67815-46-7; [Ru₃O(OAc)₆(py)₂(pyr)](PF₆), 67815-40-1; [Ru₃O-(pyr)Ru₃O]³⁺, 70812-63-4; [Ru₃O(OAc)₆(py)₂(CH₃OH)](PF₆), 67815-39-8; [Ru₃O(pyr)Ru₃O]⁻, 70812-64-5; [Ru₃O(pyr)Ru₃O]²⁻, 70812-65-6; [Ru₃O(4,4'-bpy)Ru₃O]³⁺, 70812-71-4; [Ru₃O(4,4'-bpy)Ru₃O]⁺, 70812-67-8; [Ru₃O(4,4'-bpy)Ru₃O]⁰, 70812-68-9; [Ru₃O(4,4'-bpy)Ru₃O]⁻, 70812-69-0; [Ru₃O(4,4'-bpy)Ru₃O]²⁻, 70812-70-3; [Ru₃O(BPE)Ru₃O]³⁺, 70812-75-8; [Ru₃O(BPE)Ru₃O]⁺, 70850-22-5; [Ru₃O(BPE)Ru₃O]⁰, 70812-72-5; [Ru₃O(BPE)Ru₃O]⁻, 70812-73-6; [Ru₃O(BPE)Ru₃O]²⁻, 70812-74-7; [Ru₃O(BPA)Ru₃O]³⁺, 70812-79-2; [Ru₃O(BPA)Ru₃O]⁺, 70812-76-9; [Ru₃O(BPA)Ru₃O]⁰, 70812-77-0; [Ru₃O(BPA)Ru₃O]⁻, 70812-78-1; [Ru₃O(OAc)₆-(py)₂(pyr)]²⁺, 67954-61-4; [Ru₃O(OAc)₆(py)₂(pyr)]⁰, 67951-63-7; [Ru₃O(CH₃CO₂)₆(py)₃]⁰, 37337-93-2; [Ru₃O(CH₃CO₂)₆(py)₃](PF₆), 67815-38-7.

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Intramolecular Electron Transfer in the Reaction of Hydroxyl Radicals with (Pyridine)pentaamminecobalt(III) Ion in Aqueous Solution[1]

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The reaction of radiation-generated OH radicals with Co(NH₃)₅py³⁺ in aqueous solution to form Co²⁺(aq) serves as a model of induced electron transfer. The yield of Co²⁺(aq) formation is dependent upon the radiation dose rate, pH, and the gas used to purge the solutions (N₂O, N₂, O₂). The initial reaction of OH with Co(NH₃)₅py³⁺ ($k = 6.5 \times 10^8$ M⁻¹ s⁻¹) involves addition of the radical to the aromatic ligand; pulse radiolysis reveals the absorption spectrum of this Co(III)-coordinated ligand-radical species (I) (λ_{max} 325 nm, ϵ_{max} 1.7 × 10³ M⁻¹ cm⁻¹) and shows that it is readily scavenged by O₂ ($k = 4.4 \times 10^8$ M⁻¹ s⁻¹). Species I is converted ($k = 8.5 \times 10^3$ s⁻¹) into a similarly coordinated ligand-radical species (II), possibly via solvent-assisted ligand modification. Species II undergoes bimolecular decay ($2k = 3.6 \times 10^5$ M⁻¹ s⁻¹) in competition with a deprotonation reaction with OH⁻ ($k = 1.8 \times 10^8$ M⁻¹ s⁻¹) and ligand-to-metal intramolecular electron transfer to form Co²⁺(aq) ($k = 2.3 \times 10^{-2}$ s⁻¹). The deprotonated coordinated ligand radical undergoes bimolecular decay ($2k = 3.8 \times 10^7$ M⁻¹ s⁻¹) in competition with intramolecular electron transfer to form Co²⁺(aq) ($k = 1.1 \times 10^1$ s⁻¹). A comparison of these intramolecular electron rate constants is made with those that have been obtained for other ligand radicals coordinated to Co(III) centers.

Introduction

Induced electron transfer, wherein the interaction of a one-electron oxidant with a metal complex leads to the formation of the one-electron-reduced metal center, remains an intriguing mechanistic problem.[3] Among the systems studied are a series of Co^III(NH₃)₅X complexes where X = carbinol pyridine;[4] oxidation by Ce(IV), Ag(II), or S₂O₈²⁻ results in the formation of Co²⁺(aq), albeit in less-than-quantitative yields. The proposed mechanism involves the formation of a one-electron-oxidized ligand radical coordinated to the Co(III) center which can engage in ligand-to-metal intramolecular electron transfer to form Co²⁺(aq) and the free two-electron-oxidized ligand in competition with further interaction with the oxidant. The primary questions in the induced electron transfer mechanism are the nature of the coordinated ligand-radical species and the kinetics of the intramolecular electron transfer step.

In order to gain some insight into the problem, we have used the reaction of the strongly oxidizing ($E°_{Red} = 2.8$ V)[5] OH radical with Co(NH₃)₅py³⁺ (py = pyridine) as a model for the formation of Co²⁺(aq) via induced electron transfer.[6] Hydroxyl radicals are conveniently generated in the radiolytic decomposition of water according to reaction 1 with a G value

$$H_2O \rightsquigarrow e_{aq}^-, OH, H \qquad (1)$$
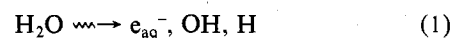
(number of radicals formed per 100 eV of energy absorbed) of 2.8; $G(e_{aq}^-) = 2.8$ and $G(H) = 0.55$. The techniques of radiation chemistry permit radicals of known stoichiometry to be generated selectively at desired rates with variable steady-state concentrations; pulse radiolytic generation of the radicals allows the kinetics and spectra of transient intermediates to be determined in the microsecond time frame. By the judicious use of scavengers, the primary radicals can be efficiently transformed: e_{aq}^- is quantitatively converted to OH
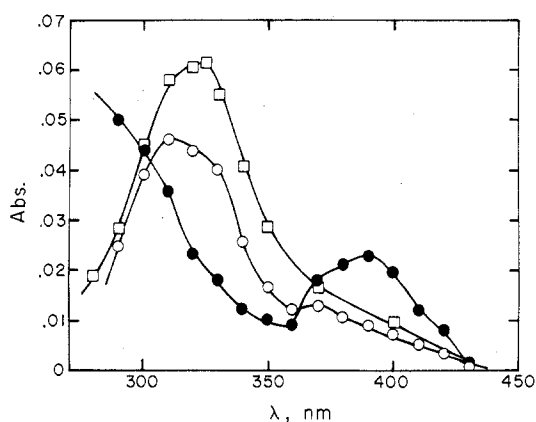
Figure 1. Absorption spectra obtained from the pulse radiolysis of N_2O-saturated solutions of 5.0×10^{-4} M $Co(NH_3)_5py^{3+}$ at pH 5.2. Spectra were taken at 10 μs ($\square$), 0.5 ms (O), and 20 s ($\bullet$) after 3.9-krad pulses; optical path length = 2 cm.

by reaction with N_2O ($k_2 = 8.7 \times 10^9$ M^{-1} s^{-1})[7] and to H by reaction with H^+ ($k_3 = 2.2 \times 10^{10}$ M^{-1} s^{-1}) (reactions 2 and 3).[7] In the presence of O_2, e_{aq}^- and H are efficiently ($k_{4,5} =$

$$e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^- \qquad (2)$$

$$e_{aq}^- + H^+ \rightarrow H \qquad (3)$$

2.0×10^{10} M^{-1} s^{-1})[7,8] scavenged according to reactions 4 and 5.

$$e_{aq}^- + O_2 \rightarrow O_2^- \qquad (4)$$

$$H + O_2 \rightarrow HO_2 \rightleftharpoons O_2^- + H^+ \quad (pK_a = 4.8) \qquad (5)$$
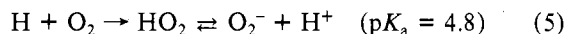
Experimental Section

Materials. $[Co(NH_3)_5py](ClO_4)_3$ was prepared according to literature procedures;[9] its purity was checked by comparison of its UV–vis spectrum with that reported in the literature (λ_{max} ±1 nm; ϵ_{max} ±2%). Doubly distilled water, which had been passed through a Millipore purification train, was used. Gases (N_2 and N_2O) were purged of O_2 by passage through two acidic Cr^{2+}(aq)-scrubbing towers followed by dilute NaOH solution and pure water. All other reagents were of analytical grade and were used without further purification.

Radiation Sources. Continuous radiolyses were carried out in a ^{60}Co-γ source with a dose rate of 4.3×10^{16} eV mL^{-1} min^{-1} (690 rad min^{-1}). Pulse radiolyses with optical absorption detection were performed by using the instrumentation at the U.S. Army Natick Research and Development Command.[10] Pulse radiolyses with kinetic conductivity detection were performed by using the instrumentation at the Hahn-Meitner Institut (Berlin).[11]

Analyses. Kitson's method[12] was used for the analysis of Co^{2+}(aq). UV–vis spectrophotometry was performed on Cary 14 and 118 instruments. Ion-exchange separations were carried out by using Dowex 50W-X8 (20–50 mesh, Na^+ form) cation-exchange resin using solutions of $NaClO_4$ or $HClO_4$ as eluents. Qualitative analyses for the organic products of the continuous radiolyses were performed according to established procedures.[13] IR spectra of extracted organic products were run in Nujol mulls or CCl_4 on a Perkin-Elmer 237B instrument.

Procedures. Aqueous solutions containing $Co(NH_3)_5py^{3+}$ in phosphate buffer were purged for 20–40 min with Ar, N_2, or N_2O (1 atm partial pressure $\equiv 2.5 \times 10^{-2}$ M) to remove residual O_2. The pH of the solutions was established with $HClO_4$, HTFMS (trifluoromethylsulfonic acid; 3 M Co), or KOH. Continuous radiolyses were conducted as described before.[14] Irradiation times were controlled so that less than 10% total destruction of the substrate occurred; only in the case of reactions for organic analysis was the decomposition as high as 20%. After continuous radiolysis, solutions were analyzed for Co^{2+}(aq) and subjected to ion-exchange chromatography. For the organic analyses, the radiolyzed solutions were made alkaline to pH 10 in order to deprotonate acidic functional groups. The solutions were then extracted with diethyl ether, and the ethereal extract was fractionally distilled to separate the volatile components from those of less volatility. Organic and IR analyses were performed on the volatile components.
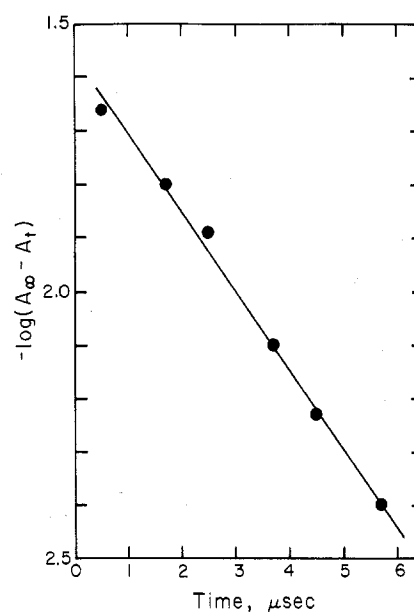
Figure 2. Kinetics of formation of the initial transient absorption obtained from the pulse radiolysis of N_2O-saturated solutions of 5.0×10^{-4} M $Co(NH_3)_5py^{3+}$ at pH 5.2. Monitoring wavelength is 330 nm, optical path length = 2 cm, and dose/pulse = 2.9 krad.

Table I. Kinetics of Conversion of Species I → II[a]

pH	dose/pulse, krad	A_{II}/A_I	$t_{1/2}$, μs
2.9	10.0	0.76	80
5.2	19.0	0.76	80
	10.0	0.74	70
	5.0	0.84	85
	1.5	0.75	85
7.2	10.0	0.81	85

[a] Monitored at 330 nm.

Results

Pulse Radiolysis. The pulse radiolysis (3.9 krad/pulse) of N_2O-saturated solutions of $Co(NH_3)_5py^{3+}$ at pH 5.2 produces initially the transient absorption spectrum (λ_{max} 325 nm) shown in Figure 1 (open squares) which is fully formed within 10 μs after the 20-ns pulse. The profile of this initial absorption (I) is independent of pH from 3 to 9. The formation of I is pseudo first order in $Co(NH_3)_5py^{3+}$ (Figure 2), corresponding to a second-order rate constant $k = 6.5 \times 10^8$ M^{-1} s^{-1} (±15%); the value of k and the quality of the pseudo-first-order kinetics are independent of pH (3–9) and $[Co(NH_3)_5py^{3+}]$ ((0.25–1.0) $\times 10^{-3}$ M). The spectrum of I undergoes a slight diminution in the course of the next millisecond resulting in a moderately stable secondary absorption (II); see Figure 1 (open circles). The conversion of I → II (Table I) shows the same $t_{1/2}$ and A_{II}/A_I ratio independent of the dose/pulse, pH, and $[Co(NH_3)_5py^{3+}]$. The species represented by spectrum I converts into the species represented by spectrum II via first-order kinetics with $k = 8.5 \times 10^3$ s^{-1}; the spectrum of II is independent of pH.

In the presence of O_2 at pH 5.2, the spectrum of I is rapidly ($k = 4.4 \times 10^8$ M^{-1} s^{-1}) quenched with very small further changes in absorbance.

The decay of II at pH 3–9 leads to a stable (20 s) final absorption spectrum (III) shown in Figure 1 (filled circles) which is not especially sensitive to pH. As Table II shows, the kinetics of decay of II are quite complicated. At pH 3.0, the reaction is clearly second order ($2k = 3.6 \times 10^5$ M^{-1} s^{-1}) as evidenced by the kinetics plot (Figure 3) and the dependence of the half-life of the reaction on the delivered radiation dose. As the solution is made less acidic, the second-order decay gives way to first-order kinetics (Figure 4) where the value of k is

Table II. Kinetics of the Decay of Species II

pH	kinetic order	k^a
3.0	II	3.6×10^5 M^{-1} s^{-1} ^{b}
5.2	I	6.0 s^{-1}
5.9	I	10.1 s^{-1}
6.4	I	17.5 s^{-1}
7.1	I	20.2 s^{-1}
7.4	I	58.0 s^{-1}
7.8	I	125 s^{-1}
9.0	II	3.8×10^7 M^{-1} s^{-1} ^{b}

^{a} $2k$ for second-order decays. ^{b} Using ϵ_{max} 1.3×10^3 M^{-1} cm^{-1} for species II (see text).

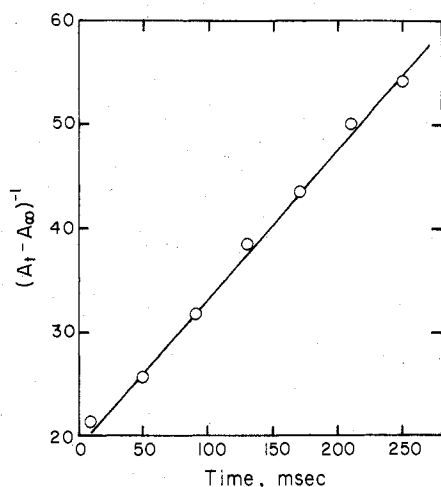**Figure 3.** Kinetics of decay of the secondary transient absorption obtained from the pulse radiolysis of N$_2$O-saturated solutions of 5.0 $\times 10^{-4}$ M Co(NH$_3$)$_5$py^{3+} at pH 3.0. Monitoring wavelength is 330 nm, optical path length = 2 cm, and dose/pulse = 2.9 krad.

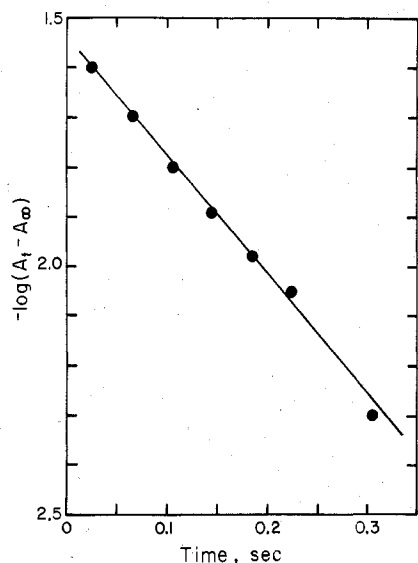**Figure 4.** Kinetics of decay of the secondary transient absorption obtained from the pulse radiolysis of N$_2$O-saturated solutions of 5.0 $\times 10^{-4}$ M Co(NH$_3$)$_5$py^{3+} at pH 5.2. Monitoring wavelength is 330 nm, optical path length = 2 cm, and dose/pulse = 2.9 krad.

proportional to [H$^+$]$^{-1}$ (Figure 5) Finally, at pH 9.0, a more rapid second-order decay ($2k$ = 3.8×10^7 M^{-1} s^{-1}) returns.

Pulse radiolyses with kinetic conductivity detection experiments were performed on buffer-free N$_2$O-saturated solutions of Co(NH$_3$)$_5$py^{3+} at pH 4.6 (dose/pulse $\sim$ 1 krad). No conductivity changes corresponding to the uptake or release of H$^+$, other than those attributable to the primary radiolysis process, could be detected within the long time frame ($\sim$1 s) of the instrumentation.
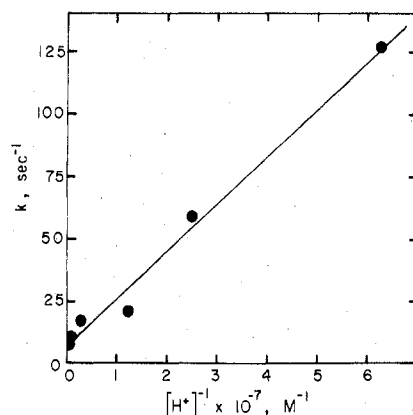

Figure 5. Dependence of the first-order rate constant for the decay of the secondary transient absorption on [H$^+$]$^{-1}$. Correlation coefficient = 0.992.
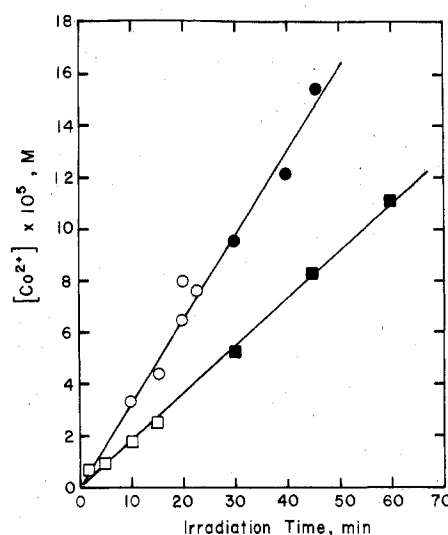

Figure 6. Yield of Co^{2+}(aq) as a function of irradiation time in the continuous radiolysis of N$_2$O-saturated solutions of Co(NH$_3$)$_5$py^{3+}: circles, pH 6.0; squares, pH 3.0; open symbols, [Co(NH$_3$)$_5$py^{3+}] = 5.0 $\times 10^{-4}$ M; filled symbols, [Co(NH$_3$)$_5$py^{3+}] = 1.0 $\times 10^{-3}$ M. Dose rate = 6.9 $\times 10^2$ rad min^{-1}.
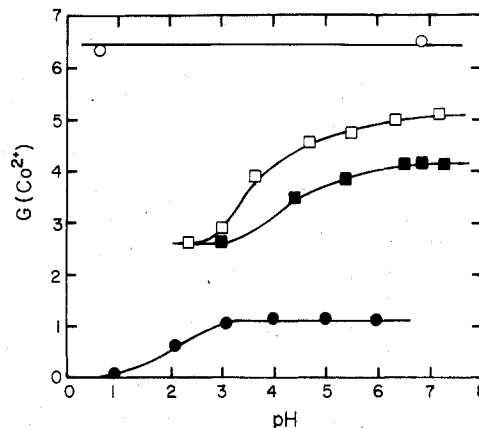
Figure 7. G(Co^{2+}(aq)) as a function of pH for the continuous radiolysis of solutions of Co(NH$_3$)$_5$py^{3+}: O, N$_2$O-saturated solutions containing 5.0 $\times 10^{-4}$ M Co(NH$_3$)$_5$py^{3+} and 1 M 2-propanol; ●, O$_2$-saturated solutions containing 1.0 $\times 10^{-4}$ M Co(NH$_3$)$_5$py^{3+}; □, N$_2$-purged solutions containing 5.0 $\times 10^{-4}$ M Co(NH$_3$)$_5$py^{3+}; ■, N$_2$O-saturated solutions containing 5.0 $\times 10^{-4}$ M Co(NH$_3$)$_5$py^{3+}.

Continuous Radiolysis. The irradiation of N$_2$O-saturated solutions of Co(NH$_3$)$_5$py^{3+} yields Co^{2+}(aq). Figure 6 shows that the rate of formation of Co^{2+}(aq) is linear and is not a
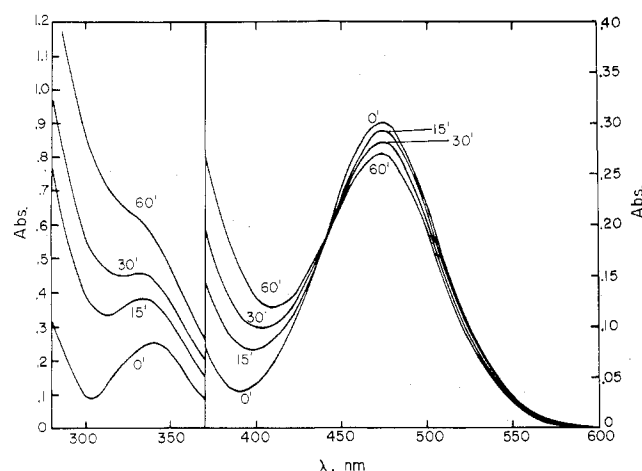
Figure 8. Spectral changes upon the continuous radiolysis of N$_2$O-saturated solutions of 1.0×10^{-3} M Co(NH$_3$)$_5$py^{3+} at pH 3.0. Optical path length = 5 cm, and dose rate = 6.9×10^2 rad min^{-1}.

function of [Co(NH$_3$)$_5$py^{3+}]. With knowledge of the dose rate of the radiation source, G(Co^{2+}(aq)) to within ±10% accuracy can be calculated from the slopes of the lines. Figure 7 shows the dependence of G(Co^{2+}(aq)) on pH for the irradiation of N$_2$O-saturated, O$_2$-saturated, and N$_2$-purged solutions and for N$_2$O-saturated solutions containing 1 M 2-propanol. In all cases, the yield of Co^{2+}(aq) was linear with irradiation time.

Figure 8 shows the spectral changes that result from the irradiation of N$_2$O-saturated solutions of Co(NH$_3$)$_5$py^{3+} at pH 3.0; virtually identical changes are seen at pH 6.0. The destruction of the substrate, as measured by the diminution of the 474-nm absorption band is stoichiometric with the yield of Co^{2+}(aq). As Figure 8 reveals, there is an isosbestic point at 442 nm. Below 280 nm, the absorbance continues to rise sharply; below 265 nm, the very intense py intraligand bands ($\epsilon > 2 \times 10^3$ M^{-1} cm^{-1}) are increased only slightly (<10%) as a result of 60 min of irradiation. No postirradiation spectral changes were ever observed under any conditions.

Ion-exchange chromatography of the radiolyzed solutions (up to 50% decomposition) did not separate any lower charged complexes, other than Co^{2+}(aq), from the tripositive substrate or reveal any new absorption bands in the substrate fraction.
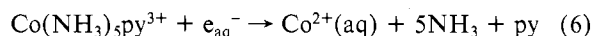
The volatile fractions distilled from the ether extract had a strong amine odor and gave positive Hinberg (primary amine) and 2,4-dinitrophenylhydrazine (carbonyl) tests. The IR spectrum of the fraction showed N–H (3350–3450 cm^{-1}), C–C (2900 cm^{-1}), and carbonyl (1720–1730 cm^{-1}) bands. The UV–vis spectrum of the fraction showed an absorption band at 295 nm. For comparison, the radiolysis of N$_2$O-saturated solutions containing pyH$^+$ (1 $\times$ 10^{-3} M) at pH 3.4 yields an absorption at 295 nm; at pH 9.5, a shoulder is seen at 295 nm and a well-resolved intense band at 363 nm is produced.
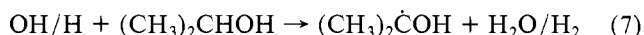
Discussion

Inasmuch as Co^{2+}(aq) is a major product of the interaction of OH radicals with Co(NH$_3$)$_5$py^{3+}, the process serves as a model for induced electron transfer. However, it is clear from the results that the mechanism, as expected, is far from simple. For example, the kinetic conductivity pulse radiolysis results at pH 4.6 indicate that Co^{2+}(aq) is *not* generated within ~1 s after the pulse; the formation of substitution-labile Co^{2+}(aq) would cause the release of NH$_3$ into the solution with the concomitant stoichiometric uptake of H$^+$ which could be readily detected.[15] Furthermore, the yield of Co^{2+}(aq) is dependent on the dose rate of the radiation source. Cohen and Meyerstein,[16] in their independent study of this reaction, report values of G(Co^{2+}(aq)) at pH 5.9 of 1.0 and 3.2 from pulse (≤3000 rad total dose from 100 to 1500 rad pulses, 0.05–0.5

μs duration) and continuous (1.8×10^4 rad min^{-1}) radiolyses, respectively, of N$_2$O-saturated solutions; our result at pH 5.9 (see Figure 7) is G(Co^{2+}(aq)) = 4.0 for 6.9×10^2 rad min^{-1}. The yield of Co^{2+}(aq) from the continuous radiolysis is strikingly pH dependent reaching plateau values at about pH 2.5 and 7.5 (Figure 7).
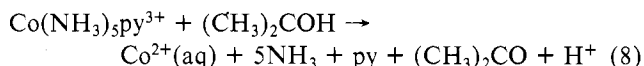
In order to construct a mechanistic model from all the data, it is necessary to maintain a catalogue of the operative reactions involving the various radical species produced in the radiolytic process. In addition to reactions 1–5, we must add the direct reduction of Co(NH$_3$)$_5$py^{3+} to Co^{2+}(aq) by the action of e$_{aq}^-$ ($k_6 = 8.0 \times 10^{10}$ M^{-1} s^{-1}) (eq 6). As can also

$$\text{Co(NH}_3\text{)}_5\text{py}^{3+} + \text{e}_{aq}^- \rightarrow \text{Co}^{2+}(\text{aq}) + 5\text{NH}_3 + \text{py} \quad (6)$$

be seen in Figure 7, Co(NH$_3$)$_5$py^{3+} reacts with (CH$_3$)$_2$ĊOH radicals (reaction 8), produced from reaction 7, to generate Co^{2+}(aq) quantitatively (G = 6.2) independent of pH.

$$\text{OH/H} + \text{(CH}_3\text{)}_2\text{CHOH} \rightarrow \text{(CH}_3\text{)}_2\text{ĊOH} + \text{H}_2\text{O/H}_2 \quad (7)$$

$$k = 1.3 \times 10^9 / 5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1 \, 8,17}$$

$$\begin{aligned}\text{Co(NH}_3\text{)}_5\text{py}^{3+} + \text{(CH}_3\text{)}_2\text{ĊOH} \rightarrow \\ \text{Co}^{2+}(\text{aq}) + 5\text{NH}_3 + \text{py} + \text{(CH}_3\text{)}_2\text{CO} + \text{H}^+ \quad (8)\end{aligned}$$
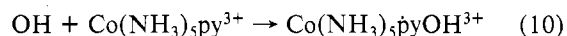
$$k \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

Primary Radical Reactions. In the radiolysis of N$_2$O-saturated solutions of Co(NH$_3$)$_5$py^{3+} at pH 3–7, reactions 2 and 6 represent the competing processes for the scavenging of e$_{aq}^-$; even at pH 3, reaction 3 is of relatively minor contribution. Thus, at pH 3.0 with [Co(NH$_3$)$_5$py^{3+}] = 5.0×10^{-4} M, for example, reactions 2, 3, and 6 comprise 78, 8, and 14%, respectively, of the e$_{aq}^-$ reactions. G(Co^{2+}(aq)) = 0.40 from reaction 6, G(OH) = 5.0 from reaction 2 and the primary yields, and G(H) = 0.75 from reaction 3 and the primary yield. If intermediate I in the pulse radiolysis is assumed to arise only from the interaction of OH radicals with Co(NH$_3$)$_5$py^{3+} and not from any reaction of H atoms, then a knowledge of the radiation dose, G(OH), and the absorbance of the transient leads to an evaluation of ϵ_{325} 1.7×10^3 M^{-1} cm^{-1} for intermediate I (Figure 1). The validity of the assumption regarding the contribution of H-atom reactions to the spectrum of I has been demonstrated by Cohen and Meyerstein,[16] who found no appreciable absorption from the pulse radiolysis of N$_2$O-saturated neutral solutions of Co(NH$_3$)$_5$py^{3+} containing 1 M *tert*-butyl alcohol which serves as an efficient ($k_9 = 4.2 \times 10^8$ M^{-1} s^{-1})[17] OH scavenger (eq 9). Our values of ϵ_{max} and λ_{max}

$$\text{OH} + \text{(CH}_3\text{)}_3\text{COH} \rightarrow \cdot\text{CH}_2\text{C(CH}_3\text{)}_2\text{OH} + \text{H}_2\text{O} \quad (9)$$

and the spectral profile of I are in complete agreement with Cohen and Meyerstein[16] and match very closely those of the OH adduct to free py or pyH$^+$.[18] On this basis, and the demonstrated fact that OH radicals add to the aromatic ligand of Co(NH$_3$)$_5$O$_2$CPh^{2+},[19] we are confident that intermediate I can be represented as a coordinated ligand-radical species arising from the addition of OH to the pyridine ring (reaction 10). Our observed value of $k_{10} = 6.5 \times 10^8$ M^{-1} s^{-1} is no more

$$\text{OH} + \text{Co(NH}_3\text{)}_5\text{py}^{3+} \rightarrow \text{Co(NH}_3\text{)}_5\dot{\text{p}}\text{yOH}^{3+} \quad (10)$$

than 15% higher than the absolute value due to competition with reaction 11 ($k_{11} = 5.2 \times 10^9$ M^{-1} s^{-1})[17] at our pulse doses.

$$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (11)$$
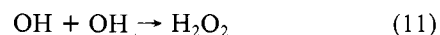
Nevertheless, it remains a matter of note that k_{10} is intermediate between the rate constant for the reaction of OH with free py (1.8×10^9 M^{-1} s^{-1}) and with free pyH$^+$ (2.0×10^7 M^{-1} s^{-1}).[18]

The structure of I can be assigned by analogy to the product of the reaction of OH with free py. ESR studies have shown[20]

that OH adds to the least electron deficient positions of the py ring, i.e., positions 3 and 5; it is probably safe to assume that the locus of attack in the complex is not the sterically inaccessible coordinating N atom. Addition of OH to the py ligand would cause the ring system to lose its aromaticity due to the formation of a quaternary carbon atom. As a result, large structural changes in the ligand would occur due to the loss of ring planarity with a concomitant gain in the stability of the coordinated radical toward intra- or intermolecular processes. Because no second-order decay of I is seen prior

I
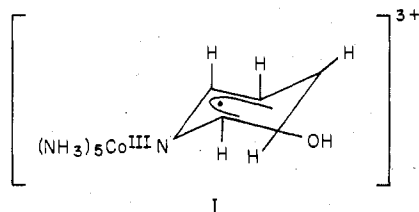
to its first-order conversion to II, any bimolecular disproportionation reaction of I would have $2k < 10^7$ M^{-1} s^{-1}.

Secondary Reactions. The conversion of I → II occurs via pH-, dose-, and [Co(NH₃)₅py³⁺]-independent first-order kinetics; the spectrum of II is very similar to that of I.[21] If one assumes that the conversion of I → II is quantitative, there being no evidence for competing modes of decay of I, then ϵ_{310} is 1.3×10^3 M^{-1} cm^{-1} for the pH-independent spectrum of II (Figure 1). The first-order decay cannot represent ligand-to-metal electron transfer; no Co²⁺(aq) is formed in that time frame. The lack of any demonstrated strong oxidizing ability of OH adducts to aromatic systems and the poor reducing ability of the Co(III) center effectively rule out metal-to-ligand electron transfer. The results suggest that a slow ($k = 8.5 \times 10^3$ s^{-1}) modification of the ligand, such as hydrate formation, occurs to yield a species that is not structurally very different from I. The spectral similarities between I and II indicate that II can also be described as an OH adduct to a modified pyridine ring.

The decay of II → III shows a smooth transition from second-order kinetics at pH 3.0 ($2k = 3.6 \times 10^5$ M^{-1} s^{-1}), to first-order kinetics at pH 5.2–7.8, and back to second-order kinetics at pH 9.0 ($2k = 3.8 \times 10^7$ M^{-1} s^{-1}); none of the processes occurring at pH 4.6 yields Co²⁺(aq). The second-order decays can be assigned to bimolecular disproportionation reactions of the coordinated radical species yielding long-lived or stable Co(III) products (III). The bimolecular reaction of II at pH 3.0 is slower than one would expect for presumably tripositive ions on electrostatic grounds. One must assume that the reaction involves further ligand modifications so that structural barriers are severe. The linear dependence of k on [H⁺]$^{-1}$ in the first-order decay region means that k is linearly dependent on [OH⁻]. From the data in Figure 5, the second-order rate constant for the reaction of II with OH⁻ can be derived; $k = 1.8 \times 10^8$ M^{-1} s^{-1}. This value is well within the range of values shown for base-catalyzed exchange of the proton of a methylene OH group in analogous OH adducts to aromatic rings.[22–24] The product of this reaction (II′) would be the conjugate base of II. Being of lower positive charge than II and, unquestionably, having a different electronic distribution in the ligand radical, II′ has a bimolecular decay at pH 9.0 which is 10² times faster than the decay of II at pH 3.0.

Reaction Mechanism. Although no Co²⁺(aq) is formed in the pulse radiolysis at pH 4.6 within ~1 s and very little Co²⁺(aq) is finally generated (G(Co²⁺(aq)) = 1.0 at pH 5.9),[16] the continuous radiolysis yields Co²⁺(aq) in appreciable, albeit less-than-quantitative, amounts. Furthermore, the spectra of the final products from the pulse and the continuous experiments are different. It is clear that the overall stoichiometry

of the reaction and the mechanistic details are affected by the rate at which the radiation is absorbed by the solution and, hence, by the concentration of the intermediates. Pulse radiolysis, with its high dose rates, generates radical concentrations of 10^{-6}–10^{-5} M within microseconds. Continuous radiolysis, being a low-dose-rate process, generates steady-state radical concentrations of the order of 10^{-9}–10^{-8} M. As a result, bimolecular processes are favored under high-dose-rate pulse conditions and unimolecular processes are favored under low-dose-rate continuous radiolysis conditions. It is necessary to invoke pathways to Co²⁺(aq) that would be operative under low-dose-rate conditions but denied under pulse conditions.

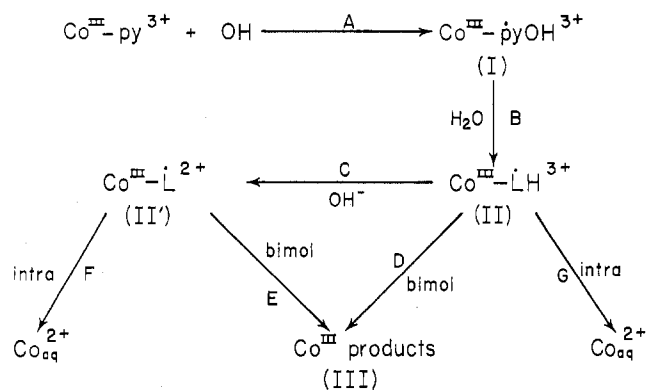Reaction of OH with Co(NH₃)₅py³⁺ is quantitative, yielding intermediate I (Co^{III}–pyOH³⁺). Formation of II is quantitative and does not involve the production of Co²⁺(aq). Deprotonation of II (Co^{III}–LH³⁺) yields II′ (Co^{III}–L²⁺). Both II and II′ show bimolecular reactions under pulse conditions which do not produce Co²⁺(aq). As mentioned above, these bimolecular reactions do not affect the Co(III) centers but cause further modifications to the py ligands resulting in final Co(III) products. The simplest route to Co²⁺(aq) would involve ligand-to-metal electron-transfer reactions[25] of II and II′ in competition with their bimolecular decays. Production of Co²⁺(aq) would be accompanied by the release of the two-electron-oxidized modified ligand. Further reactions of the organic fragments from the oxidized ligand, such as hydrolysis, would lead to the final amine and carbonyl products. It should be noted that products with similar characteristics are obtained in the radiolysis[26] and photolysis[27] of py and pyH⁺. Under continuous radiolysis conditions, where reduction of Co(III) is the predominant route, formation of any other Co(III) products is a minor component of the overall stoichiometry. As a result, the depletion of Co(NH₃)₅py³⁺ is stoichiometric with the formation of Co²⁺(aq). In any event, the visible spectra of the Co(III) products, which would be pentaammine complexes with a coordinated amine in the sixth site, could be very similar to that of Co(NH₃)₅py³⁺.

It should also be pointed out that the linear formation of Co²⁺(aq) under conditions where the total destruction of the substrate is less than 10% eliminates the possibility that Co²⁺(aq) arises from sources other than those described.

The description of species II and II′ as OH adducts to a nitrogen heterocyclic ring is not incompatible with the proposed intramolecular electron-transfer steps. The OH adduct to imidazole is a strong reducing agent;[28] it has been suggested that OH attack on the histidine ligand of ferricytochrome C results in the formation of ferrocytochrome C via ligand-to-metal intramolecular electron transfer.[29] Species II and II′ could be expected to undergo such intramolecular transfer, albeit slowly due to the large Franck–Condon barrier resulting from the distortion of the ligand.[30] Similarly, the OH adduct to Co(NH₃)₅O₂CPh²⁺ does appear to result in the formation of small quantities of Co²⁺(aq),[31] probably via a slow ($k < 10^2$ s^{-1}) intramolecular step in competition with its bimolecular reaction ($2k = 9.4 \times 10^7$ M^{-1} s^{-1}).[19]

The proposed mechanism, developed to account for all the observations, is given in Scheme I. The following rate constants are known directly from the pulse radiolysis results: $k_A = 6.5 \times 10^8$ M^{-1} s^{-1}, $k_B = 8.5 \times 10^3$ s^{-1}, $k_C = 1.8 \times 10^8$ M^{-1} s^{-1}, $2k_D = 3.6 \times 10^5$ M^{-1} s^{-1}, $2k_E = 3.8 \times 10^7$ M^{-1} s^{-1}. Values of k_F and k_G will be obtained from the continuous radiolysis yields of Co²⁺(aq). Because of the magnitude of k_A, the concentration of Co(NH₃)₅py³⁺, and the low concentration of OH, it is certain that reaction A competes quantitatively with reaction 11 in the continuous radiolysis. Therefore, G(I) = G(OH). There is no evidence to indicate that I → II is anything but quantitative so that G(II) = G(OH).

Scheme I

$$Co^{III}-py^{3+} + OH \xrightarrow{\quad A \quad} Co^{III}-pyOH^{3+}$$
$$(I)$$

$$H_2O \downarrow B$$

$$Co^{III}-L^{2+} \xleftarrow[OH^-]{\quad C \quad} Co^{III}-LH^{3+}$$
$$(II') \qquad\qquad (II)$$

$$\text{intra} \swarrow F \qquad\qquad \searrow \text{bimol} \quad D \swarrow \text{bimol} \qquad G \searrow \text{intra}$$

$$Co_{aq}^{2+} \qquad\qquad Co^{III} \text{ products} \qquad\qquad Co_{aq}^{2+}$$
$$E$$
$$(III)$$

Numerical Analysis.

We begin the numerical analysis of the data with the assumption that the effect of the reactions of H atoms with $Co(NH_3)_5py^{3+}$ at pH ≥ 3 can be ignored. Their yield is but a small fraction of the total radical yield and, although their behavior might be expected to parallel that of OH radicals, the exclusion of their reactions has essentially no effect on the results of the analysis.

At pH 3.0 in N_2-purged solutions containing 5.0×10^{-4} M $Co(NH_3)_5py^{3+}$, competition between reactions 3 and 6 results in 65% of e_{aq}^- ($G = 1.8$) reacting with the substrate to yield $Co^{2+}(aq)$ directly and 35% of e_{aq}^- ($G = 1.0$) producing H atoms; the total yield of H is $G = 1.6$. Of the observed yield of $Co^{2+}(aq)$ in the continuous radiolysis ($G = 2.9$), $G = 1.8$ can be accounted for by reaction 6. Therefore, $G(Co^{2+}(aq))$ $= 1.1$ must arise from the reaction of OH radicals ($G = 2.8$). In other words, the reaction of OH with $Co(NH_3)_5py^{3+}$ under these experimental conditions of pH, dose rate, concentration, and purging gas is 39% efficient in producing $Co^{2+}(aq)$; 61% of the OH radicals do not lead to $Co^{2+}(aq)$ and must be assumed to result, after secondary reactions, in Co(III) products which are not very different from the substrate. In N_2O-saturated solutions at pH 3.0 containing 5.0×10^{-4} M $Co(NH_3)_5py^{3+}$, competition among reactions 2, 3, and 6 leads to total yields, as discussed above, of $G(H) = 0.75$, $G(OH)$ $= 5.0$, and $G(Co^{2+}(aq)) = 0.40$. Of the observed yield of $Co^{2+}(aq)$ ($G = 2.6$), $G = 2.2$ must arise from the reactions of OH which are 44% efficient in producing $Co^{2+}(aq)$. From an average of these measured efficiencies, we conclude that, at pH 3.0 under our dose-rate conditions, 41% of II leads to $Co^{2+}(aq)$ via intramolecular path G and 59% of II disappears via bimolecular path D. Therefore, at pH 3.0, $rate_G = 0.71$ $rate_D$.

At pH 7.5, the yields of $Co^{2+}(aq)$ from N_2-purged and N_2O-saturated solutions appear to have reached plateaus so that it can be safely assumed that species II is quantitatively converted to species II' via reaction C and that $G(II') = G(OH)$. Performance of a similar analysis on the data from Figure 7 at pH 7.5 leads to the conclusion that 77% of II' leads to $Co^{2+}(aq)$ via intramolecular path F and 23% of II' disappears via bimolecular path E. Therefore, $rate_F = 3.3$ $rate_E$. It should be noted that the fraction of II or II' that leads to $Co^{2+}(aq)$ is independent of whether N_2 or N_2O has been used as the purging gas.

For a given set of experimental conditions (dose rate and purging gas), $G(II)$ at pH 3.0 is equal to $G(II')$ at pH 7.5 so that the steady-state concentrations of II and II' are equal. From the preceding analysis, $k_G = 0.71(2k_D[II])$ and $k_F = 3.3(2k_E[II'])$. Solving for the ratio of the rate constants of intramolecular steps F and G, $k_F/k_G = 4.9 \times 10^2$. On the basis of what we know about the kinetics of ligand-to-metal intramolecular electron transfer in Co(III)–ammine complexes containing coordinated radicals,[14] the direction and magnitude of the rate constants for the intramolecular reactions of

Table III. Parameters for the Conversion of Species II → II'

pH	f^a	Z^b	$k_G + 2k_D[II], s^{-1}$
3.0	0.41	0.0	
3.5	0.45	0.11	4.7×10^{-2}
4.0	0.53	0.33	3.7×10^{-2}
4.5	0.59	0.50	5.8×10^{-2}
5.0	0.65	0.67	8.9×10^{-2}
6.0	0.72	0.80	2.9×10^{-1}
7.0	0.77	1.0	
7.5	0.77	1.0	

^{a} $f = G(Co^{2+}(aq))/G(OH)$; average of values in N_2-purged and N_2O-saturated solutions. ^{b} $Z = (f - 0.41)/0.36$.

protonated II and deprotonated II' are perfectly reasonable.

Between pH 3.0 and 7.5, species II will be partitioned among reactions C, D, and G. Let $Z =$ fraction of II that forms II' via reaction C such that $Z = rate_C/(rate_C + rate_D + rate_G)$. We have already seen that at pH 3.0, where $Z = 0.0$, the fraction of II that yields $Co^{2+}(aq)$ is 0.41; at pH 7.5, where $Z = 1.0$, that fraction is 0.77. If $f =$ the fraction of all II and II' that yields $Co^{2+}(aq)$ ($f = G(Co^{2+}(aq))/G(II + II')$), a quantity that can be obtained from the data of Figure 7 and $G(OH)$ by the same analysis as conducted above, then $f = (1 - Z)(0.41) + (Z)(0.77)$ and values of Z as a function of pH can be calculated. Table III shows the result of these calculations and the smooth progression of Z from 0.0 to 1.0.

Now, from the definition of Z one can write $(k_C[OH^-]/Z)$ $- k_C[OH^-] = k_G + 2k_D[II]$. From knowledge of k_C and Z, values of $k_G + 2k_D[II]$ can be evaluated for pH 3.5–6.0 and are given in Table III. The entry at pH 6.0 is the most unreliable, being the result of the difference between numbers of very similar magnitudes; in fact, according to this treatment, the value of $k_G + 2k_D[II]$ would approach zero as $Z \to 1.0$, a situation that is physically meaningless. Actually, as $Z \to 1.0$, steps D and G become kinetically unimportant and the treatment breaks down. Taking the first four numbers as representing physically meaningful situations, the average value of $k_G + 2k_D[II]$ is 5.7×10^{-2} s^{-1}. At pH 3.0, where $Z = 0.0$ and $Co^{2+}(aq)$ is formed only from II via step G in competition with step D, $f = k_G/(k_G + 2k_D[II])$ so that $k_G = 2.3 \times 10^{-2}$ s^{-1}. Since $k_F/k_G = 4.9 \times 10^2$, $k_F = 1.1 \times 10^1$ s^{-1}.
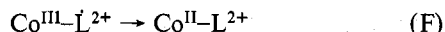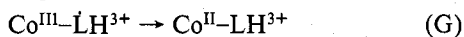
Under our continuous radiolysis conditions, where 4.4×10^{-6} M of primary radicals are generated during every minute of irradiation, the steady-state concentration of II at pH 3.0 is evaluated to be 9.1×10^{-8} M from the above analysis. It is clear that an increase in the steady-state concentration of II, which would arise for continuous irradiations at higher dose rates or pulse irradiations where the entire radiation dose is deposited into the solution in a time very short compared to the lifetimes of the transient intermediates, would result in a lowering of the fraction of II that leads to $Co^{2+}(aq)$. Similarly, for a higher value of [II], the value of Z would be lowered for a given pH. A similar analysis can be made for species II' and used to rationalize the other experimental results. For example, no $Co^{2+}(aq)$ is formed at pH 4.6 in the pulse conductivity experiments within 1 s after the 1-krad pulse. Taking $G(OH) = 5.2$, the concentration of species II generated via reactions A and B is 5.4×10^{-6} M. Under these conditions at pH 4.6, $Z = 0.035$ so that reaction C can be ignored in favor of reactons D and G. It is readily seen that reaction D is over 80 times faster than reaction G and that the lifetime of species II toward bimolecular decay is about 0.5 s. Thus, reaction D predominates and no release of $Co^{2+}(aq)$ within 1 s is detected.

It is evident from the competitive reactions involving species II and II' that the yield of $Co^{2+}(aq)$ would be lowered at any pH for an increase in radiation dose rate. Therefore, it is clear why Cohen and Meyerstein[16] obtained $G(Co^{2+}) = 3.2$ at pH 5.9 for 1.8×10^4 rad min^{-1} irradiation in N_2O-saturated
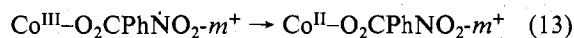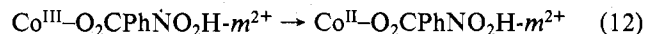
solution compared to our value of 4.0 for 6.9×10^2 rad min⁻¹ irradiation. Furthermore, they obtained $G(Co^{2+}(aq)) = 1.0$ for pulse irradiation at ≤ 3000 rad. Taking 1500 rad as their dose and $G(OH) = 5.4$ in N_2O-saturated solution containing $(1-3) \times 10^{-4}$ M Co(NH₃)₅py³⁺, the concentration of species II formed from reactions A and B is $\sim 8 \times 10^{-6}$ M. At pH 5.9, $Z \sim 0.3$ so that $\sim 30\%$ of II goes to II' via step C in competition with bimolecular step D which does not produce $Co^{2+}(aq)$; step G remains over 100 times slower than step D and can be ignored. Therefore, out of the $\sim 8 \times 10^{-6}$ M of species II initially formed, $\sim 3 \times 10^{-6}$ M of species II' is generated at pH 5.9. The fraction of II' that produces $Co^{2+}(aq)$ along path F in competition with bimolecular path E is easily calculated from knowledge of the values of $2k_E$, k_F, and [II'] and equals ~ 0.1. Therefore, $\sim 3 \times 10^{-7}$ M $Co^{2+}(aq)$ is produced representing a G value of about 0.2; an additional $G(Co^{2+}(aq)) = 0.2$ arises from reaction 6. Our mechanistic model predicts that under the conditions of Cohen and Myerstein's pulse experiments,[16] $G(Co^{2+}(aq)) \sim 0.4$. Considering their reported accuracy in the determination of $Co^{2+}(aq)$ $(G(Co^{2+}(aq)) = \pm 0.4)$ and lack of exact values for [Co(NH₃)₅py³⁺] and dose/pulse,[16] we find the agreement between their experimental value and our predicted value is quite good.

In O_2-saturated solution ($[O_2] = 1.3 \times 10^{-3}$ M) containing 1.0×10^{-4} M Co(NH₃)₅py³⁺, competition will exist among reactions 3, 4, and 6 for e_{aq}^-. At pH 3.1 where $G(Co^{2+}(aq)) = 1.0$ (Figure 7), $G(Co^{2+}(aq)) = 0.4$ from reaction 6. Species I, formed by reaction A ($G = 2.8$), will be efficiently scavenged by O_2. In order to account for the observed yield of $Co^{2+}(aq)$, the product of the reaction of I with O_2 must result in the ultimate formation of $Co^{2+}(aq)$ in $\sim 20\%$ yield. The same analysis applied to pH 6.0 gives approximately the same result.

Intramolecular Electron Transfer. It is appropriate to compare the values of the rate constants for the intramolecular transfer of an electron from the protonated and deprotonated coordinated ligand radicals into the Co(III) center with values reported[14] for reduced (nitrobenzoato)pentaamminecobalt(III) complexes. For steps G and F, $k_G = 2.3 \times 10^{-2}$ s⁻¹ and k_F

$$Co^{III}\text{–}\dot{L}H^{3+} \rightarrow Co^{II}\text{–}LH^{3+} \qquad (G)$$

$$Co^{III}\text{–}\dot{L}^{2+} \rightarrow Co^{II}\text{–}L^{2+} \qquad (F)$$

$= 1.1 \times 10$ s⁻¹. In comparison, $k_{12} \sim 10^{-2}$ s⁻¹ and $k_{13} = 1.5 \times 10^2$ s⁻¹; the meta isomers showed the lowest rates of in-

$$Co^{III}\text{–}O_2CPh\dot{N}O_2H\text{-}m^{2+} \rightarrow Co^{II}\text{–}O_2CPhNO_2H\text{-}m^{2+} \quad (12)$$

$$Co^{III}\text{–}O_2CPh\dot{N}O_2\text{-}m^+ \rightarrow Co^{II}\text{–}O_2CPhNO_2\text{-}m^+ \quad (13)$$

tramolecular electron transfer.[14] The relative slowness of these latter rates was attributed[14] partially to the low electron permeability of the carboxylate group, specifically the lack of overlap of the donor orbitals (π) and the acceptor orbital (σ), partially to the Franck–Condon barrier due to the change in the geometry of the ligand upon electron transfer, and partially to the electron density at or adjacent to the lead-in group. The same factors would be applicable in the case of the pyridine-like ligand radical of this study; the effect of symmetry mismatch in the reduction of Co(NH₃)₅py³⁺ has been pointed out by Haim and co-workers,[32] the distortion of

the coordinated ligand radical has been discussed above, and the low value of the unpaired electron spin density on the heteroatom in the OH adduct to free py has been determined.[20] It may be assumed, as has been done before,[14] that the spin densities on the free and coordinated ligand radicals, albeit modified by step B, are very similar. These factors, when coupled to the unquestionably low oxidation potential of the ligand radical, cause the intramolecular electron transfer rate to be quite low.

References and Notes

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