Intermediates in the Photochemistry of Amine–Oxalate Complexes of Cobalt(III) in Aqueous Solution[1]

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Abstract: The 254-nm photolysis of $(NH_3)_4Co(C_2O_4)^+$ and $(NH_3)_5Co(C_2O_4)^+$ generates Co^{2+} and CO_2 in a 1:1 ratio. The values of $\phi_{Co^{2+}}$ in deoxygenated acidic solution (pH 1) are 0.90 and 0.65, respectively; for the monodentate oxalate complex, $\phi_{Co^{2+}}$ is increased somewhat (0.84) when the free end of the ligand is deprotonated ($pK_a = 2.2$). The presence of O_2 reduces these $\phi_{Co^{2+}}$ values by a factor of 2. In the case of $(en)_2Co(C_2O_4)^+$, the yield of Co^{2+} is independent of the presence of O_2 at pH 1, is somewhat dependent on O_2 presence at pH 2.7–2.9, and is increased during a post-irradiation period. At pH 1, the post-irradiation formation of Co^{2+} is *via* first-order kinetics with $k = 8.7 \times 10^{-5}$ sec^{-1} at 25°. The CO_2/Co^{2+} ratio also shows this post-irradiation behavior, decreasing from 2.2 to 1.5 over a 24-hr period following irradiation. In addition, a new product is obtained by ion-exchange chromatography which is identified as the C-bonded formato linkage isomer, $(en)_2(H_2O)CoCO_2H^{2+}$ ($pK_a = 2.6$), and which spontaneously decays to Co^{2+} with an activation energy of about 21 kcal mol^{-1}. Flash photolysis of these complexes reveals two transient species, the longer lived of which is assigned as the C-bonded formato linkage isomer of that complex arising from heterolytic C–C bond scission of the oxalate ligand and rotation of the resulting "carbene" within the coordination sphere of the complex. The excited state initially populated by the absorption of radiation is seen to undergo radiationless transition to at least two other electronic states: a charge-transfer excited state which produces the direct primary yield of Co^{2+} and the accompanying oxalate radical, and a ligand excited state which gives rise to the decomposition of the oxalate within the coordination sphere. In $(en)_2Co(C_2O_4)^+$, the ratio of the formation of the C-bonded formato species to the direct, primary generation of Co^{2+} is $\sim$4. The observed photochemistry can be explained in terms of the radicals accompanying the direct primary generation of Co^{2+} and the intramolecular ligand-to-metal electron transfer in the thermal decay of the C-bonded formato species. The ammine-oxalate complexes are reduced by the protonated and deprotonated forms of $C_2O_4^-$ and CO_2^- radicals producing a secondary source of Co^{2+}; O_2 scavenges these radicals. The en complex is apparently inert to the protonated forms of these radicals but can be reduced by the basic forms. These reactivity differences are in accord with the redox potentials of the species involved.

The photochemistry of oxalate complexes of transition metals has had a long and honorable history. However, despite the importance of these compounds as standard chemical actinometers, many of the mechanistic details of the oxidation of the coordinated oxalate and the reduction of the metal center have not been established. In particular, the reaction intermediates remain virtually uncharacterized. Interestingly, the mechanisms proposed to account for the redox behavior of trivalent-metal oxalates are identical if allowance is made for secondary reactions of the reduced metal.[3] Using $Co^{III}(C_2O_4)_3^{3-}$ as an example,[4] the generally accepted mechanism proceeds *via* the generation of a radical in the primary photochemical act through one-equivalent oxidation of $C_2O_4^{2-}$ followed by the efficient scavenging of the radical by the substrate.

$$Co^{III}(C_2O_4)_3^{3-} \xrightarrow{h\nu} Co^{II}(C_2O_4)_2^{2-} + C_2O_4^- \qquad (1)$$

$$Co^{II}(C_2O_4)_2^{2-} \longrightarrow Co^{2+} + 2C_2O_4^{2-} \qquad (2)$$

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

The fact that the quantum yield of Co^{2+} production, $\phi_{Co^{2+}}$, is less than unity has been attributed to the inefficiency of the primary reaction 1. The presence of a radical has been inferred from experiments involving the polymerization of vinyl monomer and the reduction of Hg(II). It is important to note that O_2 and [substrate] were observed to have no effect on $\phi_{Co^{2+}}$ which was also independent of the intensity of absorbed radiation, I_a. These features could result if reaction 3 were much more rapid than any scavenging of the radical by O_2 or the bimolecular combination and/or disproportionation of the radicals. Thus, $\phi_{Co^{2+}}$ has been *assumed* to be twice that of the primary process 1 involving the homolytic scission of the Co–O bond.[5] It must be pointed out that in no previous study has the assumed efficiency of reaction 3 actually been demonstrated except by analogy to the $Fe(C_2O_4)_3^{3-}$ case[6] in which $\phi_{Fe^{2+}} > 1$. The flash photolysis results of Parker and Hatchard[7] did not produce any insight into the mechanism of the $Co(C_2O_4)_3^{3-}$ photolysis; they observed an initial instantaneous rise in absorption at 313 nm followed by a rapid and then slow fall in absorption. They suggested that the rapid reaction is the bimolecular reaction 3, and the slow reaction represents (2) or dissociation of the product of (3) although they recognized that there are other possibilities. Recently Gross reported[8] that

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[2] (a) Boston University; (b) Wayne State University.

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

[4] T. B. Copestake and N. Uri, *Proc. Roy. Soc., Ser. A*, **228**, 252 (1955).

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

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

[7] C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, 63, 22 (1959).

[8] R. C. Gross, Abstracts of the Sixth International Conference of Photochemistry, Bordeaux, France, Sept 1971.

$k_3 = 4 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$. However, based on our own investigation of this complex,[9] we estimate k_3 to be at least four orders of magnitude higher than this value.

The $C_2O_4^-$ radical generated in reaction 1 is believed[10] to be relatively stable with its decomposition to give CO_2^- and CO_2 at a rate slow compared to reaction 3. The reaction of OH radicals generated pulse radiolytically with $C_2O_4^{2-}$ in aqueous solution[11] produces a radical which has an absorption spectrum similar to that of CO_2^- consisting of a maximum at 235 nm with a long tail down to 350 nm; the decay of CO_2^- is second order with $2k = 1.5 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. Using the extinction coefficient of CO_2^-, the rate constant of the oxalate decay was found to be identical with that of CO_2^-. Using similar pulse radiolysis techniques, Getoff, *et al.*,[12] determined $2k_4 = 9.6 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$.

$$2C_2O_4^- \longrightarrow 2CO_2 + C_2O_4^{2-} \qquad (4)$$

In acidic solution, where the radical species would be expected to be protonated, the second-order rate constant is believed[12] to be several orders of magnitude lower although the experimental data are unclear on this point. The pK_a for $CO_2H \rightleftarrows CO_2^- + H^+$ is 3.9 ± 0.3[13] with the decay of both the protonated and deprotonated radicals following identical kinetics[11] although the CO_2H radical disproportionates to CO_2 and HCO_2H while CO_2^- combines to yield oxalate.[14] CO_2^- reacts rapidly with O_2 *via* electron transfer[13] and presumably CO_2H is also quenched by O_2. CO_2^- is a stronger reducing agent than CO_2H,[15] and presumably the same characteristics are shown by $C_2O_4^-/C_2O_4H$ although no direct determinations have been made.

Way and Filipescu[16] determined $\phi_{Co^{2+}}$ for the photolysis of ammine–oxalate complexes of Co(III) at a number of wavelengths including 254 nm. They invoked the same general mechanism for these complexes, (1)–(4), although their data could not provide a test of the mechanism. Furthermore, there is no indication that their photolyses, performed in 1-cm spectrophotometer cells, were carried out in the absence of O_2. Indeed, we had previously reported[17] that $\phi_{Co^{2+}}$ is reduced by a factor of about 2 when O_2 rather than N_2 is bubbled through $(NH_3)_4Co(C_2O_4)^+$ solutions during 254-nm irradiation.

This present study was undertaken to examine the ultraviolet photochemical behavior of $(NH_3)_4Co(C_2O_4)^+$, $(en)_2Co(C_2O_4)^+$ (where en = ethylenediamine), and $(NH_3)_5Co(C_2O_4)^+$ in aqueous solution in order to clarify some of the aspects of the general mechanism. Unlike $Co(C_2O_4)_3^{3-}$ which undergoes H^+-catalyzed thermal oxidation–reduction to give Co^{2+}, these amine–oxalate complexes are stable even in hot, acidic solutions. Because of the lower reduction potentials of these mixed ligand complexes, we expected that the radical–substrate reaction 3 would be slowed down. The generality of the effect of O_2 on $\phi_{Co^{2+}}$ for these complexes[18] indicated that the quantum yield of reaction 1 could be evaluated without resort to mechanistic hypothesis; the proof of the existence of a radical offered the possibility of studying its chemistry. Finally, the paucity of published flash photolysis data on oxalate systems and the potential this technique has when applied to Co(III) complexes[19] encouraged us to examine the amine–oxalate complexes in detail. We hoped that a critical test of the time-honored mechanism could be made.

Experimental Section

Materials. The chloride and perchlorate salts of $(NH_3)_4Co(C_2O_4)^+$, $(en)_2Co(C_2O_4)^+$, and $(NH_3)_5Co(C_2O_4)^+$ were prepared using procedures described in the literature.[20-22] The perchlorate salts were used initially until the insensitivity of the photolysis process to the presence of Cl^- was established. The spectral characteristics of the compounds agreed to within a few per cent of the literature values and elemental analysis indicated their general purity. All solutions were prepared using distilled and deionized water and reagent grade chemicals.

Apparatus and Procedures. The 254-nm radiation was generated by low-pressure mercury resonance lamps; the various units covering a range of incident intensities (I_0) from 6.6×10^{-3} to 1×10^{-6} einstein $l.^{-1}\ \mathrm{min}^{-1}$ have already been described.[23-25] Primary actinometry was carried out using uranyl oxalate[26] or potassium ferrioxalate.[6] Flash photolysis was performed using a Xenon Corp. Model 720 unit with xenon-filled flash lamps (500 J; $1/e$ time = 30 μsec) and an optical cell 22 cm in length. The 150-W xenon analyzing lamp was operated either off a bank of batteries or off a controlled voltage power supply. The output of the photomultiplier tube was displayed on a Tektronix Model 545 storage oscilloscope. For transient half-lives of greater than 5 sec, a chart recorder was used. Spectra were recorded on a Cary 14, 16 or Unicam 800 spectrophotometer.

Solutions were prepared from the solid immediately before use. If deoxygenation was required, the solution was purged with Cr^{2+}-scrubbed N_2 before irradiation. During continuous photolysis, gas bubbling and magnetic stirring ensured the homogeneity of the solution. Temperature was controlled by air or water thermostating. Samples could be removed after a desired exposure time by means of a syringe and a Teflon needle passing through a rubber serum cap. Co^{2+} determinations were performed as soon after photolysis as possible, generally within 0.5 hr. Gaseous products were detected and determined by gas chromatography from photolyses performed *in vacuo* using a F & M Model 810 instrument with thermal conductivity detection and a 12-ft molecular sieve column.

Co^{2+} was determined using a modification of Kitson's method:[27] 4 ml of the solution containing Co^{2+} ($<5 \times 10^{-3}\ M$) and 8 ml of a 50% solution of NH_4SCN were diluted to 25 ml with acetone, and the absorbance at 620 nm was recorded ($\epsilon_{620}\ 1.86 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$). Cation-exchange resin (Dowex 50W-4X, 200–400 mesh, H^+ form) was used for the separation of complex products.

For the determination of $\phi_{Co^{2+}}$ from continuous photolysis, the yield of Co^{2+} as a function of exposure time was determined for the first 20–25% of reaction; plots were generally linear with evidence of the fall-off in rate as the substrate was depleted and I_a decreased. The initial rate of the reaction was determined from such zero-order

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[9] N. S. Rowan, R. M. Milburn, and M. Z. Hoffman, *Inorg. Chem.*, 11, 2272 (1972).

[10] Z. Simon, *Rev. Roum. Chim.*, 14, 705 (1969).

[11] P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, 73, 4207 (1969).

[12] N. Getoff, F. Schwörer, V. M. Markovic, K. Sehested, and S. O. Nielsen, *ibid.*, 75, 749 (1971).

[13] A. Fojtik, G. Czapski, and A. Henglein, *ibid.*, 74, 3204 (1970).

[14] H. Fricke, E. J. Hart, and H. P. Smith, *J. Chem. Phys.*, 6, 229 (1938); E. J. Hart, *J. Amer. Chem. Soc.*, 83, 567 (1961).

[15] J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges Phys. Chem.*, 75, 458 (1971).

[16] H. Way and N. Filipescu, *Inorg. Chem.*, 8, 1609 (1969).

[17] J. F. Endicott, M. Z. Hoffman, and B. L. Mollicone, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. V38.

[18] B. L. Mollicone, M.A. Thesis, Boston University, 1966.

[19] G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 92, 6801 (1970).

[20] W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, New York, N. Y., 1954, p 547.

[21] A. Werner and A. Wilmos, *Z. Anorg. Chem.*, 21, 145 (1899).

[22] P. Saffir and H. Taube, *J. Amer. Chem. Soc.*, 82, 13 (1960).

[23] J. F. Endicott and M. Z. Hoffman, *ibid.*, 87, 3348 (1965).

[24] J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, 74, 1021 (1970).

[25] E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *ibid.*, 75, 1914 (1971).

[26] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold, New York, N. Y., 1941.

[27] R. E. Kitson, *Anal. Chem.*, 22, 664 (1950).

plots. Although primary actinometry had been performed on each photolysis unit and the dependence of I_a on the optical density of the solution was known, secondary actinometry was performed at the time of each photolysis in order to account for any variation in the output of the lamps. Specifically, each photolysis run was bracketed by an irradiation of $Co(NH_3)_5Cl^{2+}$ or $Co(NH_3)_5O_2CCH_3{}^{2+}$ under identical conditions of solution absorbance. The values of $\phi_{Co^{2+}}$ for these complexes, 0.17 and 0.19, respectively, are well established under a variety of experimental conditions.[23,25] The values of $\phi_{Co^{2+}}$ determined in this way are known at least to within ±10%.

In flash photolysis, the solution was forced into the N_2-flushed optical cell from a storage flask by a positive pressure of N_2. All solutions were discarded after one flash. For experiments in which the wavelength of the flash radiation was restricted using filter solutions, a cell with an outer jacket was employed. Experiments were normally conducted at ambient temperature; variation of temperature was accomplished either by thermostating the storage flask and/or the optical cell. Where the optical cell was not thermostated, the temperature of the flashed solution did not differ by more than 3° from that of the storage vessel. Thermostating of the optical cell ensured that the solution temperature was constant within 0.3°.

Results

Spectra. The spectra of all three complexes show the general features common to Co(III)–amine complexes with an oxygen-bonded carboxylate ligand: ligand-field (d–d) bands at 505 and 360 nm ($\epsilon \sim 100$ M^{-1} cm^{-1}) and the intense ($\epsilon > 10^3$ M^{-1} cm^{-1}) charge-transfer bands in the ultraviolet. In the case of the bidentate oxalate complexes, $(NH_3)_4Co(C_2O_4)^+$ and $(en)_2Co(C_2O_4)^+$, the spectra were independent of pH up to 2 M $HClO_4$. The spectrum of $(NH_3)_5Co(C_2O_4)^+$ showed a variation with pH in the same manner as had been described by Andrade and Taube.[28] Figure 1 shows the appearance of a new absorption band in the 290-nm region as the pH is raised, indicative of the acid dissociation reaction $(NH_3)_5Co(C_2O_4H)^{2+} \rightleftarrows (NH_3)_5Co(C_2O_4)^+ + H^+$ for which $pK_a = 2.2$. The common isosbestic point at 238 nm and the similarity of the spectra at pH 1.4 and in 2 M $HClO_4$ indicate the absence of any effect due to ionic strength.

Continuous Photolysis. Extensive photolysis converted the Co(III) quantitatively to Co^{2+}. Unbuffered solutions photolyzed at pH >3.5 became basic producing a green-brown precipitate of the hydrous oxide of Co(II). No analyses were conducted on such solutions since the uncertainty in the actinometry due to the increased opacity of the system would render quantum yield values meaningless. Oxygen bubbled for 20 min through the photolyte containing Co^{2+} produced no discernible reoxidation to Co(III) in acidic solutions.

When photolyzed, the solutions of $(NH_3)_4Co(C_2O_4)^+$ and $(NH_3)_5Co(C_2O_4)^+$ lost their pink color and became pale. In the case of $(en)_2Co(C_2O_4)^+$, the observation of a post-irradiation production of Co^{2+} and time-dependent color changes indicated that the system was more complex than originally imagined. For example, a solution at pH 2.9 under N_2 purge turned orange-gold after 8 min of photolysis. However, within 2–3 hr after photolysis, the solution had turned colorless. The effect was the same whether or not the solution, in a Pyrex flask, was exposed to fluorescent lights. When heated to 50°, the orange color bleached in less than 1 hr. At pH 1.2, the solution was orange-gold after photolysis and bleached, with the production of additional Co^{2+}, in 24 hr. The details of this post-irradiation effect will be discussed in a later section.

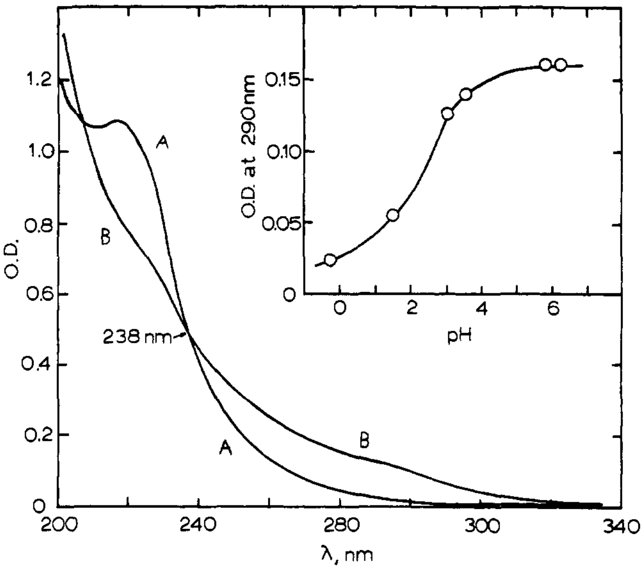

Figure 1. Uv spectrum of $(NH_3)_5Co(C_2O_4)^+$; [complex] = 6.65×10^{-4} M: (A) the acid form in 2 M $HClO_4$; (B) the basic form at pH 6.

Quantum yields for Co^{2+} production for the three complexes were determined as a function of pH in the presence of N_2 or O_2 and are given in Table I. For $(NH_3)_4Co(C_2O_4)^+$, the presence of up to 5 M methanol or 2-propanol had no effect on $\phi_{Co^{2+}}$ in N_2. Furthermore, $\phi_{Co^{2+}}$ was independent of $[(NH_3)_4Co(C_2O_4)^+]$ from 2.5×10^{-3} to 1.8×10^{-2} M, ionic strength, and the presence of Cl^- (up to 0.1 M HCl). The presence of acetate buffer (up to 10^{-2} M) in the pH 4–6 region had the effect of lowering $\phi_{Co^{2+}}$ by about 50%. Plots of log (rate of Co^{2+} production) *vs.* log (I_a) over three orders of magnitude of I_a gave straight lines with slopes greater than 0.9.

Table I. Co^{2+} Quantum Yields from the 254-nm Photolysis of Amine–Oxalate Complexes of Co(III)[a]

Complex[b]	ϵ_{254}, M^{-1} cm^{-1}	pH	Gas purge	$\phi_{Co^{2+}}$[c]
$(NH_3)_4Co(C_2O_4)^+$	4.2×10^3	1.2	N_2	0.90
		1.2	O_2	0.45
		2.4	N_2	0.81
		2.4	O_2	0.40
$(NH_3)_5Co(C_2O_4)^+$	Function of pH; see Figure 1	1.1	N_2	0.65
		1.3	O_2	0.33
		2.6	N_2	0.84
		2.6	O_2	0.41
$(en)_2Co(C_2O_4)^+$	6.7×10^3	1.2	N_2	0.084
		1.2	O_2	0.084
		1.0	N_2	0.36[d]
		1.0	O_2	0.34[d]
		2.9	N_2	0.27
		2.7	O_2	0.19

[a] $I_a \sim 5 \times 10^{-4}$ einstein l.$^{-1}$ min^{-1}. [b] [Complex] = 1.4×10^{-3}–3.4×10^{-3} M. [c] Single determinations with error estimated to be ±10%; Co^{2+} analyses performed within 0.5 hr of photolysis. [d] Co^{2+} analyses performed 24 hr after photolysis.

Photolyses of the complexes at 254 nm *in vacuo* generated Co^{2+} and CO_2 in quantities shown in Table II. As well, gas chromatographic analysis revealed that traces of H_2 and CO (<5%) were also produced.

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

Table II. Yields of Co^{2+} and CO_2 from the 254-nm Photolyses *in Vacuo*[a]

Complex	Concn, *M*	I_a, einstein $l.^{-1}$ min^{-1}	Irradiation time, min	Co^{2+}, μmol	CO_2, μmol	CO_2/Co^{2+}
$(NH_3)_4Co(C_2O_4)^+$	4.0×10^{-3}	3.5×10^{-4}	10	135	136	1.0
		5.5×10^{-3}	1.0	53.0	49.8	0.94
			1.5	181	184	1.0
$(NH_3)_5Co(C_2O_4)^+$	4.0×10^{-3}	3.5×10^{-4}	10	84.3	86.0	1.0
			10	88.4	89.4	1.0
$(en)_2Co(C_2O_4)^+$	2.0×10^{-3}	5.2×10^{-3}	3.0	37.7	82.0	2.2[b]
			3.0	106	164	1.5[c]

[a] In 0.1 *M* $HClO_4$. [b] Figures represent results of analysis immediately after photolysis; 24 hr after the initial analysis (with the solution having been opened to air), the yield of Co^{2+} had risen to 80.0 μmol. There is no comparable figure for the CO_2 yield. [c] Complete analysis performed 24 hr after photolysis.

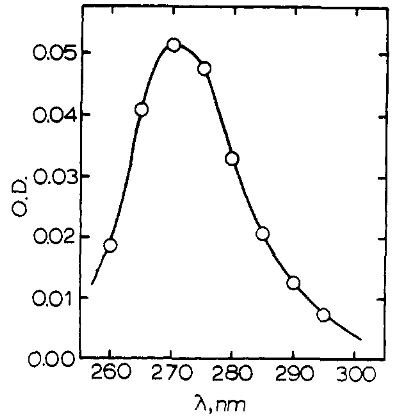

Figure 2. Spectrum of the long-lived intermediate (A_5-LL) from the flash photolysis of 5×10^{-5} *M* $(NH_3)_5Co(C_2O_4)^+$ at pH 1, 25°. OD read 50 μsec after the start of the flash.

Flash Photolysis. All three complexes showed two distinguishable transient intermediate species which absorb at $\lambda < 340$ nm, one short-lived (SL) and the other long-lived (LL). The short-lived species, SL, appeared within the lifetime of the flash and showed an absorption intensity that was independent of pH or the presence of O_2. An attempt was made to obtain the spectrum of SL ($[(NH_3)_4Co(C_2O_4)^+] = 2.8 \times 10^{-5}$ *M*; pH 3.0) by plotting the absorbance of the transient observed at 50 μsec after the start of the flash as a function of λ. Absorbance increased with decreasing λ; the high absorptivity of the substrate at $\lambda < 270$ nm made it impossible to obtain a value of λ_{max}. The decay of SL was *via* first-order kinetics, a fact that was tested by computer fit of the decay to the usual equation (standard deviation ±5%) and by the independence of $t_{1/2}$ with change in flash lamp intensity and, thus, concentration of the transient. The rate constants for the decay of SL are given in Table III and were unaffected by the presence of O_2.

Because of the overlap of the spectra of SL and LL, it is not possible to discern whether LL arises from SL or whether they are independent species. However, because of the differences in the lifetime of SL and LL, the spectrum and decay kinetics of LL can be evaluated without any contribution from SL. Figure 2 shows the spectrum of LL from the flash photolysis of $(NH_3)_5Co(C_2O_4)^+$ (A_5-LL). It should be noted that the spectrum of A_5-LL is identical with that observed[29] in the flash photolysis of $(NH_3)_5CoO_2CH^{2+}$. Very weak transient absorptions with the same kinetic characteristics as at 280 nm were observed up to 450 nm. The decay of A_5-LL followed first-order kinetics with a rate and initial amount of transient that was unaffected by the presence of O_2. The dependence of the first-order rate constant for the disappearance of A_5-LL on pH is shown in Figure 3a together with the data for $(NH_3)_5CoO_2CH^{2+}$ for comparison. The initial amount of transient was independent of pH.

The results of the first-order decay of the long-lived intermediate from the flash photolysis of $(NH_3)_4Co$-

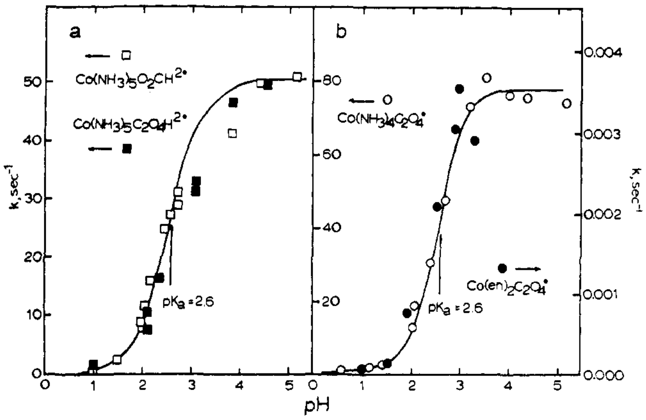

Figure 3. Rate constants for the decay of the long-lived intermediates as a function of pH (ClO_4^- medium): (a) $[(NH_3)_5CoO_2CH^{2+}]$ or $[(NH_3)_5Co(C_2O_4)^+] = 5 \times 10^{-5}$ *M*, monitoring wavelength 275 or 280 nm; (b) $[(NH_3)_4Co(C_2O_4)^+]$ or $[(en)_2Co(C_2O_4)^+] = 2\text{-}6 \times 10^{-5}$ *M*, monitoring wavelength, 280 nm. The rate constants were measured at ambient temperature with ±15–20% error.

Table III. Rate Constants for the Decay of the Short-Lived Intermediate (SL) in Flash Photolysis

Complex[a]	pH	*k*, sec^{-1} [b]
$(NH_3)_4Co(C_2O_4)^+$	−0.4[c]	32.0
	0.0[c]	190
	0.6[c]	821
	1.0	2110
	3.1	2400
	5.5	3240
$(NH_3)_5Co(C_2O_4)^+$	1.2	Very weak transient
	4.0	$\sim 10^3$
$(en)_2Co(C_2O_4)^+$	0.2[c]	1.39
	0.7[c]	2.94
	1.0	11.8
	1.4	25.6
	2.1	192
	3.0	1670

[a] [Complex] = 2×10^{-5}–6×10^{-5} *M*. [b] Monitored at 280 nm. [c] −Log [$HClO_4$].

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(29) E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, 76, 2492 (1972).

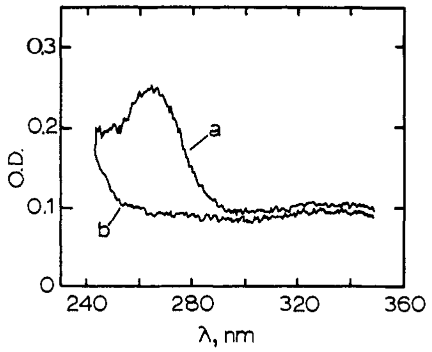

Figure 4. (a) Spectrum of flash-irradiated $(NH_3)_4Co(C_2O_4)^+$ in 2 *M* $HClO_4$; [complex] = 6.7 × 10^{-5} *M*, air-saturated solution. A flashed solution at $t = \infty$ served as the reference. Scan speed = 25 Å sec^{-1}; scan begun at 350 nm 30 sec after flash. (b) Sample ($t = \infty$) *vs.* reference.

$(C_2O_4)^+$ (A_4-LL) and $(en)_2Co(C_2O_4)^+$ (en-LL) are shown in Figure 3b. Here too, O_2 did not affect the initial amount of transient produced nor the decay kinetics. Similarly, variation of pH only affected the value of the first-order rate constant. At the higher acidities, the decay rate for A_4-LL was sufficiently slow ($t_{1/2} \sim 1$ min) to permit the recording of the transient spectrum on the Cary 14 by double beam spectrophotometry. This experiment was performed in the following manner: a solution of 6.7 × 10^{-5} *M* $(NH_3)_4Co(C_2O_4)^+$ in 2 *M* $HClO_4$, flashed in a 10-cm spectrophotometer cell and allowed to stand for 10 min, was placed in the reference beam. A second aliquot of the same solution was flashed in another 10-cm cell and its spectrum recorded at a scan rate of 25 Å sec^{-1} begun 30 sec after the flash. A distinct absorption band with $\lambda_{max} \sim 265$ nm was evident (Figure 4), the decay of which had the same first-order rate constant as obtained in the direct flash experiment monitored at 280 nm. Because of the absorption of the remaining substrate after the flash, it was not possible to obtain the spectrum of A_4-LL under these conditions at $\lambda < 240$ nm. Because of the very slow decay rate of en-LL, a similar direct determination of its spectrum could be performed without any difficulty. A difference spectrum of the solution immediately after the flash (with the solution at $t = \infty$ as the reference) was taken across the pH range. Again an absorption band at 265 nm was evident, the position and shape of which did not appear to be affected by acidity. The absorption decayed with the same kinetics as observed in the direct flash experiments monitored at 280 nm. However, a small absorption peak at 220 nm at pH 6 changed to a shoulder on an intense maximum at $\lambda < 200$ nm in acidic solution. This transition occurs between pH 2 and 5.

The addition of 0.1 *M* $NaClO_4$ to a solution of 6.2 × 10^{-5} *M* $(NH_3)_4Co(C_2O_4)^+$ at pH 4.1 had no significant effect on SL or LL. Similarly, the presence of 1.5 × 10^{-3} *M* $Na_2C_2O_4$ with $[(NH_3)_4Co(C_2O_4)^+]$ = 2.0 × 10^{-5} *M* at pH 0.3 caused no changes in the observed intermediates. The same negative results were obtained from the same experiment with $(en)_2Co(C_2O_4)$.$^+$ No transient was observed for 4.1 × 10^{-5} *M* $(NH_3)_4Co(C_2O_4)^+$ at pH 1.0 when the solution was jacketed with a solution of napthalene or anthracene so that the photolyzing flash was restricted to $\lambda > 300$ and > 380 nm, respectively. The same negative results were observed for $(NH_3)_5Co(C_2O_4)^+$.

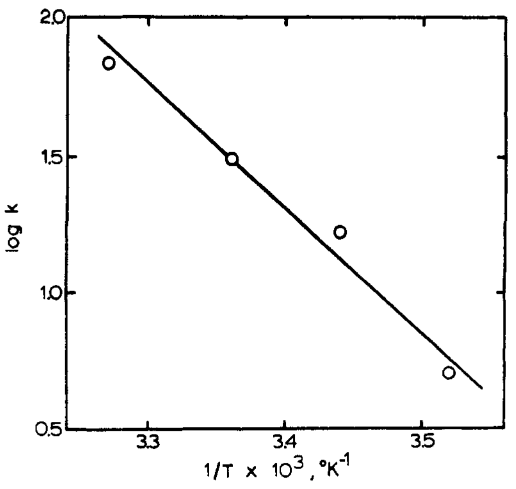

Figure 5. Dependence of the kinetics of the decay of A_5-LL on temperature: $[(NH_3)_5Co(C_2O_4)^+]$ = 5 × 10^{-5} *M*, pH 3.1, monitoring wavelength 280 nm.

The decay of en-LL was unaffected by the presence of Co^{2+} or Cl^-. When 4 × 10^{-5} *M* $(NH_3)_4Co(C_2O_4)^+$ was flashed in 95% ethanol (air saturated), A_4-LL was produced to the same extent, showed the same pH dependence on the decay, and had virtually the same rate constants as in water.

When an air-saturated solution of $(en)_2Co(C_2O_4)^+$ was monitored at 505 nm (absorption maximum of the low-energy d–d band of the complex) with very high sensitivity, the absorbance of the flashed solution was observed to decrease within the lifetime of the flash.

The activation energy of the decay of LL was determined from a plot of log *k* *vs.* 1/*T*, and such data are shown for $(NH_3)_5Co(C_2O_4)^+$ at pH 2.2 in Figure 5. The value of E_a, using a thermostated optical cell, is 21 kcal mol^{-1}. For A_4-LL and en-LL for which the optical cell was not directly thermostated, E_a has a value of 20 ± 4 kcal mol^{-1}, independent of pH.

It should be noted that the flash photolysis of free $C_2O_4^{2-}$ yields a very weak transient which absorbs in the 250–290-nm region and disappears rapidly in <0.1 msec. Furthermore, the flash photolysis of an 8 × 10^{-6} *M* solution of the binuclear Co(III) complex, $(NH_3)_4Co(NH_2,C_2O_4)Co(NH_3)_4^{4+}$,[30] at pH 2.0 revealed only a weak, rapidly decaying transient absorbing in the 270–300-nm region. Unfortunately, further work with this complex was hampered by its rapid photolysis when exposed to the analyzing lamp of the apparatus.

Post-Irradiation Effects in $(en)_2Co(C_2O_4)^+$. A 2.5 × 10^{-3} *M* $(en)_2Co(C_2O_4)^+$ solution at pH 1.0 was photolyzed at 254 nm for 10 min under a N_2 purge. The solution after photolysis was orange-gold but turned colorless after 23 hr. The photolyzed solution was kept stoppered and an analysis for Co^{2+} was performed at intervals. The results are shown in Figure 6. These data, when plotted as log $([Co^{2+}]_{t=\infty} - [Co^{2+}]_t)$ *vs.* time, yielded a straight line and a first-order rate constant of 8.7 × 10^{-5} sec^{-1}. This value is identical with that obtained for en-LL from the flash

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[30] The authors wish to thank Dr. D. Valentine, Jr., for the sample of this complex.

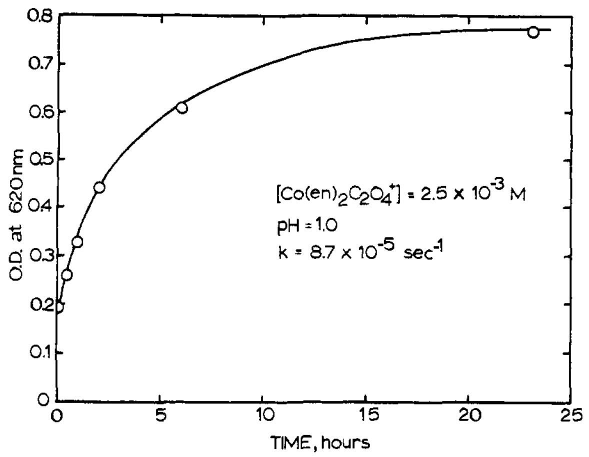


Figure 6. Post-irradiation formation of Co^{2+} from 254-nm photolysis of 2.5 × 10^{-3} $M(en)_2Co(C_2O_4)^+$; pH 1.0, N_2 purge, exposure time 10 min. Ordinate shows the absorbance at 620 nm (1-cm cell) of the Co(II)–SCN^- complex involved in the analysis of Co^{2+}.

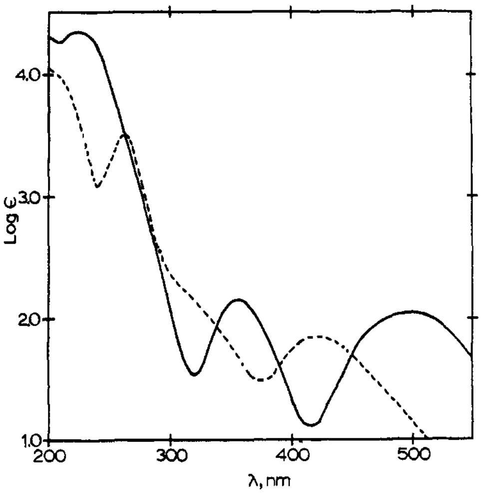


Figure 7. Spectra of $(en)_2Co(C_2O_4)^+$ (———) and en-LL = $(en)_2(H_2O)CoCO_2H^{2+}$ (- - - - -).

photolysis at pH 1. The spectrum of this solution after photolysis (with H_2O as the reference) showed characteristics of both en-LL and some unphotolyzed substrate. The 265-nm absorption band disappeared nearly in concert with the appearance of Co^{2+} and after 23 hr very little uv absorption remained. At that time, the concentration of Co^{2+} was 2.5 × 10^{-3} M, indicating quantitative destruction of the substrate. It is also evident from Figure 6 that a significant quantity of Co^{2+} is generated during the 10-min photolysis period at a rate that is considerably greater than the post-irradiation effect. The Co^{2+} generated during the direct photolysis accounts for 20–25% of the total Co^{2+} formed. This ratio is further supported by the data for $(en)_2Co(C_2O_4)^+$ in Table I and by the following experiment: a 1.0 × 10^{-4} M solution of $(en)_2Co(C_2O_4)^+$ at pH 1.0 was flashed once and an analysis for Co^{2+} conducted immediately (within 0.5 hr) and then after 24 hr. The yields of Co^{2+} were <2.7 × 10^{-6} and 1.0 × 10^{-5} M, respectively. In comparison, the Co^{2+} generated from a single flash of $(NH_3)_4Co(C_2O_4)^+$ under identical conditions (6.7 × 10^{-6} M) did not change over a period of time.

Characterization of en-LL. A 2.7 × 10^{-3} M solution (100 ml) of $(en)_2Co(C_2O_4)^+$ at pH 1.0 was photolyzed at 254 nm for 10 min under a N_2 purge. After photolysis, 96 ml of this solution was placed on the ion-exchange column which had been rinsed with distilled water. The remaining 4 ml was used for a Co^{2+} analysis. To the column was added 50 ml of 0.2 M $HClO_4$ and the eluent examined spectrophotometrically. All the residual $(en)_2Co(C_2O_4)^+$ was eluted and collected in a volumetric flask; there were no signs that the eluent contained en-LL. The addition of 50 ml of 0.8 M $HClO_4$ eluted a yellow species; all this material was collected in a volumetric flask. Further elution with higher acid concentrations did not produce any additional material. The elution characteristics of en-LL are consistent with the species having a 2+ charge in acid solution. Photolysis had produced 5.9 × 10^{-5} mol of Co^{2+}, and 6.9 × 10^{-5} mol of $(en)_2Co(C_2O_4)^+$ had been eluted from the column. A material balance requires that 1.4 × 10^{-4} mol of en-LL be produced. The spectrum of en-LL is shown in Figure 7 with that of $(en)_2Co(C_2O_4)^+$ for a comparison. From the absorbance and the concentration, the following extinction coefficients are calculated: ϵ_{421} 71.6 M^{-1} cm^{-1} and ϵ_{262} 3000 M^{-1} cm^{-1}.

The post-irradiation production of Co^{2+} from en-LL does not require the presence of Co^{2+} or the substrate. A 2.3 × 10^{-3} M $(en)_2Co(C_2O_4)^+$ solution at pH 1.0 was photolyzed at 254 nm for 10 min under a N_2 purge, separated by ion-exchange, and analyzed for Co^{2+}. In 24 hr, 5.8 × 10^{-5} mol of en-LL was destroyed while 6.7 × 10^{-5} mol of Co^{2+} was produced. The quantities of substrate and Co^{2+} present after photolysis were unchanged beyond 24 hr.

Intermediate en-LL undergoes base-catalyzed hydrolysis. The rate of this hydrolysis is accelerated greatly at pH 9; only several minutes was required for the yellow en-LL solution to become a deep gold. Upon acidification and ion-exchange of the intermediate, a 3+ complex was eluted from the column with a spectrum identical with that of $(en)_2Co(OH_2)_2^{3+}$.

The behavior of en-LL in Cl^- medium was identical with that just described for ClO_4^- solutions. A sample of ion-exchanged en-LL at pH 1 was photolyzed at 254 nm under a N_2 purge and a Co^{2+} analysis performed immediately. $\phi_{Co^{2+}}$ had a value of 0.13. During the same period of time, the thermal contribution from the decay of en-LL is negligible.

All attempts to isolate the solid en-LL intermediate failed. Approximately 50 ml of a solution of ion-exchanged en-LL in 0.5 M $HClO_4$ was cooled to 0° and its volume reduced to ~5 ml using a rotary evaporator. No solid appeared; safety considerations required that this attempt be terminated at this point. The same procedure was followed using the Cl^- salt in HCl solution. Continued reduction of the volume caused the yellow solution to become viscous and deeper in color. Just as it appeared that crystals would form, the solution suddenly turned blue-green. In order to avoid the problems apparently associated with having massive quantities of ClO_4^- or Cl^- in solution, an ion-exchanged solution of en-LL in 0.5 M $HClO_4$ was neutralized with K_2CO_3. $KClO_4$ precipitated and CO_2 was evolved but no solid en-LL was produced at 0°.

Unsuccessful attempts were made to bring en-LL out of solution using various ethanol–ether mixtures and BF_4^-, $B(C_6H_5)_4^-$, $F_3CSO_3^-$, and $Cr_2O_7^{2-}$ as counterions.

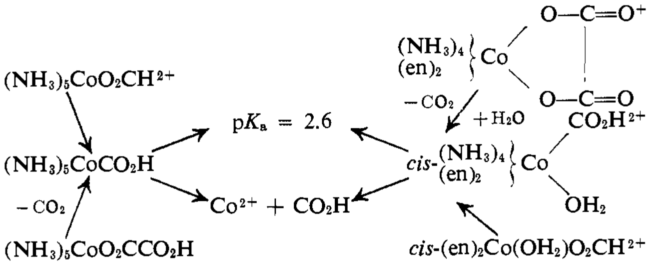
Discussion

Except for the magnitudes of the rates and quantum yields, it is obvious that the behavior of the bidentate amine–oxalate complexes, $(NH_3)_4Co(C_2O_4)^+$ and $(en)_2Co(C_2O_4)^+$, and the monodentate complex, $(NH_3)_5Co(C_2O_4)^+$, when irradiated in their ligand-to-metal charge-transfer band, is extremely similar so that a common mechanism can be assumed to be applicable. Central to any mechanism must be the inclusion of the long-lived intermediate which is an important source of Co^{2+} in the case of $(en)_2Co(C_2O_4)^+$ and, by analogy, in the case of the other complexes. From all the spectral and kinetic evidence, it is apparent that intermediates LL in all the cases have the same fundamental structure. It is important to note that the behavior of A_5-LL and LL from $(NH_3)_5CoO_2CH^{2+}$[29] is identical.

Identification of Intermediate LL. An examination of all the experimental data reveals the following facts: (1) LL has an absorption spectrum as shown in Figure 7 with maxima at 421, 320, 262, and <200 nm; (2) in acidic solution it displays the behavior of a 2+ species on the ion-exchange column; (3) the extent of its formation and its decay rate are unaffected by the presence of Co^{2+}, $C_2O_4^{2-}$, substrate, O_2, alcohols, Cl^-, and (except for the rate of decay) H^+; (4) it undergoes first-order decay to form Co^{2+} with an activation energy of about 21 kcal mol^{-1}; the decay also produces CO_2 and is independent of ionic strength; (5) LL undergoes protonation–deprotonation with $pK_a = 2.6$ with the rate of decay to Co^{2+} dependent upon the state of protonation; protonation retards the rate; (6) LL undergoes base-catalyzed hydrolysis to form a Co(III) diaquo species.

In a preliminary communication[31] we reviewed these facts and concluded that LL could not be a free radical coordinated to a Co(II) center because of its lifetime and insensitivity to O_2, an excited state of Co(III) or Co(II) for the same lifetime reasons, or a Co(III) complex retaining the original O-bonded carboxylate configuration on the basis of its spectrum. Consideration of charge rules out binuclear complexes. We proposed that A_5-LL and the intermediate from $(NH_3)_5CoO_2CH^{2+}$ were $(NH_3)_5CoCO_2H^{2+}$, a C-bonded formato linkage isomer which is both kinetically and thermodynamically unstable with respect to Co^{2+} and which undergoes internal electron-transfer to generate Co^{2+} and the release of the CO_2H radical. A_5-LL would thus arise from heterolytic C–C bond scission, loss of CO_2, and carbon → oxygen linkage isomerization. For the bidentate oxalato complexes, excitation causes similar heterolytic bond breakage, loss of CO_2, and linkage isomerization; here, however, water substitution into the sixth coordination site yields A_4-LL and en-LL, designated as *cis*-$A_4Co(OH_2)CO_2H^{2+}$ (where A = coordinated N atom). It is to be noted that the flash photolysis of *cis*-$(en)_2Co(OH_2)O_2CH^{2+}$ gives an intermediate with characteristics identical with en-LL.[29] The decay of the LL intermediates as a function of pH shows that the rate of intramolecular electron transfer from the C-bonded formato ligands to the Co(III) center is strongly dependent on the state of protonation of the carboxylate group with an apparent pK_a for deprotonation of 2.6; formate is a more powerful reducing agent than is formic acid.[32] Although the pK_a of free formic acid is 3.8, the greater electron-withdrawing character of the 3+ metal center would strengthen the C-bonded acid and lower its pK_a. Thus, upon photolysis the reactions in Scheme I take place.

Scheme I



The differences in the rate constants for the intramolecular decay of the LL species from the bidentate oxalato compounds are consistent with the generally lower reactivity of en compounds in simple electron-transfer reactions[33] and photoredox processes.[3] The slightly higher rate for the decay of A_4-LL as compared to A_5-LL may reflect the somewhat lessened stability (with respect to Co(II)) of complexes in which an ammine group is replaced by a lower crystal field strength aquo ligand.

The spectrum of LL, certainly not that of a Co(III) complex containing O-bonded carboxylate ligands, is consistent with the assignment of its structure. In order to give such blue-shifted d–d bands, LL must contain a ligand that lies very high in the spectrochemical series, perhaps even higher than C-bonded cyanide which has the largest crystal field strength of common ligands. C-Bonded formate would be expected to have a larger crystal field strength than the O-bonded carboxylate ligand inasmuch as the deprotonated formate carbon is a stronger Lewis base than is the carboxylate oxygen. It is this extremely low acidity of the carbon hydrogen which has rendered thermally induced oxygen → carbon linkage isomerization of formate unobservable. By analogy, the ultraviolet irradiation of $(NH_3)_5CoNO_2^{2+}$ results in the formation of the linkage isomer, $(NH_3)_5CoONO^{2+}$, in addition to the direct generation of Co^{2+};[34] formate, HCO_2^-, is isoelectronic with NO_2^-. The N-bonded nitrite has a higher ligand field strength than does the O-bonded isomer and shows blue-shifted d–d bands in a manner similar to that observed for LL.[34] The band at 262 nm is assigned as a C-bonded formate → metal charge-transfer band. This ligand is certainly more easily oxidizable than is its O-bonded isomer and would be expected to show a charge-transfer band shifted toward the red. Examination of Figure 7 shows that this indeed is the case. A similar shift is observed for the nitro–nitrito isomers.[34]

The assigned structure of LL is consistent with the observation that its first-order conversion to Co^{2+} is independent of ionic strength and the presence of O_2,

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(31) A. F. Vaudo, E. R. Kantrowitz, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **93**, 6698 (1971).

(32) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952, p 130.

(33) D. P Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem., Soc.*, **94**, 394 (1972).

(34) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

alcohols, Cl^-, Co^{2+}, and $C_2O_4^{2-}$. The lack of a marked effect even in the presence of 95% ethanol means either that water is still preferentially bound to the sixth coordination site or that the factors that govern the ligand-to-metal intramolecular electron transfer are not influenced significantly by the nature of that sixth ligand. The similarity in the decay rates of A_4-LL and A_5-LL indicates that this latter possibility is not unreasonable. The fact that the amount of LL formed in the flash is not affected by the presence of other solutes, including H^+, means that the precursor to LL is likewise unreactive toward those solutes and is not quenched or scavenged.

The identification of LL is further supported by the formation of Co^{2+} in the 254-nm photolysis of en-LL with $\phi_{Co^{2+}} = 0.13$ and by the formation of a Co(III) diaquo species upon base hydrolysis. In the latter experiment, no attempt was made to define the cis or trans nature of the product or to analyze for the ligand lost into solution, presumably formate. It is difficult to analyze quantitatively for formate, especially when secondary radical reactions can also generate this species.

The Photochemical Mechanism. A complete photochemical mechanism will have to take into account the existence of intermediate LL and its decay into Co^{2+} and a radical, the effect of O_2 on $\phi_{Co^{2+}}$, the apparent insensitivity of $\phi_{Co^{2+}}$ to I_a and the presence of alcohols, and the direct formation of Co^{2+} and radical species. The data for $(en)_2Co(C_2O_4)^+$ involving $\phi_{Co^{2+}}$ (Table I), the decay of en-LL(Figure 6), and the generation of Co^{2+} in the flash demonstrate that 20–25% of the total Co^{2+} yield arises directly from the photochemical act and the remainder as a result of the decay of en-LL. There is, of course, no direct way of establishing this ratio for the other complexes because of the short lifetimes of their LL intermediates. Here, the analysis for Co^{2+} reflects the production of Co^{2+} by both paths which cannot be distinguished. However, it is probably not unreasonable to expect these two complexes to show a similar ratio as that demonstrated by the en complex.

Both $(NH_3)_4Co(C_2O_4)^+$ and $(NH_3)_5Co(C_2O_4)^+$ exhibit a reduction in $\phi_{Co^{2+}}$ by a factor of 2 when O_2 is present during photolysis. This establishes that O_2 scavenges a species which normally generates additional Co^{2+}. The direct production of Co^{2+} would be accompanied by the formation of a radical ($C_2O_4^-$ or CO_2^-; in acidic solution, C_2O_4H or CO_2H) arising from the one-electron oxidation of oxalate. In the presence of the Co(III) substrate, electron transfer to the complex would generate additional Co^{2+}. However, in an O_2-saturated solution ($[O_2] = 1.3 \times 10^{-3}$ *M*), the radicals would be preferentially scavenged by O_2. A similar situation would exist for the radical generated by the rapid decay of A_4-LL and A_5-LL. Thus, the factor of 2 between the values of $\phi_{Co^{2+}}$ in the presence of N_2 and O_2 can be completely rationalized if the radicals from the direct and indirect generation of Co^{2+} normally reduce the complex to Co^{2+} but are scavenged by O_2. Concentrating on the oxalate ligand

$$CoC_2O_4^+ \xrightarrow{h\nu} [CoC_2O_4^+]^* \qquad (5)$$

$$[CoC_2O_4^+]^* \begin{cases} \rightarrow Co^{2+} + C_2O_4^-/C_2O_4H & (6) \\ \rightarrow LL + CO_2 & (7) \end{cases}$$

$$LL \longrightarrow Co^{2+} + CO_2^-/CO_2H \qquad (8)$$

$$C_2O_4^-/C_2O_4H + CoC_2O_4^+ \longrightarrow Co^{2+} + 2CO_2 \qquad (9)$$

$$CO_2^-/CO_2H + CoC_2O_4^+ \longrightarrow Co^{2+} + CO_2 \qquad (10)$$

$$C_2O_4^-/C_2O_4H/CO_2^-/CO_2H + O_2 \longrightarrow O_2^- + 2CO_2/CO_2 \qquad (11)$$

It should be noted that, under the conditions of all the quantum yield determinations, the O_2^- radical would exist in its acidic form, HO_2,[35] which does not appear to be effective in reducing Co(III) complexes.[36] This mechanism also accounts for the CO_2/Co^{2+} ratio of 1.0 for these ammine complexes *in vacuo*. It is apparent that *regardless of the ratio of reactions 6 and 7*, CO_2 and Co^{2+} will be produced in a 1:1 stoichiometry as long as the radicals disappear *via* reactions 9 and 10 and not by combination and/or disproportionation. With these complexes, the short lifetimes of A_4-LL and A_5-LL prevent a buildup in concentration allowing all complications due to photolysis of the intermediate or reaction with the radicals to be ignored.

In the case of $(en)_2Co(C_2O_4)^+$, however, it is evident that the photolysis of en-LL and the post-irradation production of Co^{2+} and CO_2 must be considered in accounting for the product yields. Concerning the $\phi_{Co^{2+}}$ values at pH 1.2 in Table I, the analyses for Co^{2+} were performed within a half-hour of the photolysis before very much en-LL had thermally decomposed. In these continuous photolysis experiments run to < 25% completion, the extent of photochemical decomposition of en-LL would likewise be small. The lack of an effect of O_2 on $\phi_{Co^{2+}}$ at pH 1.2 indicates that the primary radical, in its protonated form, does not react with the substrate at a concentration of $\sim 10^{-3}$ *M* to produce additional Co^{2+} but rather disappears *via* disproportionation. Similarly, the CO_2H radical generated in the decay of en-LL must also disappear in the same way as evidenced by the $\phi_{Co^{2+}}$ values at pH 1.0 where the analysis for Co^{2+} is delayed for 24 hr.

$$2C_2O_4H \longrightarrow 2CO_2 + H_2C_2O_4 \qquad (12)$$

$$2CO_2H \longrightarrow CO_2 + HCO_2H \qquad (13)$$

At pH 2.7–2.9, on the other hand, by the time the Co^{2+} analyses had been performed, a substantial amount of en-LL had decayed according to reaction 8. During the photolysis period, the concentration of en-LL would build up and may even contribute to its direct photolysis. In addition, the release of base during the photolysis into the unbuffered solution would raise the pH. Thus, the radicals, with pK_a values of 3–5 (3.9 for CO_2H and probably not more than 1 p*K* unit lower for C_2O_4H), would exist in their various protonated and deprotonated forms. If the CO_2H and C_2O_4H radicals are inert to $(en)_2Co(C_2O_4)^+$ but CO_2^- and $C_2O_4^-$ reduce the complex, then $\phi_{Co^{2+}}$ will consist of a component which is O_2-scavengable and a component which is not. The effect of O_2 on $\phi_{Co^{2+}}$ at pH 2.7–2.9 demonstrates this contention. If the quantum yields of the primary photoprocesses are independent of pH, then $\Delta\phi_{Co^{2+}}(N_2) \approx 2\Delta\phi_{Co^{2+}}(O_2)$ where $\Delta\phi_{Co^{2+}} = (\phi_{Co^{2+}}$ at pH 2.7–2.9$) - (\phi_{Co^{2+}}$ at pH 1.2$)$. As is seen in Table I, the $\phi_{Co^{2+}}$ values are in accord with the reducing ability of the protonated and deprotonated radicals.[15]

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[35] B. H. J. Bielski and J. M. Gebicki, *Advan. Radiat. Chem.*, **2**, 177 (1970).

[36] (a) N. Zevos, *J. Phys. Chem.*, **72**, 1506 (1968); (b) E. P. Vanek and M. Z. Hoffman, manuscript in preparation.

If $\phi_7/\phi_6 \sim 4$ for $(en)_2Co(C_2O_4)^+$ and if $\sim 20\%$ of en-LL is destroyed by secondary photolysis during a 3-min exposure at high light intensity, then the CO_2/Co^{2+} data given in Table II are also rationalized. At pH 1, where reactions 5–8 and 12 and 13 would be applicable, $CO_2/Co^{2+} \sim 2.2$ would be predicted when the Co^{2+} analysis is performed immediately after photolysis before an appreciable amount of en-LL is destroyed. After 24 hr, when nearly all of the en-LL has disappeared, the ratio is predicted to be ~ 1.4. The agreement between prediction and experiment is excellent. It is assumed here that the photolysis of en-LL to Co^{2+} is *via* the usual charge-transfer route.

$$LL \xrightarrow{h\nu} Co^{2+} + CO_2^-/CO_2H \qquad (14)$$

It is further assumed that the protonated radicals are inert to en-LL as they apparently are to the parent complex.

It is possible to place limits on the values of the rate constant for radical reattack on the complex substrate from the O_2-scavenging data. If $k_{11} \sim 10^9\ M^{-1}\ sec^{-1}$, then for O_2 (at a concentration of $1.3 \times 10^{-3}\ M$) to scavenge the radicals preferentially in competition with reattack on the substrate present at $> 10^{-3}\ M$ concentration, $k_{9,10} \leq 10^7\ M^{-1}\ sec^{-1}$ for the ammine complexes. This limit is probably also valid for the deprotonated radicals with the en complex. However, at pH 1.2, radical reattack on the en complex does not apparently occur at all so that the radicals disappear *via* reactions 12 and 13. Replacement of the ammine ligands by the chelating en group lowers the reactivity of the complex toward radical attack in accord with the lowering of the reduction potential. Similarly, coordination of three oxalate ligands as in $Co(C_2O_4)_3^{3-}$ raises the reduction potential and increases the complex's reactivity toward radical attack in accord with linear free energy relations for electron-transfer reactions.[33] Indeed, we find[9] $k_{9,10}/k_{11} \sim 10$ for this latter complex, indicating that the rate of radical attack is very near to the diffusion-controlled limit; note that $k(e_{aq}^- + Co(C_2O_4)_3^{3-}) = 1.2 \times 10^{10}\ M^{-1}\ sec^{-1}$.[37] Thus, no effect of O_2 on the redox decomposition of $Co(C_2O_4)_3^{3-}$ is seen[4] unless $[Co(C_2O_4)_3^{3-}] \ll [O_2]$.[9]

The independence of $\phi_{Co^{2+}}$ on changes in I_a is consistent with the general mechanism. The lack of any effect on $\phi_{Co^{2+}}$ in N_2 from the presence of relatively high concentrations of alcohols is not unexpected. Even if the radicals did react rapidly with the alcohol *via* a H atom transfer mechanism, the resulting alcohol radical would reduce the complex to Co^{2+}.[25,36b] Thus, one source of Co^{2+} would be exchanged for another.

The observation that $\phi_{Co^{2+}}$ for $(NH_3)_4Co(C_2O_4)^+$ is reduced by about 50% in the presence of acetate buffer at pH 4–6 may indicate that the primary processes leading directly and indirectly (*via* LL) to Co^{2+} are pH dependent above pH 2.4. However, it is more likely that acetate can interfere with the free radical mechanism by serving as a scavenger, thus diminishing the secondary reduction of the complex; we have found that the acetate radical does not appear to reduce $(NH_3)_5CoO_2CCH_2CO_2H^{2+}$. In this regard, concern must be expressed over previous work involving $Co(C_2O_4)_3^{3-}$ in which $\phi_{Co^{2+}}$ values were determined at pH 4 in an acetate buffer.[5]

The Primary Process. The flash photolysis experiments involving the use of anthracene and napththalene to filter solutions to restrict the wavelength of the light demonstrated that only absorption in the intense band at $\lambda < 280$ nm was effective in generating the LL intermediate. This absorption band, also illuminated in the case of the steady-state photolysis at 254 nm, is assigned as arising from a spin-allowed ligand-to-metal charge-transfer transition in which a ligand electron is propagated into a molecular orbital more closely associated with the metal center.[3] Such irradiations of Co(III) amine complexes have always been observed to generate Co^{2+} and a one-electron oxidized ligand.[3] Other processes arising from this excitation have also been observed: NH_3 aquation [$Co(NH_3)_5Cl^{2+}$ [38] and $Co(NH_3)_5N_3^{2+}$ [24]], X-ligand aquation [$Co(NH_3)_4CO_3^+$ [39]], and linkage isomerization [$Co(NH_3)_5NO_2^{2+}$ [34] and $Co(NH_3)_5O_2CH^{2+}$ [31]]. Consideration of the range of these processes, and the possibility that other examples will be found in the future, makes it unlikely that all the products arise directly from a single precursor, whether a "radical-pair" or a discrete excited state. It has been reasonably argued[40] that the various processes are independent and arise from distinct excited states, all linked *via* radiationless transitions from the excited state populated in the primary absorption process. In addition to those electronic states that must be proposed to account for these observations, the oxalato complexes require consideration of a state that gives rise to the heterolytic C–C bond scission in the oxalate ligand leading to the eventual formation of the C-bonded formato linkage isomer. This excited state must be closely associated with the ligand and may involve a π^* oxalate orbital. The free ligand, protonated or deprotonated, has a very low extinction at $\lambda > 200$ nm, thereby making it highly unlikely that direct ligand absorption is involved.[41]

We propose that absorption in the ligand-to-metal charge-transfer bond of the complex generates the primary CTTM excited state of singlet multiplicity (^1CT) which, *via* radiationless transition, generates the reactive charge-transfer triplet (^3CT) and a ligand excited state (L*). Because of the fact that the total quantum yield of observed products is less than unity and no luminescence is observed from Co(III) complexes of this type,[42] radiationless return from these excited states to the ground state must be an important process. There is mounting evidence from sensitization studies[43] on Co(III) complexes that the oxidation–reduction products arise from the ^3CT states and aquation products from the ligand field excited states of triplet spin multiplicity. In the same way, the ligand excited state here that leads to the decomposition of the oxalate

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[37] J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Nature (London)*, **201**, 468 (1964).

[38] L. Moggi, N. Sabbatini, and V. Balzani, *Gazz. Chim. Ital.*, **97**, 980 (1967).

[39] V. W. Cope and M. Z. Hoffman, *Chem. Commun.*, 227 (1972).

[40] V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, **1**, 7 (1967).

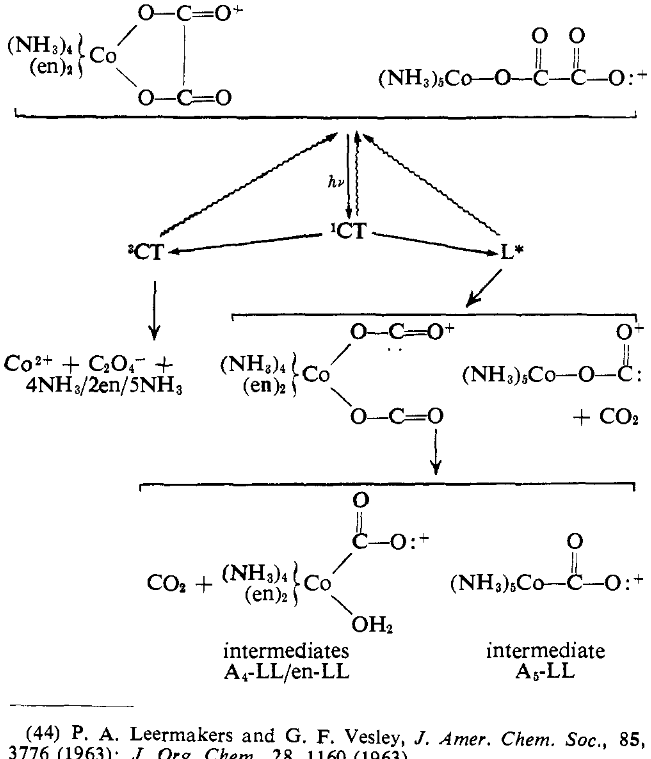
[41] To date there has been no indication that strictly intraligand transitions are substantially affected by coordination to the Co(III) center; see A. W. Adamson, A. Vogler, and I. Lantzke, *J. Phys. Chem.*, **73**, 4183 (1969), for the case of *trans*-4-stilbenecarboxylatopentaamminecobalt(III).

[42] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

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

ligand and formation of the C-bonded formato linkage isomer may be a triplet. Because of the low absorptivity of free oxalate, the photochemistry of this species has not been studied to any extent. However, the photochemistry of pyruvic acid (CH_3COCO_2H) in aqueous solution, an analogous α-diketo acid, proceeds *via* a triplet state and a carbene intermediate[44] suggesting that a similar process could be operative in the case of oxalate. We suggest that the "intramolecular sensitization" of the coordinated oxalate causes its decomposition *via* heterolytic C–C bond scission which leaves a doubly deprotonated formate ion, CO_2^{2-}, coordinated to the Co(III) center. The resulting "carbene" carbon would be an extremely strong Lewis base capable of displacing the carboxylate oxygen either *via* direct attack or the formation of a transitory seven-coordinate species. Irrespective of these mechanistic details, linkage isomerization must occur rapidly within the first coordination sphere of the complex in a time short compared with entrance of the solvent into the coordination shell and protonation of the "carbene." Inasmuch as water exchange with coordinated H_2O (in $Co(NH_3)_5OH_2^{3+}$) is rather slow[45] and linkage isomerization of $Co(NH_3)_5NO_2^{2+}$ (as studied by flash photolysis)[29] occurs within the lifetime of the flash, it appears certain that linkage isomerization of the "carbene" competes favorably with any processes involving the solvent. Presumably the remaining CO_2 ligand then aquates. Its interesting to note that the "intramolecular sensitization" of the coordinated oxalate ligand also takes place with the monodentate oxalate complex irrespective of the state of protonation of the free end of the ligand. Here bond scission will cause CO_2 to be released directly into the solution rather than from a coordination site as in the case of the bidentate oxalate complexes. Either way, the formation of LL is accompanied by the loss of one molecule of CO_2.

Scheme II



The values of $\phi_{Co^{2+}}$ in O_2 (after 24 hr in the case of the en complex) in Table I represent the sum of the quantum yields for the direct (*via* ^3CT) and indirect (*via* L* and the LL intermediates) formation of Co^{2+} ($\phi_6 + \phi_7$); in the presence of O_2, secondary production of Co^{2+} *via* radical–substrate reaction is quenched. In the case of $(en)_2Co(C_2O_4)^+$, $\phi_7/\phi_6 \sim 4$; this ratio is unlikely to be very different for the other complexes. Thus, the quantum yield for the direct primary formation of Co^{2+} (ϕ_6) for the ammine complexes has a value of 0.1–0.2. It is interesting to note that the observed value of $\phi_{Co^{2+}}$ for a large number of cobalt(III) pentaammine complexes containing aliphatic carboxylic acids as the sixth ligand is also in that range.[25,29,46] For some that have been studied extensively, such as $(NH_3)_5CoO_2CCH_3^{2+}$ and $(NH_3)_5$-$CoO_2CCH_2CO_2H^{2+}$, there do not appear to be any sources of an appreciable yield of Co^{2+} other than from direct primary formation. Inasmuch as the amine–oxalate complexes appear to be the first reported cases of intramolecular ligand excitation in Co(III) complexes, it is hard to judge if the extent of this process ($\phi_7 \sim 0.4$) is unusual. Indeed, this may be one of the energy degradation routes normally followed by Co(III) complexes; failure to recognize it up to now merely means that the clues have not been as obvious. Ligand excitation that does not result in bond scission, luminescence, or transient absorption would not be detected other than by inference from the less than unity values of $\phi_{Co^{2+}}$. Our failure to observe anything other than a short-lived weak transient in the case of the oxalate-bridged binuclear complex can be attributed to an unfavorable ratio of ϕ_7/ϕ_6. Coordination of the oxalate to two Co(III) centers apparently causes the charge-transfer excited state initially populated to undergo transition to the dissociative state leading to Co^{2+} with a high probability. As a result, the complex is extremely photosensitive; the transient observed was probably the $C_2O_4^-$ radical.

It is not possible, on the basis of the results presented in this paper, to make sweeping generalizations about the dependence of the quantum yields of the various degradative and nondegradative radiationless transitions on the nature of the ligands coordinated to the metal center. However, certain trends should be noted. The slightly lower quantum yield values for the en complex is in accord with generally lower values for such chelated complexes.[3] Although the $\phi_{Co^{2+}}$ values for $(NH_3)_4Co(C_2O_4)^+$ are pH independent within the precision of the measurement, the pH effect for $(NH_3)_5Co(C_2O_4)^+$ is probably real and could reflect changes in the internal processes due to protonation of the ligand ($pK_a = 2.2$). At the same time, the yield of A_5-LL is not affected by $[H^+]$ implying that some transitions are pH dependent and some are not.

The short-lived intermediate, SL, could be a precursor to LL or a completely independent species. However, the pH-dependent first-order decay of its tail absorption suggests that SL is either the ligand excitation species (L*) or the "carbene." Unfortunately, we have not been able to obtain direct evidence on this point, and further speculation is inappropriate at this time.

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[44] P. A. Leermakers and G. F. Vesley, *J. Amer. Chem. Soc.*, 85, 3776 (1963); *J. Org. Chem.*, 28, 1160 (1963).

[45] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 80, 2642 (1958).

[46] D. D. Campano, E. R. Kantrowitz, and M. Z. Hoffman, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, INOR 23.

Implications to Other Systems. Extension of the ideas presented here to other tripositive metal–oxalate complexes must be made with caution because of the unknown effect of the nature of the ligands on the photochemical processes. Thus, conclusions about the detailed behavior of $Co(C_2O_4)_3^{3-}$, for example, cannot be drawn by analogy to the amine–oxalate systems. We have already indicated, however, that the secondary formation of Co^{2+} in the photolysis of $Co(C_2O_4)_3^{3-}$ *via* reaction 9 is so rapid as to compete successfully with the removal of the radicals by O_2 in reaction 11. Only at low complex concentrations is the yield of Co^{2+} affected by the presence of O_2.[9] Thus, the assumption made in earlier work[5] that the quantum yield of primary Co^{2+} formation is one-half of the observed value of $\phi_{Co^{2+}}$ is correct. It is interesting to note that Cooper and DeGraff[47] obtained a rate constant of $>5 \times 10^7$ M^{-1} sec^{-1} for $C_2O_4^-/CO_2^- + Fe(C_2O_4)_3^{3-}$ from their flash photolysis study indicating a fast secondary formation of Fe^{2+}. They also obtained a long-lived intermediate absorbing at $\lambda < 460$ nm which they could only identify very tentativly. Future work on these and related systems will be directed toward answering the many questions raised by the study reported here.

Summary

The ultraviolet photochemistry of the amine–oxalate complexes of Co(III), $(NH_3)_5Co(C_2O_4)^+$, $(NH_3)_4Co(C_2O_4)^+$, and $(en)_2Co(C_2O_4)^+$ generates, in addition to Co^{2+} and a radical derived from the one-electron oxidation of oxalate ($C_2O_4^-$, CO_2^- or their protonated analogs), excitation localized on the oxalate ligand. This "intramolecular sensitized" ligand excitation results in heterolytic C–C bond scission and leads to the formation of CO_2 and a C-bonded formato linkage isomer complex of Co(III). This C-bonded formato species is unstable with respect to Co^{2+} and undergoes thermal intramolecular electron transfer with a rate that is dependent upon the state of protonation of the formato ligand and the nature of the amine ligands. The production of Co^{2+} by this indirect route is accompanied by the generation of radicals (CO_2^- or CO_2H). The radicals formed here and in the primary direct production of Co^{2+} reattack and reduce the complex (except for the protonated radicals and the en complex) to generate a secondary source of Co^{2+}. The radicals can be scavenged by O_2 to reduce the value of $\phi_{Co^{2+}}$ by a factor of 2.

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(47) G. D. Cooper and B. A. DeGraff, *J. Phys. Chem.*, 75, 2897 (1971).

Photochemical Reaction Pathways of Ruthenium(II) Complexes. III.[1] Metal-to-Ligand Charge-Transfer Excitation of the Pentaamminepyridineruthenium(II) Cation and Related Species[2]

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Abstract: Product analyses and quantum yields are reported for the photoreactions resulting from metal-to-ligand charge-transfer excitation of the complex ion $Ru(NH_3)_5py^{2+}$. Photoaquation of pyridine and of cis and trans ammonias are the principal reaction pathways. Quantum yields for pyridine photoaquation show an unusual dependence on solution pH plateauing at ~0.04 mol/einstein at high pH and appearing to level at ~0.12 mol/einstein for low pH (2.0 M ionic strength). Ammonia photoaquation is apparently pH insensitive. Quantum yields were also measured for the photoaquation of L from the complexes $Ru(NH_3)_5L^{2+}$ (L = benzonitrile, 3-chloropyridine, 4-methylpyridine). These were independent of pH for L = benzonitrile and for L = 3-chloropyridine except at very low pH's. In contrast, the quantum yields for L = 4-methylpyridine followed a pH pattern similar to that observed for L = pyridine. In the higher pH region, the Φ_L values followed the order L = benzonitrile > 3-chloropyridine > pyridine > 4-methylpyridine. Photolysis of $Ru(NH_3)_5py^{2+}$ in acidic D_2O gave small yields of H/D exchange on the pyridine ring. The quantum yield of this pathway, however, was too small to indicate a major role in the photoaquation. These data are interpreted in terms of proposed photoaquation mechanisms which for $Ru(NH_3)_5py^{2+}$ involve competitive protonation of an excited state or intermediate.

In recent years, there has been considerable interest in the mechanistic photochemistry of octahedral metal ammine complexes.[4–7] These studies have principally

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(1) Papers I and II are respectively (a) P. C. Ford, D. H. Stuermer, and D. P. McDonald, *J. Amer. Chem. Soc.*, 91, 6209 (1969); (b) P. C. Ford, D. A. Chaisson, and D. H. Stuermer, *Chem. Commun.*, 530 (1971).

(2) Taken in part from the M.A. dissertation of D. A. C., University of California, Santa Barbara, 1971. This work has been presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

(3) (a) National Science Foundation Undergraduate Research Participant, summer 1969; (b) Camille and Henry Dreyfus Foundation Teacher–Scholar.

(4) For comprehensive reviews, see (a) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press,

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