Intermediates in the Photochemistry of Carbonato–Amine Complexes of Cobalt(III). CO_3^- Radicals and the Aquocarbonato Complex[1]

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Abstract: The 254-nm irradiation of neutral, buffered, solutions of $Co(NH_3)_4CO_3^+$ and $Co(en)_2CO_3^+$ produces Co_{aq}^{2+} with a relatively low quantum yield (0.06 and 0.02, respectively); $Co(NH_3)_5CO_3^+$ also is photoreduced. The irradiation of $Co(NH_3)_4CO_3^+$ also generates $Co(NH_3)_4(OH_2)_2^{3+}$ with a quantum yield of 0.11 ± 0.03. The flash photolysis of the three complexes yields a transient intermediate which has λ_{max} 600 nm and which is identified as the CO_3^- radical. The flash photolysis of the bidentate carbonato complexes also reveals a long-lived tail absorption in the 300-nm region which decays *via* pH-dependent first-order kinetics. The behavior of this intermediate is identical with that of the aquocarbonato species proposed as an intermediate in the acid-catalyzed aquation of the bidentate carbonato complexes. It is proposed that photochemical excitation of these complexes in the intense ligand-to-metal charge-transfer band produces the charge-transfer singlet state (^{1}CT) which generates, *via* radiationless transition, the charge-transfer triplet state (^{3}CT) and a ligand excited state (L*). The ^{3}CT state is the precursor to the oxidation–reduction products; protonation of the carbonato ligand in the L* state is viewed as causing ring opening and aquation.

It has been amply demonstrated[3–9] that the predominant process resulting from the irradiation of amine complexes of Co(III) in their intense ligand-to-metal charge-transfer band is the generation of Co_{aq}^{2+} and a free radical derived from the one-electron oxidation of a ligand. In addition, other processes arising from this excitation have been observed such as NH_3 aquation [$Co(NH_3)_5Cl^{2+}$ [10] and $Co(NH_3)_5N_3^{2+}$ [5]], linkage isomerization [$Co(NH_3)_5NO_2^{2+}$ [11] and $Co(NH_3)_5O_2CH^{2+}$ [12]], and ligand decomposition [$Co(NH_3)_5C_2O_4^+$ and $Co(NH_3)_4C_2O_4^+$ [8]]. In the case of the bidentate oxalato complex, no evidence of photochemically induced ring opening, aquation, and subsequent loss of oxalate was obtained.[8] As one part of our continuing study of the effect of multidentate chelation on the photochemistry of transition metal complexes, we chose to examine the carbonato–amine complexes of Co(III). These bidentate carbonato complexes are known to undergo thermal ring opening and aquation and most of the mechanistic details have been well clarified.[13,14] The properties of these compounds offer a unique opportunity to compare the photochemical and thermal behavior of coordination complexes.

$Co(NH_3)_5CO_3^+$ decarboxylates quite rapidly[15] in a first-order manner for which $k_{obsd} = k_1[H^+]/([H^+] + K_2)$, where k_1 is the rate constant for the unimolecular decarboxylation of the protonated form of the complex

$$Co(NH_3)_5CO_3H^{2+} \longrightarrow Co(NH_3)_5OH^{2+} + CO_2 \quad (1)$$

and K_2 is the equilibrium constant for

$$Co(NH_3)_5CO_3H^{2+} \rightleftharpoons Co(NH_3)_5CO_3^+ + H^+ \quad (2)$$

At the low pH limit $k_1 = 1.25$ sec^{-1} and $pK_2 = 6.4$. The value of k_{obsd} at pH >8 is as much as two orders of magnitude slower than in acidic solution.[16] The activation parameters for reaction 2 are $\Delta H^\ddagger = 17.0 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = -0.5 \pm 1.0$ eu.[15]

The aquation of $Co(NH_4)_4CO_3^+$ occurs through reaction with H_2O and H_3O^+ and has been postulated to proceed *via* the formation of a ring-opened aquocarbonato intermediate.[17]

$$Co(NH_3)_4CO_3^+ + H_2O \rightleftharpoons cis\text{-}Co(NH_3)_4(OH)(CO_3H)^+ \quad (3)$$

where $k_3 = 1.3 \times 10^{-4}$ sec^{-1} and $k_{-3} \sim 10^{-1}$ sec^{-1}

$$Co(NH_3)_4CO_3^+ + H_3O^+ \longrightarrow cis\text{-}Co(NH_3)_4(OH_2)(CO_3H)^{2+} \quad (4)$$

with $k_4 = 1.5\ M^{-1}$ sec^{-1}. The various acid–base forms of the aquocarbonato intermediate are related by the following equilibria

$$cis\text{-}Co(NH_3)_4(OH_2)(CO_3H)^{2+} \rightleftharpoons cis\text{-}Co(NH_3)_4(OH)(CO_3H)^+ + H^+ \quad (5)$$

$$cis\text{-}Co(NH_3)_4(OH)(CO_3H)^+ \rightleftharpoons cis\text{-}Co(NH_3)_4(OH)(CO_3)^0 + H^+ \quad (6)$$

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where pK_5 is estimated[18] to be $\sim$6 and $pK_6 \sim 8.6$.[19] The decarboxylation reactions

$$Co(NH_3)_4(OH_2)(CO_3H)^{2+} \longrightarrow Co(NH_3)_4(OH_2)(OH)^{2+} + CO_2 \quad (7)$$

$$Co(NH_3)_4(OH)(CO_3H)^{+} \longrightarrow Co(NH_3)_4(OH)_2^{+} + CO_2 \quad (8)$$

have rate constants estimated to be $k_7 \sim 2$ sec^{-1} and $k_8 \sim 1 \times 10^{-2}$ sec^{-1}. Isomerization of the *cis*-aquocarbonato intermediate is too slow to be considered in this competitive scheme[19] and the neutral deprotonated product $Co(NH_3)_4(OH)(CO_3)^0$ is fairly resistant to hydrolysis or isomerization.[19,20] Because of the complex ring-opening and decarboxylation mechanism, measured activation parameters reflect the combined contributions from the individual steps. However, the point must be made that the decarboxylation of the aquocarbonato intermediate (reaction 7) is kinetically very similar to the direct decarboxylation of $Co(NH_3)_5CO_3^+$ (reaction 1).

For $Co(en)_2CO_3^+$, the same mechanism has been found to hold[18] with $k_7 \sim 2$ sec^{-1} and $pK_5 \sim 5.3$.[19]

Because the slow ring opening of the bidentate carbonate is the rate determining step, the presence and disappearance of the aquocarbonato intermediate has not been directly observable in the thermal reaction in neutral or mildly acidic solution. In 2 *M* $HClO_4$, where the H_3O^+-catalyzed ring-opening step would be somewhat faster than the subsequent decarboxylation of the intermediate, experiments using stopped-flow techniques[21] have shown the formation and decay of the intermediate from $Co(tren)CO_3^+$ with the complex consecutive reaction kinetics analyzed in terms of the estimated rate constants. From these experiments it is known that the spectra of the proposed aquocarbonato species in the ultraviolet region is more intense than that of the chelated carbonato complex.

In this paper we report the results of the continuous and flash photolysis of carbonato–amine complexes of Co(III) [$Co(NH_3)_5CO_3^+$, $Co(NH_3)_4CO_3^+$, $Co(en)_2CO_3^+$] and the observation of photoinduced ring opening of the chelated ligand.

Experimental Section

Chemicals. $Co(NH_3)_5CO_3^+$ (as the nitrate salt) was prepared according to literature procedures[22] as was $Co(NH_3)_4CO_3^+$ (as the chloride salt).[23] Conversion of the bidentate complex to the perchlorate salt was accomplished by dissolving the chloride salt in a minimum volume of water at 60°, filtering quickly, and adding the filtrate to an equal volume of 50% $NaClO_4$ solution (w/v). A bright purple solid was obtained after 1 hr at 0° which was filtered, washed with alcohol–ether, and air dried. Recrystallization did not change the absorption spectrum of the complex which compared very well with the literature.[24]

$[Co(en)_2CO_3]ClO_4$ was prepared[25] from $[Co(en)_2Cl]Cl$ which in turn had been prepared by the procedure of Bailar.[26] The spectrum of the complex was unchanged by recrystallization but showed slight deviations from the literature values[24] (found: λ_{max} 511, 359 nm, ϵ_{max} 129, 118 M^{-1} cm^{-1}; literature: λ_{max} 514, 362 nm, ϵ_{max} 135, 123 M^{-1} cm^{-1}).

A phosphate buffer stock solution was prepared to pH 6.5 by the addition of concentrated NaOH to 0.4 *M* NaH_2PO_4 solution. The solutions for continuous photolysis were prepared from this stock solution so that [total phosphate] = 0.02 *M*; pH was adjusted using concentrated $HClO_4$ or NaOH and measured with a Beckman Expandomatic pH meter.

All solutions were prepared using distilled water. In some of the flash photolysis experiments, the solutions were prepared from triply distilled water which had been radiolyzed and photolyzed.

Photochemical Apparatus. The 254-nm photolysis units have already been described.[6] Quantum yields were determined relative to the photolysis of $Co(NH_3)_5O_2CCH_3^{2+}$ in 0.1 *M* $HClO_4$ taking $\phi_{Co^{2+}} = 0.19$.[6] Flash photolysis was performed using a 22-cm optical cell and procedures which have already been reported.[4,8] For monitoring the 300-nm region, a RCA 1P28 photomultiplier was used; for the 600-nm region, a Hamamatsu R136 PM tube was operated at about 600 V. The linearity of the detection system was checked and found to be satisfactory. A glass filter (for short-wavelength monitoring, Vycor filter; for long-wavelength, Corning 3-72) was always in place between the analyzing lamp (Osram 150w Xe lamp) and the cell and an electric shutter restricted the exposure of the solution to the light. The solutions used were very dilute ($\sim 5 \times 10^{-5}$ *M*) to ensure homogeneous absorption of the photolyzing flash and the distribution of transient species in the cell. Transient absorption spectra were obtained from the optical density of the absorption measured 50 μsec after the start of the flash as a function of monitoring wavelength. Rate constants were calculated from a least-square computer fit of the data to the appropriate rate law.

Procedures. Because of the acid-catalyzed thermal aquation of these carbonato complexes, the solid salt was added to the buffer solution at the last moment and all subsequent procedures were carried out as rapidly as possible. In the continuous photolysis experiments, we found the optimum conditions for the bidentate complexes to be pH 6.4 and 2×10^{-3} *M* complex in the phosphate buffer. Under these conditions the thermal aquation is relatively slow and the solution does not change by more than 0.2 unit during photolysis. Photolyses were run to 20–25% completion (aliquots were taken periodically for Co_{aq}^{2+} analysis) and no Co(II) hydroxide or phosphate precipitated. Plots of Co_{aq}^{2+} yield *vs.* time, from which $\phi_{Co^{2+}}$ values were obtained, were linear. Co_{aq}^{2+} analyses were performed using the thiocyanate complexation method described previously;[6] the presence of the phosphate buffer had no effect on the analytical procedure. Analysis for Co^{2+} was carried out immediately. The photolyte was first acidified with $HClO_4$ to pH 1 in order to destroy the carbonato substrate and to dissolve any microcrystals of Co(II) salts. In the flash photolysis experiments, solutions were prepared without the complex which was added as the solid immediately prior to the experiment. This was particularly critical at pH 4 or at elevated temperatures where the useful life of the solution was about 5 min. Alternatively, in neutral or mildly alkaline solution, a fresh stock solution or 0.01 *M* $Co(NH_3)_4CO_3^+$ was used to prepare the solutions for flashing. The solutions for flashing were prepared in less than 1 min and the stock solution was discarded within 2 hr of preparation. Under these experimental conditions thermal aquation is never an important feature. For $Co(NH_3)_4CO_3^+$, $t_{1/2} \sim 80$ min for thermal aquation at pH >5; even at pH 4, $t_{1/2} > 30$ min. Solutions were rarely used for as much as 15 min and considerably less at lower pH values and elevated temperatures. Thus, we are confident that our bidentate carbonato solutions contained <10% thermal aquation products at the time they were flashed. For $Co(NH_3)_5CO_3^+$, the flash solution was prepared directly from the solid. All solutions were discarded after one flash. Since O_2 had no effect on the kinetics of the transient species, air-saturated solutions were used directly as prepared. The ionic strength of the solution was established by the phosphate buffer, added $NaClO_4$, or the NaOH in alkaline solution.

Ion exchange separation of the photolysis products was carried out on a Dowex 50-4X, 200–400 mesh resin in a 5 × 0.6 cm column. The resin was first washed with 15 ml of 1 *M* $NaClO_4$ to convert it to the Na^+ form, then washed with 5 ml of water. This final eluate was neutral to pH paper. A sample of the neutral photolyte solution (or, alternatively, an unphotolyzed blank solution) was placed on the column and washed with two 1-ml portions of water. The column was then eluted with 0.2 *M* $NaClO_4$ which caused the material on the solumn to separate into a moving purple band, $Co(NH_3)_4CO_3^+$, and a stationary orange band which could only be eluted at higher $NaClO_4$ concentrations. The orange band, the elution characteristics of which indicated that its charge was greater than 2+, was identified as $Co(NH_3)_4(OH_2)_2^{3+}$. The total Co

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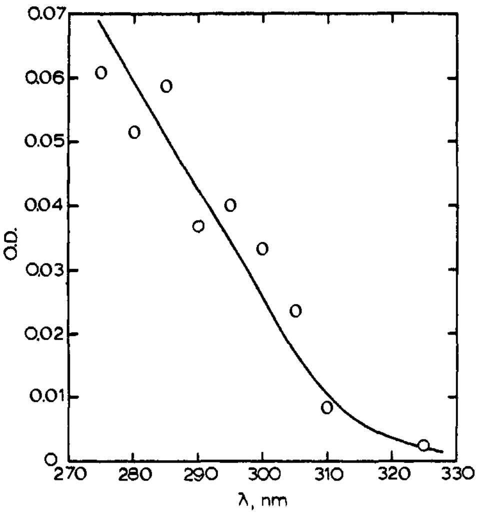

Figure 1. The spectrum of the long-lived intermediate from the flash photolysis of 7.4 × 10^{-5} M $Co(NH_3)_4CO_3^+$, pH 6.4. Optical density read 50 μsec after the start of the flash.

present before photolysis and in the eluted purple band was determined by converting the material to Co_{aq}^{2+} by boiling the solution in concentrated NaOH, acidifying, and analyzing for Co_{aq}^{2+} in the usual way.[6] Thus, by knowing the loss of carbonato complex by thermal aquation and photoreduction, an estimate of the yield of photoaquation could be made.

Gas analysis for noncondensable gases was performed by gas chromatography on solutions photolyzed *in vacuo*.[6]

Results

Continuous Photolysis Studies. The quantum yields for the formation of Co_{aq}^{2+}, $\phi_{Co^{2+}}$, for the 254-nm irradiation of $Co(NH_3)_4CO_3^+$ and $Co(en)_2CO_3^+$ are given in Table I together with some data for $Co(NH_3)_5CO_3^+$, $Co(NH_3)_4(OH_2)_2^{3+}$, and $Co(en)_2(OH_2)_2^{3+}$. The 254-nm photolysis of $Co(NH_3)_4CO_3^+$ at pH 6.4 *in vacuo* revealed the absence of N_2, O_2, and NO as gaseous products. The thermal yield of CO_2 as well as the appreciable solubility of the gas at pH 6.4 rendered its determination of no significance. Note that the presence of O_2 had no effect on the values of $\phi_{Co^{2+}}$ but that 1 M 2-propanol in the absence of O_2 caused the quantum yields to double.

Table I. Quantum Yields of Co_{aq}^{2+} Formation[a]

Complex	Purge gas	Additional solute	$\phi_{Co^{2+}}$[b]
$Co(NH_3)_4CO_3^+$	N_2		0.06
	O_2		0.06
	O_2	1 M 2-propanol	0.07
	N_2	1 M 2-propanol	0.15
$Co(en)_2CO_3^+$	N_2		0.02
	O_2		0.02
	O_2	1 M 2-propanol	0.01
	N_2	1 M 2-propanol	0.03
$Co(NH_3)_5CO_3^+$	N_2		0.06[c,d]
$Co(NH_3)_4(OH_2)_2^{3+}$	N_2		0.05[c]
$Co(en)_2(OH_2)_2^{3+}$	N_2		0.01[c]

[a] [complex] = 2.0 × 10^{-3} M; 25.0°; pH 6.4; [total phosphate] = 0.02 M; $I_a \sim 6 \times 10^{-4}$ einstein $l.^{-1}$ min^{-1}; average of two determinations. [b] Values known to ±0.01. [c] [complex] = 5.0 × 10^{-3} M; single determinations. The other conditions remained the same. [d] pH 8.3.

Separation of the products by ion exchange chromatography enabled a determination of the quantum yield of photoaquation to be made. Since the extent of thermal aquation of an unphotolyzed 2 × 10^{-3} M $Co(NH_3)_4CO_3^+$ solution at pH 6.4 and room temperature (handled in exactly the same way as a photolyzed solution) was about 35% and represented almost ten times the extent of apparent photoaquation, a reliable estimate of the quantum yield of photoaquation could not be made under these conditions. Rather, the solutions were prepared and photolyzed at 5°. Table II shows the results of these duplicate experiments from which is calculated ϕ_{aq} = 0.11 ± 0.03 based on $\phi_{Co^{2+}}$ = 0.07 which was determined relative to ferrioxalate actinometry.

Table II. Determination of Photoaquation Quantum Yield[a]

Initial concentration of $Co(NH_3)_4CO_3^+$	2.11 × 10^{-3} M
$[Co(NH_3)_4CO_3^+]$ remaining after 8-min exposure	1.30 × 10^{-3} M
Thermal aquation (9 ± 1%)	0.19 × 10^{-3} M
Co_{aq}^{2+} yield	0.23 × 10^{-3} M
Photoaquation yield	0.39 × 10^{-3} M
$\phi_{Co^{2+}}$ = 0.07	
ϕ_{aq} = 0.11 ± 0.03	

[a] Results of duplicate determinations; T = 5°.

Flash Photolysis Studies. The flash photolysis of the three complexes generated a transient absorption at 600 nm that has been characterized as the CO_3^- radical.[27-29] In addition, $Co(NH_3)_4CO_3^+$ and $Co(en)_2CO_3^+$ generated a long-lived transient species which absorbed in the 300-nm region with no evident absorption maximum (Figure 1). Because of the absorption of the substrate, spectral measurements below 270 nm were not possible and depletion of the substrate was seen as a shift in the base line to lower absorbance after the flash. In the spectral region examined, the absorption due to the transient exceeded the loss of substrate in the flash. $Co(NH_3)_5CO_3^+$ did not yield a corresponding long-lived absorption in the 300-nm region.

The full absorption was formed during the time of the flash and decayed very slowly *via* first-order kinetics (Figure 2) which were independent of the presence of O_2, 2-propanol (0.1 M), and methanol (0.5 M). The observed first-order rate constant, k_{obsd}, was dependent on the pH of the solution as shown in Figure 3. For $Co(NH_3)_4CO_3^+$, k_{obsd} exhibited a rather complex dependence on ionic strength. At pH 4.0 and 8.0, no dependence was found, but at pH 6.4, a plot of log k *vs.* $\mu^{1/2}$ (Figure 4) gave a linear plot with a slope of 1.1. Activation parameters, determined from a plot of ln k/T *vs.* $1/T$ (Figure 5) for $Co(NH_3)_4CO_3^+$ at pH 4.3, had values of $\Delta H^{\ddagger}$ = 19.2 ± 3.4 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 5 ± 10 eu. Because of the problems associated with the stability of the carbonato complex at this pH and elevated temperatures, the data show considerable scatter. Nevertheless, the values quoted are considered reliable within the standard deviations indicated.

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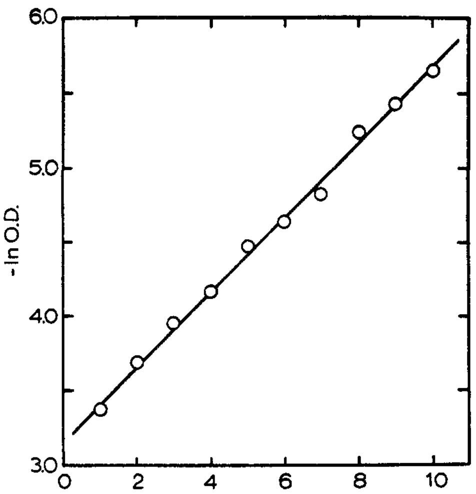

Figure 2. First-order decay kinetics of the long-lived intermediate from the flash photolysis of 7.4 × 10^{-5} M $Co(NH_3)_4CO_3^+$, pH 6.4, 23°, monitoring wavelength 300 nm.

Discussion

The identification of $Co(NH_3)_4(OH_2)_2^{3+}$ as a product from the 254-nm irradiation of $Co(NH_3)_4CO_3^+$ adds ring opening and aquation to the growing list of processes that can result from charge-transfer excitation of Co(III) complexes. However, regardless of the mechanistic origins of the final products, the quantum yield values given in Table I follow some trends that have been seen before. The slightly lower ϕ values for the en complexes (compared to the tetraamines) are in accord with the generally lower values for such chelated complexes.[3] Tetraammine complexes with bismonodentate ligands (of the form $Co(NH_3)_4X_2$) also tend to show diminished values of $\phi_{Co^{2+}}$.[3] The other quantum yield values for the carbonato complexes can be rationalized in terms of the presence of the CO_3^- radical generated in the photolysis. The radical is not affected by O_2 and does not exhibit any reactivity toward $Co(NH_3)_4CO_3^+$.[29] Thus, $\phi_{Co^{2+}}$ in the presence of N_2 and O_2 is constant and must reflect the generation of Co^{2+} in the primary photochemical processes. In the presence of a relatively high concentration of 2-propanol, CO_3^- is scavenged, perhaps *via* H atom transfer (or, alternatively, electron transfer followed by deprotonation), to generate the $(CH_3)_2\dot{C}OH$ radical

$$CO_3^- + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + CO_3H^- \quad (9)$$

where $k_9 \leqslant 4.0 \times 10^4$ M^{-1} sec^{-1}. The $(CH_3)_2\dot{C}OH$ radical is well established as a good reducing agent[30] capable of converting Co(III) complexes to Co_{aq}^{2+}[6–8] with rate constants in the order of 10^{7}–10^{9} M^{-1} sec^{-1}.[31,32]

$$(CH_3)_2\dot{C}OH + Co(III) \longrightarrow Co_{aq}^{2+} + (CH_3)_2CO \quad (10)$$

Thus, the oxidizing CO_3^- radical is converted into a reducing radical by reaction 9 and $\phi_{Co^{2+}}$ is doubled. In the presence of 2-propanol and O_2, the $(CH_3)_2\dot{C}OH$ radical is scavenged by O_2, probably at diffusion-controlled rates, and $\phi_{Co^{2+}}$ returns to its value in the absence of scavengers. Although CO_3^- reacts with Co_{aq}^{2+} and $Co(NH_3)_4(OH_2)_2^{3+}$ with rate constants of 4.4 × 10^6 and 1.4 × 10^7 M^{-1} sec^{-1}, respectively,[29] these reactions would be of only minor concern due to the relatively low extent of reaction (10–15%) in the continuous photolysis. It is not known if the reaction of CO_3^- with $Co(NH_3)_4(OH_2)_2^{3+}$ eventually yields Co_{aq}^{2+} as does the reaction of other oxidizing radials with Co(III) complexes.[33,34] As far as the $CO_3^- + Co_{aq}^{2+}$ reaction is concerned, the formation of a CO_3^{2-}–Co(III) complex cannot be ruled out; a similar reaction of free radicals with Cr_{aq}^{2+} has been shown to generate Cr(III) transient intermediates.[35] However, instability of the CO_3^{2-}–Co(III) complex relative to Co_{aq}^{2+} and the oxidation of water would be expected so that no net loss of Co_{aq}^{2+} would be experienced.

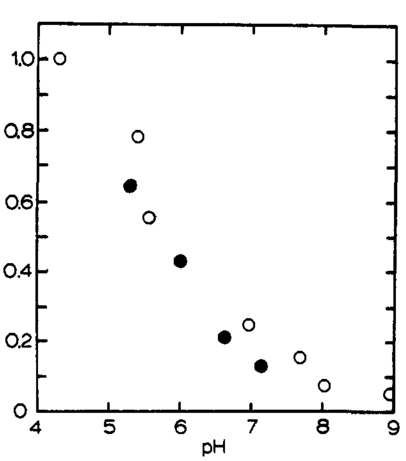

Figure 3. First-order rate constants for the decay of the long-lived intermediate from $Co(NH_3)_4CO_3^+$ (○) and $Co(en)_2CO_3^+$ (●). [complex] = 6.0–9.0 × 10^{-5} M, ionic strength = 0.026–0.036 M, 23°.

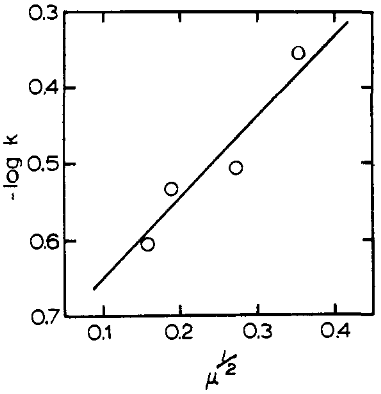

Figure 4. The dependence of the first-order rate constant for the decay of the long-lived intermediate on ionic strength (varied with $NaClO_4$). [$Co(NH_3)_4CO_3^+$] = 6.0–9.0 × 10^{-5} M, pH 6.4, 23°.

Aquocarbonato Intermediate. The behavior of the 300-nm absorption observed in the flash photolysis is completely consistent with the assignment of the intermediate as the aquocarbonato complex generated directly in the flash from the opening of the carbonate

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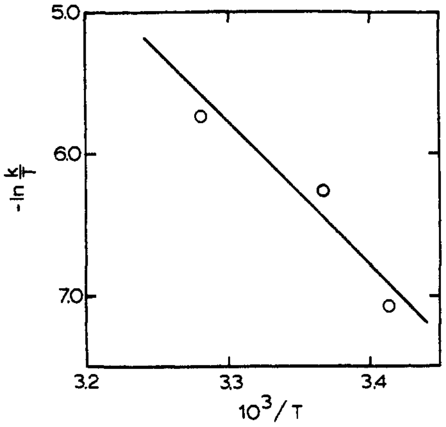

Figure 5. A Eyring–Polanyi plot of the decay of the long-lived intermediate. $[Co(NH_3)_4CO_3^+] = 6.0–9.0 \times 10^{-5}$ *M*, ionic strength = 0.026 *M*, pH 4.0.

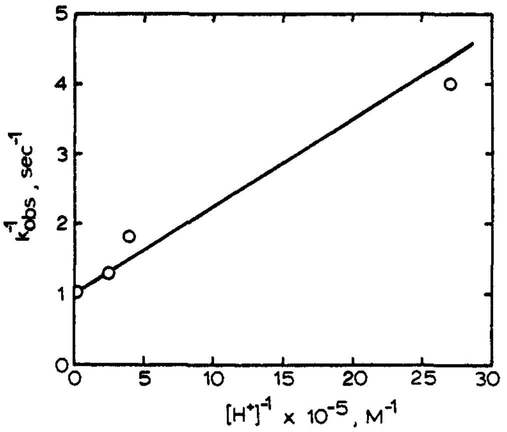

Figure 6. The variation of the observed first-order rate constant, k_{obsd}, as a function of $[H^+]$: double reciprocal plot. $[Co(NH_3)_4CO_3^+] = 5.5–9.4 \times 10^{-5}$ *M*, 24°, ionic strength = 0.026 *M*,

ring with subsequent rapid aquation in the cis position. Reactions 5–8 will be applicable in the conversion of this intermediate to the diaquo final product.

The data shown in Figure 3 are almost identical with those of the thermal aquation of $Co(NH_3)_5CO_3^+$ presented by Francis and Jordan[16] and Dasgupta and Harris[15] and can be treated in terms of reactions 5–8 where the acid–base equilibria (reactions 5 and 6) are fast and reaction 8 is slow compared to reaction 7. Then, $k_{obsd} = k_7[H^+] + K_5$ so that $1/k_{obsd} = 1/k_7 + K_5/k_7[H^+]$. Figure 6 shows the data for $Co(NH_3)_4CO_3^+$ plotted in reciprocal form from which the intercept at high acidity $k_{obsd} = k_7 = 1.0 \pm 0.1$ sec^{-1}; from the slope, a value of $K_5 = 1.0 \pm 0.2 \times 10^{-6}$ *M* ($pK_6 = 6.0$) is obtained. The excellent correlation between our observed values and those of Dasgupta and Harris[17] leaves little doubt that the species we are observing directly is the aquocarbonato intermediate. The spectrum of the intermediate we observe is at least consistent with that of the charge-transfer region of a Co(III)–amine complex with an absorbance in the observed spectral region greater than that of $Co(NH_3)_4CO_3^+$. Despite the uncertainty in our values of the activation parameters, the coincidence between these results and those for $Co(NH_3)_5CO_3^+$ involving direct decarboxylation[15] is extremely good.

At higher pH values (up to 8.9), the deviations from the plot of Figure 6 become large as k_{obsd} approaches a limiting value of about 5×10^{-2} sec^{-1}. In this pH range the intermediate is in its $Co(NH_3)_4(OH)(CO_3H)^+$ form with somewhat greater stability due to the internal hydrogen bonding bridge between the ligands.[14] At pH 4.3, k_{obsd} is independent of ionic strength which is consistent with the unimolecular nature of reaction 7. At pH 8.0, where no ionic strength dependence is also seen, the rate-controlling steps must be the unimolecular decarboxylation of $Co(NH_3)_4(OH)(CO_3H)^+$ and $Co(NH_3)_4(OH)(CO_3)^0$. At pH 6.4 where a positive ionic strength effect is observed (Figure 4), the value of the slope indicates the kinetic importance of a reaction between two +1 (or −1) charged species. At this pH, where ~75% of the intermediate is in the hydroxybicarbonato form protonation of this +1 species (reverse of reaction 5) must occur at a rate greater than that of reaction 7 for the ionic strength effect to be seen. Taking protonation rates as being at or near the diffusion-controlled limit (10^{10} M^{-1} sec^{-1}), it is easily seen that this analysis is numerically valid.

For $Co(en)_2CO_3^+$, the data give the following results: $k_7 = 0.88 \pm 0.08$ sec^{-1} and $K_5 = 2.0 \pm 0.1 \times 10^{-6}$ *M* ($pK_5 = 5.7$).

The Primary Process. The observation that the intermediates from the flash photolysis are generated within the lifetime of the flash indicates that all processes involving the precursors to these species are over in less than 30 μsec. The initial absorption of the radiation within the intense ultraviolet band produces 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] This primary CTTM excited state of singlet multiplicity (^{1}CT) may decay to the ground state, but without the generation of detectable luminescence,[36] or undergo radiationless relaxation to other excited states which lead to the observable products. Some recent sensitization results[37] have shown that the oxidation–reduction products in Co(III) photochemistry arise from a reactive charge-transfer triplet state (^{3}CT) which may also undergo radiationless return to the ground state in order to account for the less-than-unity value of the quantum yield. Thus, in the cases reported here, the generation of Co_{aq}^{2+} and the CO_3^- radical is attributed to the reactive decay of the ^{3}CT state. The lifetime of the intermediate Co(II)–CO_3^- species is clearly shorter than the instrumental time resolution of the flash. The rapid aquation of the Co(II) intermediate would release the CO_3^- radical into the bulk solution.

The fact that ring opening and aquation is the predominant product from the charge-transfer excitation of the bidentate carbonato complexes may not be surprising within the context of their thermal chemistry but it is a novel observation in the 254-nm photochemistry of Co(III)–amine complexes. In the photochemistry of the analogous bidentate oxalato complexes, no ring opening was observed to occur.[8] The only other cases of loss of a ligand other than NH_3 at 254 nm that appear to have been observed are various dichloro– and aquochloro–tetraammine and bis-

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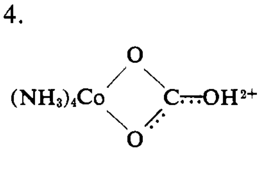
(36) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

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

ethylenediamine complexes.[10] Aquation processes involving the nonamine ligand, albeit with very low quantum yields, appear to be the general case, however, in the irradiation of the ligand field (d–d) absorption bands of these complexes.[3,38] From the sensitization studies[37] it has also been concluded that the aquation products arise from the ligand field excited states of triplet spin multiplicity. It is still a matter of conjecture whether CTTM excited states deactivate *via* the ligand field states. Regardless, it is hard to account for the relatively high yield of ring opening and aquation of bidentate carbonate on the basis that this process originates from the ligand field states of the complex either directly or indirectly populated. There are no obvious properties of carbonate that would enhance intersystem crossing or the reactivity of the d–d excited states.

It is hard to visualize how the aquocarbonato intermediate could arise except *via* heterolytic Co–O bond scission and rapid aquation at the vacant sixth coordination site. The properties of the transient absorption at 300 nm in no way resemble those of the long-lived intermediates observed in the flash photolysis of formato- and oxalato-amine complexes of Co(III).[7,8] In the latter cases, a C-bonded formato species was generated by heterolytic C–C bond scission followed by linkage isomerization of the resulting fragment. There is absolutely no evidence that the mode of formation of the intermediate absorbing at 300 nm in the case of the carbonato complexes is in any way related to the intermediate derived from the oxalato complexes. Neither is there any evidence to show that it is not related to the initiation of the thermal aquation process.

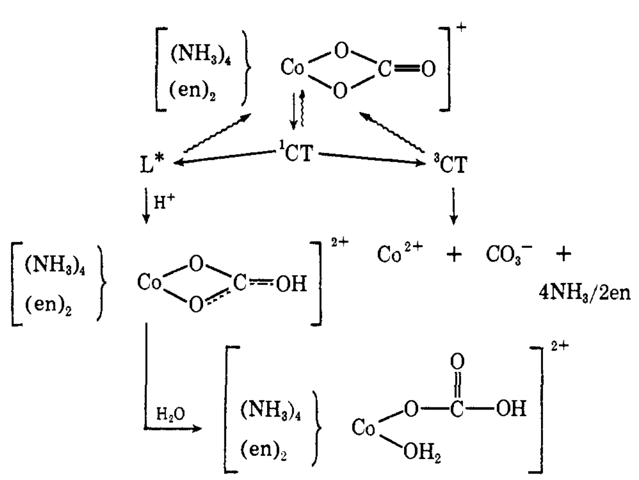
It has been pointed out a number of times[8,39] that the various processes exhibited by Co(III) complexes are independent and arise from distinct excited states, all linked *via* radiationless transitions from the excited state populated in the primary absorption process. Let L* be a ligand excited state not normally populated upon irradiation of the free ligand (due to absorptivity restrictions) which can be generated *via* radiationless transition from ^{1}CT. If this L* state involved population of a π^* orbital of the ketonic C–O bond system with an increase in electron density on the oxygen atom, rapid protonation by H_3O^+ or the solvent could generate the same species that Dasgupta and Harris[17] postulated, for the transition state of reaction 4.



This protonation would weaken one of the Co–O bonds causing heterolytic scission and the formation of the resultant aquocarbonato intermediate. Such a sequence could not, of course, be observed in free carbonate; furthermore, the absorption exhibited by CO_3^{2-} in the 200-nm region is charge-transfer-to-solvent in nature and irradiation results in ionization.[40]

The results of this study can be summarized in Scheme I. The quantum yields for the formation of Co_{aq}^{2+} and the products of intramolecular ligand excitation are rather low indicating that radiationless return to the ground state from the various excited states is quite facile. Inasmuch as the molecular parameters that govern the efficiency of these processes are not known, it is sufficient only to note that the ϕ values are lower than the corresponding values for the analogous oxalato complexes;[8] in particular, the carbonato complexes are rather inert to photoreduction. There is no evidence to indicate that $Co(NH_3)_5CO_3^+$ shows any photoaquation of the carbonato ligand. Finally, it is important to note that O_2 has no apparent effect on the quantum yields in these systems. Except where O_2 scavenges radicals which contribute to the generation of Co_{aq}^{2+} in secondary reactions, O_2 generally does not affect the yield of Co_{aq}^{2+} from the photolysis of Co(III) complexes. This fact implies that O_2 cannot quench the various excited states generated because of either a low intrinsic reactivity or very short lifetimes of the excited states. To date, no transient absorption spectra have been observed in conventional microsecond flash photolysis that can be attributed to these excited states.

Scheme I



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[38] However, ammonia aquation was observed in the 366-nm irradiation of $Co(NH_3)_5O_2CCH_3^{2+}$ [6] and, although with less certainty, $Co(NH_3)_5O_2CH^{2+}$.[7]

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

[40] E. Hayon and J. J. McGarvey, *J. Phys. Chem.*, **71**, 1472 (1967).