Notes

Mechanism of CO₃H Generation in the Charge-Transfer Photochemistry of Co(NH₃)₄CO₃⁺. A Picosecond to Microsecond Flash Photochemical Investigation of the Reaction Intermediates
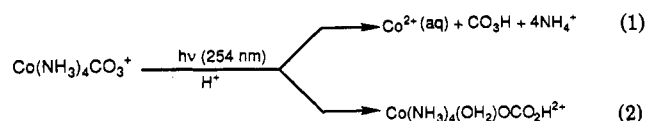
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Introduction

A considerable amount of flash photochemical work has been concerned with the nature of microsecond- to millisecond-lived intermediates that were generated in the charge-transfer photochemistry of Co(III) complexes.[1-3] However, the investigation of early events, from several picoseconds to several nanoseconds, has been considerably more sparse. One example is the observation of the radical–Co(II) ion pairs generated by photohomolysis of alkyl–metal bonds in alkylcobalamines.[4] A number of features associated with fast reactions following the population of reactive charge-transfer states remain to be investigated.

In the UV excitation of the carbonato ammine complex Co-(NH₃)₄CO₃⁺, the photoproducts (Co²⁺(aq), Co(NH₃)₄(OH₂)-OCO₂H⁺, and free radical CO₃H) and their reactions after 50 μs have been well characterized (eqs 1 and 2).[5-7] Neither the

$$Co(NH_3)_4CO_3^+ \xrightarrow[\text{H}^+]{\text{hv (254 nm)}} \begin{cases} Co^{2+}(aq) + CO_3H + 4NH_4^+ & (1) \\ Co(NH_3)_4(OH_2)OCO_2H^{2+} & (2) \end{cases}$$

detachment of the carbonato radical from the metal center nor the origin of the aqua carbonato complex could be established in such time scales. These processes have been investigated in this work with flash photochemical techniques which allow us to follow chemical reactions in a picosecond to microsecond time domain.

Experimental Section

Materials. [Co(NH₃)₄CO₃]ClO₄ and [Co(en)₂CO₃]ClO₄ (en = ethylenediamine) were prepared according to a literature procedure, and the purities of the compounds were ascertained from their absorption spectra.[5,8,9] [Co(cyclen)CO₃]ClO₄ (cyclen = 1,4,7,10-tetraazacyclododecane) was prepared by a modification of a literature procedure.[10] Small fractions of solid [Co(CO₃)₃]Na₃ were added to a 10⁻² M solution of (cyclenH₄)(ClO₄)₄ in ethanol at 40 °C until they were in an equimolar proportion. The mixture of Co(III) complex and macrocyclic ligand was stirred with a magnetic bar and maintained at 40 °C for 45 min. A dark red solid was filtered out and washed with cold ethanol. The purity of the material was based on its Co elemental analysis. Anal. Calcd for CoC₉N₄O₇ClH₂₀: Co, 15.10. Found: Co, 15.05. [Co(NH₃)₅Br]Br₂ was

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(2) Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 4.
(3) Balzani, V.; Carrasiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.
(4) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 4000.
(5) Cope, V. W.; Chen, S.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1973**, *95*, 3116.
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(7) Cope, V. W.; Hoffman, M. Z.; Chen, S. *J. Phys. Chem.* **1978**, *82*, 2665.
(8) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 171.
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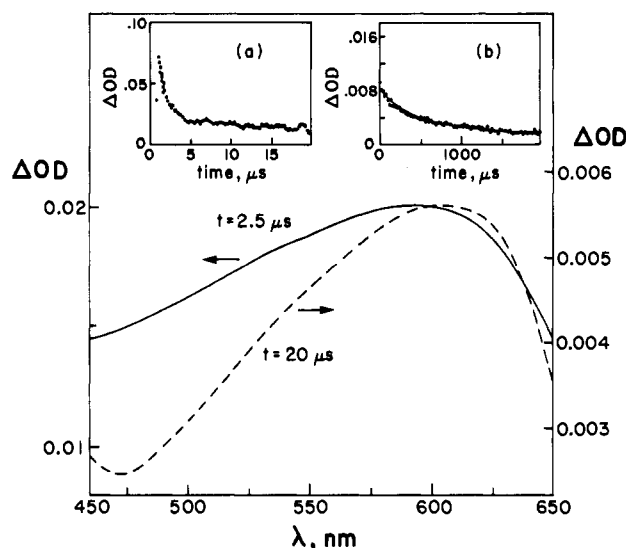
Figure 1. Transient spectra recorded in 249-nm flash photolyses of 10⁻⁴ M Co(NH₃)₄CO₃⁺ in a deaerated pH 5.7 buffer solution. The inserts show (a) the 510-nm decay of the optical density when a short-lived intermediate decomposes into CO₃H radicals and (b) the 600-nm optical density decay associated with the disappearance of CO₃H.

available from a previous work.[11] Other chemicals were of reagent grade and were used without further purification.

Photochemical Procedures. Solutions of the Co(III) complex for photochemical experiments were prepared by adding given weights of the solid compound to appropriate volumes of (5.5 < pH < 6.5) acetic acid/sodium acetate or phosphate buffers. The liquids were deaerated with streams of N₂, handled in dim light, and discarded after 1 h in order to minimize decomposition of the photolyte. The flash photolysis apparatus with picosecond and microsecond time resolutions were described elsewhere.[11,12] Steady-state irradiations at 253.8 nm were carried out with a low-pressure Hg lamp. The light intensity was measured with acidic solutions of Co(NH₃)₅Br²⁺.[11,13] Co²⁺(aq) analyses were performed by using the thiocyanate method.[11,13] Figures for quantum yields and rate constants are reported with their "confidence intervals" as an average of a given number (between 5 and 10) of determinations.

Results

Time-resolved spectra recorded in 249-nm flash irradiations of 5 × 10⁻⁴ M Co(NH₃)₄CO₃⁺ aqueous solutions, 5.3 < pH < 6.5, reveal two transients in a microsecond to a millisecond time domain (Figure 1). Spectra and decay kinetics measured with a delay equal to or longer than 20 μs from the flash are in accord with one reported in the literature for CO₃H.[14] A rate constant $k = (5.0 \pm 0.3) \times 10^8$ M⁻¹ s⁻¹ was calculated for the decay of the (λ_{ob} = 600 nm) optical density via a reaction with second-order dependence on the radical concentration. Concentrations of CO₃H, required for such calculations, were estimated by using the literature value $\epsilon \sim 1.83 \times 10^3$ M⁻¹ cm⁻¹ for the extinction coefficient at 600 nm.[15] The rate constant measured in these experiments compares very well with those determined in previous works concerned with the dimerization/disproportionation of CO₃H at various pH values and ionic strengths. Experimental observations between 0.2 and 20 μs (Figure 1) reveal strong

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(12) Kraut, B.; Ferraudi, G. *Inorg. Chem.* **1990**, *29*, 4384.
(13) Endicott, J. F.; Ferraudi, G.; Barber, J. R. *J. Phys. Chem.* **1975**, *79*, 630.
(14) For a review of the photochemically- and radiolytically-generated CO₃H radical, see ref 6 and references therein.
(15) Hug, G. L. *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solutions*; NSRDS-NBS 69; GPO: Washington, DC, 1981.
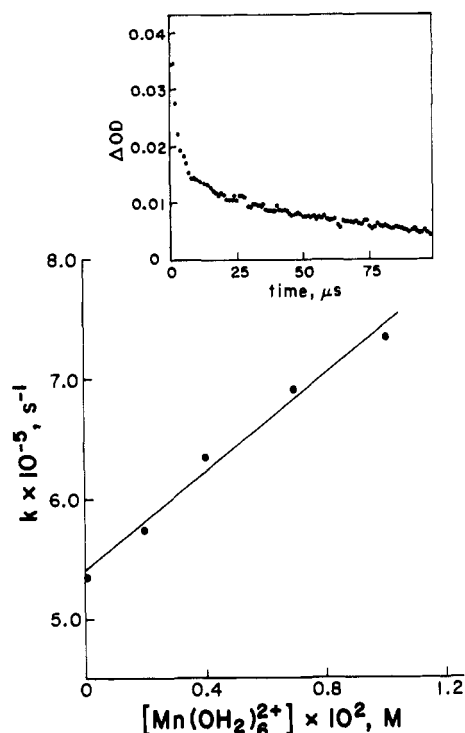
Figure 2. Dependence of the rate constant for the disappearance of CO_3H on $Mn(OH_2)_6{}^{2+}$ concentration. Ionic strength, $I = 0.1$ M, adjusted with $NaClO_4$. For other conditions see Figure 1. The insert shows a trace at 600 nm recorded with a scavenger concentration $[Mn(OH_2)_6{}^{2+}] = 4.0 \times 10^{-3}$ M (i.e., for a partial scavenging of CO_3H).

absorptions between 400 and 700 nm. Transient spectra evolve toward the spectrum of CO_3H in 20 μs. The optical changes at 510 or 600 nm are kinetically of a first order with a pH-independent rate constant $k = (5.3 \pm 0.5) \times 10^5$ s^{-1}.

Scavenging of the flash-generated transient species with $Mn(OH_2)_6{}^{2+}$ put in evidence differences between the corresponding reactions of CO_3H and its precursor. Indeed, a rate constant $k_1 = (2.8 \pm 0.2) \times 10^7$ M^{-1} s^{-1} was measured ($\lambda_{ob} = 600$ nm) for the disappearance of the radical when Mn(II) concentrations were equal to or smaller than 2.0×10^{-2} M (Figure 2). This value is in good agreement with a literature report.[7] No appreciable reaction between $Mn(OH_2)_6{}^{2+}$ and the CO_3H precursor could be detected at such Mn(II) concentrations. Concentrations of scavenger larger than 4.0×10^{-2} M were necessary in order to observe ($\lambda_{ob} = 470$ nm) a linear dependence of the rate of decay of the CO_3H precursors on the Mn(II) concentration. A rate constant $k_2 = (1.8 \pm 0.2) \times 10^7$ M^{-1} s^{-1} was measured from the slope of the rate constant vs scavenger concentration. It must be noted that the reaction of the CO_3H precursor with $Mn(OH_2)_6{}^{2+}$ is slower than the corresponding reaction of the free CO_3H but is still of the same order of magnitude.

Processes leading to the formation of the free CO_3H radical were also investigated in a picosecond to nanosecond time domain. Spectra recorded with 0.1- and 5-ns delays with respect to the 266-nm flash (Figure 3a) show the large absorptions at $\lambda_{ob} \leq 550$ and $\lambda_{ob} \geq 650$ nm that were observed between 0.2 and 5 μs (Figure 1) for the CO_3H precursor. Time resolution of the optical density changes reveal that this transient is generated within the 30-ps laser flash (Figure 3b) and undergoes two decays. The respective rate constants $k = (3.2 \pm 0.5) \times 10^9$ s^{-1} and $k = (5.5 \pm 0.7) \times 10^7$ s^{-1} were calculated for these two processes from a double-exponential curve fitting.

The appearance of the free CO_3H radical is also a slow process in the flash irradiations ($\lambda_{exc} = 266$ nm) of the polyamine complexes $CoLCO_3{}^+$ (L = (en)$_2$, cyclen). Indeed, transient spectra, maxima between 650 and 750 nm, in a picosecond to
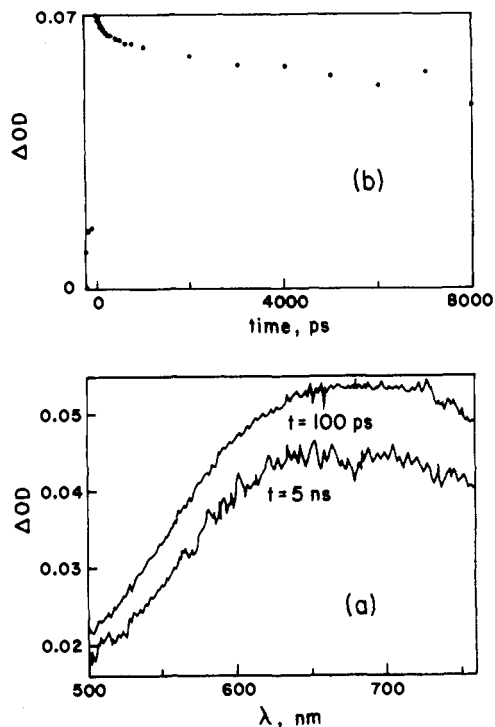
Figure 3. (a) Transient spectra recorded in 266-nm flash irradiations of deaerated 10^{-4} M $Co(NH_3)_4CO_3{}^+$ in a 10^{-2} M acetic/sodium acetate buffer solution. (b) Time-resolved ($\lambda_{ob} = 650$ nm) optical density changes.

nanosecond time domain differed from the spectrum of CO_3H. The rate constant determined for the first-exponential decay of the flash-generated optical density (Figure 4) has the same order of magnitude of the one reported above for the tetraammine complex, i.e. $k = (5.9 \pm 0.7) \times 10^9$ s^{-1} when L = (en)$_2$ and $k = (6.7 \pm 0.7) \times 10^9$ s^{-1} when L = cyclen. The second-exponential decay of the optical density in a nanosecond to microsecond time domain was only observed in flash irradiations of the $Co(en)_2CO_3{}^+$ complex (Figure 4). In this last case, the rate constant is larger, $k = (8.0 \pm 0.4) \times 10^8$ s^{-1}, than the corresponding rate constant measured with the tetraammine complex.

Steady-state photolyses, $\lambda_{exc} = 254$ nm, of 4.0×10^{-3} M $Co(NH_3)_4CO_3{}^+$, in pH 5.8 buffer solutions were carried out for periods of time which produced $Co^+(aq)$ in concentrations equal to or less than 10% of the initial Co(III) complex concentration. The quantum yield of $Co^{2+}(aq)$ measured when 10^{-1} M $Mn(OH_2)_6{}^{2+}$ was added as a scavenger of the intermediates, $\phi = 0.058 \pm 0.006$, was nearly the same as one determined in the absence of scavenger, $\phi = 0.063 \pm 0.005$.

Discussion

While late events (i.e. $t_{1/2} \gg 10$ μs) in the charge-transfer photochemistry of $Co(NH_3)_4CO_3{}^+$ have been previously characterized,[5] the results described above provide more details on the mechanism of the CO_3H radical and $Co^{2+}(aq)$ photogeneration. In terms of the transient spectra (Figure 1) and the kinetics of the optical changes (Figures 1 and 2), it is necessary to conclude that the detachment of the CO_3H radical is not concurrent with the relaxation of the charge-transfer state, LMCT.[16,17] Indeed, the results show that the oxidized carbonato ligand remains at a contact distance to the reduced metal center for nearly 1 μs. Intermediates different of radical-ion pairs must be considered in order to account for the transient spectra preceding the appearance of the free CO_3H.
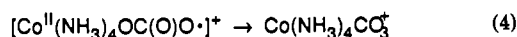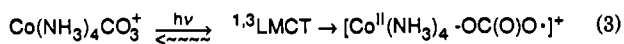
(16) For a review of the charge-transfer photochemistry of Co(III) complexes see refs 1–3, 17.

(17) Langford, C. H.; Lindsay, E. *Inorg. Chem.* **1990**, *29*, 3961.
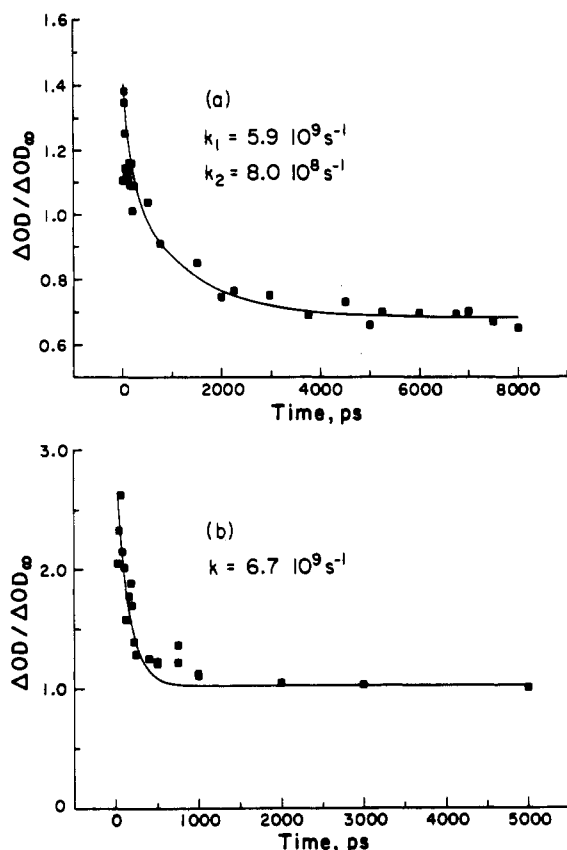
Figure 4. Traces for the decay of flash-generated 650-nm optical absorptions in (a) 5×10^{-4} M $Co(en)_2CO_3^+$ and (b) 6×10^{-4} M Co-(cyclen)CO_3^+ deaerated solutions. Solid lines are for curve fittings with (a) a double-exponential decay and (b) a single-exponential decay. Corresponding rate constants are given in the figure.

A mechanism for the photogeneration of CO_3H and Co^{2+}(aq) can be written in terms of the transformation of singlet and/or triplet LMCT states[1-3] into primary species by a homolytic dissociation of one cobalt–oxygen bond (eqs 3 and 4).

$$Co(NH_3)_4CO_3^+ \xrightarrow[\xleftarrow{\;\;\;\;}]{h\nu} {}^{1,3}LMCT \rightarrow [Co^{II}(NH_3)_4 \text{-}OC(O)O\cdot]^+ \quad (3)$$

$$[Co^{II}(NH_3)_4OC(O)O\cdot]^+ \rightarrow Co(NH_3)_4CO_3^+ \quad (4)$$

The differences between the well-known absorption spectrum of the free CO_3H radical and the spectra recorded with less than 1-μs delay from the flash can be associated with low-energy metal to ligand charge-transfer transitions (i.e. $CO_3H \leftarrow Co(II)$) in such Co(II)–ligand radical species. Similar electronic transitions in a radical-ion pair are expected at wavelengths shorter than 400 nm, and metal-centered transitions at the Co(II) center are expected to have small extinction coefficients by comparison to those centered in the ligand radical. It must be noted that these arguments are in agreement with literature reports about the properties of various Co(II) and Co(III) complexes with radicals functioning as ligands.[18-20] These species exhibit, for example, a much larger kinetic stability than the one expected on the basis of the nuclear factor alone.[21-23] In these regards, lifetimes between tens of picoseconds and several microseconds are expected for back electron transfers in the high- and low-spin Co(II) intermediates considered in this work.

The rates of flash-induced optical transformations observed in less than 1 ns, (Figures 3b and 4) show only a little dependence on the aza ligands coordinated to Co. Aquation or isomerization processes involving these ligands do not provide, therefore, an appropriate rationale of the experimental observations. Literature reports concerned with magnetic field effects on the charge-transfer photochemistry of Co(III) complexes reveal that low-spin Co(II) photoproducts must have a lifetime that is very short but significant in terms of their chemical reactions.[24] A doublet–quartet relaxation lifetime for the Co(II) metal ion in such tetraaza environments, $10^{-11} > t > 10^{-10}$ s, can be calculated by comparison with related Co(II) complexes.[25-27] It is possible that a fast back-electron-transfer reaction of the kind indicated in eq 4 can compete with the relaxation of the low-spin configuration, namely the spin flip.
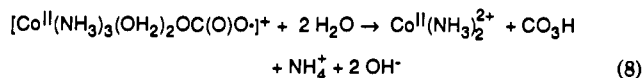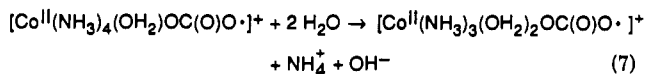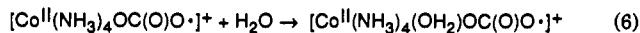
Optical changes in a nanosecond time domain that were observed in the respective irradiations of $Co(en)_2CO_3^+$ and $Co(NH_3)_4CO_3^+$ (Figures 3 and 4) cannot be rationalized only on the basis of various ligand aquations and/or back-electron-transfer processes. In terms of structural contributions to the reaction rate,[28] a configurational isomerization, e.g. of the type indicated in eq 7,[29,30] is expected to have a faster rate in $[Co^{II}(en)_2OC(O)O\cdot]^+$ than in $[Co^{II}(NH_3)_4OC(O)O\cdot]^+$ and be completely inhibited in the cyclen complex.
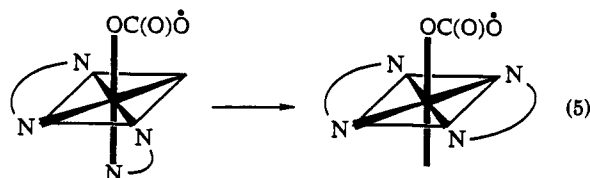
A number of NH_3 ligands from the ammine intermediates can be aquated, however, at longer reaction times in accordance with rates reported in the literature for such Co(II) complexes.[31-33] Reactions in eqs 6–9 must be considered as viable steps leading to the separation of the CO_3H radical from the Co(II). The reaction in eq 8 could be expected to be the rate-determining step
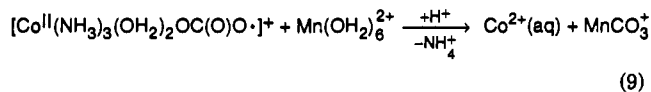
(18) Whitburn, K. D.; Hoffman, M. Z.; Brezniak, N. V.; Simic, M. G. *Inorg. Chem.* **1986**, *25*, 3037.

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(21) The rate constant, k_{ct}, for electron transfer between metal centers in a ligand-bridged binuclear complex is given by the expression[22] $\kappa_{ct} = \nu_n\kappa_{el}\kappa_n$, where $\nu_n \approx 10^{13}$ s^{-1} is the "effective nuclear frequency" and κ_{el} is the "electronic transmission coefficient"; i.e., $\kappa_{el} \approx 1$ for an adiabatic reaction. The factor κ_n is the "nuclear factor" and can be related to the reorganization energy, $\lambda = \lambda_0 + \lambda_i$, and the free energy of the reaction, ΔG°, by $\kappa_n = \exp(-\Delta G^*/RT)$; $\Delta G^* = (\lambda + \Delta G^\circ)^2/4\lambda$. These relationships were applied to the calculation of the rate of intramolecular electron-transfer reactions reported for Co(II) and Co(III) complexes with ligand radicals in refs 18–20. Calculated values of $\kappa_{ct} \approx 10^{13}\kappa_n$ were between 3 and 5 orders of magnitude larger than the corresponding experimental results. These discrepancies are much larger than those that could be introduced by calculating λ with data from (outer-sphere) self-exchange electron-transfer reactions of related Co complexes and radicals. While various reasons could be advanced to explain these departures, magnetic field effects on the rates of intramolecular electron transfers suggest that electronic restrictions can make $\kappa_{el} \ll 1$.[23]

(22) For a comprehensive review, see: Wilkins, R. G. In *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: New York, 1991; Chapter 5, pp 279–282 and references therein.

(23) Ferraudi, G. F. Unpublished observations.

(24) Ferraudi, G. F. *Chem. Phys. Lett.* **1993**, *203*, 487.

(25) Literature reports[26,27] give values between 10^{-9} and 10^{-10} s to the lifetime of the doublet state in Co(bipy)$_2^{2+}$. Corrections for a larger doublet–quartet energy gap in the tetraaza complexes reduces the relaxation lifetime by 1 order of magnitude.

(26) Beattie, J. K. *Adv. Inorg. Chem.* **1980**, *102*, 2918.

(27) Song, X.; Lei, Y.; Van Wallendal, S.; Perkovic, M. W.; Jackman, D. C.; Endicott, J. F.; Rillema, D. P. *J. Phys. Chem.*, in press.

(28) Consideration must be given to competitive contributions to the activation energy, namely from changes in the ligand field stabilization energy and in ligand strain.

(29) While the species in eq 5 can be pentacoordinated, the sixth position can also be occupied by a solvent molecule in accordance with the structure of Co(II) complexes.[30]

(30) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431.

$$[Co^{II}(NH_3)_4OC(O)O\cdot]^+ + H_2O \rightarrow [Co^{II}(NH_3)_4(OH_2)OC(O)O\cdot]^+ \quad (6)$$

$$[Co^{II}(NH_3)_4(OH_2)OC(O)O\cdot]^+ + 2\,H_2O \rightarrow [Co^{II}(NH_3)_3(OH_2)_2OC(O)O\cdot]^+$$
$$+ NH_4^+ + OH^- \quad (7)$$

$$[Co^{II}(NH_3)_3(OH_2)_2OC(O)O\cdot]^+ + 2\,H_2O \rightarrow Co^{II}(NH_3)_2^{2+} + CO_3H$$
$$+ NH_4^+ + 2\,OH^- \quad (8)$$

(i.e., $k = (5.5 \pm 0.5) \times 10^5$ s^{-1}) by comparison to the rate of ammonia hydrolysis in $Co(NH_3)_3^{2+}$.[31-33] If hydrolysis of CO_3H competes with the hydrolysis of ammonia, the spectra of the radical and its precursor would not be time-resolved in flash photolysis.
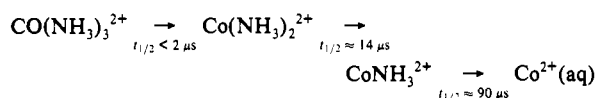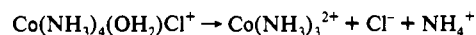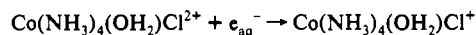
Results from steady-state photolysis show that scavenging of CO_3H and [$Co^{II}(NH_3)_3(OH_2)_2OC(O)O\cdot$] with $Mn(OH_2)_6^{2+}$ (eqs 9 and 10) does not change the quantum yield of Co(II). In the

$$[Co^{II}(NH_3)_3(OH_2)_2OC(O)O\cdot]^+ + Mn(OH_2)_6^{2+} \xrightarrow[-NH_4^+]{+H^+} Co^{2+}(aq) + MnCO_3^+$$
$$\quad (9)$$

$$CO_3H + Mn(OH_2)_6^{2+} \rightarrow MnCO_3^+ + H^+ \quad (10)$$

absence of the scavenger, the quantitative dissociation of the Co-(II)–ligand–radical species in CO_3H radicals (eq 8) gives a possible rationale for the lack of dependence of the quantum yield on $Mn(OH_2)_6^{2+}$ concentration.

(31) It is known that upon the reduction of Co(II) ammine complexes a number of ammonia ligands are lost in less than 2 μs[32,33]

$$Co(NH_3)_4(OH_2)Cl^{2+} + e_{aq}^- \rightarrow Co(NH_3)_4(OH_2)Cl^+$$

$$Co(NH_3)_4(OH_2)Cl^+ \rightarrow Co(NH_3)_3^{2+} + Cl^- + NH_4^+$$

$$CO(NH_3)_3^{2+} \underset{t_{1/2} < 2\,\mu s}{\rightarrow} Co(NH_3)_2^{2+} \underset{t_{1/2} \approx 14\,\mu s}{\rightarrow}$$

$$CoNH_3^{2+} \underset{t_{1/2} \approx 90\,\mu s}{\rightarrow} Co^{2+}(aq)$$

The rates measured for the aquation of en from Co(en)$_2^{2+}$, slower than those for equivalent aquation reactions of ammonia, have no significance in the time frame of our experimental observations.

(32) Lilie, J.; Shinohara, N.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6516.

(33) Shinohara, N.; Lilie, J.; Simic, M. G. *Inorg. Chem.* **1977**, *16*, 2809.