Oxidation of Benzoatopentaamminecobalt(III) by Hydroxyl Radicals

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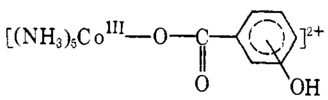
Abstract: The reaction of hydroxyl radicals with benzoatopentaamminecobalt(III) yields a radical formed by the addition of the OH to the aromatic ring. The spectrum of the radical formed is very similar to that formed by the reaction of OH radicals with free benzoate ions. The specific rates of formation and disappearance of the radical were measured. The disappearance follows a second-order mechanism. The yield of Co^{2+} depends on the steady-state concentration of the radicals formed and is always considerably less than one, based on the concentration of OH radicals introduced. It is concluded that the overlap between the orbitals on the central Co(III) atom and the conjugated double bond system of the radical is small. Furthermore, if an inner-electron transfer from the radical to the central Co(III) atom takes place, the specific rate of this reaction is less than 10^2 sec^{-1}.

The reduction of cobalt(III) complexes of the type $Co^{III}(NH_3)_5L$, where L is an organic ligand with a system of conjugated double bonds, by attack of a reductant at a remote site on L has been the subject of several recent studies.[1] It has been concluded that electron transfer from the reductant through the conjugated double bond system to the central Co(III) atom takes place. It has been suggested[1] that the mechanism of these reactions involves bonding of the reductant, R, to the remote site on L, forming a complex of the type $(NH_3)_5Co^{III}LR$, followed by reduction of the ligand L by R forming $(NH_3)_5Co^{III}L^{-}R^{+}$, and finally reduction of the central Co(III) atom. However, the intermediate $(NH_3)_5Co^{III}L^{-}R^{+}$ has not been observed.

It has been shown that the oxidation of complexes of the type $Co^{III}(NH_3)_5L$ by external one-electron oxidizing agents yields in several cases as one of the final products Co^{2+}.[2-6] It has been suggested that the first step in the oxidations of *p*-hydroxymethylbenzoatopentaamminecobalt(III)[5] and of pentaammine(pyridinemethanol)cobalt(III)[6] is the formation of a radical on the methanolic group of the type $Z\text{-}\dot{C}HOH$. The results indicated that the central Co(III) atom may oxidize this radical to an aldehyde group *via* the system of conjugated double bonds, and that the lifetime of the radical is of the order of 10^7 sec. Also in this case the intermediate radicals could not be observed.

It seemed of interest to form an organic radical on a site conjugated by double bonds to a central Co(III) atom and to study its properties. A convenient method for the production of such a radical in a concentration high enough to be physically observed is the pulse radiolysis technique.

We have chosen to study radical I, formed by the oxidation of benzoatopentaamminecobalt(III) with hydroxyl radicals, as all the radicals formed are nearly identical and all are conjugated to the central Co(III) atom.



I

Experimental Section

Materials. All solutions were prepared from triply distilled water.

Benzoatopentaamminecobalt(III) as the perchlorate salt was prepared according to the procedure described by Robson and Taube[5] for the synthesis of *p*-hydroxymethylbenzoatopentaamminecobalt(III). *Anal.* Calcd for $C_7H_{20}N_5O_{10}Cl_2Co$: C, 18.11; H, 4.34; N, 15.07; Cl, 15.28. Found: C, 17.84; H, 4.45; N, 14.60; Cl, 14.37.

NH_4CNS, Merck AR grade, was dissolved in triply distilled water to yield a 6 *M* solution, filtered, and then further purified by extraction with methyl isobutyl ketone to eliminate iron impurities.

Nitrous oxide, Matheson, was purified from oxygen by bubbling through three washing bottles containing basic pyrogallol solutions and then through two washing bottles containing triply distilled water.

All other materials were of AR grade and were used without further treatment. pH was controlled by adding perchloric acid.

Procedure. The procedure of preparation of samples for the pulse radiolysis experiments was identical with that described earlier in detail.[7,8] The pulse radiolysis experiments were carried out using 0.1–1.3-μsec, 5-MeV, 200-mA pulses from the linear accelerator at the Hebrew University of Jerusalem. The dose per pulse was $1\text{-}10 \times 10^{19}$ eV l.$^{-1}$. The formation and disappearance of the intermediate were followed at 345 nm unless otherwise stated. The irradiation cell was 2 or 4 cm long, the analyzing light traveling three times through the cell. The experimental setup in Jerusalem and the method used for evaluating the results have been described elsewhere in detail.[9]

Low-dose-rate irradiations were carried out using a ^{60}Co γ-ray source (Gammacell 200, Atomic Energy Commission of Canada Ltd.). The dose rate was of the order of 3×10^{20} eV l.$^{-1}$ min^{-1}. The samples, in uniform test tubes, were saturated with N_2O or Ar by bubbling through a capillary and sealed with a rubber stopcock.

Dosimetry of the ^{60}Co source was carried out by the Fricke dosimeter.[10] The dose delivered by the linear accelerator was determined by the modified Fricke dosimeter for high dose rates.[11]

The yield of Co^{2+} was determined by the method described by Allen and Katakis.[12]

Spectrophotometric determinations were carried out using a Cary 14 for measuring the spectra of products and a Hilger Uvispec or a Beckman DB spectrophotometer for determining yields.

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(1) H. Taube and S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).
(2) P. Saffir and H. Taube, *J. Amer. Chem. Soc.*, **82**, 13 (1960).
(3) R. T. M. Fraser and H. Taube, *ibid.*, **82**, 4152 (1960).
(4) J. P. Candlin and J. Halpern, *ibid.*, **85**, 2518 (1963).
(5) R. Robson and H. Taube, *ibid.*, **89**, 6487 (1967).
(6) J. E. French and H. Taube, *ibid.*, **91**, 6951 (1969).
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(9) Internal Report of the Accelerator Laboratory, Hebrew University, Jerusalem, Israel.
(10) J. Weiss, A. O. Allen, and H. A. Schwarz, *Proc. Int. Conf. Peaceful Uses At. Energy*, 14, 179 (1956).
(11) J. K. Thomas and E. J. Hart, *Radiat. Res.*, **17**, 408 (1963).
(12) D. Katakis and A. O. Allen, *J. Phys. Chem.*, **68**, 1359 (1964).

Table I. Yield of Intermediates Formed by the Pulse[a]

	Additive				
	N_2O, pH 6.0	Ar, pH 6.0	N_2O, pH 6.0, 1 × 10^{-2} *M* CH_3OH	Ar, pH 1.0	Ar, pH 1.0, 1 × 10^{-2} *M* CH_3OH
Exptl	5.7 ± 0.5	3.3 ± 0.3	1.0 ± 0.15	7.2 ± 0.6	4.2 ± 0.4
Calcd[b]	5.7	3.2	1.1	6.6	3.6
Calcd[c]	5.1	2.6	0.6	3.2	0.4

[a] All solutions contained 1 × 10^{-4} *M* $[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$. The pulse intensity was 2.1 × 10^{16} eV ml^{-1}. The yields were measured at 345 nm assuming ϵ_{345} 3700 M^{-1} cm^{-1}. [b] Calculated yields assuming that both OH radicals and H atoms react with the complex yielding an absorbing intermediate. The following specific rates of reaction were used: $k_{OH+[Co(NH_3)_5O_2CC_6H_5]^{2+}} = 6.4 \times 10^9$ M^{-1} sec^{-1}, $k_{H+[Co(NH_3)_5O_2CC_6H_5]^{2+}} = 1.6 \times 10^9$ M^{-1} sec^{-1}, $k_{e_{aq}^{-}+[Co(NH_3)_5O_2CC_6H_5]^{2+}} = 6.0 \times 10^{10}$ M^{-1} sec^{-1}, $k_{e_{aq}^{-}+N_2O} = 5.9 \times 10^9$ M^{-1} sec^{-1}, $k_{OH+CH_3OH} = 5 \times 10^8$ M^{-1} sec^{-1}, and $k_{H+CH_3OH} = 1.6 \times 10^6$ M^{-1} sec^{-1}. [c] Calculated yields assuming that only OH radicals contribute to the formation of the absorbing intermediate.

Results

The absorption spectrum of the intermediates formed by a pulse of 2.5 × 10^{16} eV/ml in a N_2O-saturated solution containing 1 × 10^{-4} *M* $[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$ at pH 6.0 was measured and found to have a maximum at 345 ± 5 nm (Figure 1). The absolute absorption coefficient, ϵ_{max} (3.7 ± 0.5) × 10^3 M^{-1} cm^{-1}, was determined by comparison with the yield of $Fe(CN)_6^{3-}$ formed by an identical pulse in an N_2O-saturated solution containing 1 × 10^{-3} *M* $K_4Fe(CN)_6$. It was assumed that the yield of the intermediates in the first solution was equal to the $Fe(CN)_6^{3-}$ yield. The absorption spectra of the intermediates formed by a pulse of 5 × 10^{16} eV/ml in an Ar-saturated solution containing 1 × 10^{-4} *M* $[Co(NH_3)_5O_2CC_6H_5]^{2+}$ at pH 6.0 and in an Ar-saturated solution at pH 1.0 containing 1 × 10^{-4} *M* $[Co(NH_3)_5O_2CC_6H_5]^{2+}$ and 1 × 10^{-2} *M* methanol were also measured (Figure 1). The absolute absorption coefficients in these cases were fitted so that the spectra should best fit Figure 1. For comparison the absorption spectrum of the intermediates formed by a pulse of 2.5 × 10^{16} eV/ml in a N_2O-saturated solution containing 1 × 10^{-4} *M* $NaO_2CC_6H_5$ at pH 7.0 was measured (Figure 1) and found to be in good agreement with the results reported in the literature.

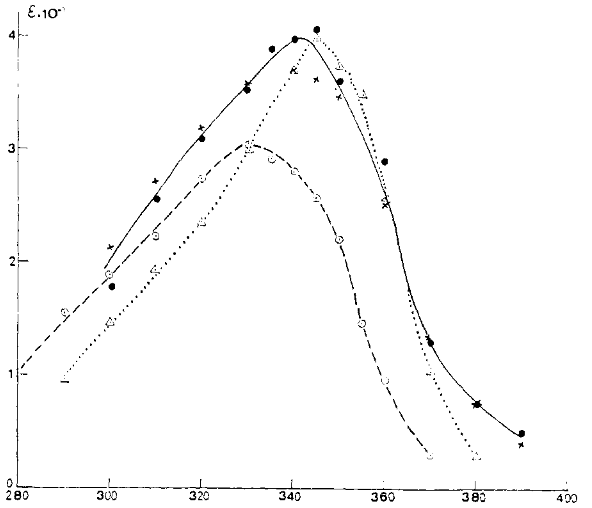

Figure 1. Absorption spectra of the intermediates formed by pulse radiolysis of the following solutions: ×, 1 × 10^{-4} *M* $[(NH_3)_5Co^{III}O_2CC_6H_5](ClO_4)_2$, pH 6.0, N_2O saturated; ●, 1 × 10^{-4} *M* $[(NH_3)_5Co^{III}O_2CC_6H_5](ClO_4)_2$, pH 6.0, Ar saturated (the height of the band has been adjusted so that the absorption at 330 nm would be identical with that in the N_2O-saturated solution); △, 1 × 10^{-4} *M* $[(NH_3)_5Co^{III}O_2CC_6H_5](ClO_4)_2$, 1 × 10^{-2} *M* methanol, pH 1.0, Ar saturated (the height of the band has been adjusted so that the absorption at 340 nm would be identical with that in the N_2O-saturated solution); ○, 1 × 10^{-4} *M* sodium benzoate, pH 7.0, N_2O saturated.

In order to identify the intermediates formed, the optical density at 345 nm immediately after their formation ended was measured in the presence of different scavengers. The pulse intensity in these experiments was 2.1 × 10^{16} eV/ml. The yields of the intermediates formed, assuming ϵ_{345} 3700 M^{-1} cm^{-1}, in the presence of N_2O, Ar, methanol, and H_3O^+ were calculated. The results are summarized in Table I.

The specific rate of the reaction

$$OH + Co(NH_3)_5O_2CC_6H_5^{2+} \longrightarrow \text{radical I} \qquad (1)$$

was measured by two techniques: (a) by following the rate of formation of the absorption due to radical I at 345 nm in neutral N_2O-saturated solutions containing different concentrations of the complex and (b) by competition between reactions 1 and 2, assuming k_2 =

$$OH + CNS^- \longrightarrow CNS \qquad (2)$$

$$CNS^- + CNS \longrightarrow (CNS)_2^- \qquad (3)$$

2.0 × 10^{10} M^{-1} sec^{-1},[13] and observing the absorption due to $(CNS)_2^-$ at 500 nm.[14] The results are summarized in Table II. It is concluded that k_1 = (6.4 ±

Table II. Specific Rate of Reaction of OH Radicals with the Complex[a]

$[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$, *M*	$[CNS^-]$, *M*	$k_1 \times 10^{-9}$ M^{-1} sec^{-1}	Method used[b]
1 × 10^{-5}		6.7 ± 1	a
3 × 10^{-5}		6.3 ± 1	a
1 × 10^{-4}		6.5 ± 1	a
5 × 10^{-5}	7 × 10^{-5}	7.0 ± 1	b
1 × 10^{-4}	7 × 10^{-5}	6.0 ± 0.6	b
2 × 10^{-4}	7 × 10^{-5}	6.0 ± 0.6	b
2 × 10^{-4}	2 × 10^{-4}	6.0 ± 0.6	b
3 × 10^{-4}	2 × 10^{-4}	6.3 ± 0.6	b

[a] Pulse intensities used, 2–2.5 × 10^{16} eV ml^{-1}. [b] (a) Measured by following the formation of the intermediates at 345 nm in N_2O-saturated solutions. (b) Measured by competition with CNS^- observing the yield of $(CNS)_2^-$ at 500 nm in O_2-saturated solutions.

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(13) J. H. Baxendale and D. A. Stott, *Chem. Commun.*, 1699 (1967).

(14) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael in "Pulse Radiolysis," J. H. Baxendale, M. Ebert, J. P. Keene, and A. J. Swallow, Ed., Academic Press, New York, N. Y., 1965, p 131.

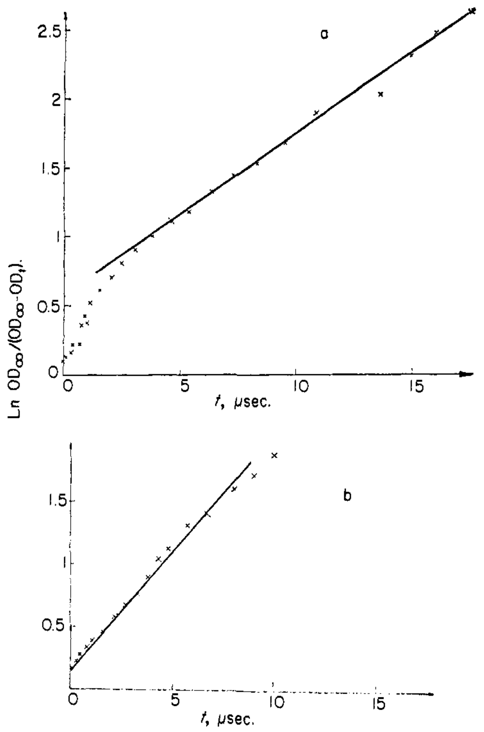
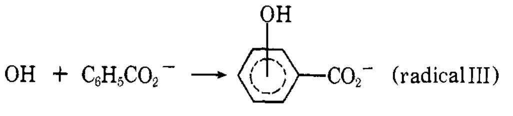


Figure 2. First-order formation plot of the intermediates formed by a 2.5 × 10^{16} eV ml^{-1} pulse to (a) Ar-saturated solution containing 1 × 10^{-4} M $[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$ at pH 1.0, (b) Ar-saturated solution containing 1 × 10^{-4} M $[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$ and 1 × 10^{-2} M CH_3OH at pH 1.0.

0.6) × 10^9 M^{-1} sec^{-1}. For comparison the specific rate of reaction

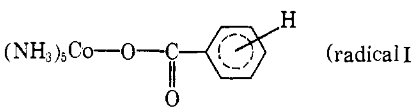


(4)

was measured by technique a and found to be k_4 = (5.7 ± 0.6) × 10^9 M^{-1} sec^{-1}. The latter value is higher than that found in the literature,[15] but this is based on k_2 = 6.6 × 10^9 M^{-1} sec^{-1} and should therefore be corrected.[13]

The specific rate of reaction of hydrogen atoms with the complex

$$H + Co(NH_3)_5O_2CC_6H_5{}^{2+} \longrightarrow$$



(5)

was measured by two techniques. (a) The rate of formation of the intermediates at 345 nm in Ar-saturated solutions containing 2–10 × 10^{-5} M $[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$ at pH 1.0 was followed. The first-order plot of the results (Figure 2a) shows two distinct parts, a fast reaction attributed to the OH radicals followed by a slower reaction with k_5 = (1.4 ± 0.3) × 10^9 M^{-1} sec^{-1} attributed to reaction 5. (b) The rate of formation of the products in an Ar-saturated solution at pH 1.0 containing 1 × 10^{-2} M CH_3OH and 2–10 × 10^{-5} M $[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$ was followed.

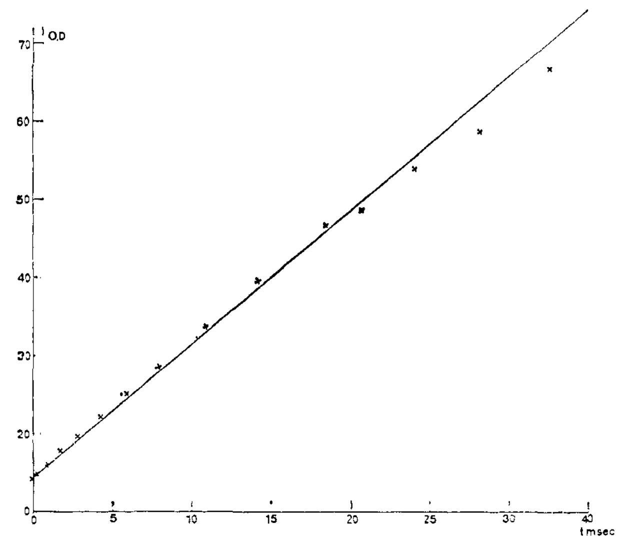


Figure 3. Second-order disappearance plot for radical I. Solution composition: 1 × 10^{-4} M $[(NH_3)_5Co^{III}O_2CC_6H_5](ClO_4)_2$, pH 6.0, N_2O saturated.

Under these conditions nearly all of the OH radicals react with the methanol, whereas nearly all of the H atoms react with the complex.[15] Therefore, only one reaction is observed (Figure 2b), for which k_5 = (1.6 ± 0.4) × 10^9 M^{-1} sec^{-1} was calculated.

The disappearance of radical I in Ar- and N_2O-saturated solutions was followed and found to obey a second-order mechanism (Figure 3). The specific rate of this reaction was found to be $2k$ = (6.5 ± 0.6) × 10^7 M^{-1} sec^{-1} for a solution containing 1 × 10^{-4} M of the complex and $2k$ = (3.7 ± 0.4) × 10^8 M^{-1} sec^{-1} in a solution containing 0.1 M $NaClO_4$ in addition to the complex. An experiment to plot the results according to a first-order mechanism shows that any first-order disappearance reaction of radical I has to be slower than 10^2 sec^{-1}. The disappearance of the mixture of radicals I and II formed at pH 1 also followed a second-order mechanism with $2k$ = (4.0 ± 0.5) × 10^8 M^{-1} sec^{-1}. The difference in the rates between neutral and acid solutions is evidently mainly due to the changes in the ionic strength of the solution. The disappearance of the radical $C_6H_5(OH\cdot)CO_2^-$ in neutral solutions containing 1 × 10^{-4} M $NaO_2CC_6H_5$ was also found to follow a second-order mechanism, with $2k$ = (3.9 ± 0.4) × 10^8 M^{-1} sec^{-1}. The specific rate of disappearance of radical I was independent of the wavelength at which it was measured. However, on the uv side of the band a residual absorption seemed to remain and at 300 nm nearly no disappearance reaction was observed. The spectra of the solutes was, therefore, recorded long after irradiation (Figure 4) and it was found that the stable products caused a small shoulder around 290 nm on the absorption band of the parent complex. This spectrum was not changed by allowing the solutions to stand for 24 hr. The nature of the product causing this shoulder was not elucidated, as it could not be formed at concentrations higher than 1 × 10^{-5} M (as the rate of disappearance of the intermediates was increased after ten pulses (2.5 × 10^{16} eV ml^{-1} $pulse^{-1}$) were delivered to the solution).

The yield of Co^{2+} formed as a stable product after the chemical reactions induced by the radiation ended was

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(15) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, 18, 493 (1967).

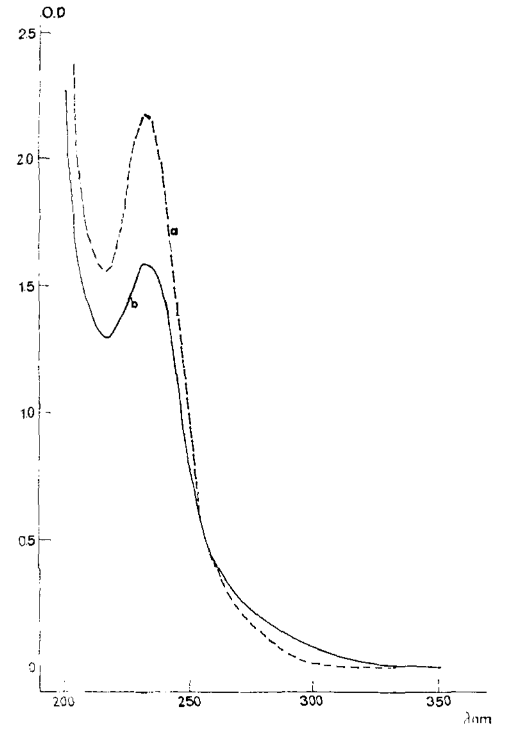


Figure 4. Absorption spectra of the solutions before and after irradiation. Solution composition: 1 × 10^{-4} M $[(NH_3)_5Co^{III}O_2CC_6H_5](ClO_4)_2$, pH 6.0, N_2O saturated. The spectra below 250 nm were measured after dilution by a factor of 2. (a) Before irradiation, (b) after irradiation of ~10^4 rads by the linac. Identical after 1 and 24 hr.

measured. The effect of dose rate on this yield was determined by using two radiation sources: (a) the linear accelerator with a dose rate of ~3 × 10^{27} eV min^{-1} and (b) a Co^{60} source with a dose rate of 3 × 10^{20} eV l.^{-1} min^{-1}. The results are summarized in Table III.

Table III. Co^{2+} Yields[a]

Gas present	Additive	Radiation source	$G_{Co^{2+}}$
N_2O		Linac	0.7
N_2O		Linac	0.9[b]
N_2O		^{60}Co	1.6
Ar		Linac	2.4
Ar		^{60}Co	2.9
N_2O	1 × 10^{2} M CH_3OH	Linac	3.4
N_2O	1 × 10^{-2} M CH_3OH	^{60}Co	3.7
N_2O	1 × 10^{-1} M CH_3OH	^{60}Co	4.6

[a] All solutions contained 1 × 10^{-4} M $[(NH_3)_5Co(III)O_2CC_6H_5](ClO_4)_2$ and were at pH 6.0. The error limit on $G_{Co^{2+}}$ is ± 0.2. [b] 2 × 10^{-4} M complex.

Discussion

The radiolysis of water may be described by

$$H_2O \xrightarrow{\gamma,\ e^-} e_{aq}^-,\ H,\ OH,\ H_2,\ H_2O_2,\ H_3O^+ \qquad (6)$$

the yields of the products in neutral solutions being[16] $G_{e_{aq}^-} = 2.6$, $G_{OH} = 2.65$, $G_H = 0.6$, $G_{H_2O_2} = 0.75$, and $G_{H_2} = 0.45$. (G is defined as the number of molecules of product formed by absorption of 100 eV by the sample.) The hydrated electron reacts with N_2O according to

$$\begin{aligned} N_2O + e_{aq}^- &\xrightarrow{k_7} N_2 + O^- \\ O^- + H_2O &\longrightarrow OH + OH^- \end{aligned} \qquad (7)$$

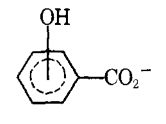
the specific rate of reaction 7 being $k_7 = 5.6 \times 10^9$ M^{-1} sec^{-1}.[15] In neutral solutions saturated with 2 × 10^{-2} M N_2O, the yield of OH is, therefore, increased to $G(OH) = G_{e_{aq}^-} + G_{OH} = 5.25$. (A somewhat higher yield is plausible owing to the effect of N_2O on G_{H_2}.[17]) The hydrated electron reacts also with H_3O^+ according to

$$H_3O^+ + e_{aq}^- \xrightarrow{k_8} H \qquad (8)$$

the specific rate of reaction being $k_8 = 2.3 \times 10^{10}$ M^{-1} sec^{-1}.[15] Therefore, in acid solutions all the hydrated electrons are transformed into hydrogen atoms.

The specific rates of reaction of the hydrated electron with Co(III) complexes are diffusion controlled, all being in the range of 4–9 × 10^{10} M^{-1} sec^{-1}.[18] On the other hand, the reaction of hydrogen atoms with $Co(NH_3)_6^{3+}$ is relatively slow, $k_{H+Co(NH_3)_6^{3+}} = 1.7 \times 10^6$ M^{-1} sec^{-1}.[19–21] Hydrogen atoms reduce other Co(III) complexes *via* the inner-sphere mechanism[19–21] with higher specific rates of reaction. It has been suggested that in some cases the high specific rates of reaction of H atoms with Co(III) complexes are due to reaction with the ligand and not with the central cobalt atom.[21] Specific rates of reaction of OH radicals with Co(III) complexes have not been reported; however, it has been suggested that the specific rate of reaction of OH with $Co(NH_3)_6^{3+}$ is relatively low.[12]

The specific rates of reaction of hydrogen atoms and hydroxyl radicals with benzoic acid and its derivatives are high. It was therefore expected that in neutral N_2O-saturated solutions containing less than 1 × 10^{-4} M $[Co(NH_3)_5O_2CC_6H_5](ClO_4)_2$, the OH radicals, $G_{OH} \simeq 5.2$, and the H atoms, $G(H) \simeq 0.6$, would react with the benzoate ligand. Under these conditions over 92% of the e_{aq}^-'s react with N_2O. This expectation is confirmed by the following results. (a) The spectra of the intermediates formed under these conditions, λ_{max} 345 ± 5 nm, ϵ_{max} (3.7 ± 0.5) × 10^3 M^{-1} cm^{-1}, and half-band width 70 nm are very similar to those of



(radical III), for which the corresponding values are λ_{max} 335 ± 5 nm, ϵ_{max} (3.0 ± 0.4) × 10^3 M^{-1} cm^{-1}, and half-width ~50 nm (Figure 1). A similar spectrum is obtained in Ar-saturated acid solutions, indicating that the spectrum of radical II is similar to that of radical I. (b) The yields of the intermediates formed assuming that the molar extinction coefficients of radical I and radical II are identical in the presence of different scavengers are in good agreement with those calculated assuming that both OH and H react with the complex

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[16] M. S. Matheson and L. M. Dorfman, "Pulse Radiolysis," MIT Press, Boston, Mass., 1969.

(17) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, 61, 492 (1965).

(18) D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 73, 1091 (1969).

(19) G. Navon and G. Stein, *ibid.*, 69, 1391 (1965).

(20) M. Anbar and D. Meyerstein, *Nature (London)*, 206, 818 (1965).

(21) J. Halpern and J. Rabani, *J. Amer. Chem. Soc.*, 88, 699 (1966).

(Table I). The scavengers in these experiments, N_2O, CH_3OH, and H_3O^+, and their concentrations were chosen so that in each experiment one of the primary radicals formed, e_{aq}^-, H, or OH, was scavenged, whereas the rest were unaffected. Thus N_2O scavenges e_{aq}^-, producing OH radicals, H_3O^+ scavenges e_{aq}^-, producing H atoms, and CH_3OH in the concentration used scavenges nearly all the OH radicals, producing CH_2OH radicals, but still does not compete seriously with the reaction of H atoms with the complex.[14] The agreement between the observed and calculated yields also indicates that the products of the reactions of e_{aq}^- and CH_2OH with the complex do not absorb at 345 nm. (c) The specific rate of reaction of the hydroxyl radicals with the complex, $k_1 = 6.4 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, is very similar to $k_{OH+C_6H_6CO_2^-} = 5.7 \times 10^9\ M^{-1}$ sec. On the other hand, $k_{OH+Co(NH_3)_6^{3+}} < 2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ (determined by competition with CNS^-) is much lower than k_1. Furthermore, the specific rate of reaction of hydrogen atoms with the complex, $k_5 = 1.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, resembles $k_{H+C_6H_5CO_2^-} = 8.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$[15] and is much higher than $k_{H+Co(NH_3)_6^{3+}} = 1.6 \times 10^6\ M^{-1}\ \text{sec}^{-1}$.[18-21] The fact that the specific rates of reaction of both OH radicals and H atoms with the complex are much higher than those for the corresponding reactions with $Co(NH_3)_6^{3+}$ and are similar to their specific rates of reaction with benzoate ions indicates that the radicals react with the complex *via* the aromatic ring of the ligand and not with the $(NH_3)_5Co^{III}$ group.

It is therefore concluded that the mechanism of reaction of hydroxyl radicals and hydrogen atoms with the complex involves in the first stage addition to the π system of the system of the benzoate ligand, forming radicals I and II. The results also indicate that the central cobalt ion has only minor effects on the reactivity of the benzoate ligand toward these radicals, as well as on the spectra of the intermediates formed. Therefore, it is suggested that there is nearly no overlap between the orbitals of the central Co(III) atom and the conjugated double bond system of the radical.

The fact that radical I in neutral solutions as well as the mixture of radicals I and II disappear *via* a second-order mechanism indicates that no intramolecular oxidation of these radicals by the central Co(III) ion takes place. In fact, it can be shown from the results that the specific rate of the latter reaction has to be less than 10^2 sec^{-1}.

This conclusion is corroborated by the low yields of Co^{2+} formed under high-dose-rate conditions (Table III). It is evident from the yields in Ar-saturated solutions that all the hydrated electrons reacting with $Co(NH_3)_5O_2CC_6H_5^{2+}$ yield Co^{2+}. Part of the yield in N_2O-saturated solutions is due to the competition between the reaction of e_{aq}^- with the complex and with N_2O; this can be seen from the effect of complex concentration on $G(Co^{2+})$ and calculated from the known corresponding rates of reaction. It is concluded that $G(Co^{2+})$ due to OH reaction is of the order of 0.4–05 under the high-dose-rate conditions, or 8% of the OH yield. Even the latter value might be too high, as we have noticed that the mechanism of disappearance of radical I is changed after 10 pulses (see above), and these yields were measured after 20 pulses (owing to the low G value).

Under low-dose-rate conditions $G(Co^{2+})$ in N_2O-saturated solutions is much higher, being about 25% of G_{OH}. This can be interpreted as proving that under these conditions internal electron transfer takes place. However, the possibility that under these conditions the reaction of radical I with the products of reaction begins to contribute at lower concentrations of products cannot be ruled out.

The increased yield of Co^{2+} in the presence of methanol is believed to be due to the reaction

$$\cdot CH_2OH + Co(NH_3)_5O_2CC_6H_5^{2+} \longrightarrow CH_2O + Co^{2+} + 5NH_3 + C_6H_5CO_2^- + H_3O^+ \quad (9)$$

The parallel reaction

$$\cdot CH_2OH + Co(NH_3)_6^{3+} \xrightarrow{k_{10}} CH_2O + Co^{2+} + 6NH_3 + H_3O^+ \quad (10)$$

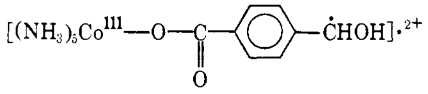
has been observed,[22] the specific rate of reaction being $k_{10} = 1.8 \times 10^8\ M^{-1}\ \text{sec}^{-1}$.[23] The effect of CH_3OH concentration on $G(Co^{2+})$ is due to the competition between the reactions of OH radicals with the complex and with methanol. The dose rate effect on $G(Co^{2+})$ in this case is due to the competition between reactions 9 and 11.

$$\cdot CH_2OH + CH_2OH \xrightarrow{k_{11}} HOCH_2CH_2OH \quad (11)$$

$$2k_{11} = 2.4 \times 10^9\ M^{-1}\ \text{sec}^{-1}\ {}^{24}$$

The fact that the specific rates of reduction of Co(III) complexes by $R\dot{C}HOH$ radicals are high[23] suggests that this reaction might contribute also to the mechanism of oxidation of *p*-hydroxymethylbenzoatopentaamminecobalt(III)[5] and of pentaammine(pyridinemethanol)cobalt(III).[6]

It has to be concluded that the intramolecular electron-transfer reaction in radical I is slow, $k < 10^2\ \text{sec}^{-1}$, though it seems to occur. The relative low rate of this reaction in comparison with that suggested for the parallel reaction in the radical[5]



might be explained by the fact that radicals of the type $R\dot{C}HOH$ are much stronger reducing agents than phenyl radicals. We are not fully satisfied with this explanation and plan to study the chemical properties of other radicals bound to a Co(III) central atom with hope of getting a better understanding of the factors influencing the specific rates of intramolecular electron transfer reactions.[25]

Acknowledgments. The authors are indebted to Professor F. S. Klein for his encouragement and discussions throughout this work. We wish to thank Mr. J. Ogdan for his careful operation of the linear accelerator and the electronic equipment.

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