Kinetics of Ligand-to-Metal Intramolecular Electron Transfer in Cobalt(III)-Ammine Complexes Containing a Coordinated Radical[1a]

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Abstract: Reducing radicals (e_{aq}^-, CO_2^-, and $(CH_3)_2\dot{C}OH$) undergo intermolecular electron transfer to pentaamminecobalt(III) complexes containing a mono- or dinitrobenzoato ligand to generate a coordinated reduced nitrobenzoato ligand radical. In neutral solution, the coordinated radical disappears via unimolecular kinetics, which represents ligand-to-metal intramolecular electron transfer with the quantitative formation of Co^{2+}. The value of the electron transfer rate constant (10^2–10^5 s^{-1}) is dependent upon the number and position of nitro groups substituted on the aromatic ring; the highest rates are shown by the ortho isomers and the slowest by the meta. The rate appears to depend upon the electron spin density at or adjacent to the lead-in carboxylate group. Orbital overlap between the ortho radical group and the lead-in group facilitates electron transfer. The coordinated nitrobenzoato radical can be protonated (pK_a = 2–3) at the nitro group resulting in bimolecular disproportionation at high radical concentration; bimolecular decay does not yield Co^{2+}. The only exception is the *o*-nitrobenzoato isomer, the protonated coordinated radical of which decays via intramolecular transfer and quantitative generation of Co^{2+}. The yields of Co^{2+} and the spectral changes that result as a function of pH can be rationalized in terms of the reaction mechanism. Evidence is also offered that reduction of the complexes by e_{aq}^- may occur via the formation of some initial electronically excited molecular species which then partitions to yield the coordinated reduced ligand and the reduced metal center.

The transport of electrons through molecules is of fundamental chemical importance bearing on the intramolecular pathway of transfer through large biological molecules involved in redox processes which occur in the chloroplasts and the mitochondria.[2] In simpler metal ion coordination complexes, the inner-sphere electron transfer mechanism involves the formation of a precursor binuclear complex between oxidant and reductant with the two metal centers bridged by a ligand, followed by electron transfer through the ligand.[3] Whether or not this ligand-mediated electron transfer occurs via reduction of the ligand to form a radical coordinated to the metal center must be evaluated for each system. Nevertheless, knowledge of the factors that govern the rate of intramolecular electron transfer from a coordinated radical to a metal center is necessary to the understanding of the overall redox process.

Ligand radicals coordinated to both cobalt and chromium centers have been suggested as intermediates in the Cr(II) reduction of many Co(III)-ammine complexes.[4] The detection of such intermediates and their unambiguous characterization have been frustrated by their short lifetimes and their lack of unique absorption spectra. Under extremely favorable circumstances, detection can be accomplished by stopped-flow spectrophotometry,[5] although the overlap of intermediate, reactant, and product spectra and the multiple pathways followed by the reaction have made interpretation difficult.[6] In the few cases where intramolecular electron transfer rates have been measured in precursor binuclear complexes involving aromatic bridging ligands,[7-9] little concern has been given to the possibility of forming coordinated ligand radicals as intermediates, partially on grounds of the energetics of forming such ligand radicals and partially because the lifetimes of such species are expected to be short compared with the half-life of the overall electron transfer reaction.

The fast kinetics technique of pulse radiolysis lends itself extremely well to investigations into the problem of intramolecular electron transfer. The time resolution of the technique (<1 μs) permits the detection and characterization, by optical absorption spectrophotometry and kinetic conductivity, of the intermediates produced from the fast reaction of radiation-generated free radicals. In a preliminary publication[10] we showed that radiation-generated reducing radicals (e_{aq}^-, CO_2^-, and $(CH_3)_2\dot{C}OH$) react with *p*-nitrobenzoatopentaamminecobalt(III) ion, $p\text{-}O_2NC_6H_4CO_2Co^{III}(NH_3)_5^{2+}$, generating a coordinated one-electron reduced ligand radical which decays via ligand-to-metal intramolecular electron transfer to form Co^{2+}. The rate constant for electron transfer was found to be 2.6×10^3 s^{-1} at pH 5.5–7.7. In this paper we examine the effect of pH and the number and position of nitro-substitution on the kinetics of intramolecular electron transfer in cobalt(III)-ammine complexes containing a coordinated nitrobenzoato ligand radical.

Experimental Section

Preparation of Complexes. The general method of Dockal, Everhart, and Gould[11] was used to prepare the nitrobenzoatopentaamminecobalt(III) complexes as the perchlorate salts. The parent nitrobenzoic acid (20 mmol) (obtained from Aldrich and Eastman and used without further purification) was dissolved in 8 mL of diethylene glycol at 70–80 °C to which 0.75 g of $[Co(NH_3)_5CO_3]NO_3$ was added with stirring. The mixture was heated at 70 °C for 25 min and extracted into water from ether. Additional ether washings were used to remove the free parent acid from the aqueous solution; extraction was continued (up to four cycles) until the intense ($\epsilon \sim 10^4$ M^{-1} cm^{-1}) UV absorption of the free acid could no longer be detected in the ethereal wash. Air was drawn through the aqueous solution for at least 10 min to remove dissolved ether. The Co(III) salt was precipitated in $HClO_4$ at −5 °C, then filtered and recrystallized from warm water. Recrystallization was repeated (usually two cycles were necessary) until the optical absorption maximum at 501–503 nm reached a constant and maximum ($\epsilon_{530} \sim 80$ M^{-1} cm^{-1}) value. Microanalysis (Galbraith Laboratories) further demonstrated the purity of the complexes. The following pentaammine complexes of Co(III) (as their ClO_4^- salts) were prepared: *o*-nitrobenzoato (ON), *m*-nitrobenzoato (MN), *p*-nitrobenzoato (PN), 2,4-dinitrobenzoato (2,4D), and 3,5-dinitrobenzoato (3,5D). Despite prolonged heating in the preparation, the following complexes could not be isolated: 3,4-dinitrobenzoato, 2,5-dinitrobenzoato, and 2,4,6-trinitrobenzoato. Table I shows the analytical and spectral data for the complexes used.

Radiation Techniques. Pulse radiolyses were conducted using the apparatus[12] at the U.S. Army Natick Research and Development Command. Transient absorption spectra were obtained by optical spectrophotometry with a time resolution of ~0.5 μs. The radiation dose per pulse was established by the use of SCN^- dosimetry.[13] Reagent grade chemicals and high purity water were used to prepare the solutions, which were buffered using phosphate or $HClO_4$. Solutions were purged of O_2 by bubbling (~30 min) with high purity Ar or N_2O (1 atm partial pressure ≡ 2.5×10^{-2} M).

Continuous radiolyses were conducted in a well-type ^{60}Co γ-ray source at Boston University with a dose rate of about 4×10^{16} eV

Table I. Chemical and Spectral Analysis of Complexes

Complex[a]	%Co	%C	%H	λ_{max}, nm	ϵ_{max}, $M^{-1} cm^{-1}$
ON	11.34	16.35	3.52	503	70
MN	11.81	16.27	3.76	503	80
PN	10.85	15.89	3.86	502	83
2,4D	10.43	15.41	3.46	503	81
3,5D	10.36	15.04	3.44	501	75

[a] As ClO_4^- salt with unknown number of waters of hydration.

$mL^{-1} min^{-1}$. The Fricke chemical dosimeter[14] was used to evaluate the exact radiation dose received by the solutions. The solutions were prepared for irradiation as described above and contained in sealed Pyrex vessels that had provision for a preirradiation gas purge. After irradiation for a measured length of time, analysis for Co^{2+} was performed according to Kitson's method[15] from which the G value[16] of Co^{2+} formation was calculated. Spectra were recorded on a Cary 118 spectrophotometer. The yield of Co^{2+} was linear with radiation dose and the extent of reaction was always <15%.

Generation of the Reducing Radicals. The radiolysis of water and aqueous solutions generates e_{aq}^-, OH radicals, and H atoms according to the overall reaction $H_2O \rightsquigarrow e_{aq}^-$ (2.8), OH (2.8), H (0.55) where the numbers in parentheses represent the G values of the species. By the use of selected scavengers, a particular reactive radical can be chosen to be the principal reactant in the solution. Thus, in the presence of *tert*-butyl alcohol, the OH radials are effectively scavenged: $OH + (CH_3)_3COH \rightarrow \cdot CH_2C(CH_3)_2OH + H_2O$ ($k = 5.2 \times 10^8$ $M^{-1} s^{-1}$);[17] the resultant radical is relatively inert and its weak optical absorption[12] below 280 nm can easily be taken into account when transient absorption spectra are determined. In N_2O-saturated solution, e_{aq}^- is efficiently scavenged: $e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^-$ ($k = 8.7 \times 10^9$ $M^{-1} s^{-1}$);[18] in acidic solution e_{aq}^- is converted to H atoms: $e_{aq}^- + H^+ \rightarrow H$ ($k = 2.2 \times 10^{10}$ $M^{-1} s^{-1}$).[18] The reducing radicals CO_2^- and $(CH_3)_2\dot{C}OH$ can be generated conveniently from solutions containing formate or 2-propanol:

$$OH/H + HCO_2^- \rightarrow CO_2^- + H_2O/H_2 \; (k = 2.5 \times 10^9/5.0 \times 10^7 \; M^{-1} s^{-1})^{19,20}$$

$$OH/H + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O/H_2 \; (k = 1.3 \times 10^9/5.0 \times 10^7 \; M^{-1} s^{-1})^{19,20}$$

Thus, by the judicious choice of scavengers, reducing radicals with an upper-limit yield of $G = 6.2$ can be generated.

Results

Formation and Decay of Transient Intermediates. The reaction of reducing radicals (e_{aq}^-, CO_2^-, and $(CH_3)_2\dot{C}OH$) with the complexes gave rise to transient absorption spectra that were virtually identical with those obtained from the free radical reduction of the parent nitrobenzoic acids.[21] Figure 1 shows the results for PN and *p*-nitrobenzoic acid in detail. In both cases the absorption spectra are a function of the pH, giving rise to a typical "titration curve" from which the pK_a of the intermediate species can be evaluated inasmuch as protonation-deprotonation reactions are faster than the decays of the intermediates. For both PN and its parent acid,[21] the pK_a of the reduced intermediate is 2.8. The spectral and pK_a data for the complexes are given in Table II. Except for ON and 2,4D, where the formations and decays of the intermediates overlapped, the absorption spectra were recorded after completion of the formation reaction and before any decay could be observed. Any contribution by the weak absorption of CO_2^- and $(CH_3)_2\dot{C}OH$ could be ignored.[12,22] The spectra at λ < 330 nm were obtained at low solute concentration (<10^{-4} M) because of the strong absorption by the complexes and free ligands. In addition, a correction was always applied for the loss of substrate absorption due to reaction with the radicals.

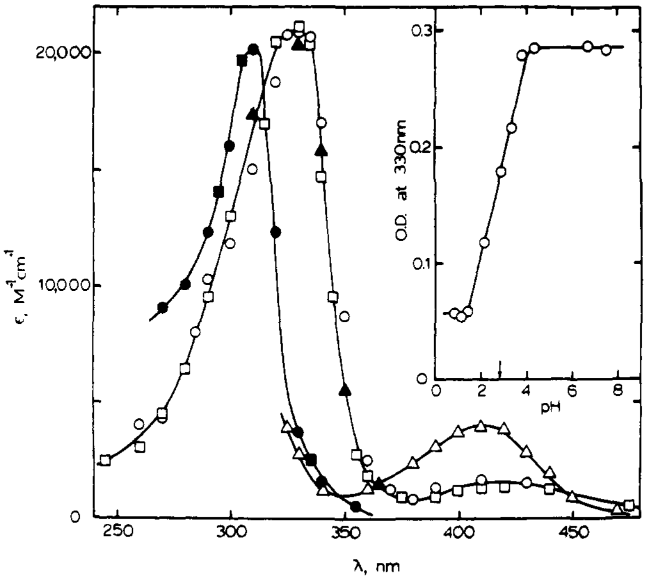

Figure 1. Transient absorption spectra from the pulse radiolysis of p-O_2NPhCO_2H, p-$O_2NPhCO_2^-$, and p-$O_2NPhCO_2Co(NH_3)_5^{2+}$. All spectra corrected for loss of substrate absorption. Dose/pulse = 1.5 krad. ○: p-$O_2\dot{N}PhCO_2Co(NH_3)_5^+$ from CO_2^- reaction (2×10^{-4} M p-$O_2NPhCO_2Co(NH_3)_5^{2+}$, 0.1 M HCO_2^-, N_2O saturated, pH 7.2). □: p-$O_2\dot{N}PhCO_2^{2-}$ from CO_2^- reaction (5×10^{-4} M p-$O_2NPhCO_2^-$, 0.1 M HCO_2^-, N_2O saturated, pH 7.0). ▲: p-$O_2\dot{N}PhCO_2Co(NH_3)_5^+$ from e_{aq}^- reaction (1×10^{-4} M p-$O_2NPhCO_2Co(NH_3)_5^{2+}$, 1 M *tert*-butyl alcohol, Ar purged, pH 6.9; spectrum normalized to that of ○). ●: p-$HO_2\dot{N}PhCO_2Co(NH_3)_5^{2+}$ from $(CH_3)\dot{C}OH$ reaction (5×10^{-5} M p-$O_2NPhCO_2Co(NH_3)_5^{2+}$, 1 M 2-propanol, Ar purged, pH 1.2). ■: p-$HO_2\dot{N}PhCO_2H$ from $(CH_3)_2COH$ reaction (5×10^{-4} M p-O_2N-$PhCO_2H$, 1 M 2-propanol, Ar purged. pH 1.0). △: p-$O_2NPh(H)$-$CO_2Co(NH_3)_5^{2+}$ from H atom reaction (5×10^{-4} M p-O_2NPh-$CO_2Co(NH_3)_5^{2+}$, 1 M *tert*-butyl alcohol, Ar purged. pH 1.0). Insert: A at 330 nm as a function of pH for 5×10^{-5} M p-$O_2NPhCO_2Co(NH_3)_5^{2+}$, 1 M 2-propanol, N_2O saturated.

The rate constants for all the formation of the transient intermediates were established from the pseudo-first-order kinetics of the build-in of the transient absorptions. The data for all five complexes are given in Table III. The reactions of CO_2^-

Table II. Spectral and pK_a Data of Transient Intermediates

	pH 0.8		pH 7.0		
Complex	λ_{max}, nm	ϵ_{max},[a] $M^{-1} cm^{-1}$	λ_{max}, nm	ϵ_{max},[a] $M^{-1} cm^{-1}$	pK_a of intermediate
ON	280	$\geq 7.8 \times 10^3$	*b*	*b*	*b*
MN	280	1.0×10^4	290	1.3×10^4	2.8
PN	310	2.0×10^4	330	2.1×10^4	2.8
2,4D	*b*	*b*	*b*	*b*	*b*
3,5D	265	1.5×10^4	285	1.9×10^4	2.3

[a] ϵ values ±20%. [b] Unobtainable due to overlap of formation and decay of intermediate.

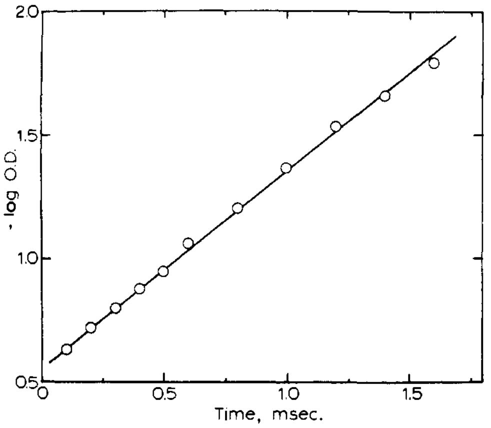

Figure 2. First-order kinetics of the decay of p-$O_2NPhCO_2Co(NH_3)_5^+$; 5×10^{-4} M complex, 0.1 M HCO_2^-, N_2O saturated, pH 7.1, λ 350 nm, dose/pulse = 2.4 krad.

Table III. Kinetics of Formation of Transient Intermediates

Complex	$k(CO_2^- + \text{complex})$,[a] $M^{-1}\ s^{-1}$	$k((CH_3)_2\dot{C}OH + \text{complex})$,[a] $M^{-1}\ s^{-1}$
ON	2.0×10^9	1.7×10^9
MN	1.5×10^9	1.5×10^9
PN	1.9×10^9	2.6×10^9
2,4D	7.5×10^9	4.3×10^9
3,5D	8.1×10^9	2.9×10^9

[a] Measured at pH 7.0; [complex] = $1\text{-}3 \times 10^{-4}$ M; [buffer] = $\sim 10^{-4}$ M.

were obtained in neutral solution, while those for $(CH_3)_2\dot{C}OH$ were obtained in both acidic and neutral solution. The observed formation rate constants of the order of $10^9\ M^{-1}\ s^{-1}$ were not a function of pH. In comparison, k for the reaction of e_{aq}^- with the complexes in neutral solution was $8.0 \times 10^{10}\ M^{-1}\ s^{-1}$.

The kinetics of the decays of the intermediates were dependent upon the nature of the nitrobenzoato ligand and the pH. In neutral solution, the intermediates of all the complexes decayed via first-order kinetics (Figure 2) with values of k that were independent of [complex], radiation dose, i.e., [intermediate], or the nature of the radical reactant. In acidic solution, the intermediate from ON decayed via first-order kinetics, while the others showed distinctly second-order kinetics (Figure 3). The data for all five complexes are given in Table IV.

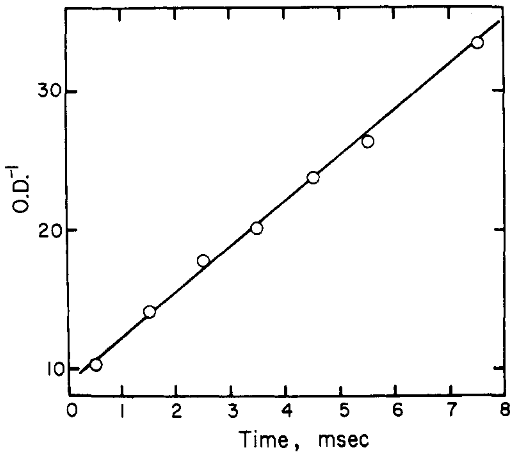

Figure 3. Second-order kinetics of the decay of m-$HO_2NPhCO_2Co(NH_3)_5^{2+}$; 5×10^{-5} M complex, 1 M 2-propanol, Ar purged, pH 0.8, λ 280 nm, dose/pulse = 2.4 krad.

The intermediate from the reduction of PN in neutral solution could be scavenged by electron acceptors if the rate of the scavenging reaction were greater than the rate of first-order decay of the intermediate. Thus, for a 1×10^{-3} M solution of PN containing 0.1 M HCO_2^-, 1×10^{-4} M O_2, and 2.5×10^{-2} M N_2O at pH 6.9, the intermediate was formed from the reaction of CO_2^- and PN in the usual manner, but decayed with $[O_2]$-dependent pseudo-first-order kinetics due to reaction with O_2 for which $k = 2.2 \times 10^9\ M^{-1}\ s^{-1}$. Similar reaction of the intermediate was observed with menaquinone (2-methyl-1,4-naphthaquinone; MQ) for a 2×10^{-3} M solution of PN containing 0.1 M HCO_2^-, 5×10^{-5} M MQ, and 2.5×10^{-2} M N_2O at pH 6.7. From the disappearance of the intermediate and the formation of $\cdot MQ^-$ (ϵ_{400} $1.0 \times 10^4\ M^{-1}\ cm^{-1}$),[23] a value of $k = 1.6 \times 10^9\ M^{-1}\ s^{-1}$ was obtained. The second-order decay of $\cdot MQ^-$ was unaffected ($k = 2.4 \times 10^8\ M^{-1}\ s^{-1}$) by the presence of PN.

It was pointed out at the beginning of this section and demonstrated in Figure 1 that the transient absorption spectra from the reduction of the complexes by CO_2^- and $(CH_3)_2\dot{C}OH$ and the parent free acids by all the radicals were virtually identical with regard to absorption band maxima and values of the extinction coefficients. In the case of reduction of the complexes by e_{aq}^- in neutral solution, λ_{max} were unchanged, but the values of ϵ were uniformly diminished throughout the entire spectral region. The ratios of the apparent ϵ from e_{aq}^- reduction to that from CO_2^- or $(CH_3)_2\dot{C}OH$ reduction were 0.70, 0.50, and 0.47 for PN, MN, and 3,5D respectively. Unfortunately, the overlapping formations and decays in the cases of ON and 2,4D prevented similar evaluations to be made.

Figure 1 also shows the spectrum obtained from the reaction of H atoms at pH 1 with PN in 1 M *tert*-butyl alcohol. This transient spectrum (λ_{max} 410 nm; ϵ_{410} 4000 $M^{-1}\ cm^{-1}$) and its formation kinetics ($k = 1.9 \times 10^9\ M^{-1}\ s^{-1}$) are to be compared with the reaction of H atoms with $(NH_3)_5$-

Table IV. Kinetics of Decay of Transient Intermediates

	pH 0.8[a]			pH 7.0[b]		
Complex	λ monitored, nm	Kinetic order	k[c]	λ monitored, nm	Kinetic order	k[c]
ON	290	I	9.5×10^3	330	I	4.0×10^5
MN	290	II	1.0×10^8	300	I	1.5×10^2
PN	310	II	1.5×10^8	330	I	2.6×10^3
2,4D	320	II	9.0×10^8[d]	330	I	3.5×10^4
3,5D	300	II	3.4×10^8	300	I	1.3×10^2

[a] 5×10^{-5} M complex, 1 M 2-propanol, Ar purged, dose/pulse = 2.4 krad. [b] 5×10^{-5} M complex, 1 M 2-propanol or 0.1 M HCO_2^-, N_2O-saturated, $\sim 10^{-4}$ M buffer, dose/pulse = 2.4 krad. [c] First-order rate constants in units of s^{-1}; second-order rate constants in units of $M^{-1}\ s^{-1}$. [d] Calculated using ϵ_{320} for the reduced free ligand at pH 0.8.

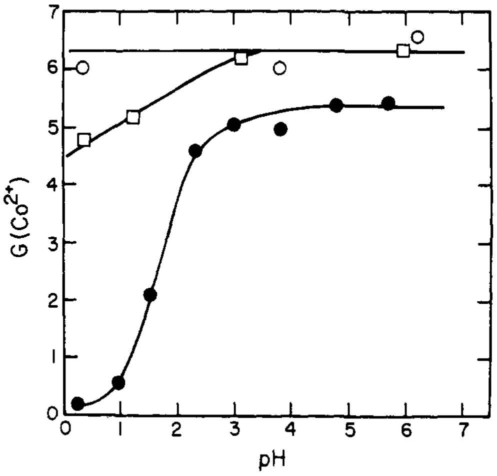

Figure 4. $G(\mathrm{Co}^{2+})$ as a function of pH: ○ *o*-$O_2NPhCO_2Co(NH_3)_5^{2+}$; ● *m*-$O_2NPhCO_2Co(NH_3)_5^{2+}$; □ *p*-$O_2NPhCO_2Co(NH_3)_5^{2+}$.

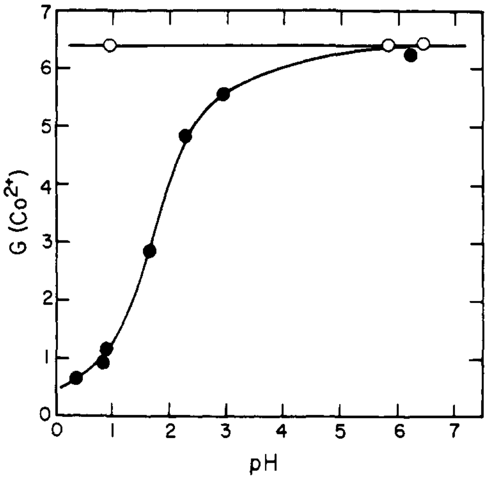

Figure 5. $G(\mathrm{Co}^{2+})$ as a function of pH: ○ 2,4-$(O_2N)_2PhCO_2Co(NH_3)_5^{2+}$; ● 3,5-$(O_2N)_2PhCO_2Co(NH_3)_5^{2+}$.

CoO_2Ph^{2+} ($k = 1.5 \times 10^9$ M^{-1} s^{-1}), which yields a spectrum with λ_{max} 350 nm and ϵ_{350} 3600 M^{-1} s^{-1}.

Yield of $\mathbf{Co^{2+}}$. In neutral solution, the reaction of $(CH_3)_2\dot{C}OH$ with 5×10^{-4} M complex in N_2O-saturated 1 M 2-propanol solution under continuous irradiation conditions led to the quantitative ($G = 6.2$) formation of Co^{2+} in the case of all nitrobenzoato complexes except MN; this latter complex gave $G(Co^{2+}) = 5.4$ or 87% yield. The yields of Co^{2+} were independent of pH for ON and 2,4D, but were a function of pH for the others (Figures 4 and 5). It is of importance to note that in highly acidic medium, reaction of $(CH_3)_2\dot{C}OH$ with MN and 3,5D generates Co^{2+} in a yield of <10%, whereas the yield for PN is 77%. For comparison, $G(Co^{2+}) = 6.2 \pm 0.4$ for the reaction of CO_2^- with ON, MN, and PN at pH 3.6.

Figure 6 shows the spectrum of MN under continuous irradiation conditions as a function of radiation dose. The first d-d band at 503 nm shows a regular decrease, but no spectral changes are seen in the 270-395-nm region. Below 270 nm the absorbance decreases slightly upon irradiation, with the maximum of the band at 223 nm shifting somewhat to shorter wavelengths (~5 nm). In 1 M acid, equivalent radiation dose results in virtually no spectral changes. For comparison, Figure 7 shows the result of irradiating free *m*-nitrobenzoic acid in 1 M 2-propanol in acidic and neutral solution.

Discussion

The one-electron reduction of the free nitrobenzoate anions yields radicals which are capable of acting as reducing agents ($E' \sim -0.3$ to -0.4 V at pH 7) and in which ~50% of the spin density is on the nitro group.[21] Therefore, it is hardly surprising that these free radicals reduce Co(III)-ammine complexes[24] or, when coordinated to a Co(III) center, engage in intramolecular electron transfer.[10] The virtual identity of the absorption spectra and acid-base properties of the free and coordinated ligand radicals suggest that the spin distributions and structures of these species are very similar and, to the first approximation, identical. Thus, coordination of the radicals to the +3 metal center through the carboxylate group has no obvious effect on the energy levels and oscillator strengths of the electronic transitions, presumably localized on the nitro group, that give rise to the absorption spectra. Similarly, the equilibrium constants for the deprotonation of the acid form of the radicals is unaffected by coordination to the positive metal center or its presence in a positively charged complex. One must conclude that the carboxylate group serves to insulate the aromatic and nitro group electronic systems from the metal center orbitals to a rather large extent.

The reduction of the Co(III) complexes discussed in this paper and their subsequent acid-base behavior can be represented by the reactions

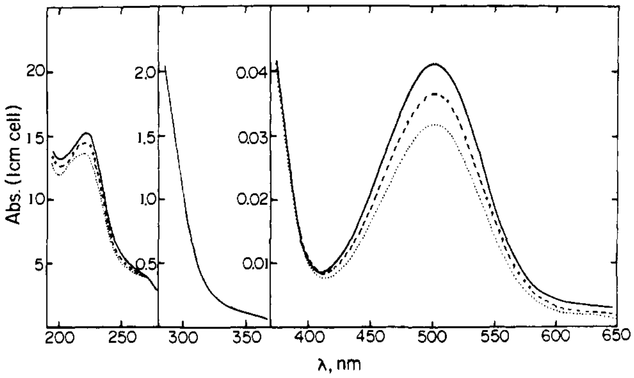

Figure 6. Spectral changes upon continuous γ-radiolysis of *m*-O_2N-$PhCO_2Co(NH_3)_5^{2+}$, 5×10^{-4} M complex, 1 M 2-propanol, N_2O saturated, pH 6.1: —, $t = 0$; - - - -, $t = 13$ min; . . . , $t = 26$ min. Dose rate = 4×10^{16} eV ml^{-1} min^{-1}.

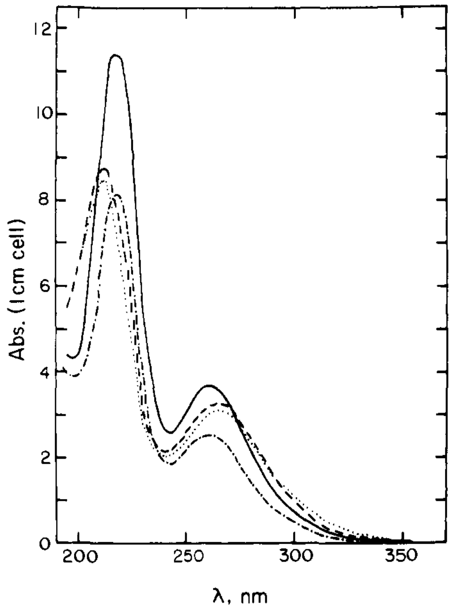

Figure 7. Spectral changes upon continuous γ-radiolysis of *m*-O_2N-$PhCO_2H$, 5×10^{-4} M substrate, 1 M 2-propanol, N_2O saturated: —, $t = 0$, 1 M acid; - • - •, $t = 26$ min, 1 M acid; - - -, $t = 0$, pH 6.1; . ., $t = 26$ min, pH 6.1. Dose rate = 4×10^{16} eV ml^{-1} min^{-1}.

$$\mathrm{Co^{III}O_2CPhNO_2{}^{2+} + \mathit{Red} \rightarrow Co^{III}O_2CPh\dot{N}O_2{}^{+} + \mathit{Ox}} \quad (1)$$

$$\mathrm{Co^{III}O_2CPh\dot{N}O_2{}^{+} + H^+ \rightleftarrows Co^{III}O_2CPh\dot{N}O_2H^{2+}} \quad (2)$$

Red represents the radiation-generated reducing agent and the pK_a of the intermediate given in Table II represents reaction 2. In the case of the dinitrobenzoato complexes, it is recognized that the spin density may be distributed between the nitro groups as well as within the aromatic system. Nevertheless, the same notation as given in reactions 1 and 2 will be used for these complexes as well.

The value of k_1 for the reaction of $e_{aq}{}^-$ with the complexes (8.0×10^{10} M^{-1} s^{-1}) is not significantly different than the corresponding value for $\mathrm{Co(NH_3)_5O_2Ph^{2+}}$.[25] On the other hand, values of k_1 for $\mathrm{CO_2{}^-}$ and $\mathrm{(CH_3)_2\dot{C}OH}$ radicals (Table II) are substantially higher for the nitro complexes than those shown by other Co(III) complexes;[26,27] the generally higher rates shown by the dinitro complexes may reflect a statistical factor in the selection of a site of attack.

Reduction of the Ligand and the Metal Center. Whereas reduction by $\mathrm{CO_2{}^-}$ and $\mathrm{(CH_3)_2\dot{C}OH}$ leads to quantitative formation of the coordinated radical intermediate, rapid reduction by $e_{aq}{}^-$ in neutral solution leads to less-than-quantitative formation for PN, MN, and 3,5D (and presumably ON and 2,4D as well). Inasmuch as the overall reaction yields $\mathrm{Co^{2+}}$ quantitatively, we conclude that reduction by $e_{aq}{}^-$ proceeds via two paths, the direct formation of $\mathrm{Co^{2+}}$ and the generation of the coordinated radical intermediate. Kinetic conductivity studies[28] on the reaction of $e_{aq}{}^-$ with PN have independently verified that ~30% $\mathrm{Co^{2+}}$ is formed, with concomitant release of $\mathrm{NH_3}$, directly upon reduction; the formation of the remaining ~70% of $\mathrm{Co^{2+}}$ coincides with the intramolecular transfer of an electron from the coordinated ligand radical to the metal center.[10] Whether $e_{aq}{}^-$ attack produces a common intermediate which then partitions, or proceeds via electron addition directly to either ligand-localized or metal-centered orbitals could not be established by these experiments. No precursor to the coordinated radical could be observed; the build-in of the intermediate absorption reflected the rate of reaction of the substrate complex with $e_{aq}{}^-$.

If a common intermediate were produced initially upon $e_{aq}{}^-$ attack, it could be visualized as a short-lived ($\tau < 10^{-7}$ s) species corresponding to the addition of the electron to an unoccupied molecular orbital of higher energy than the unoccupied e_g orbital (reaction 3). This would be equivalent to an excited state of the reduced acceptor molecule.[25] Decay of this excited state by electron transition into metal-centered orbitals (leading to Co(II)) and ligand-localized orbitals (leading to the coordinated radical intermediate) would be expected to be rapid. In support of this speculation, the reaction of $e_{aq}{}^-$ with $\mathrm{Ru(bipy)_3{}^{3+}}$ produces the luminescence characteristic of excited $\mathrm{Ru(bipy)_3{}^{2+}}$ because of the very large free-energy change involved in the $e_{aq}{}^-$ reduction.[29] Furthermore, multiple decay pathways of initially formed excited states of Co(III) complexes leading to metal-centered and ligand-localized excited states are known.[30] The ratio of coordinated radical to direct Co(II) formation upon $e_{aq}{}^-$ reaction would reflect the relative probability of the decay modes of the initially formed excited state (reactions 4a and 4b). Formation of $\mathrm{Co^{II}O_2CPhNO_2{}^+}$ via reaction 4b would presumably result in a low-spin product; spin equilibrium to high-spin Co(II) is believed to be very fast (~10^{-7} s)[31] and ligand labilization of high-spin Co(II)-ammine complexes (reaction 5) is known to take place in the submicrosecond time range.[28] Thus, 4a/(4a + 4b) would equal 0.70, 0.50, and 0.47 for PN, MN, and 3,5D, respectively.

$$\mathrm{Co^{III}O_2CPhNO_2{}^{2+} + e_{aq}{}^- \rightarrow [CoO_2CPhNO_2{}^+]^*} \quad (3)$$

$$\mathrm{[CoO_2CPhNO_2{}^+]^* \nearrow Co^{III}O_2PhNO_2{}^+} \quad (4a)$$

$$\mathrm{[CoO_2CPhNO_2{}^+]^* \searrow Co^{II}O_2PhNO_2{}^+} \quad (4b)$$

$$\mathrm{Co^{II}O_2CPhNO_2{}^+ \rightarrow Co^{2+} + 5NH_3 + O_2NPhCO_2{}^-} \quad (5)$$

The similar ratios calculated for MN and 3,5D could be due to their common meta isomeric configuration. The significantly higher ratio calculated for PN could reflect a closer matching of the energies, symmetries, and spatial orientations of the initially formed excited molecular species and the ligand-localized excited state. It should be noted that we have never observed any transient coordinated radical intermediate from the reaction of $e_{aq}{}^-$ with $\mathrm{(NH_3)_5Co^{III}O_2CPh^{2+}}$ or $\mathrm{(NH_3)_5Co^{III}py^{3+}}$, implying either that the 4a/(4a + 4b) ratio in those cases is zero or that the lifetime of the coordinated radical toward intramolecular electron transfer is extremely short (<10^{-7} s). Conversely, the reaction of $\mathrm{CO_2{}^-}$ and $\mathrm{(CH_3)_2\dot{C}OH}$ radicals with the nitro complexes yields the coordinated radicals quantitatively. These free radicals are weaker reducing agents than $e_{aq}{}^-$ and so the free energy change in the reaction is less. As a result, the electron would not be transferred into the excited molecular orbitals as with $e_{aq}{}^-$, but would enter directly into the lower ligand-localized orbital (reaction 1).

This apparent ability of $e_{aq}{}^-$ to partition between the metal center and the ligands has implications for the study of electron transfer pathways in metalloproteins. The $e_{aq}{}^-$ is often used as a probe to mimic biological reducing agents which, with E' less negative than ~−0.5 V, are even weaker reductants than $\mathrm{CO_2{}^-}$ and $\mathrm{(CH_3)_2\dot{C}OH}$ radicals. Thus, the intermediates formed upon reaction with $e_{aq}{}^-$ are not necessarily related to those generated in the biological system.

Reactions of H Atoms. A completely different situation exists when the reactive radical is the H atom. Reaction with PN at pH 1 is rapid ($k = 1.9 \times 10^9$ M^{-1} s^{-1}), but electron transfer does not occur, as evidenced by the fact that the resulting transient absorption spectrum is not the same as that produced by the reaction of $\mathrm{(CH_3)_2\dot{C}OH}$ radicals in acidic solution. H atoms, in spite of being strong reductants ($E° = 2.0$ V), add to aromatic ligands[32] to yield a coordinated cyclohexadienyl radical. The H adduct to PN would be isomeric with the protonated reduced coordinated radical, but shows an absorption spectrum similar to that of the H adduct to $\mathrm{Co^{III}O_2CPh^{2+}}$. The difference in λ_{max} reflects the increased conjugation provided by the nitro group causing a decrease in the energy of the electronic transition.

$$\mathrm{Co^{III}O_2CPhNO_2{}^{2+} + H \rightarrow Co^{III}O_2C\dot{P}h(H)NO_2{}^{2+}} \quad (6)$$

The fate of the H adducts is second-order decay, presumably disproportionation.

Intramolecular Electron Transfer. Inasmuch as the reduction of the nitro complexes in neutral solution results in quantitative generation of $\mathrm{Co^{2+}}$ (with the exception of MN which gives on 87% yield), the first-order decay of the intermediate is taken to represent the unimolecular transfer of an electron from the coordinated ligand radical to the metal center. Electron transfer into the e_g acceptor orbital results in the formation of a Co(II) metal center (reaction 7)

$$\mathrm{Co^{III}O_2CPh\dot{N}O_2{}^+ \rightarrow Co^{II}O_2CPhNO_2{}^+} \quad (7)$$

which rapidly undergoes ligand labilization (reaction 5). The values at pH 7.0 given in Table IV therefore represent k_7.

Several things are evident about the values of k_7: firstly, the 3000-fold range of the values is dependent upon the number and position of nitro groups substituted on the aromatic ring and, secondly, the rate of this intramolecular electron transfer is astonishingly slow relative to vibrational motions and electronic transitions. Comparison of the values of k_7 with the redox potentials of the free ligand anion radicals[21] does not reveal any obvious correlation except that internal electron transfer should be facile due to the reducing ability of the coordinated radical. This reducing ability is further demonstrated by its very rapid reaction with O_2 and MQ. On the other hand, the ESR parameters of the nitroaromatic radical anions[21] provide a basis for rationalizing the range of the values of k_7 assuming the spin densities on the free and coordinated ligand radicals are the same. In the mononitrobenzoate radical anions, 50–55% of the spin density is on the nitro group with ~15% on each of the ring carbon atoms ortho to the nitro group, ~16–17% para, and virtually nothing (or negative spin density) meta. Therefore, if the coordinated carboxylate group is ortho or para to the nitro group, a substantial spin density resides adjacent to that group; very little spin density exists there for the meta isomer. As a result, k_7 for MN is the lowest for the mononitrobenzoato complexes. ON and PN would be predicted to have the same values of k_7; the significantly higher rate for ON must be due to other factors. Now for the symmetric 3,5D, the proton splittings for the ortho and para positions (relative to one of the nitro groups) are only slightly higher than those for MN and the sum of the nitrogen splittings slightly lower.[21] As a result, there is a little more spin on the ring of 3,5D compared to MN, although the effect on the carbon adjacent to the carboxylate group is negligible. Hence, k_7 for 3,5D is practically the same as for MN. In 2,4D, ~98% of the nitrogen spin density is on the nitro group para to the carboxylate group; otherwise the proton splittings are virtually the same as those for PN. On this basis, one might expect 2,4D to behave similar to PN except for the contribution of the radical site on the ortho position. Assuming that the ortho radical transfers the electron at the same rate as ON and the para radical the same as PN, the value of k_7 can be rationalized in terms of ~8% contribution from the ortho radical. Considering the crudeness of the model, the order-of-magnitude correlation with the ESR data[21] is probably remarkable.

The relative slowness of intramolecular electron transfer from the coordinated ligand radical into the metal center reflects the low electron permeability of the carboxylate group and, specifically, the lack of overlap of the donor orbitals (π) and the acceptor orbital (σ). Part of the effect may be due to a change in the geometry of the ligand upon reduction, which introduces a Franck–Condon barrier toward electron transfer.[33] In any event, these symmetry and energetic barriers render slow the transfer of the electron from the ligand orbitals into the metal robitals via the π^* orbitals of the lead-in carboxylate group. When the nitro radical is ortho to the carboxylate group, significant orbital overlap can occur, thereby increasing the electron density on the carboxylate group, resulting in an increase in the intramolecular rate. Alternatively, the ortho radical may be in a position to overlap with metal orbitals, thereby facilitating electron transfer. We reject any need to invoke mediation of electron transfer through adjacent ammine ligands.[34]

Reactions of Protonated Intermediates. Protonation of the nitro group on the coordinated radical would be expected to lower the energies of the ligand orbitals, lower the reducing ability of the ligand radical, and substantially reduce the electron spin densities on the ligand and particularly the lead-in carboxylate group. Hence, the rate constant for intramolecular transfer is expected to be diminished. ON is the only complex which shows first-order decay of the reduced intermediate in acidic solution; the yield of Co^{2+} is also quantitative. We conclude that the 40-fold reduction in the rate constant can be attributed to the reduction of spin density on the carboxylate group; k_8 represents an intramolecular reaction not essentially different from those represented by k_7.

$$Co^{III}O_2CPh\dot{N}O_2H^{2+} \rightarrow Co^{II}O_2CPhNO_2H^{2+} \qquad (8)$$

For MN and PN, the corresponding values of k_8 are not experimentally obtainable because the reduced intermediate decays via second-order kinetics under pulse radiolysis conditions, even at relatively low radiation doses (~1 krad/pulse). We would estimate that k_8 for MN and PN are at least a factor of 40 less than k_7; because of the lack of direct overlap of the orbitals of the nitro and carboxylate groups for these complexes according to our model, the factor may be much greater than 40. As a result, the second-order decay of the reduced intermediate,

$$2Co^{III}O_2CPh\dot{N}O_2H^{2+} \rightarrow \text{products} \qquad (9)$$

presumably via disproportionation, is kinetically competitive with reaction 8 under pulse radiolysis conditions where the intermediate concentration is $\sim 10^{-6}$ M. (A discussion of the nature of reaction 9 will be presented in the next section.) Thus, in acidic solution under pulse conditions for all the complexes except ON, k_9[intermediate] > k_8; for ON, $k_8 > k_9$[intermediate]. By extension, in neutral solution reaction 7 is kinetically competitive with the analogue of reaction 9.

The values of k_9 for the dinitro derivatives are significantly greater than those for MN and PN. This can be due to the delocalization of the radical site between the nitro group, thereby providing a statistical and steric advantage for electron transfer via disproportionation. The values of k_9 for the complexes studied are of the same order of magnitude as the disproportionation rate constants of the free ligand radicals in acidic solution.[21]

Formation of Co^{2+}. Under continuous radiolysis conditions, the steady-state concentration of the intermediates is very low ($\sim 10^{-9}$ M), so that the kinetic competition between first- and second-order reactions of the intermediates can be very different than for pulse radiolysis conditions. The relative contributions of first-order intramolecular reactions and second-order intermolecular processes are seen from the effect of pH on the continuous radiolysis yield of Co^{2+}. The yield of Co^{2+} is quantitative when the intermediate decays unimolecularly. In acidic solution, neither MN nor 3,5D yields Co^{2+}, which leads to the conclusion that reaction 9 predominates over reaction 8 for these complexes even under very low steady-state intermediate concentration conditions, and that reaction 9 does not lead to Co^{2+}. The results lead to an estimate of k_8 for MN and 3,5D of $\sim 10^{-2}$ s^{-1} and $k_7/k_8 \sim 10^4$; $k_7/k_8 \sim 40$ for ON. The pH dependence shown by the Co^{2+} yield for these complexes is a result of the change of reaction 9 to reaction 7 as the intermediate is deprotonated (reaction 2). For 2,4D the yield of Co^{2+} is quantitative even in acidic solution, indicating that $k_8 > k_9$[intermediate] so that k_8 could be $\sim 10^1$ s^{-1} or greater. PN provides an intermediate case where in acidic solution the Co^{2+} yield is 77% of the quantitative yield. Thus, $k_8 \approx k_9 \cdot$[intermediate] and $k_8 \sim 10^{-1}$ s^{-1}. It is interesting to note that the estimates of k_8 and the experimentally determined value for ON are in the same relative order as k_7, suggesting the importance of spin densities in establishing the intramolecular electron transfer rate and demonstrating the efficacy of the model proposed here.

The results for MN given in Figure 6 show that in neutral solution containing 2-propanol, the yield of Co^{2+} is 87% of the quantitative value based on the radical stoichiometry. We feel that this deviation is outside experimental error considering the quantitative yields obtained for the other complexes in neutral solution and for MN upon its reaction with CO_2^-. We further believe that the specter of impurities cannot be raised in this case. Aside from the satisfactory microanalysis of the complex, any impurity present would have to scavenge 13% of the $(CH_3)_2\dot{C}OH$ radicals in competition with MN ($k = 1.5 \times 10^9$ M^{-1} s^{-1}). The most probable impurities would be free

MN ligand or $Co(NH_3)_5OH_2^{3+}$. The former compound reacts with $(CH_3)_2\dot{C}OH$ with $k = 9.0 \times 10^8$ M^{-1} s^{-1} [21] and the latter with a rate constant that can be estimated to be $\sim 10^8$ M^{-1} s^{-1} from values for other Co(III)-ammine complexes.[27] Thus, the free ligand would have to be present as a 20% impurity or $Co(NH_3)_5OH_2^{3+}$ as a major constituent. We prefer to attribute the results to the failure of the β-radical, $\cdot CH_2C(CH_3)HOH$, to reduce the MN complex. This β-radical is known[35] to be generated in 13–15% yield upon the reaction of OH radicals with 2-propanol and is a much weaker reducing agent than is the α-radical, $(CH_3)_2\dot{C}OH$. Inasmuch as the free MN ligand has the most negative E' value[21] of the ligands involved in this study, we conclude that the β-radical is capable of transferring an electron to all the coordinated nitrobenzoato ligands except MN.

The spectral changes exhibited by MN upon irradiation at pH 6 in N_2O-saturated 2-propanol solutions (Figure 6) can be now rationalized in terms of the overall mechanism. Reactions 1, 7, and 5 lead to the formation of Co^{2+} and the free ligands; loss of the complex is represented by the decrease of the 503-nm band. The near UV absorption of the complex largely reflects ligand-localized electronic transitions (Figure 7); labilization of the MN ligand would not be expected to lead to absorption changes. The second d–d band of the complex at ~360 nm is only a minor contributor in that region. A decrease in the charge-transfer band of the complex is superimposed upon the high energy intraligand band resulting in slight spectral shifts. On the other hand, in 1 M acid, virtually no spectral changes are seen at all as well as the generation of no Co^{2+}. This is consistent with the products of reaction 9 being Co(III) complexes as the result of the electron-transfer disproportionation reaction. One product is the MN substrate and the other would initially be a nitrosobenzoato complex which would not be expected to have a significantly different absorption spectrum.

$$2Co^{III}O_2CPh\dot{N}O_2H^{2+} \rightarrow Co^{III}O_2CPhNO_2^{2+} + Co^{III}O_2CPhNO^{2+} + H_2O \quad (10)$$

The large spectral changes seen for the free ligand in acidic solution must be indicative of other reaction modes available to the uncomplexed species.

Implications for Cr^{2+} Reduction. The results presented here are relevant to the extensive work by Gould[36] on the Cr^{2+} reduction of the mononitrobenzoatopentaamminecobalt(III) complexes in 1.2 M acid. Cr^{2+} (1 equiv) did not result in the formation of any Co^{2+} for MN and PN; 15% yield of Co^{2+} came from ON. In addition, reduction of PN and MN gave rise to intensely colored stable intermediates which were attributed to Cr-bound species. The question raised was the proportion of the Cr^{2+} reaction that occurs by initial reduction of the ligand via electron transfer (outer-sphere) and the proportion by Cr binding to the ligand (inner-sphere). Although our results do not contribute to the clarification of the nature and subsequent chemistry of the Cr-bound intermediates, our radiolytically-generated reduced species should be the same as those resulting from direct outer-sphere electron transfer from Cr^{2+}. Thus, irrespective of the mode of Cr^{2+} reduction, we can see that no Co^{2+} should result from the reduction of MN in 1.2 M acid. However, Co^{2+} is a product of the radiolytic reduction of PN in acidic solution through a competition between reactions 8 and 9. If the rate of electron transfer from Cr^{2+} to PN were rapid so that a modestly high ($\sim 10^{-6}$ M) initial concentration of the reduced species were formed, then the rate of reaction 9 would be greater than the rate of reaction 8 and no Co^{2+} would result. However, Co^{2+} is rapidly and quantitatively released from the reduction of ON in acidic solution so that any radical species from the Cr^{2+} reduction would yield Co^{2+}. We wish to suggest that the 15% yield of Co^{2+} from ON that Gould observed represents the proportion of the Cr^{2+} reduction that occurs via direct electron transfer with 85% occurring via Cr binding. The increased yield of Co^{2+} (10%) from PN in 0.012 M acid is obviously a direct result of reactions 2 and 7 being operative to some extent at that pH.

Conclusions

The rate at which an electron is transferred intramolecularly from a coordinated aromatic ligand radical into the metal center appears to depend upon the electron spin density at or adjacent to the lead-in group. Especially facile internal electron transfer for ortho isomers is to be expected due to orbital overlap between the ortho radical group and the lead-in group. The relatively slow rate of electron transfer in Co(III) complexes appears to be due to the poor overlap of the π orbitals of the ligand with the σ acceptor orbital of the metal center. No need is seen to invoke electron mediation through ammine ligands.

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References and Notes

(1) (a) The support of this research by the National Science Foundation through Grant No. MPS73-05025 is gratefully acknowledged. Aspects of the work were presented at the XIV International Coordination Chemistry Conference, Toronto, Ontario, June 1972, p 501. (b) Visiting Professor, Boston University, 1975.
(2) For example, L. E. Bennett, *Prog. Inorg. Chem.*, **18,** 1 (1973).
(3) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, N.Y., 1970.
(4) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86,** 1318 (1964); E. S. Gould, *ibid.*, **87**, 4730 (1965); F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).
(5) E. S. Gould, *J. Am. Chem. Soc.*, **94,** 4360 (1972); A. Zanella and H. Taube, *ibid.*, **94,** 6403 (1972).
(6) E. S. Gould, *J. Am. Chem. Soc.*, **96,** 2373 (1974).
(7) R. D. Cannon and J. Gardiner, *J. Am. Chem. Soc.*, **92,** 3800 (1970).
(8) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96,** 7845 (1974); J-J. Jwo and A. Haim, *ibid.*, **98,** 1172 (1976).
(9) S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95,** 8198 (1973).
(10) M. Z. Hoffman and M. Simic, *J. Am. Chem. Soc.*, **94,** 1757 (1972).
(11) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Am. Chem. Soc.*, **93,** 5661 (1971).
(12) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73,** 3794 (1969).
(13) J. H. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, **64,** 2398 (1968).
(14) M. S. Matheson and L. M. Dorfman, "Pulse Radiolysis", The M.I.T. Press, Cambridge, Mass., 1969.
(15) R. E. Kitson, *Anal. Chem.*, **22,** 664 (1950).
(16) *G* = number of radicals or ions produced per 100 eV of energy absorbed by the solution.
(17) R. L. Willson, C. L. Greenstock, G. E. Adams, R. Wageman, and L. M. Dorfman, *Int. J. Radiat. Phys. Chem.*, **3,** 211 (1971).
(18) M. Anbar, M. Bambenek, and A. B. Ross, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 43,** 1 (1972).
(19) L. M. Dorfman and G. E. Adams, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 46,** 1 (1973).
(20) P. Neta, *Chem. Rev.*, **72,** 533 (1972).
(21) P. Neta, M. G. Simic, and M. Z. Hoffman, *J. Phys. Chem.*, **80,** 2018 (1976).
(22) P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, **73,** 4207 (1969).
(23) E. Hayon and M. Simic, *J. Am. Chem. Soc.*, **95,** 1029 (1973).
(24) H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 2478 (1975).
(25) E. J. Hart and M. Anbar, "The Hydrated Electron", Wiley, New York, N.Y., 1972.
(26) M. Z. Hoffman and M. Simic, *Inorg. Chem.*, **12,** 2471 (1973).
(27) H. Cohen and D. Meyerstein, private communication of unpublished results.
(28) M. Simic and J. Lilie, *J. Am. Chem. Soc.*, **96,** 291 (1974).
(29) J. E. Martin, E. J. Hart, A. W. Adamson, H. Gafney, and J. Halpern, *J. Am. Chem. Soc.*, **94,** 9238 (1972).
(30) A. F. Vaudo, E. R. Kantrowitz, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, *J. Am. Chem. Soc.*, **94,** 6655 (1972); E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, **76,** 2492 (1972).
(31) J. F. Endicott in "Concepts in Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, Chapter 3.
(32) M. Simic and M. Z. Hoffman, *J. Phys. Chem.*, **76,** 1398 (1972).
(33) P. Natarajan and J. F. Endicott, *J. Am. Chem. Soc.*, **94,** 5909 (1972).
(34) H. Cohen and D. Meyerstein, private communication quoted by R. J. Balahura, *J. Am. Chem. Soc.*, **98,** 1487 (1976).
(35) M. Simic and E. Hayon, *Int. J. Radiat. Biol.*, **22,** 507 (1972); *Biochem. Biophys. Res. Commun.*, **50,** 364 (1973); K.-D. Asmus, H. Möckel, and A. Henglein, *J. Phys. Chem.* **77,** 1218 (1973).
(36) E. S. Gould, *J. Am. Chem. Soc.*, **88,** 2983 (1966).