

Intermediates in the Photochemistry of Tris(oxalato)cobaltate(III) Ion in Aqueous Solution. Free and Coordinated Radicals¹

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Abstract: The flash photolysis of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in aqueous solution generates an intermediate, I, absorbing weakly in the 360-nm region, which is seen as arising from ligand-to-metal charge transfer followed by rapid spin relaxation of the resulting Co(II) center. This intermediate, considered to involve a bidentate oxalate radical ion coordinated to the high spin Co(II), $[(\text{C}_2\text{O}_4)_2\text{Co}^{\text{II}}(\text{C}_2\text{O}_4^-)]^{3-}$, is viewed as being in rapid equilibrium with a minor component, intermediate II, in which the oxalate radical is monodentate with water occupying the sixth coordination site, $[(\text{C}_2\text{O}_4)_2\text{Co}^{\text{II}}(\text{C}_2\text{O}_4^-)(\text{H}_2\text{O})]^{3-}$. The latter species is designated as the direct precursor to free C_2O_4^- radicals. These radicals normally react rapidly with the substrate to generate a second equivalent of Co(II), but at high free radical and low substrate concentrations bimolecular dismutation reactions remove the C_2O_4^- . The slow first-order decay of intermediate I ($k = 58 \text{ sec}^{-1}$ at pH 6 and 23°), which corresponds to a larger specific rate for unimolecular loss of the coordinated radical from intermediate II, is accelerated by acid ($k = 82 \text{ sec}^{-1}$ at pH <1 and 23°) in a way which indicates the monodentate coordinated radical possesses acid-base character with a $\text{p}K_a \sim 2.5$. In the presence of O_2 , intermediate I decays more rapidly; the observed $k = 3.4 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ gives an upper limit for the bimolecular reactivity of I toward O_2 . Activation parameters for these processes have been obtained. The presence of added oxalate has a pronounced effect on the spectrum and decay kinetics of the intermediates. From the retardation of the decay and the significant increase in absorption and change in spectrum, it is concluded that free oxalate converts I and II into a new intermediate, III, related to II by substitution of a monodentate $\text{C}_2\text{O}_4^{2-}$ for H_2O in the sixth coordination site. The dissociation equilibrium quotient for the conversion of species III to I and free oxalate is $\sim 1 \times 10^{-3}$.

The photochemistry of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ has been extensively studied as an example of the general behavior of coordinated oxalates.² In aqueous solution, irradiation in the charge-transfer spectral region ($\lambda < 350 \text{ nm}$) or within the 350–480-nm d–d band results in the formation of Co^{2+} ;^{3,4} irradiation of the optically active complex with visible light causes photoracemization.⁵ Recently, Demas and Adamson⁶ reported on the photosensitized reduction of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ using Ru(bipy)₃³⁺ as the donor. Irradiation of the complex in frozen solution causes esr signals to be generated which have been attributed to intermediate species.^{7,8} As well, a number of papers have dealt with the photolysis of solid $\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3$.^{9–11}

Interestingly, the flash photolysis of this complex in aqueous solution has received scant attention. Parker and Hatchard,¹² in a paper dealing almost exclusively with $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, presented very preliminary results

on $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$: “Cobaltioxalate [shows] three distinct stages, an initial ‘instantaneous’ rise in absorption (at 313 nm), a rapid (though measurably slow) fall in absorption and finally a slow fall in absorption.” No mechanistic conclusions could be drawn from this information except by analogy to $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$. Recent work by Cordemans, *et al.*,¹³ on the flash photolysis of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in the presence of $3 \times 10^{-3} \text{ M}$ oxalic acid has characterized some aspects of the behavior of the intermediate species formed in that system.

Recently we reported¹⁴ that amine–oxalate complexes of Co(III) [$\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$, $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$, and $\text{Co}(\text{en})_2\text{C}_2\text{O}_4^+$] exhibit a photochemical pathway in which oxalate ligand decomposition occurs by means of heterolytic C–C bond scission leading to the formation of the C-bonded formato linkage isomer. One of the objectives of the flash photolysis study reported here was to ascertain the possible involvement of similar ligand-localized excited states in the photochemistry of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$. We also wished to evaluate the role of the oxidized ligand radical, C_2O_4^- , or its equivalent, CO_2^- , in the photoredox process and to determine the nature of the intermediate species which act as precursors to the final products.

Experimental Section

The flash photolysis apparatus and the procedures followed have already been described.¹⁴ Continuous photolysis was performed in the 22-cm flash photolysis cell using the 150-W xenon analyzing lamp as the source. $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ was prepared according to the literature¹⁵ or by recrystallization of the material obtained

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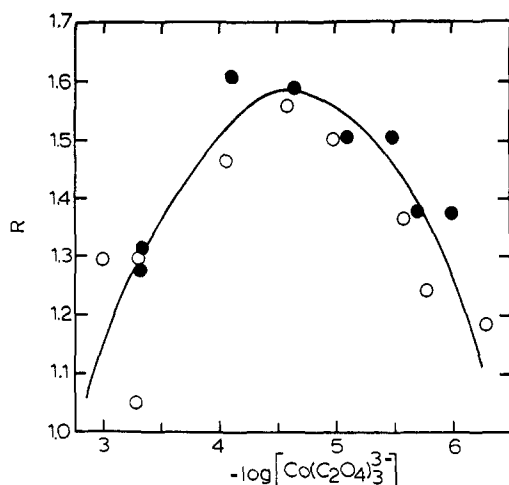


Figure 1. Dependence of R (the ratio of the amount of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ destroyed in the flash of N_2 -purged solutions to that destroyed in O_2 -saturated solutions) on the concentration of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$: \circ , pH 1; \bullet , pH 6.

from Alfa Inorganics from water and ethanol until the spectrum of the complex showed no further change. Spectra were run on Cary 14 and 16 spectrophotometers and the pH values of the solutions were measured using a calibrated Beckman Zeromatic pH meter. All experiments were performed at ambient temperature (23°) using an unjacketed flash photolysis cell except for those in which activation parameters were measured; then a water thermostated cell was used. All solutions were purged with high purity N_2 unless the presence of O_2 was desired.

Because of the photosensitivity of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$, exposure of the solution to the analyzing lamp in the flash photolysis experiments was minimized by the use of an electric shutter which was opened for short periods of time (a few seconds) during the experiment. In addition, filters were always in place in front of the analyzing lamp to remove the light of wavelengths < 300 nm unless shorter wavelengths were being monitored.

Results

Destruction of Substrate. In the continuous photolysis study by Copestake and Uri,³ the presence or absence of air in the solutions had no effect on the quantum yield of Co^{2+} formation when the substrate concentration was $5 \times 10^{-3} M$. We recently showed¹⁶ that, in the acid-catalyzed thermal redox decomposition of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$, the rate of destruction of the substrate depended on the presence of O_2 in a way which demonstrated that at low substrate concentrations scavenging of the C_2O_4^- radicals (in their conjugate acid form, $\text{C}_2\text{O}_4\text{H}$) by O_2 was competitive with reduction of the complex by the radical. In order to demonstrate the same scavenging mechanism in the photochemistry, solutions of varying substrate concentration at pH 6 were photolyzed for a fixed time (corresponding to less than 10% of the complex destroyed) in the presence and absence of O_2 , and the amount of substrate lost was determined spectrophotometrically. In these preliminary experiments the value of R , the ratio of the amount of complex destroyed in a N_2 -purged solution to the amount destroyed in an O_2 -saturated ($1.3 \times 10^{-3} M$) solution, varied from $1.3 (\pm 0.2)$ for $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1 \times 10^{-3} M$ to $1.9 (\pm 0.2)$ for $1 \times 10^{-5} M$ solution.

This same test was applied to solutions photolyzed by means of the flash lamps. Because of the high photon flux from the unfiltered flash, the extent of reaction for the very dilute complex solutions was very high ($> 90\%$) even for a single flash. For concentrated solutions (1

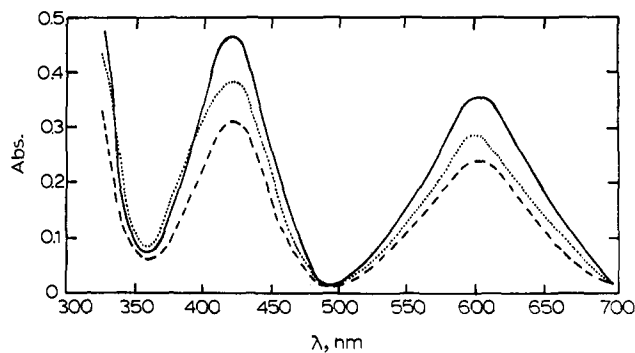


Figure 2. Spectrum of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ before the flash (—), immediately after the flash (.....), and at $t = \infty$ after the flash (---): $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1.0 \times 10^{-4} M$, pH 6.0, optical path length 22 cm, N_2 -purged solution.

$\times 10^{-3} M$), the per cent decomposition was so low in a single flash that the same solution had to be flashed five times in order to obtain reliable absorbance changes in the spectrum of the substrate. The values of R as a function of $-\log [\text{Co}(\text{C}_2\text{O}_4)_3^{3-}]$ are shown in Figure 1. Each point is the average of at least two determinations and the error in the knowledge of R is $\pm 10\%$. Despite variations in the flash intensity between pairs of runs and the problems of inhomogeneous light absorption at high concentrations and large depletion of substrate at low concentrations, it is clear the value of R reaches a maximum in the middle of the concentration range, although it never reaches a value of 2, and that it approaches the theoretical limit of unity at both higher and lower substrate concentrations. In all cases the final spectrum of the solution after the flash was the same as before, except for the decrease in absorbance due to loss of substrate.

Transient Spectrum. Upon exposure to a 500-J unfiltered flash, the absorbance of a $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ solution at $t = \infty$ was less than that at $t = 0$ by amounts corresponding to the total amount of complex destroyed by the flash. The total decrease in absorbance as measured by the flash spectrophotometry, whether for a N_2 - or O_2 -purged solution, could be correlated within experimental error with the changes measured on the Cary spectrophotometer as described in the previous section. But immediately after the flash (30–50 μsec after initiation), the absorbance of the solution was greater or less than the original absorbance, depending upon the monitoring wavelength. For example, in the region from 330 to 400 nm, the absorbance of a N_2 -purged solution *increased* upon flashing and then decayed slowly to its $t = \infty$ value. At $\lambda > 400$ and < 330 nm (limited in practice by the photomultiplier response and the intense charge-transfer absorption of the complex), the absorbance of the solution *decreased* instantaneously upon flashing and then further decreased slowly to its $t = \infty$ value. A plot of these transient spectral data (Figure 2) reveals that, except in the region from 320 to 440 nm, the spectrum of the solution immediately after the flash is identical with that of the substrate. Furthermore, the extent of the immediate decrease in the region $320 > \lambda > 440$ nm can be correlated perfectly with the absorptivity of the substrate. The conclusion must be drawn that a certain amount of substrate is destroyed initially by the flash with an additional amount lost by the slow reaction. Having

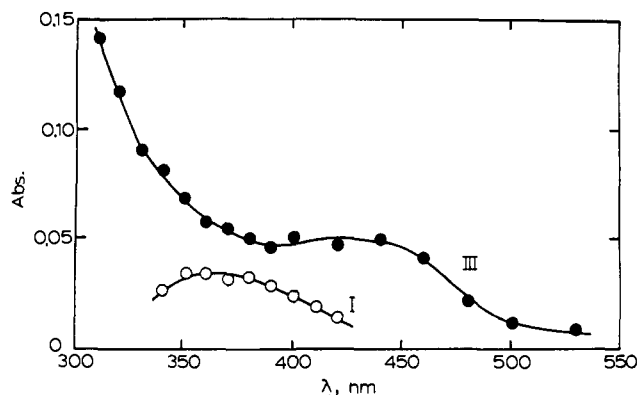


Figure 3. Spectra of intermediates I and III recorded immediately after the flash: O, $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1.0 \times 10^{-4} \text{ M}$, pH 6.0, N_2 -purged solutions; ●, $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 2.5 \times 10^{-5} \text{ M}$, $[\text{C}_2\text{O}_4^{2-}] = 1.0 \times 10^{-2} \text{ M}$, pH 6.0, N_2 -purged solutions.

drawn this conclusion, it was then possible to calculate the absorbance of the substrate destroyed by the flash and to evaluate the absorbance at $\lambda < 440 \text{ nm}$ due to another species. The open-circled points in Figure 3, obtained in this way, show the spectrum of an intermediate (I) formed by the flash. It should be noted from Figure 2 that the correction for the loss of the substrate was minimal at 360 nm where $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ exhibits a spectral window. Admittedly, the absorbance of the intermediate is weak and, because of the strong absorption of the substrate at the shorter wavelengths, its exact profile could not be precisely determined. These spectral characteristics were independent of solution acidity between pH 1 and 6.

In the presence of O_2 , as indicated in the previous section, the total amount of substrate destroyed was less (except at the highest substrate concentrations) than in N_2 -purged solutions. However, the *initial* changes in the absorbance of the solution upon flashing were the same for both N_2 - and O_2 -purged solutions. Thus, the spectrum of the transient intermediate in the 320–440-nm region and the amount of substrate destroyed initially by the flash (as monitored at 600 nm) were unchanged by the presence of O_2 , but the secondary slow loss of substrate was largely quenched, with at most only an additional 25% of the complex being destroyed in O_2 compared with the additional 100% loss in the presence of N_2 . As before, these spectral characteristics were independent of pH (1–6).

When the flash photolysis cell was surrounded by a Pyrex sleeve in order to restrict the flash to $\lambda > 320 \text{ nm}$, only a small decrease in the substrate concentration at 600 nm was observed. Any transient absorption in the 360-nm region was too weak to characterize.

A number of experiments were conducted at a substrate concentration of $4 \times 10^{-6} \text{ M}$ in order to observe the short wavelength spectral region. Under these conditions the absorbance changes at 360 and 600 nm were too small to observe. The absorption at $\lambda < 320 \text{ nm}$ showed the same behavior patterns as did the 600-nm absorption at higher substrate concentrations. There was no evidence for a separate intermediate in the 280-nm region.

Decay Kinetics. The decay of the transient intermediate (I) was monitored at 360 nm and the secondary loss of the substrate was monitored at 600 nm. Both these decays were established to be first order from a

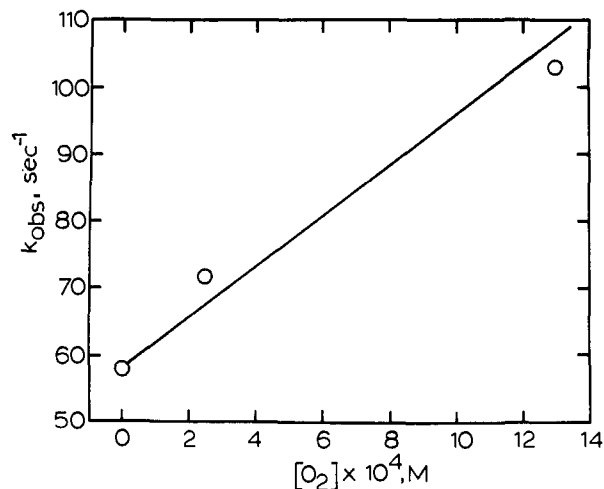


Figure 4. Dependence of the observed rate constant for intermediate decay on $[\text{O}_2]$: $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1.0 \times 10^{-4} \text{ M}$, pH 6.0, $\lambda 360 \text{ nm}$.

computer plot of the data and from the independence of the half-life of the decay when the flash intensity (and thus initial concentration of transient species) was changed. The decays were also independent of the initial substrate concentration ($5\text{--}10 \times 10^{-6} \text{ M}$). At pH 6.0 in a N_2 -purged solution ($[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1 \times 10^{-4} \text{ M}$), the decay of the transient intermediate and the secondary loss of the substrate were identical within experimental error with $k = 58 \text{ sec}^{-1}$ ($\pm 15\%$ standard deviation).

In addition to quenching the secondary loss of substrate, O_2 had a pronounced effect on the decay of the intermediate. Figure 4 shows that the observed first-order rate constant increased in a linear manner as the concentration of dissolved O_2 was increased. This behavior demonstrates that the observed rate constant can be written as the sum of two terms, $k_{\text{obsd}} = k_1 + k_2[\text{O}_2]$, where $k_1 = 58 \text{ sec}^{-1}$ and $k_2 = 3.4 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$.

The observed first-order rate constant for the decay of the transient intermediate and the coupled secondary loss of the substrate were dependent upon the pH of the solution in the same way as shown in Figure 5. From the shape of the pH-dependence plot, it can be concluded that the species involved in the reaction very likely possesses acid–base character with an apparent $\text{p}K_a$ of ~ 2.5 .

Activation parameters for k_1 and k_2 were obtained for solutions containing a $1 \times 10^{-4} \text{ M}$ complex at pH 6.0. The values of k_{obsd} were obtained at 15.7, 25.2, and 34.7° in the presence of N_2 or O_2 with monitoring at 360 and 600 nm. The values are given in Table I.

Table I. Activation Parameters for k_1 and k_2^a

	k_1		k_2
	600 nm, N_2 -purge	360 nm, N_2 -purge	360 nm, O_2 -purge
E_a , kcal mol $^{-1}$	18 ± 2	19 ± 2	15 ± 2
ΔH^\ddagger , kcal mol $^{-1}$	17 ± 2	18 ± 2	14 ± 2
ΔS^\ddagger , eu	8.4 ± 1.6	12 ± 2	9.5 ± 1.0

^a $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1 \times 10^{-4} \text{ M}$, pH 6.0.

The following added solutes had little or no effect on the value of k_{obsd} in N_2 or O_2 at both monitoring wave-

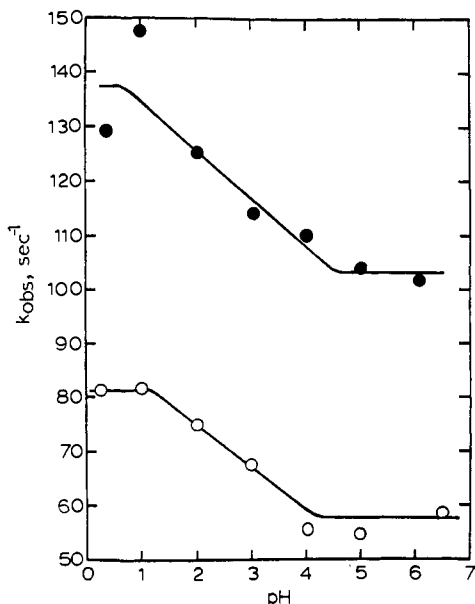


Figure 5. Dependence of the observed rate constant for intermediate decay on pH ($[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1.0 \times 10^{-4} M$): O, λ 600 nm, N_2 -purged solutions; ●, λ 360 nm, O_2 -saturated solutions.

lengths with $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1 \times 10^{-4} M$ at pH 6–7: NaClO_4 (0.1 M), Co^{2+} ($5 \times 10^{-4} M$), 2-propanol (1 M), sodium formate ($5 \times 10^{-3} M$), and sodium acetate ($5 \times 10^{-3} M$). As far as could be determined, these materials as well did not affect the nature of the transient absorption at 360 nm. On the other hand, the decay of the transient and the coupled loss of substrate were doubled in rate in solutions containing 90–100% methanol. Oxygen had the same effect as in aqueous solution; the rate of disappearance of the intermediate was increased and the secondary loss of substrate was quenched. The O_2 effect in methanol is magnified because of the higher solubility of O_2 in that solvent than in water but the value of k_2 remains virtually unchanged.

Effect of Added Oxalate. A pronounced effect on the spectrum of the intermediate and its decay kinetics is caused by the presence of added oxalate. Figure 3 shows the spectrum of the transient intermediate in the presence of $1.0 \times 10^{-2} M \text{C}_2\text{O}_4^{2-}$ (III); the transient spectrum in the absence of added oxalate is also shown for comparison (I). The change in the spectrum upon addition of oxalate is smooth, with the greatest change in absorption occurring when $[\text{C}_2\text{O}_4^{2-}] \sim 10^{-3} M$. In parallel with this spectral change is the decrease in the decay rate of the transient with increase in $[\text{C}_2\text{O}_4^{2-}]$ and the secondary loss of substrate as shown in Figure 6; here again the transient did not absorb significantly at 600 nm. The pH dependence of the rate of transient decay was determined in the presence of 0.01 M $\text{C}_2\text{O}_4^{2-}$ by monitoring the transient decay in O_2 at 360 nm and the substrate loss in N_2 at 600 nm. As before, transient decay and secondary substrate loss occurred in concert. These results are shown in Figure 7. As in the case of the decay of the transient in the absence of added oxalate, the observed first-order rate constant is increased in acidic solution with an apparent $\text{p}K_a$ value of ~ 2 . The presence of O_2 has the same effect as described before, causing an increase in the rate of disappearance of the transient intermediate. In 2×10^{-2}

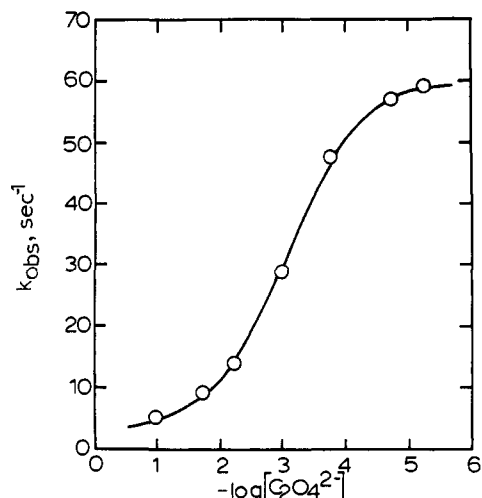


Figure 6. Dependence of k_{obs} on $[\text{C}_2\text{O}_4^{2-}]$: $[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1.0 \times 10^{-4} M$, pH 6.9, λ 600 nm, N_2 -purged solutions.

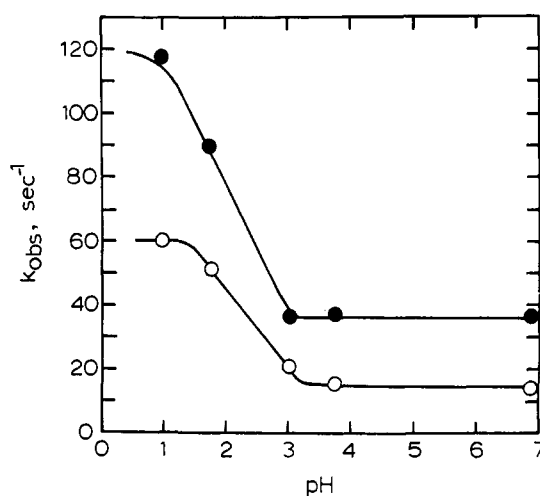


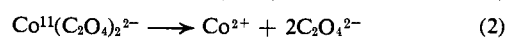
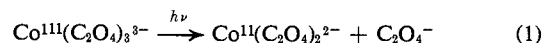
Figure 7. Dependence of k_{obs} on pH in the presence of added oxalate ($[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] = 1.0 \times 10^{-4} M$, $[\text{C}_2\text{O}_4^{2-}] = 1.0 \times 10^{-2} M$): O, λ 600 nm, N_2 -purged solutions; ●, λ 360 nm, O_2 -saturated solutions.

$M \text{C}_2\text{O}_4^{2-}$ at pH 7, the value of k_2 is reduced to about $1.3 \times 10^4 M^{-1} \text{sec}^{-1}$.

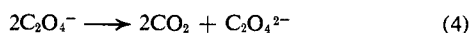
A number of experiments were performed at a substrate concentration of $4 \times 10^{-6} M$ with added $\text{C}_2\text{O}_4^{2-}$ at pH 6. The monitoring wavelength was 280 nm and the decay of the transient intermediate in a N_2 -purged solution followed the same trend as the points shown in Figure 6.

Discussion

Copstake and Uri³ found that, at a given photolysis wavelength, the quantum yield of formation of Co^{2+} , $\phi_{\text{Co}^{2+}}$, from the irradiation of aqueous solutions of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$, was independent of $[\text{complex}]$, $[\text{H}^+]$, $[\text{C}_2\text{O}_4^{2-}]$, and $[\text{Co}^{2+}]$, the presence of alcohol, and the deaeration of the solutions. They proposed a photochemical mechanism that has served as the model for the behavior of other tripositive transition metal oxalato complexes.⁴



In the continuous photolysis, the steady-state concentration of $C_2O_4^-$ radicals is very low, so that the rate of reaction 3 ($k_3 \sim 10^{10} M^{-1} sec^{-1}$)¹⁶ far exceeds the rate of the radical disproportionation for which $2k_4 = 9.6 \times 10^8 M^{-1} sec^{-1}$ in neutral solution.¹⁷ In acidic solution,



where the radical is expected to be protonated, the value of k_4 is believed¹⁷ to be several orders of magnitude smaller, although the experimental data are not conclusive on this point.

In the flash photolysis experiments reported here, the total amount of substrate destroyed by one flash, as determined spectrophotometrically, was independent of $[H^+]$, $[C_2O_4^{2-}]$ (up to $1 \times 10^{-2} M$), $[Co^{2+}]$, alcohols, and the other solutes added to the system (except O_2) as long as the substrate concentration and flash intensity remained constant from one flash to another. Naturally, variation of these latter two conditions affects the intensity of the absorbed radiation; in the Copestake and Uri work,³ the concentration of the complex was relatively high, usually $5 \times 10^{-3} M$, so that complete light absorption was ensured. Their failure to observe an effect on $\phi_{Co^{2+}}$ upon the deaeration of their solutions is understood in terms of the competition for the $C_2O_4^-$ radical by substrate (reaction 3) and O_2



for which $k_5 = 10^9-10^{10} M^{-1} sec^{-1}$ by analogy to the similar reaction involving CO_2^- .¹⁸

This comparison of the gross features of the continuous and flash photolysis of $Co(C_2O_4)_3^{3-}$ indicates that the high photon flux available from the flash does not alter the overall mechanism of the reaction. The mechanism deduced from the flash photolysis results can be taken as representing the behavior of the system under lower continuous light intensities. In that case, the initial absorption of light generates, after completion of the various rapid excited state processes, an intermediate (I) which absorbs in the 360-nm region. This intermediate then decays *via* a first-order process with a rate that is dependent upon temperature, pH, O_2 , and the presence of other solutes. It is clear that the decay of I monitored at 360 nm parallels the decay of the substrate monitored at 600 nm and that, while O_2 accelerates the rate of decay of I, O_2 effectively quenches the secondary loss of the substrate. This leads to the conclusion that the slow decay of I results in the formation of a species that reacts very rapidly with $Co(C_2O_4)_3^{3-}$. Such a species is undoubtedly the $C_2O_4^-$ radical, and the remainder of this discussion will deal with the identification of I, the manner in which it gives rise to $C_2O_4^-$, and the behavior of the $C_2O_4^-$ free radicals.

Free Radicals. The generation of free $C_2O_4^-$ radicals (or alternatively CO_2^-) in the photolysis of $Co(C_2O_4)_3^{3-}$ was established earlier by experiments involving the polymerization of vinyl monomer and the reduction of Hg(II) when those species were present in the photolysis mixture.³ The generation of radicals has been further confirmed in the continuous and flash photolysis by the

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determination of the value of R , the ratio of the amount of complex destroyed in a N_2 -purged solution to the amount destroyed in an O_2 -saturated solution, as a function of the concentration of substrate (Figure 1). The increase in the value of R from 1 at high substrate concentrations toward 2 at lower concentrations is in accord with reactions 3 and 5. The further diminution of the value of R toward 1 as the substrate concentration is further reduced is due to the introduction of reaction 4 in the flash photolysis experiments. The concentration of radicals from the flash is 10^{-5} – $10^{-6} M$ which encourages their bimolecular disproportionation at the expense of substrate reduction at low complex concentration. Thus, reaction 4 competes with reaction 3 and the presence of O_2 has no effect on the loss of substrate. The behavior shown in Figure 1 is completely consistent with the values of the rate constants quoted earlier.

It is to be noted that the dependence of R on $[Co(C_2O_4)_3^{3-}]$ shown in Figure 1 is the same at both pH 1 and 6. Although the acid-base properties of the $C_2O_4^-$ radical are not known, it is reasonable to assume that the pK_a of C_2O_4H lies somewhere between the pK_a of $C_2O_4H^-$ (4.1) and the pK_a of the CO_2H radical (1.4).¹⁹ Thus, at pH 1, the $C_2O_4^-$ radical is most likely in its conjugate acid form. It may be concluded, therefore, that the ratios of the rate constants for reactions 3–5 are the same irrespective of the state of protonation of the radical.

The product of reaction 5 is the O_2^- free radical. From the diminution of the extent of loss of substrate from reaction 3 in the presence O_2 , the conclusion must be drawn that the O_2^- radical does not further reduce $Co(C_2O_4)_3^{3-}$.

In a recently reported experiment,⁶ $C_2O_4^-$ radicals (or C_2O_4H) were generated by the action of $Ru(bipy)_3^{3+}$ on oxalic acid at pH 1 in the presence of $Co(C_2O_4)_3^{3-}$. Very little reduction of the cobalt complex was noted and the conclusion was drawn that radical attack on $Ru(bipy)_3^{3+}$ was at least 100 times faster than reaction 3. It is certainly possible that the reaction of C_2O_4H with $Ru(bipy)_3^{3+}$ occurs with diffusion controlled rates and that reaction 3 (with the radical protonated) has a rate constant of $\sim 10^8 M^{-1} sec^{-1}$; C_2O_4H would not be expected to be as facile an electron transfer agent as $C_2O_4^-$.

All the evidence indicates that free $C_2O_4^-$ radicals arise from the decomposition of the transient intermediate I. However, the question of whether $C_2O_4^-$ radicals are produced directly in a primary process as in reaction 1 must be examined. If $C_2O_4^-$ radicals were produced during the duration of the flash, fast reaction 3 would be the destructive mode for the radicals with the elimination of another equivalent of substrate. The addition of O_2 should make reaction 5 operative in competition with reaction 3 under the conditions of the experiment ($[Co(C_2O_4)_3^{3-}] = 1 \times 10^{-4} M$; $[O_2] = 1.3 \times 10^{-3} M$) thereby causing the amount of substrate destroyed initially by the flash to be reduced. We have already seen that such conditions virtually eliminate the slow, secondary loss of substrate by the radicals formed from I. The fact is that the amount of substrate destroyed initially by the flash is independent of the presence of O_2 . The conclusion must be drawn that

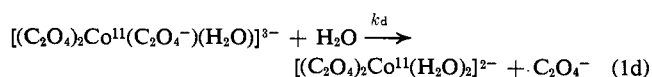
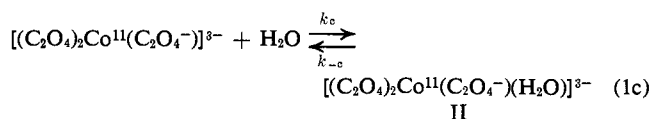
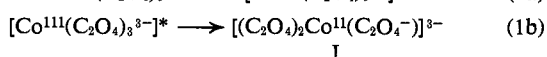
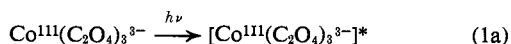
(19) G. V. Buxton and R. M. Sellers, *J. Chem. Soc., Faraday Trans. 1*, **69**, 555 (1973).

free $C_2O_4^-$ radicals are not generated in the primary step and that reaction 1 is not a valid representation of the mechanism. Rather, the intermediate I, formed initially, is a precursor of the $C_2O_4^-$ radicals and the Co^{2+} final product.

Nature of the Transient Intermediate. At the start it must be noted that the intermediate I does not exhibit the kinetics characteristics observed for the C-bonded formate isomer formed in the case of the amine-oxalato complexes.¹⁴ Specifically, the intermediate from the flash photolysis of $Co(NH_3)_4C_2O_4^+$ and $Co(en)_2C_2O_4^+$ decays more rapidly in neutral solution than in acidic and is unaffected by the presence of O_2 or free oxalate. The conclusion must be drawn that the intermediate arising from $Co(C_2O_4)_3^{3-}$ cannot be identified with that from the amine-oxalato complexes.

Instead, we see intermediate I as arising simply from the initial charge-transfer excitation with electron transfer from ligand to the e_g orbital of the metal center forming low-spin ($t_{2g}^6e_g$) Co(II). However, spin relaxation to the high-spin ($t_{2g}^5e_g^2$) configuration may be presumed to occur in less than 10^{-6} sec.²⁰ Thus, the intermediate produced in the flash photolysis would be in the high-spin Co(II) state long before observations would have begun.

Intermediate I can then be viewed as involving a $C_2O_4^-$ radical coordinated to a high-spin Co(II) metal center. Of course, a species such as $[(C_2O_4)_2Co^{II}(C_2O_4^-)]^{3-}$, in which the radical maintains bidentate coordination, has been proposed in the past,^{12,13} and a similar speculative proposal of a monodentate coordinated radical has also been made.⁸ The suggestion that intermediate I is of the latter type seems unlikely, particularly in view of the observed slow loss of $C_2O_4^-$ to solvent. Thus, compare our values of $k = 58 \text{ sec}^{-1}$ (pH 6, 23°) and $\Delta H^\ddagger \sim 18 \text{ kcal mol}^{-1}$ (Table I) with values for H_2O exchange in $Co(H_2O)_6^{2+}$: $k = 2.2 \times 10^6 \text{ sec}^{-1}$ at 25°, $\Delta H^\ddagger = 10.3 \text{ kcal mol}^{-1}$.²¹ A more reasonable view is that I, the spectrally observed species, involves chelated $C_2O_4^-$ and that this intermediate is in a rapidly established equilibrium (or pseudo-equilibrium) with a small amount of a second intermediate, II, involving monodentate $C_2O_4^-$, with the sixth coordination site filled by a water molecule. The latter intermediate is, accordingly, the direct precursor to the free $C_2O_4^-$ radical. Thus, we suggest reaction 1 can be replaced by the more detailed mechanism



where all the above Co(II) species are high spin and where $k_c \ll k_{-c} \gg k_d$. The complex $[(C_2O_4)_2Co^{II}(H_2O)_2]^{2-}$ would then equilibrate with $Co^{II}(C_2O_4)$ -

(20) J. F. Endicott in "Concepts of Inorganic Photochemistry," A. W. Adamson and P. D. Fleischauer, Ed., Chapter 3, Wiley-Interscience, New York, N. Y., in press.

(21) P. E. Hoggard, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **10**, 959 (1971).

$(H_2O)_4$, $Co(H_2O)_6^{2+}$ and free oxalate, the specific distribution depending on the concentrations of cobalt(II), free oxalate, pH, etc. That any equilibrium of the latter type could be associated with the slow spectral changes in the 360-nm region can be ruled out, in view of the exact equivalence between the rates of decay for the observed transient and for the secondary loss of substrate (see above). Our representation of I is, of course, approximate in the sense that one anticipates a large degree of delocalization of the unpaired electron among the three bidentate ligands; perhaps $[Co^{II}\{(C_2O_4)_3^{5-}\}]^{3-}$ would be a better representation. A ring-opening process for I, which destroys this possible equivalence between the three oxalate residues, would be most likely to occur for $C_2O_4^-$ (in comparison to the more basic $C_2O_4^{2-}$, although an opening and closing of a $C_2O_4^{2-}$ ring would be irrelevant to the process we wish to describe); at this point the unpaired electron is likely to become more localized on the now monodentate oxalate residue. The assumption that the sixth coordination site is rapidly filled by a water molecule is reasonable and would almost certainly occur before any complete loss of the $C_2O_4^-$.

The above view, with the suggestion that ring closing is much more rapid than either ring opening or loss of $C_2O_4^-$ to solvent, is essentially the same as the proposal made earlier for $Pt(C_2O_4)_2^{2-}$.²² Here, it was necessary to explain why all oxalate oxygens exchange with solvent at apparently equivalent rates while the exchange between free and coordinated oxalate is extremely slow (rate constants for the latter process being *ca.* four orders of magnitude smaller than values for substitution processes involving monodentate ligands for otherwise comparable complexes^{22a}). For cobalt(II) similar kinds of observations have been made; thus, although the half-life for $Co(NH_3)_6^{2+}$ is of the order of microseconds,^{23,24} the chelate complexes $Co(en)_3^{2+}$ and $Co(bipy)_3^{2+}$ aquate with half-lives of the order of milliseconds²⁵ and seconds,²⁶ respectively. For the present case, where $k_c \ll k_{-c} \gg k_d$, the observed first-order rate constant for disappearance of the spectrally observed intermediate would be equal to $(k_c/k_{-c})k_d$ (where k_c/k_{-c} is, of course, the equilibrium quotient for reaction 1c). One can easily see how the rather small observed first-order rate constant can arise; for example, if $k_c/k_{-c} \sim 10^{-3}$ and $k_d \sim 10^5 \text{ sec}^{-1}$, the observed value would be $\sim 10^2 \text{ sec}^{-1}$ which is approximately what we observe. Again, the rather high value of ΔH^\ddagger of $\sim 18 \text{ kcal mol}^{-1}$ presumably arises because it is a summation of ΔH for reaction 1c and ΔH^\ddagger for reaction 1d.

Behavior of the Coordinated Radical. The behavior of the observed intermediate I can be reconciled with the presumed structure in which the unpaired electron is considerably delocalized throughout the π -system of the three chelated oxalate residues. Unfortunately, the observed weak and structureless spectrum of the intermediate ($\epsilon_{360} \sim 100 \text{ M}^{-1} \text{ cm}^{-1}$) does not assist in its characterization.

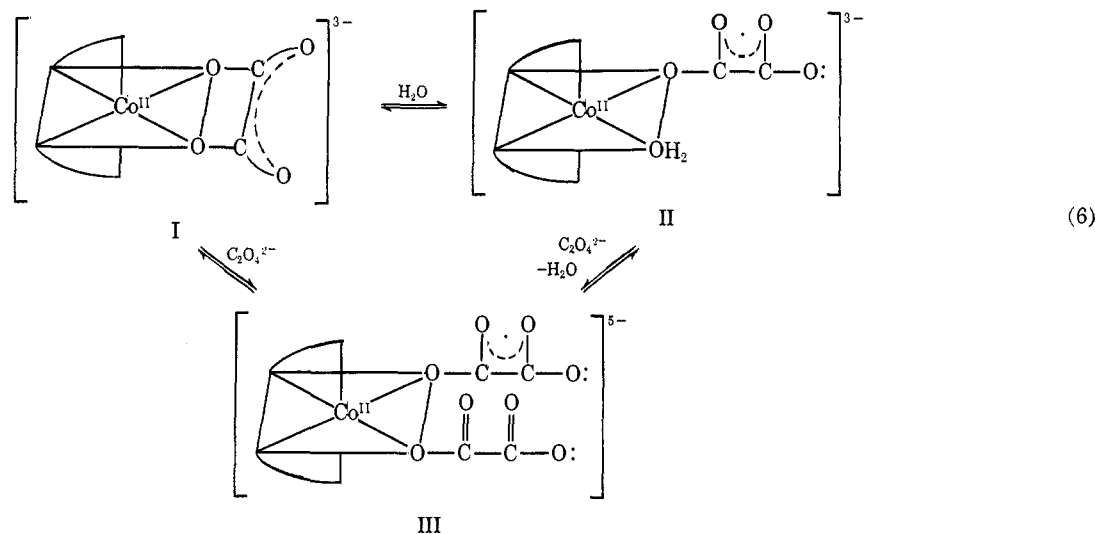
(22) (a) J. E. Teggin and R. M. Milburn, *Inorg. Chem.*, **3**, 364 (1964); (b) *ibid.*, **4**, 793 (1965).

(23) R. Murray, S. F. Lincoln, H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **8**, 544 (1969).

(24) M. Simic and J. Lilie, *J. Amer. Chem. Soc.*, **96**, 291 (1974).

(25) J. Lilie and M. Simic, personal communication of unpublished results.

(26) R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, **7**, 170 (1968).



The rate of decay of intermediate I is accelerated in acidic solution with a pH dependence suggestive of the intermediate possessing acid-base character with an apparent $pK_a \sim 2.5$. In view of our mechanism it, however, seems more likely that the protonation involves the monodentate oxalate radical ion of intermediate II. Such protonation could cause an increase in the pre-equilibrium concentration of the monodentate oxalato species, as well as a reduction in the basicity of the ligand with an increase in its lability. The pK_a for the monodentate oxalate ligand in $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$ is 2.2,²⁷ and, although the pK_a for the free C_2O_4^- radical has not been established nor is the pK_a for monodentate oxalate coordinated to Co(II) known, a value of 2.5 for the monodentate oxalate radical is deemed reasonable.

The spectrally observed intermediate, I, reacts with O_2 with an observed rate constant of $3.4 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ and activation parameters as shown in Table I. It is not immediately obvious whether the bimolecular reaction is between O_2 and intermediate I or O_2 and intermediate II or both, but, whatever the case, the one-electron transfer will lead to rapid loss of the resulting C_2O_4^0 ligand as CO_2 with aquation of the residual species. If II is the species reactive toward O_2 , the second-order rate constant for the process would be several orders of magnitude greater than the observed value above, although it is still likely to be significantly less than the value for reaction 5. Certainly the observed value of $3.4 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ gives an upper limit to the specific rate for the reaction of I with O_2 , and this is $\sim 10^6$ times lower than the value for reaction 5. The low reactivity of I toward O_2 can be reconciled in terms of the greater steric requirements and the delocalization of the unpaired electron among the three chelate ligands. It is to be noted that, even in O_2 -saturated solutions at 1 atm partial pressure, reaction 1d is competitive with the O_2 -scavenging reaction. Thus, some small contribution from reaction 3 is seen as a secondary loss of substrate in the flash photolysis of O_2 -purged solutions monitored at 600 nm. These competitive processes lead to the values of R given in Figure 1 and the lack of a dependence of $\phi_{\text{Co}^{2+}}$ upon deaeration of the solutions in the original Copstake and Uri work.³

The activation parameters for k_2 are very similar to those for k_1 . Diffusion- and near-diffusion-con-

trolled reactions in aqueous solution, such as reaction 5, have very little activation energy other than that arising from the diffusion process itself. In the slower O_2 -scavenging reaction, the activation energy is significant. If II is the reactive species, a major part of the observed ΔH^\ddagger would be attributable to the ring-opening process (*i.e.*, to reaction 1c). The effect of the presence of O_2^- radicals has been discussed in a previous section.

The failure of various added solutes (except oxalate) to affect the value of k_1 must be attributed to the lack of involvement of those species in any reactions of either I or II and to the absence of an ionic strength effect. Certainly one does not expect an ionic strength effect for an equilibrium reaction type 1c or for the forward reaction 1d. Indeed, the rate of C_2O_4^- loss should be fairly independent of the medium unless substitution for the water in the sixth coordination site occurs. Such substitution would be likely in the presence of 90–100% methanol; the increase in the value of k_1 could then arise through a different specific influence by methanol in reactions analogous to 1c and 1d (with methanol taking the place of entering H_2O). In any event, k_2 for the reaction of O_2 with the coordinated radical species is unchanged in methanol.

As has been described, in the presence of excess free oxalate the spectrum attributable to I undergoes a marked change, which we attribute to the generation of a new intermediate (III) which is structurally different from I. We suggest III is related to II by substitution of the coordinated H_2O by a monodentate $\text{C}_2\text{O}_4^{2-}$ ion. As before, II will be present only at very low concentrations and so will not contribute to the spectra observed for the intermediates. The structure of III would involve a monodentate oxalate ligand cis to the monodentate coordinated radical, thereby providing spatial proximity for electron overlap and considerable delocalization of the unpaired electron over the two ligands. Such a ligand-ligand interaction could be the cause of the marked changes observed in the transient spectrum upon the addition of free oxalate. A similar effect is noted when $\text{C}_2\text{O}_4^{2-}$ is added to $\text{Co}(\text{C}_2\text{O}_4)_2^{2-}$ inasmuch as $\text{Co}(\text{C}_2\text{O}_4)_3^{4-}$ shows a higher absorptivity than does $\text{Co}(\text{C}_2\text{O}_4)_2^{2-}$.²⁸ The species III is kinetically more

(27) C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

(28) A. W. Adamson, H. Ogato, J. Grossman, and R. Newburg, *J. Inorg. Nucl. Chem.*, **6**, 319 (1958).

stable than intermediate I due to the presence of the free oxalate and, presumably, the resonance stabilization of III. From the data in Figure 6, we estimate $pK_{\text{equil}} \sim 3$ for the reaction $\text{III} \rightleftharpoons \text{I} + \text{C}_2\text{O}_4^{2-}$. This value is comparable to the dissociation constants reported for other Co(II)-oxalato species such as $\text{Co}(\text{C}_2\text{O}_4)_3^{4-}$ ($\sim 10^{-1}$)²⁸ and $\text{Co}(\text{C}_2\text{O}_4)_2^{2-}$ ($\sim 7 \times 10^{-3}$).²⁹ The pH dependence of the decay of III (Figure 7) shows that the pK_a of that species is ~ 2 , which reflects the acid-base properties of the coordinated oxalate radical and the monodentate oxalato ligand.

Further Considerations. The flash photolysis of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ did not give any indication of the formation of the C-bonded formate linkage isomer that had been characteristic of the amine-oxalate complexes.¹⁴ Conversely, the amine-oxalate complexes did not show any evidence for the existence of a long-lived Co(II) species with a coordinated radical. This latter fact is easily understood in terms of the lability of Co(II)-amine complexes which renders the lifetime of any Co(II)-coordinated radical species shorter than the time resolution of the flash. The heterolytic C-C bond scission in the amine-oxalate complexes was attributed¹⁴ to ligand-localized excitation arising *via* intersystem crossing from the initially populated charge-transfer singlet state. The failure to detect such a process in $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ could be due to the instrumental limitations of time resolution and spectral sensitivity at short wavelengths; the formate linkage isomer could absorb at $\lambda < 270$ nm and be very short lived in $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$. Alternatively, there may exist a barrier to such ligand-localized excitation in the symmetrical, negatively-charged tris-oxalato complex. This matter warrants further examination.

The results in this paper are all in accord with the general mechanism proposed by Copestake and Uri.³ It appears that the fate of the transient intermediates is

(29) R. G. Seys and C. B. Monk, *J. Chem. Soc.*, 2452 (1965).

the same regardless of the pH of the solution or the presence of added solutes; the rates of the decay reactions vary, but, inasmuch as there are apparently no competing reactions, the end products are the same. Great caution must be exercised in attempting to extrapolate the results presented here to other trivalent metal oxalato complexes such as $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ or $\text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$ merely because of the apparent similarity in their overall photochemistries.^{2,4} It is not possible to use the $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ case to adjudicate between the redox mechanism proposed by Cooper and DeGraff³⁰ for $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ and the formation of a Fe(III) oxalate diradical as suggested by Perone and coworkers.³¹

Our results can be compared with those obtained by Cordemans, *et al.*,¹³ for the flash photolysis of $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in the presence of 3×10^{-3} M oxalic acid. Although the pH of their experiments was not specified, if one assumes that no acidity adjustment was made, the pH of that weak acid system would be approximately 2.8. The spectrum they observed immediately after the flash correlates well with the spectrum of our species III, and, although an exact comparison of rates is not possible because of differences in the conditions, their values of k_{obsd} are well within the range of ours. It is evident that the intermediate species they write as $[\text{Co}^{2+}(\text{C}_2\text{O}_4^{2-})_2\text{C}_2\text{O}_4 \cdot]^{3-}$ should be presented as III. The secondary photolysis of III that Cordemans, *et al.*,¹³ observe, which they attribute to the formation of e_{aq}^- and $[\text{Co}^{2+}(\text{C}_2\text{O}_4^{2-})(\text{C}_2\text{O}_4 \cdot)_2]^{2-}$, is consistent with the low temperature esr studies of Poznyak and Shagisultanova.⁷ In terms of III, such electron ejection could arise from charge-transfer to solvent excitation of the coordinated monodentate oxalato ligand.

(30) G. D. Cooper and B. A. DeGraff, *J. Phys. Chem.*, 75, 2897 (1971); 76, 2618 (1972).

(31) R. A. Jamieson and S. P. Perone, *J. Phys. Chem.*, 76, 830 (1972); J. I. H. Patterson and S. P. Perone, *ibid.*, 77, 2437 (1973).