Comparison Between the Inter- and Intra-molecular Kinetics of Reduction of Penta-ammine(ligand)cobalt(III) Complexes by the *para*-Nitrobenzoate Radical: A Pulse-radiolytic Study

By **Haim Cohen** and **Dan Meyerstein**,* Chemistry Department, Nuclear Research Centre Negev, Beer-Sheva, Israel

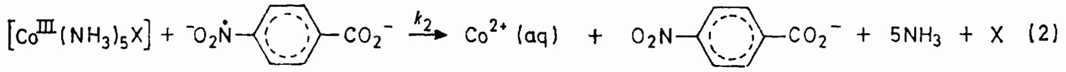
Second-order rate constants for reduction by the *p*-nitrobenzoate radical of the complexes $[Co^{III}(NH_3)_5X]$ [X = NH_3, $PhCO_2^-$, *p*-$O_2NC_6H_4CO_2^-$, Br^-, pyridine (py), and *m*-$H_2NCOC_5H_4N$] have been measured and are in the range 10^5—10^7 l mol^{-1} s^{-1}. The rates of the first three reactions are considerably faster than those expected from the intramolecular rate of electron transfer in $[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2^-p)]^+$ and suggest poor 'electron permeability' of the carboxylate group.

THE rate constant for the intramolecular electron-transfer reaction (1) has been recently measured.[1] This is the

$$[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^+ \longrightarrow Co^{2+}(aq) + 5NH_3 + p\text{-}O_2NC_6H_4CO_2^-; \quad k_1 = 2.6 \times 10^3\ s^{-1} \quad (1)$$

first study reporting the rate of reduction of a central cation by a ligand bound to the metal by a carboxylate group. The study is of general interest as it has been suggested previously [2] that the mechanism of reduction of several $[Co^{III}(NH_3)_5L]$ complexes, where L is bound to the cobalt atom by a carboxylate group, involves reduction of L as an intermediate stage. Furthermore, rates of intramolecular electron-transfer reactions in complexes of the type $[(H_3N)_5Co^{III}\{O_2C(CH_2)_nC_5H_4N\}Ru^{II}(NH_3)_4(OH_2)]^{4+}$ ($n = 0$ or 1 and the substitution is *para* or *meta* to the ring nitrogen) have recently been reported.[3]

It seemed of interest to assess the role of the carboxylate group in these intramolecular redox processes. We have measured the rates of reactions (2). It was hoped that a comparison of k_1 with k_2 would yield information on the efficiency of the carboxylate group as an intramolecular electron-transfer mediator.



(2)

X = NH_3, $PhCO_2^-$, *p*-$O_2NC_6H_4CO_2^-$, Br^-, pyridine (py), and *m*-$H_2NCOC_5H_4N$

EXPERIMENTAL

Materials.—The complexes $[Co(NH_3)_5(O_2CPh)][ClO_4]_2$, $[Co(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)][ClO_4]_2$, $[Co(NH_3)_5Br][ClO_4]_2$, $[Co(NH_3)_5(py)][ClO_4]_3$ (py = pyridine), and $[Co(NH_3)_5(NC_5H_4CONH_2\text{-}m)][ClO_4]_3$ were prepared according to procedures described in the literature.[4] Their purity was checked spectrophotometrically; in all cases $\lambda_{max.}$ was within ±2 nm and $\varepsilon_{max.}$ was within ±5% of the reported values. The salt $[Co(NH_3)_6][ClO_4]_3$ was prepared from $[Co(NH_3)_6]Cl_3$ (K & K) and twice recrystallized. All other chemicals used were of AnalaR grade and were used without further purification. All the water used was triple distilled. Argon and N_2O gases were bubbled through three wash bottles containing $V[SO_4]$ in dilute H_2SO_4 over Zn amalgam, dilute NaOH, and triple-distilled water respectively; thus trace amounts of O_2 were eliminated. The pH was adjusted with NaOH or $HClO_4$.

Irradiations.—The pulse-radiolytic experiments were carried out using 0.5 μs, 5 MeV, 200 mA pulses from the linear electron accelerator at the Hebrew University of Jerusalem. The dose per pulse was 1 500 rad.† The experimental set-up in Jerusalem and the method used for evaluation of the results have been described elsewhere in detail.[5] The kinetics of reduction of the Co^{III} complexes were measured by following spectrophotometrically the disappearance of absorbance due to the $^-O_2\dot{N}C_6H_4CO_2^-$ radical at 410 nm. γ Irradiations were carried out using a ^{60}Co γ source with a dose rate of 2 700 rad min^{-1}. The yield of $Co^{2+}(aq)$ was determined by the method described by Katakis and Allen.[6] All the experiments were made at room temperature, 22 ± 2 °C.

RESULTS

Dinitrogen oxide- or argon-saturated solutions (both solutions gave the same results) containing 1.0M-isopropyl alcohol, 1×10^{-2}—4×10^{-2}M-*p*-nitrobenzoate in the pH range 5.7—6.0, and various concentrations of the cobalt complexes (1×10^{-4}—100×10^{-4}M) were irradiated. In the presence of the complex the absorbance due to the *p*-nitrobenzoate radical anion [7] disappeared *via* a pseudo-first-order rate law. A correction for the disappearance of the radical in the absence of the complexes was included when needed; it was always ⩽20% of the observed rate. For every second-order rate constant determined at least 10 kinetic traces were analyzed; these were obtained by pulse radiolyzing 10 sample solutions which had been prepared from at least two different stock solutions diluted to several different concentrations. The dependence of

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† 1 rad = 10^{-2} J kg^{-1}, 1M = 1 mol dm^{-3}, 1 cal = 4.184 J.

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TABLE 1

Effects of $[Co(NH_3)_6]^{3+}$ concentration on the rate of reaction (2)

$10^3[Co(NH_3)_6{}^{3+}]/M$	$10^{-2}k_{obs.}{}^a/s^{-1}$	$10^{-5}k_2(calc.)^b$/ $l\ mol^{-1}\ s^{-1}$	$10^{-2}k_{obs.}(calc.)^c/s^{-1}$ $K_{eq} = 1\,000$	200	100 l mol^{-1}
10	11	1.1	11	11	11
5	6.5	1.3	9.6	8.2	7.3
1.5 [d]	2.7	1.8	6.9	3.8	3.1
0.5 [d]	0.9	1.8	3.7	1.5	1.1

[a] The rate of disappearance of absorption due to $p\text{-}^-O_2\dot{N}C_6H_4CO_2^-$ {after correcting for that in the absence of added $[Co(NH_3)_6]^{3+}$}. [b] From $k_{obs.}$ assuming a simple bimolecular reaction. [c] Assuming $k_{obs.} = 1.1 \times 10^3\ s^{-1}$ for solutions containing 1×10^{-2}M-$[Co(NH_3)_6]^{3+}$ and different K_{eq}. The equation used was $k_{obs.} = k_{2b}K_{eq}/\{1 + K_{eq}[Co(NH_3)_6{}^{3+}]\}$. [d] In all these solutions the correction due to the second-order disappearance of the radical was larger than 20%. Therefore the average of the results at higher concentrations is used in Table 2.

the rate constant on the complex concentration for the hexa-ammine complex is given in Table 1. For the other complexes studied a smaller concentration range, 1×10^{-4}—4×10^{-3}M, was used because of their higher rates of reaction and no significant dependence of the rates of reaction on concentration was observed (Table 2). The yield of $Co^{2+}(aq)$ in identical solutions irradiated in the ^{60}Co γ source was measured; $G[Co^{2+}(aq)] = 6.3 \pm 0.4$ for all the complexes studied.

DISCUSSION

The radiolysis of water can be described by equation (3). The yields of the products are known: [8]

$$H_2O \xrightarrow{\gamma,e} e^-(aq),\ OH,\ H,\ H_2O_2,\ H_2,\ [H_3O]^+ \quad (3)$$

$G[e^-(aq)] = 2.65$, $G(OH) = 2.65$, $G(H) = 0.60$, $G(H_2) = 0.45$, and $G(H_2O_2) = 0.75$. (Somewhat higher yields are expected in concentrated solutions.[8]) These products are homogeneously distributed in the solution within less than 10^{-7} s after the pulse. Under our experimental conditions, reactions (4)—(9) may occur. Thus all

$$e^-(aq) + N_2O \xrightarrow{k_4} O^- + N_2,\ O^- + H_2O \longrightarrow OH + OH^-;\quad k_4 = 5.6 \times 10^9\ l\ mol^{-1}\ s^{-1}\ \text{(ref. 9)} \quad (4)$$

$$OH + Pr^iOH \xrightarrow{k_5} Me_2\dot{C}OH + H_2O;\quad k_5 = 1.2 \times 10^9\ l\ mol^{-1}\ s^{-1}\ \text{(ref. 9)} \quad (5)$$

$$H + Pr^iOH \xrightarrow{k_6} Me_2\dot{C}OH + H_2;\quad k_6 = 5 \times 10^7\ l\ mol^{-1}\ s^{-1}\ \text{(ref. 9)} \quad (6)$$

$$e^-(aq) + p\text{-}O_2NC_6H_4CO_2^- \xrightarrow{k_7} p\text{-}^-O_2\dot{N}C_6H_4CO_2^-;\quad k_7 = 1.5 \times 10^{10}\ l\ mol^{-1}\ s^{-1}\ \text{(ref. 7)} \quad (7)$$

$$Me_2\dot{C}OH + p\text{-}O_2NC_6H_4CO_2^- \xrightarrow{k_8} p\text{-}^-O_2\dot{N}C_6H_4CO_2^-;\quad k_8 = 3.3 \times 10^9\ l\ mol^{-1}\ s^{-1}\ \text{(ref. 7)} \quad (8)$$

$$e^-(aq) + [Co^{III}(NH_3)_5X] \longrightarrow Co^{2+}(aq) + 5NH_3 + X \quad (9)$$

primary radicals formed on irradiation are transformed into the $p\text{-}^-O_2\dot{N}C_6H_4CO_2^-$ radical. [If reaction (9) competes with (8) in the presence of a high concentration of the complex the yield of the desired radical is somewhat diminished, but the new products do not absorb at 410 nm and therefore do not interfere with the kinetics of reaction studied.] We observed the formation of an intermediate with an absorption spectrum identical to that of $p\text{-}^-O_2\dot{N}C_6H_4CO_2^-$. It is evident from the results that this radical reacts with the different Co^{III} complexes. Furthermore the observation that $G[Co^{2+}(aq)] = 6.4 = G[e^-(aq)] + G(H) + G(OH) = G(p\text{-}^-O_2\dot{N}C_6H_4CO_2)^-$ confirms that these reactions are redox processes.

TABLE 2

Rate constants for reduction of $[Co^{III}(NH_3)_5X]$ complexes by $p\text{-}O_2\dot{N}C_6H_4CO_2^-$

X	$10^{-6}k/l\ mol^{-1}\ s^{-1}$
NH_3	0.12 ± 0.04
$PhCO_2^-$	0.21 ± 0.05
$p\text{-}O_2NC_6H_4CO_2^-$	0.60 ± 0.15
Br^-	2.4 ± 0.6
py	3.5 ± 0.5
$m\text{-}H_2NCOC_5H_4N$	11 ± 3

In order to compare the measured second-order rate constants, k_2, with the first-order rate constant k_1, we make the following assumption. The mechanism of the second-order reaction can be written in principle as in equations (2a) and (2b) where the first step represents

$$[Co^{III}(NH_3)_5X] + {}^-O_2CC_6H_4\dot{N}O_2{}^-\text{-}p \overset{K_{eq}}{\rightleftharpoons} [Co^{III}(NH_3)_5X,\ {}^-O_2CC_6H_4\dot{N}O_2{}^-\text{-}p] \quad (2a)$$

$$[Co^{III}(NH_3)_5X,\ {}^-O_2CC_6H_4NO_2{}^-\text{-}p] \xrightarrow{k_{2b}} Co^{2+}(aq) + 5NH_3 + X + p\text{-}O_2NC_6H_4CO_2^- \quad (2b)$$

formation of an outer-sphere ion pair, or the approach of the two reactants to a reaction distance, and the second step is the electron-transfer reaction. With this assumption the rate law is as in (10) where R_T =

$$-\frac{d[R_T]}{dt} = \frac{d[Co^{2+}(aq)]}{dt} = k_{2b}K_{eq}\frac{[R_T][Co^{III}(NH_3)_5X]}{1 + K_{eq}[Co^{III}(NH_3)_5X]} \quad (10)$$

$[p\text{-}^-O_2\dot{N}C_6H_4CO_2^-] + [Co^{III}(NH_3)_5X,\ {}^-O_2CC_6H_4\dot{N}O_2{}^-\text{-}p]$. (The spectrum of the radical in the ion pair is assumed to

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be identical with that of the free radical as is that of the chemically bound radical.) From the dependence of the observed rate constants, $k_{obs.} = k_{2b}K_{eq}/\{1 + K_{eq}[Co^{III}(NH_3)_5X]\}$, on the complex concentration, K_{eq} can be estimated. Such calculations (Table 1) clearly indicate that for $[Co(NH_3)_6]^{3+}$, $K_{eq} < 100$ l mol^{-1}. It should be pointed out that the decrease in k_2 with increasing $[Co(NH_3)_6]^{3+}$ concentration is expected to be due at least in part also to the increase in the ionic strength of the solutions.[10] We were unable to measure the dependence of $k_{obs.}$ on the concentration of $[Co(NH_3)_5(O_2CPh)]^{2+}$ and $[Co(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^{2+}$ due to the limited solubility of these complexes. However, as the charge of these complexes is less than that of $[Co(NH_3)_6]^{3+}$, K_{eq} is expected to be also less for them. We therefore conclude that $k_{2b} \geqslant 2 \times 10^3$, 2.1×10^3, and 6.0×10^3 s^{-1} for $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5(O_2CPh)]^{2+}$, and $[Co(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^{2+}$ respectively. Thus our findings indicate that $k_{2b} \geqslant k_1$, *i.e.* the intramolecular electron transfer is not significantly faster than the similar intermolecular outer-sphere reaction (2b).*

The free-energy gain in reaction (1) is expected to be similar to that of (2b), which is larger than 14 kcal mol^{-1}.† It is reasonable to assume that the ligand-rearrangement parameters are similar for outer-sphere reductions of $[Co(NH_3)_5(O_2CPh)]^{2+}$ and $[Co(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^{2+}$. The most likely explanation for the slowness of reaction (1) relative to (2b) is that the carboxylate group has a relatively low ' electron permeability '.

The rate constant of reaction (11) is $k_{11} = 4.0 \times 10^5$ s^{-1}.[1] This reaction is expected to have the same

$$[Co(NH_3)_5(O_2CC_6H_4NO_2\text{-}o)]^+ \longrightarrow Co^{2+}(aq) + 5NH_3 + o\text{-}O_2NC_6H_4CO_2^- \quad (11)$$

free-energy gain and ligand-rearrangement requirements as (1). However, $k_{11} \gg k_1$ and a value of K_{eq} *ca.* 1 l mol^{-1} only would be in agreement in a comparison of reaction (2) with (11). It seems that the difference between reactions (1) and (11) arises because in (11) the electron is not transferred to the central Co^{III} through the bridging carboxylate group. A similar mechanism has been suggested for the intramolecular electron-transfer reaction in $[(H_3N)_5Co^{III}\{O_2CCH_2C_5H_4N\}Ru^{II}(NH_3)_4(OH_2)]^{4+}$.[3] This is corroborated by the observation that reaction (11) occurs also for the protonated form of *o*-nitrobenzoate $[Co(NH_3)_5(O_2CC_6H_4NO_2H\text{-}o)]^{2+}$ but not for *p*-nitrobenzoate.[1] In the protonated form of the radicals the spin density on the aromatic ring is expected to be much lower than in their unprotonated form. Therefore the rate of reaction is more affected for a mechanism involving ' electron transfer through the carboxylate group ' than for ' electron transfer at an ammine group '. From e.s.r. measurements it is known that the spin density on the aromatic ring in radicals of the type of $p\text{-}{}^-O_2\dot{N}C_6H_4CO_2^-$ is of the order of 0.35.[12-14] It is reasonable also that in $[Co^{III}(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^+$ a considerable spin density exists on the aromatic ring. The relatively low k_1 indicates therefore that the ' electron permeability ' of the carboxylate group is rather low in this case. The reason might be poor overlap between the e_g orbitals of the Co^{III} ion with the π system of the ligand in the complex. It is of interest also that all inner-sphere reductions of Co^{III} complexes that proceed *via* remote attack on a ligand bound to Co^{III} by a carboxylate group have a prominent path which calls for external H$^+$.[15] It was suggested that this H$^+$ is bound to the carboxylate group.[16] Its role seems to be either to change the geometry or electronic configuration of the carboxylate group thus increasing the ' electron permeability '. We could not check the pH effect on reaction (2b) due to the pK of the radical $p\text{-}{}^-O_2\dot{N}C_6H_4CO_2H$.[7] The difference in the specific rate of reaction of $p\text{-}{}^-O_2\dot{N}C_6H_4CO_2^-$ with $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5Br]^{2+}$ is rather small. The relatively high rate of reaction of $p\text{-}{}^-O_2\dot{N}C_6H_4CO_2^-$ with $[Co(NH_3)_5(NC_5H_4CONH_2\text{-}m)]^{3+}$ and $[Co(NH_3)_5(py)]^{3+}$ may indicate that in these cases the ligand is reduced in the rate-determining step. Similar mechanisms were suggested for the reduction of these complexes by other reductants.[2,4c,17,18] No intermediate, such as the expected Co^{III} complex with a reduced ligand, was found in agreement with other observations.[19]

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* This is correct for X = NH$_3$ and PhCO$_2^-$ where the *p*-nitrobenzoate radical reduces directly the Co^{III} centre as its redox potential is too low to reduce the ligands in a stepwise mechanism. For $[Co(NH_3)_5(O_2CC_6H_4NO_2\text{-}p)]^{2+}$ we cannot confirm that the reaction does not involve reduction of the ligand in the rate-determining step. The observed rate suggests, however, that the mechanism of this reaction is similar to the rest. Confirmation would require the use of complex concentrations higher than 3×10^{-3}M which are not possible as the complex is insoluble in the presence of 4×10^{-2}M-*p*-nitrobenzoate.

† Calculated from the redox potentials of $[Co(NH_3)_6]^{3+}$ and $p\text{-}O_2NC_6H_4CO_2^-$. The latter was obtained from its reversible half-wave polarographic oxidation state.[11]

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