_2O_4^{2-}$	quencher = H_2edta^{2-}
5-Cl-phen	1.10 (8)	1.35 (5)
phen	0.82 (4)	1.68 (7)
bpy		1.41 (7)

Acidic Solutions. Quenching does not occur at pH ≤4, indicating that both $H_2C_2O_4$ and $HC_2O_4^-$ are ineffective quenchers. Similarly, the Co(III) complex $(NH_3)_4CoC_2O_4^+$ is also an ineffective electron-transfer quencher.

Discussion

Oxalate Quenching. The dependences of k_{obsd} upon oxalate ion concentration suggest a preequilibrium ion pairing followed by electron transfer to form CrL_3^{2+} and $CO_2^{\bullet -}$, as shown in Scheme I for L = bpy. The $CO_2^{\bullet -}$ formed then reacts with a second CrL_3^{3+} as in eq 11.

Scheme I

$$Cr(bpy)_3^{3+} + h\nu \rightarrow {*}Cr(bpy)_3^{3+}$$

$${*}Cr(bpy)_3^{3+} \rightarrow Cr(bpy)_3^{3+} + h\nu' \quad k_0$$

$${*}Cr(bpy)_3^{3+} + C_2O_4^{2-} \rightleftarrows {*}Cr(bpy)_3^{3+},C_2O_4^{2-} \quad K_1$$

$${*}Cr(bpy)_3^{3+},C_2O_4^{2-} \rightarrow Cr(bpy)_3^{2+} + CO_2^{\bullet -} + CO_2 \quad k_{ox}$$

$${*}Cr(bpy)_3^{3+},C_2O_4^{2-} \rightarrow Cr(bpy)_3^{3+},C_2O_4^{2-} \quad k_0'$$

If one considers this scheme for the quenching of the excited state, the observed rate constant is given by eq 6. The fit of the data to Scheme I is shown by how well k_{obsd} values are fit to eq 6, by using at each point the Fuoss-calculated value of K_1 and the given oxalate ion concentration (Figure 1).

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(19) Barshop, B. A.; Wrenn, R. F.; Frieden, C. J. *Anal. Biochem.* **1983**, *130*, 134.

(20) Jamieson, M. A.; Serpone, N. *Coord. Chem. Rev.* **1981**, *39*, 121.

Consider next the determinations of the quenching rate constant carried out at constant ionic strength (0.75 or 2.00 M). In these experiments sodium sulfate was added to maintain the ionic strength. This introduces a second ion-pairing term (K_2) and also a rate constant k_0'' for the deactivation of the sulfate ion pair. The resulting description can be simplified by assuming the two ion-pairing constants are identical ($K = K_1 \cong K_2$),[21] yielding the equation

$$k_{\text{obsd}} = \frac{k_0 + k_0''KC + (k_{\text{ox}} + k_0' - k_0'')K[\mathrm{C_2O_4}^{2-}]}{1 + KC} \qquad (12)$$

where C is the sum $[\mathrm{C_2O_4}^{2-}] + [\mathrm{SO_4}^{2-}]$. According to this equation the constant a of eq 10 is equal to $(k_0 + k_0''KC)/(1 + KC)$, and $k_q = \{K(k_{\text{ox}} + k_0' - k_0'')\}/(1 + KC)$. The difference in the values of k_q for the two series can be shown to be due to the dependence of the ion-pairing constant on ionic strength. The Fuoss equation gives $K = 6.7$ M^{-1} ($\mu = 0.75$ M) and $K = 4.3$ M^{-1} ($\mu = 2.00$ M). The theoretical ratio of the slope at $\mu = 2.00$ M to that at 0.75 M is then 0.44. The experimental ratio is $(1.57 \times 10^5)/(3.59 \times 10^5) = 0.43$. This agreement validates the reaction scheme and the data treatment.

The values of k_{ox}, the unimolecular rate constant for quenching within the ion pair, are listed in Table I. They were calculated from the values of k_q and K under the assumption that $k_0' \simeq k_0''$. In that case $k_{\text{ox}} = k_q(1 + KC)/K$. A radius of 6.8 Å was used in the calculations for all the complexes examined.

The Transient Intermediate. The quenching of $\mathrm{Cr(phen)_3}^{3+}$, $\mathrm{Cr(5\text{-}Cl\text{-}phen)_3}^{3+}$, and $\mathrm{Cr(5\text{-}Mephen)_3}^{3+}$ by oxalate yields an intermediate, T. In these cases the $\mathrm{CO_2}^{\bullet-}$, formed in reactions 3 and 4, apparently does not transfer an electron directly to $\mathrm{CrL_3}^{3+}$ to produce $\mathrm{CrL_3}^{2+}$ and $\mathrm{CO_2}$, as it does for $\mathrm{Cr(bpy)_3}^{3+}$ and $\mathrm{Cr(4,4'\text{-}Me_2bpy)_3}^{3+}$. T has a broad absorption in the visible region, as shown by the spectrum obtained by quenching of $^*\mathrm{Cr(5\text{-}Cl\text{-}phen)_3}^{3+}$ by oxalate ions, Figure 4.

Two possibilities seem likely for the identity of T. Electron transfer from $\mathrm{CO_2}^{\bullet-}$ to the phenanthroline ring may produce a ligand radical species, $\mathrm{T} = [\mathrm{Cr^{III}L_2(L^{\bullet-})}]^{2+}$, analogous to the known[23] $\mathrm{Li^+bpy^{\bullet-}}$. Alternatively, $\mathrm{CO_2}^{\bullet-}$ may add to the ligand, producing a substituted-ring radical, $\mathrm{T} = [\mathrm{Cr^{III}L_2(L'^{\bullet-})}]^{2+}$. In either case the visible spectrum will have the features of a $\mathrm{phen}^{\bullet-}$ species. Examples of both types of reactivity of coordinated polypyridines exist. A ligand radical species was proposed in the reaction of $\mathrm{Ru(bpy)_3}^{3+}$ with $\mathrm{e_{aq}}^-$,[24] and a ligand addition species, in the reaction of $^\bullet\mathrm{CH_2OH}$ with $\mathrm{Cr(phen)_3}^{3+}$.[25] The assignment is a difficult one to make for the latter reaction, since the spectral data given[25] for the intermediate do not rule out the ligand radical species.[26,27]

It is interesting to note that $\mathrm{Cr(bpy)_3}^{3+}$ reacts with $^\bullet\mathrm{CH_2OH}$ to give $\mathrm{Cr(bpy)_3}^{2+}$ directly.[25] Thus, the difference between the bipyridine and phenanthroline complexes observed in our work with $\mathrm{CO_2}^{\bullet-}$ parallels that found with $^\bullet\mathrm{CH_2OH}$. The radical produced by the oxidation of $\mathrm{H_2edta}^{2-}$, on the other hand, yields long-lived intermediates with both types of complexes. Ultimately, however, we arrive at no convincing rationale as to the different species formed with bpy and phen complexes.

T reacts with ground-state $\mathrm{CrL_3}^{3+}$ to produce what appears to be $\mathrm{CrL_3}^{2+}$ by its electronic spectrum. The following seems to be the process occurring:

$$[\mathrm{Cr^{III}L_2(L'^{\bullet-})}]^{2+} + \mathrm{CrL_3}^{3+} \rightarrow (\mathrm{CrL_2L'})^{3+} + \mathrm{CrL_3}^{2+} \quad k_T \qquad (13)$$

The rate constants for reaction 13 vary somewhat with the nature of the quencher, implying that different quenchers ($\mathrm{H_2edta}^{2-}$ or oxalate) produce different intermediates T. This would be consistent with ligand addition. The differences in the rate constants are, however, not large enough to permit unambiguous distinction between the two possibilities.

Finally, we should consider the thermodynamics of the quenching process. The calculated one-electron reduction potential for $\mathrm{C_2O_4}^{2-}$ is

$$\mathrm{C_2O_4}^- + \mathrm{e}^- \rightarrow \mathrm{C_2O_4}^{2-} \qquad (14)$$

$E° = 0.60$ V.[28] The initial step of the quenching process

$$^*\mathrm{Cr(bpy)_3}^{3+} + \mathrm{C_2O_4}^{2-} \rightarrow \mathrm{Cr(bpy)_3}^{3+} + \mathrm{C_2O_4}^{\bullet-}$$

is therefore a favorable one, with $\Delta E = 0.86$ V.

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(21) This is a reasonable proposition, since $\mathrm{SO_4}^{2-}$ and $\mathrm{C_2O_4}^{2-}$ have very similar radii: Pringle, G. E.; Broadbent, T. A. *Acta Crystallogr.* **1965**, *19*, 426.

(22) This approximation is a reasonable one. Indeed the value of k_0'' (3.3×10^4 s^{-1}, from the intercept of k_{obsd} vs $[\mathrm{C_2O_4}^{2-}]$ in the absence of $\mathrm{SO_4}^{2-}$) is close to that of k_0 (1.4×10^4 s^{-1}) for the tris(bipyridine) complex. It is, however, not possible to evaluate k_0', and so further direct comparisons cannot be made.

(23) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(24) Jonah, C. D.; Matheson, M. S.; Meisel, D. *J. Am. Chem. Soc.* **1978**, *100*, 1449.

(25) Venturi, M.; Emmi, S.; Fuochi, P. G.; Mulazzani, Q. G. *J. Phys. Chem.* **1980**, *84*, 2160.

(26) Konig, E.; Kremer, S. *Chem. Phys. Lett.* **1970**, *5*, 87.

(27) Calculated from the two-electron potential ($\mathrm{H_2C_2O_4/CO_2}$) and the $\mathrm{CO_2/CO_2}^{\bullet-}$ potential (−1.9 V) and the K_{a_1} and K_{a_2} values for $\mathrm{H_2C_2O_4}$.

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Photochemical Cleavage of Carbonate in $\mathrm{Cp^*Rh(CO_3)\cdot 2H_2O}$

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Irradiation of $\mathrm{Cp^*Rh(CO_3)\cdot 2H_2O}$ in THF at 351 nm leads to photochemical cleavage of the carbonate ligand to form carbon dioxide and a metal–oxo intermediate that reacts with the starting material to produce the dimeric $[\{\mathrm{Cp^*Rh}\}_2(\mathrm{OH})_3]^+$ complex. The photoreaction is wavelength dependent. The reaction quantum yield in THF is 0.24 ± 0.03 with 351-nm irradiation and is immeasurably small at wavelengths longer than 488 nm. The characterization of the photoproducts and the photochemical mechanism are discussed.

The photochemical reactivity of metal–carbonato complexes has not been well studied. Most earlier work shows that ready elimination of $\mathrm{CO_2}$ occurs with the concomitant formation of highly reactive species.[1–3] The carbonato ligand is photochem-

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(1) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.

(2) Krishnamurty, K. V.; Harris, G. M.; Sastri, V. S. *Chem. Rev.* **1970**, *70*, 171.