Aliphatic Radicals as Reducing Agents of Cobalt(III) and Ruthenium(III) Complexes: A Pulse Radiolytic Study

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The pH effect on the rate of the reduction reaction $\dot{C}H_2OH + [Co(NH_3)_6]^{3+}$ has been studied. The results indicate that this reaction does not proceed *via* the outer-sphere mechanism. The pH effect on the reactivity of $R^1\dot{C}(OH)CO_2H$ [R^1 = H, CH_3, or $HO_2CCH(OH)$] towards $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{3+}$ has been studied. The results indicate that the radicals $R^1\dot{C}(OH)CO_2^-$ are considerably more reactive than $R^1\dot{C}(OH)CO_2H$. The reasons for this effect are discussed. The rate of water loss from the radical derived from tartaric acid has been measured. The kinetics of reduction of $[CoX(NH_3)_5]^{2+}$ and $[RuX(NH_3)_5]^{3+}$ (X = halide) and $[Co^{III}(en)_2XY]$ (en = ethylenediamine; X,Y = F, Cl, Br, NH_3, or H_2O) by the radicals $\dot{C}H_2OH$, $Me\dot{C}HOH$, $Me_2\dot{C}OH$, $Me\dot{C}HOEt$, and $\overline{O{-}\dot{C}H{-}CH_2{-}O{-}CH_2{-}CH_2}$ have been examined. The results suggest that these reactions proceed *via* a bridged mechanism.

THE mechanism of reduction of many cobalt(III) and ruthenium(III) complexes by different reducing agents has been studied. It is commonly accepted that the reduction of $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{3+}$ always proceeds *via* the outer-sphere mechanism.[1] Recently we reported some unexpected kinetic results for the reduction of these complexes by $R^1R^2\dot{C}OH$ radicals (R^1, R^2 = H, Me, or CO_2^-).[2] Assuming that these reactions also proceed *via* the outer-sphere mechanism, the results were interpreted as indicating that the symmetry properties of the orbital in which the unpaired electron is located affect the specific rates of reaction.[2]

It seemed of interest to check the latter speculation and we decided to investigate the following aspects of these reactions. (*a*) The effect of small changes in the radical structure on its reactivity towards $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{3+}$, *e.g.* a comparison between the reactivity of $R\dot{C}(OH)CO_2H$ and $R\dot{C}(OH)CO_2^-$ radicals. (*b*) The effect of the structure of the radicals on redox processes which proceed *via* a 'bridged' mechanism.[3] The reduction of $[Co^{III}(NH_3)_5X]$, $[Ru^{III}(NH_3)_5X]$, and $[Co^{III}(en)_2XY]$ ($X \neq NH_3$; en = ethylenediamine) might proceed *via* this mechanism. Therefore the specific rates of reaction of several aliphatic radicals with complexes of this type were measured. (*c*) During this study Hoffman and his co-workers[4] reported that the reduction of $[Co(NH_3)_6]^{3+}$ by $\dot{C}H_2OH$ radicals is pH dependent.[4] The mechanism suggested involved the co-ordination of the radical to the cobalt yielding a seven-co-ordinate intermediate, and was based on results obtained by steady-state radiolysis. We decided to recheck (by the pulse-radiolytic technique) the pH dependence of the reactivity of $\dot{C}H_2OH$ radicals towards different complexes. The results indicate that the reduction of $[Co(NH_3)_6]^{3+}$ by aliphatic alcohol radicals is not *via* a simple outer-sphere mechanism, and the reduction of some of the other complexes seems to proceed *via* a 'bridged' mechanism.

EXPERIMENTAL

Materials.—The complexes $[Co(NH_3)_6][ClO_4]_3$, $[CoF(NH_3)_5][ClO_4]_2$, $[CoCl(NH_3)_5][ClO_4]_2$, $[CoBr(NH_3)_5][ClO_4]_2$, $[Co(en)_3][ClO_4]_3$, *cis*-$[CoCl(en)_2(OH_2)][SO_4]$, *cis*-$[CoCl(en)_2(NH_3)]Cl_2$, *cis*-$[CoCl_2(en)_2]Cl$, *trans*-$[CoCl_2(en)_2]Cl$, *cis*-$[CoBrF(en)_2]Br$, *trans*-$[CoBr_2(en)_2]Br$, *cis*-$[CoF_2(en)_2][ClO_4]$, $[Ru(NH_3)_6][ClO_4]_3$, $[RuCl(NH_3)_5][ClO_4]_2$, and $[RuBr(NH_3)_5][ClO_4]_2$ were prepared according to procedures described in the literature.[5] Their purity was checked spectrophotometrically: in all the cases $\lambda_{max.}$ was within 2 nm and $\varepsilon_{max.}$ was within 5% of the reported values. All the other chemicals used were of AnalaR grade and were used without further purification. The water used was triple distilled. Dinitrogen oxide used was bubbled through three wash bottles containing $V[SO_4]$ in dilute H_2SO_4 over zinc amalgam, followed by one containing Na[OH] and one containing triple distilled water; thus trace amounts of oxygen were eliminated. The pH was adjusted with $HClO_4$ and Na[OH].

Complexes containing Cl^- or Br^- as a ligand were used within 1 h of the preparation of the solutions in order to prevent hydrolysis. In order to minimize photochemical decomposition of the complexes by the analyzing light, appropriate filters when needed were introduced between the xenon lamp and the cell. Furthermore, a mechanical shutter was kept closed until shortly before the pulse, and all the solutions were kept in the dark.

Irradiations.—The pulse-radiolytic experiments were carried out using 0.05—1 μs, 5-meV, 200-mA pulses from the linear electron accelerator at the Hebrew University of Jerusalem. The dose per pulse was 150—3 000 rad.* The experimental set-up in Jerusalem and the method used for evaluating the results have been described elsewhere in detail.[6] γ-Irradiations were carried out using a ^{60}Co γ-source with a dose rate of 2 300 rad min^{-1}. The yield of $Co^{2+}(aq)$ was determined by the method of Katakis and Allen.[7]

Kinetics.—Solutions saturated with N_2O or argon and

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* Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 eV ≈ 1.60×10^{-19} J.

[1] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' Wiley, New York, 1967.

[2] H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.*, 1972, **94**, 6944.

[3] H. Taube, 'Electron Transfer Reactions of Complex Ions in Solution,' Academic Press, New York, London, 1970.

[4] (*a*) D. C. Campano, E. R. Kantrowvitz, M. Z. Hoffman, and M. S. Weinberg, *J. Phys. Chem.*, 1974, **78**, 686; (*b*) K. R. Olson, N. V. Brezniak, and M. Z. Hoffman, *Inorg. Chem.*, 1974, **13**, 117; (*c*) K. R. Olson and M. Z. Hoffman, *J.C.S. Chem. Comm.*, 1974, 938.

[5] R. G. Pearson, C. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, 1953, **75**, 3089; *J. Phys. Chem.*, 1955, **59**, 304; S. C. Chan, *J. Chem. Soc.*, 1963, 5137; J. W. Palmer and F. Basolo, *J. Inorg. Nuclear Chem.*, 1960, **15**, 279; J. A. Stritar and H. Taube, *Inorg. Chem.*, 1969, **8**, 2284; *Inorg. Synth.*, 1939, **1**, 186; 1953, **4**, 171.

[6] (*a*) H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434; (*b*) H. Harel and D. Meyerstein, *J. Amer. Chem. Soc.*, 1974, **96**, 2720.

[7] D. Katakis and A. O. Allen, *J. Phys. Chem.*, 1964, **68**, 1359.

containing 0.01—1 mol dm^{-3} of different organic solutes at pH 0.7—11 were irradiated. The kinetics of disappearance of the radicals formed were followed. In the absence of complexes, these reactions obeyed second-order rate laws. The effect of added complexes at different concentrations in the range 3×10^{-5}—4×10^{-3} mol dm^{-3} on the kinetics of disappearance of the organic radicals was studied. For most of the radicals their disappearance changed from second- to pseudo-first-order on adding complex. Pseudo-first-order rates were calculated when a plot of a good first-order decay was linear for at least three half-lives. A correction for the disappearance of the aliphatic radicals in the absence of the complexes was included when needed All the experiments were at room temperature (22 ± 2 °C).

RESULTS AND DISCUSSION

The radiolysis of water may be described[8] by equation (1), the yields of the products in neutral dilute solutions

$$H_2O \xrightarrow{\gamma,e^-} e^-(aq), H, OH, H_2, H_2O_2, [H_3O]^+ \quad (1)$$

being 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 (G is defined as the number of product molecules formed by the absorption of 100 eV by the sample). The hydrated electron reacts with N_2O according to equation (2), the yield of OH radicals in neutral

$$N_2O + e^-(aq) \xrightarrow{[H_3O]^+} N_2 + OH; \quad k_2\ 8.7 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ (\text{ref. 9}) \quad (2)$$

solutions saturated with N_2O (2×10^{-2} mol dm^{-3}) being G(OH) 5.3. (A somewhat higher yield is plausible in concentrated solutions.[8]) Hydroxyl radicals and hydrogen atoms abstract hydrogen atoms from saturated organic solutes *via* reaction (3). Thus in neutral

$$RH_2 + H \text{ or } OH \longrightarrow \dot{R}H + H_2 \text{ or } H_2O \quad (3)$$

N_2O saturated solutions containing sufficiently high concentrations of organic solute the only intermediate formed is the organic radical $\dot{R}H$. The nature of the radicals formed in the presence of different organic solutes, as well as their u.v. and e.s.r. spectra and irreversible polarographic half-wave potentials, are known.[9]

Table 1

pH Dependence of the rate of reaction [a] of $\dot{C}H_2OH$ radicals with $[Co(NH_3)_6]^{3+}$ and $[CoBr(NH_3)_5]^{2+}$

(*i*) $[Co(NH_3)_6]^{3+}$

pH	6.1	5.75	4.9	4.5	3.5	5.5 [b]	5.7 [c]	5.7 [d]
k/dm^3 mol^{-1} s^{-1}	1.4×10^8	1.4×10^8	6×10^7	4.5×10^7	$\leqslant 1 \times 10^7$	$\leqslant 1 \times 10^7$	1.4×10^8	2.7×10^8

(*ii*) $[CoBr(NH_3)_5]^{2+}$

pH	6.1	4.9	4.5	3.5	2.0	1.0
k/dm^3 mol^{-1} s^{-1}	9.0×10^7	2.5×10^7	2.0×10^7	1.8×10^7	1.8×10^7	1.8×10^7

[a] All the solutions contained 1 mol dm^{-3} methanol and were saturated with N_2O. The standard deviation of the rate constants is ±15%. The dose per pulse was 100—500 rad. [b] The solution also contained 1×10^{-3} mol dm^{-3} acetate buffer (see footnote on p. 1060). [c] Dose per pulse, 4 500 rad. [d] As *c* but second pulse.

The Reduction of $[M^{III}(NH_3)_6]^{3+}$ (M = Co *or* Ru) *by Aliphatic Radicals:* pH *Dependence.*—(*a*) $\dot{C}H_2OH$ *Radicals.* The rates of reduction of $[Co(NH_3)_6]^{3+}$ and $[CoBr(NH_3)_5]^{2+}$ by $\dot{C}H_2OH$ radicals in the range pH 0—7 were measured and are summarized in Table 1. The results clearly support the conclusion of Hoffman and his co-workers that the rate of reaction of $\dot{C}H_2OH$ with

$$[Co(NH_3)_6]^{3+} + \dot{C}H_2OH \longrightarrow [Co(NH_3)_6]^{2+} + CH_2O + [H_3O]^+ \quad (4)$$

$$[Co(NH_3)_6]^{3+} + e^-(aq) \longrightarrow [Co(NH_3)_6]^{2+}; \quad k_5\ 9 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ (\text{ref. 10}) \quad (5)$$

$$[Co(NH_3)_6]^{2+} \longrightarrow [Co(NH_3)_3(OH_2)_3]^{2+} + 3NH_3; \quad k_6 > 10^6\ \mathrm{s^{-1}}\ (\text{ref. 11}) \quad (6)$$

$$[Co(NH_3)_3(OH_2)_3]^{2+} \longrightarrow [Co(NH_3)_2(OH_2)_4]^{2+} + NH_3; \quad k_{7a} \simeq 6 \times 10^4\ \mathrm{s^{-1}}\ (\text{ref. 11}) \quad (7)$$

$[Co(NH_3)_6]^{3+}$ decreases with decreasing pH. The reduction of $[Co(NH_3)_6]^{3+}$ *via* reactions (4) and (5) (CH_2O is the product, see ref. 2) is followed by (6)—(8). Therefore the pH of the solutions increases immediately after the pulse. This increase might affect k_6 if a high pH is obtained during the reaction through (9) and (10). We checked this point by irradiating relatively dilute solutions of the complex [so reaction (5) does not compete considerably with (4)] with a small pulse (<110 rad per

$$[Co(NH_3)_2(OH_2)_4]^{2+} \longrightarrow \text{further hydrolysis}; \quad k_{7b} < 1 \times 10^4\ \mathrm{s^{-1}}$$

$$NH_3 + [H_3O]^+ \rightleftharpoons [NH_4]^+; \quad K_8\ 1.8 \times 10^{-5}\ \mathrm{dm^3\ mol^{-1}}\ (\text{ref. 12}) \quad (8)$$

pulse). The concentration of radicals produced by this pulse was $<6 \times 10^{-7}$ mol dm^{-3}. Thus the pH after receipt of a single pulse by a solution at pH 5.7 could reach at most the value of 8.2, and during the reaction

$$\dot{C}H_2OH \rightleftharpoons \dot{C}H_2O^- + [H_3O]^+; \quad pK_9\ 10.7\ (\text{ref. } 9a) \quad (9)$$

$$\dot{C}H_2O^- + [Co(NH_3)_6]^{3+} \longrightarrow [Co(NH_3)_6]^{2+} + CH_2O; \quad k_{10}\ 9 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ (\text{ref. 2}) \quad (10)$$

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[8] M. Matheson and L. M. Dorfman, 'Pulse Radiolysis,' Massachusetts Institute of Technology Press, Cambridge, 1969.

[9] (*a*) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794; (*b*) P. Neta, M. Simic, and E. Hayon, *ibid.*, p. 4207; (*c*) M. Simic, P. Neta, and E. Hayon, *ibid.*, p. 4214; (*d*) K. Eiben and R. W. Fessenden, *ibid.*, 1971, **75**, 1186; (*e*) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124; (*f*) J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 458.

[10] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493.

[11] M. Simic and J. Lilie, *J. Amer. Chem. Soc.*, 1974, **96**, 291.

[12] L. G. Sillen and A. E. Martell, 'Stability Constants of Metal–Ion Complexes,' *Special Publ.* No. 17, The Chemical Society, London, 1964, p. 149.

(50 μs) only reaction (6) occurs, and $pH < 8$ is maintained. Therefore the maximum contribution of reaction (10) to k under the experimental conditions was less than 10%. The rate of reaction observed after a second pulse was higher as expected. The observation that a similar pH effect is observed for the reactions of $Me_2\dot{C}OH$ and $Me\dot{C}HOH$ radicals, which have pK values of 12.2 and 11.7 respectively,[9a] can also not be explained by the increase in pH during the reaction. It is concluded that the rate of reaction (4) at pH *ca.* 6.0 is not due to the change in pH caused by the hydrolysis of ammine molecules during the reaction.

Our results thus confirm the conclusion of Hoffman and his co-workers[4] that the reduction of $[Co(NH_3)_6]^{3+}$ by $\dot{C}H_2OH$ radicals does not occur *via* the simple outer-sphere mechanism.* However, we feel that their mechanism [equations (11) and (12)] does not explain the

$$\dot{C}H_2OH + [Co(NH_3)_6]^{3+} \underset{k_{-I}^{11}}{\overset{k_I^{11}}{\rightleftharpoons}} \underset{(A)}{[Co^{III}(CH_2OH)(NH_3)_6]^{3+}} \underset{k_{-II}^{11}}{\overset{k_{II}^{11}}{\rightleftharpoons}} H^+ + \underset{(B)}{[Co^{III}(CH_2O)(NH_3)_6]^{2+}} \xrightarrow{k_{III}^{11}} Co^{2+}(aq) + CH_2O + 6NH_3 \quad (11)$$

$$2\dot{C}H_2OH \longrightarrow \text{products}; \quad k_{12}\ 2.4 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}\ (\text{ref. } 9a) \quad (12)$$

experimental observations.† This mechanism assumes the formation of a seven-co-ordinate intermediate (A) with pK 4.2. {At this pH, $G[Co^{2+}(aq)] = \frac{1}{2}G[Co^{2+}(aq)$ at pH 6].} At pH 4.2 only half the $\dot{C}H_2OH$ radicals reduce $[Co(NH_3)_6]^{3+}$, *i.e.* the half-life of intermediate (B) is $> 0.7/k_{-II}^{11}[H_3O^+] > 1$ μs (if k_{-II}^{11} approaches the diffusion-controlled limit of 1×10^{10} dm^3 mol^{-1} s^{-1}). This conclusion seems unreasonable for the following reasons. The free $\dot{C}H_2O^-$ radical in a homogeneous solution reduces $[Co(NH_3)_6]^{3+}$ with k_{10} 9×10^9 dm^3 mol^{-1} s^{-1}.[2] Thus even in solutions containing only 5×10^{-5} mol dm^{-3} $[Co(NH_3)_6]^{3+}$ the half-life of the free radical was found to be 1.5 μs. It does not seem reasonable that the half-life of (B) should be similar to this value. Moreover, Hoffman and his co-workers suggested[4b] that the pK of the intermediate $[Co^{III}(CH_2OH)(NH_3)_5(O_2CMe)]^{2+}$ is 5.2; thus the half-life of $[Co^{III}(CH_2O)(NH_3)_5(O_2CMe)]^+$ should be larger than 10 μs.

If the reaction is neither a simple outer-sphere redox process nor proceeds *via* a seven-co-ordinate intermediate an alternative mechanism must be considered. This mechanism will be clearly an unconventional one. We believe that the most plausible speculation involves attack of the radical on one of the ammine groups yielding an intermediate of the type $[Co^{III}(NH_3)_5(NH_2CH_2OH)]^{3+}$. However, the experimental information available is not sufficient to elucidate the nature of this intermediate. A similar pH effect was also found for the rates of reduction of $[Co(NH_3)_6]^{3+}$ by the $Me\dot{C}HOH$ and $Me_2\dot{C}OH$ radicals. Thus $k\{Me_2\dot{C}OH + [Co(NH_3)_6]^{3+}\} = 1.3 \times 10^7$, 7×10^6, *ca.* 5×10^6, and $\leqslant 1 \times 10^6$ dm^3 mol^{-1} s^{-1} at pH 6.1, 5.6, 5.2, and 4.5 respectively. However, $G[Co^{2+}(aq)]$ is 6.2 ± 0.5 down to pH 1.0 in the presence of isopropanol. These results indicate that $k\{Me_2\dot{C}OH + [Co(NH_3)_6]^{3+}\}$ *ca.* 1×10^6 dm^3 mol^{-1} s^{-1} at pH $\leqslant 4.0$, and also that $k\{Me_2\dot{C}OH + [Co(NH_3)_6]^{3+}\} \geqslant k\{\dot{C}H_2OH + [Co(NH_3)_6]^{3+}\}$ at pH $\leqslant 4.0$ as would be expected from the redox potentials.

However, no pH effect at $1.0 \leqslant pH \leqslant 6.0$ was found for the corresponding reaction with $[Ru(NH_3)_6]^{3+}$. Thus our earlier conclusions relating the rates of reduction of $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{3+}$ by $R^1R^2\dot{C}OH$ radicals to the symmetry properties of the orbital containing the unpaired electrons[2] have to be reconsidered. The order of reactivities of $\dot{C}H_2OH$, $Me\dot{C}HOH$, and $Me_2\dot{C}OH$ towards $[Co(NH_3)_6]^{3+}$ might be due to inductive effects and/or to steric effects according to the proposed mechanism.

(*b*) $\dot{C}H(OH)CO_2H$, $Me\dot{C}(OH)CO_2H$, *and* $HO_2CCH(OH)\dot{C}(OH)CO_2H$ *radicals.* The pH effect on the rates of reaction of the radicals formed by hydrogen abstraction from glycolic, lactic, and tartaric acids with $[Ru(NH_3)_6]^{3+}$ was measured. The results are plotted in Figure 1. Thus in all the cases studied, the basic forms reduce $[Ru(NH_3)_6]^{3+}$ with a rate approaching the diffusion-controlled limit. On the other hand, the acidic forms of these radicals are much less reactive; thus $k \leqslant 5 \times 10^5$ dm^3 mol^{-1} s^{-1} for $\dot{C}H(OH)CO_2H$ and $Me\dot{C}(OH)CO_2H$ radicals, and $k = (5 \pm 1) \times 10^7$ dm^3 mol^{-1} s^{-1} for the $HO_2CCH(OH)\dot{C}(OH)CO_2H$ radical. The apparent pK values of these radicals (derived from Figure 1) are 4.6, 5.2, and 4.5 respectively, in good agreement with those obtained by other techniques.[9c] The results thus confirm that the effect of pH on the rates of reduction of $[Ru(NH_3)_6]^{3+}$ by these radicals is due to the dissociation of the CO_2H group.

The following factors should be considered in explaining the enhanced reactivity of the basic forms of the radicals towards $[Ru(NH_3)_6]^{3+}$. (*i*) The change in the charge on the radical from zero to 1− on acid dissociation is expected to increase the rate of reaction with $[Ru(NH_3)_6]^{3+}$ by a factor of *ca.* 10. The observed effects, at least for the $\dot{C}H(OH)CO_2H$ and $Me\dot{C}(OH)CO_2H$ radicals, are considerably larger and cannot be explained by the effect of the charge alone. (*ii*) The acid dissociation of the radical might in principle affect the driving force of the redox process. However for reactions (13) and (14) the pH effect on the driving force should be

$$R\dot{C}(OH)CO_2^- \longrightarrow RC(O)CO_2^- + [H_3O]^+ + e^- \quad (13)$$

identical, except for the pH range where the product is in its basic form and the radical in its acidic form.

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* From polarographic, spectroscopic, and especially e.s.r. measurements it was shown that $\dot{C}H_2OH$ radicals have no pK in the range pH 0—10 and the pK observed for the hydroxyl group is 10.7.[9a] The first acid dissociation of an ammine group of $[Co(NH_3)_6]^{3+}$ has p$K > 14$ (R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **78**, 4878).

† In principle, intermediate (A) could be formulated as $[Co(NH_3)_6(HO{\cdot}CH_2)]^{3+} \rightleftharpoons [Co(NH_3)_6(OCH_2)]^{2+} + [H_3O]^+$. Hoffman and his co-workers do not point out the exact nature of the intermediate.

Therefore this factor also does not explain the observed enhancement of the rates with acidic dissociation.

$$R\dot{C}(OH)CO_2H \longrightarrow RC(O)CO_2H + [H_3O]^+ + e^- \quad (14)$$

Thus it seems that the radicals studied attack $[Ru(NH_3)_6]^{3+}$ *via* an outer-sphere mechanism or *via* a seven-co-ordinate transition state.[13] The latter, if it exists, is very short lived and thus unaffected by pH. (Such a mechanism is more probable for the larger Ru^{III} as central atom than for Co^{III}.) In both cases the additional increase in the reduction rates above the charge effect seems to be due to the larger resonance stabilization of the radicals in their basic forms. Therefore the unpaired electron is located in an orbital with a larger π character and overlaps better with the empty t_{2g} orbital of Ru^{III}.[2]

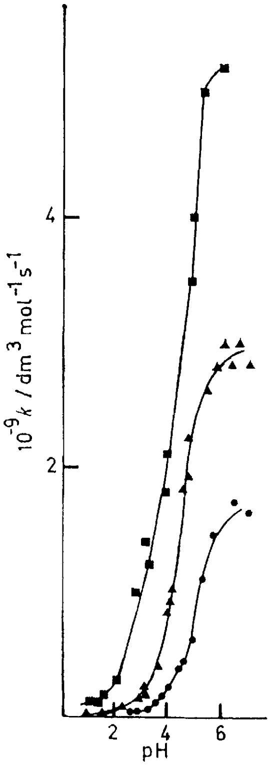

FIGURE 1 pH Dependence of the rate of reduction of $[Ru(NH_3)_6]^{3+}$ by the radicals formed by hydrogen abstraction from glycolic, lactic, and tartaric acids. (▲) The solutions contained 0.1 mol dm^{-3} glycolic acid and 3×10^{-5}—2×10^{-4} mol dm^{-3} of $[Ru(NH_3)_6]^{3+}$ and were saturated with argon at pH <3 and with N_2O at pH >3. Measured at 280 nm. Solid line calculated assuming p*K* 4.6, $k\{\dot{C}H(OH)CO_2^- + [Ru(NH_3)_6]^{3+}\} = 3.0 \times 10^9$ dm^3 mol^{-1} s^{-1}, and $k\{\dot{C}H(OH)CO_2H + [Ru(NH_3)_6]^{3+}\} = 5 \times 10^5$ dm^3 mol^{-1} s^{-1}. (●) The solutions contained 0.1 mol dm^{-3} lactic acid and 3×10^{-5}—2×10^{-4} mol dm^{-3} of $[Ru(NH_3)_6]^{3+}$ and were saturated with argon at pH <3 and with N_2O at pH >3. Measured at 300 nm. Solid line calculated assuming p*K* 5.3, $k\{Me\dot{C}(OH)CO_2^- + [Ru(NH_3)_6]^{3+}\} = 1.7 \times 10^9$ dm^3 mol^{-1} s^{-1}, and $k\{Me\dot{C}(OH)CO_2H + [Ru(NH_3)_6]^{3+}\} = 5 \times 10^5$ dm^3 mol^{-1} s^{-1}. (■) The solutions contained 1×10^{-2} mol dm^{-3} tartaric acid and 3×10^{-5}—2×10^{-4} mol dm^{-3} of $[Ru(NH_3)_6]^{3+}$. At pH <3, the solutions were saturated with argon and at pH >3 with N_2O. Measured at 280 nm. Solid line calculated assuming p*K* 4.5, $k\{^-O_2CCH(OH)\dot{C}(OH)CO_2^- + [Ru(NH_3)_6]^{3+}\} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1}, and $k\{^-O_2CCH(OH)\dot{C}(OH)CO_2H + [Ru(NH_3)_6]^{3+}\} = 5 \times 10^7$ dm^3 mol^{-1} s^{-1}. It is also assumed that the reactivity of $HO_2CCH(OH)\dot{C}(OH)CO_2H$ is identical with that of $^-O_2CCH(OH)\dot{C}(OH)CO_2H$. The small deviation at pH *ca.* 3 might be due to the inaccuracy of the latter assumption

The kinetics of reaction of these radicals with $[Co(NH_3)_6]^{3+}$ were followed. The following rates of reaction were observed: $k\{CH(O^-)CO_2^- + [Co(NH_3)_6]^{3+}\} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1} at pH 10.2 and $k\{Me\dot{C}(O^-)CO_2^- + [Co(NH_3)_6]^{3+}\} = 2.4 \times 10^{10}$ dm^3 mol^{-1} s^{-1} at pH 12.0. These rates approach the diffusion-controlled limit. At pH < 6 the reactions are too slow to be measured by the pulse-radiolysis technique, $k[R\dot{C}(OH)CO_2H/CO_2^-] \leqslant 5 \times 10^5$ dm^3 mol^{-1} s^{-1} for R = H or Me. The large effect of the acid dissociation of the hydroxyl group on these rates is in accord with that reported for the $\dot{C}H_2OH$, $Me\dot{C}HOH$, and $Me_2\dot{C}OH$ radicals.[2] This effect has been attributed to the fact that in reaction (15) no bond breaking, the OH bond, is required prior to the electron-transfer reaction. The pH dependence of the rates of reduction of $[Co(NH_3)_6]^{3+}$ by the radicals derived from tartaric acid (Figure 2) indicates three apparent p*K* values at 10.5 ± 0.3, 5.7 ± 0.3, and 2.3 ± 0.4. [The separation between the latter two processes is not apparent in Figure 2. However, the results clearly indicate that $k = (2 \pm 0.5) \times 10^6$ dm^3 mol^{-1} s^{-1} is nearly pH independent for $3.5 < pH < 4.5$.] These apparent p*K* values differ considerably from the p*K* values obtained by the spectroscopic method and from the $[Ru(NH_3)_6]^{3+}$ system (see above). The deviation of the observed apparent p*K* values at pH 10.5 and 2.3 from the spectroscopic data[9] is attributed to the acid- and

$$R^1R^2\dot{C}O^- + [M(NH_3)_6]^{3+} \longrightarrow R^1R^2CO + [M(NH_3)_6]^{2+} \quad (15)$$

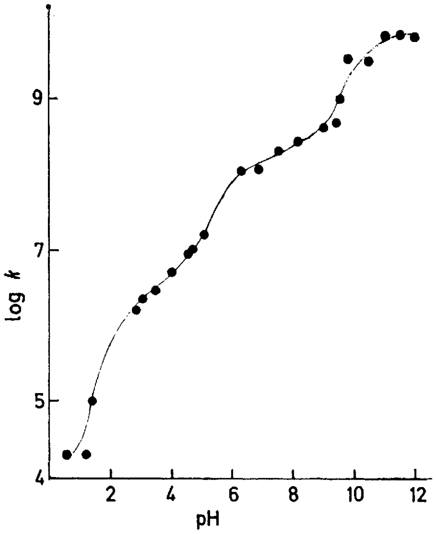

FIGURE 2 pH Dependence of the rate of reduction of $[Co(NH_3)_6]^{3+}$ by the radical formed by hydrogen abstraction from tartaric acid. The solution contained 1×10^{-2} mol dm^{-3} tartaric acid and 3×10^{-5}—5×10^{-3} mol dm^{-3} of $[Co(NH_3)_6]^{3+}$. At pH <3 the solutions were saturated with argon and at pH >3 with N_2O. Measured at 280 nm

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[13] G. Navon and D. Meyerstein, *J. Phys. Chem.*, 1970, **74**, 4067.

base-catalyzed water-elimination reaction (16) which is known to occur for all *gem*-diols.[14] We also studied the apparent p*K* at 2.3 by measuring the pH dependence of the yield of $Co^{2+}(aq)$ in this system. Assuming that the

$$R^1\dot{C}(OH)C(OH)R^2R^3 \longrightarrow R^1C(O)\dot{C}R^2R^3 + H_2O \quad (16)$$

radical produced in reaction (16) in acidic solutions does not reduce $[Co(NH_3)_6]^{3+}$, the yield of $Co^{2+}(aq)$, $G[Co^{2+}(aq)]$, will be $k_{17}G^0[Co^{2+}(aq)][Co(NH_3)_6{}^{3+}]/\{k_{17}[Co(NH_3)_6{}^{3+}] + k_{16}\}$, where $G^0[Co^{2+}(aq)]$ is the yield of $Co^{2+}(aq)$ in neutral solutions, $5 < pH < 7$, where all the radicals react *via* (17). Using these assumptions, k_{16}

$$HO_2C\dot{C}(OH)CH(OH)CO_2H + [Co(NH_3)_6]^{3+} \longrightarrow HO_2CCOCH(OH)CO_2H + Co^{2+}(aq) + 6NH_3 + [H_3O]^+ \quad (17)$$

was calculated (Table 2) from the experimental results. The pH dependence observed is similar to that reported for the corresponding reaction of the $\dot{C}H(OH)CH_2OH$ radical[15] although the reaction studied here is considerably slower.

TABLE 2

pH Dependence of the rate of water elimination from the $HO_2C\dot{C}(OH)CH(OH)CO_2H$ radical *

pH	k_{16}/s^{-1}	$G[Co^{2+}(aq)]$†	$[Co(NH_3)_6{}^{3+}]$/ mol dm^{-3}
5—6	20	5.1	5×10^{-5}
3.8	50	4.9	1×10^{-4}
2.8	70	4.6	1×10^{-4}
2.4	90	4.2	1×10^{-4}
1.3	800	1.3	1×10^{-4}
1.0	4 000	2.1	1×10^{-3}

* Accuracy ±50%; for the method of calculation see Discussion section.

† A correction for the yield of $Co^{2+}(aq)$ from the competition between the reactions $e^-(aq) + [Co^{III}(NH_3)_5X] \rightarrow Co^{2+}(aq)$ and $e^-(aq) + N_2O \rightarrow N_2 + OH$ was included.

The apparent p*K*, 5.7 ± 0.3, is significantly higher than that (4.5 ± 0.2) obtained in the corresponding reaction with $[Ru(NH_3)_6]^{3+}$. (The latter value is identical with that reported by Simic *et al.*[9c] from spectroscopic data.) This difference indicates that the reduction of $[Co(NH_3)_6]^{3+}$ by $^-O_2C\dot{C}(OH)CH(OH)CO_2{}^-$ does not proceed *via* the outer-sphere mechanism but *via* a path similar to that suggested above for $\dot{C}H_2OH$ radicals. The fact that reduction is also observed below the p*K* value indicates the existance of a parallel mechanism, possibly outer sphere, with $k = (2 \pm 0.5) \times 10^6$ dm³ mol⁻¹ s⁻¹.

TABLE 3

Rates of reaction ($dm^3\ mol^{-1}\ s^{-1}$) of some aliphatic radicals with $[Co^{III}(NH_3)_5X]$ complexes [a]

Complex / Radical	$[Co(NH_3)_6]^{3+}$	$[CoCl(NH_3)_5]^{2+}$	$[CoBr(NH_3)_5]^{2+}$
$\dot{C}H_2OH$	1.4×10^{8} [b]	$(3 \pm 1) \times 10^{6}$ [c]	1.8×10^{7}
$Me\dot{C}HOH$	5.2×10^{7} [b]	3.0×10^{6}	1.5×10^{8}
$Me_2\dot{C}OH$	1.3×10^{7} [b]	4.0×10^{7}	3.0×10^{8}
$Me\dot{C}HOEt$	$\leqslant 5 \times 10^{6}$ [d]	1.4×10^{7}	1.6×10^{8}
$\overline{O{-}\dot{C}H{-}CH_2{-}O{-}CH_2{-}CH_2}$	$\leqslant 2 \times 10^{6}$	$\leqslant 2 \times 10^{6}$	$\leqslant 2 \times 10^{6}$

[a] All the solutions contained 0.5—1 mol dm^{-3} of the organic solute and were saturated with N_2O at pH 3.5—4.0. Unless otherwise stated, the standard deviation of the rate constant is ±15%. [b] From ref. 2. [c] From Table 6. [d] pH 5.5—6.0.

Reactivity of Aliphatic Radicals towards $[Co^{III}(NH_3)_5X]$, $[Co^{III}(en)_2XY]$, *and* $[Ru^{III}(NH_3)_5X]$ *Complexes.*—The rates of reaction of several aliphatic radicals with $[Co^{III}(NH_3)_5X]$, $[Co^{III}(en)_2XY]$, and $[Ru^{III}(NH_3)_5X]$ at $3.5 \leqslant pH \leqslant 4.0$ are summarized in Tables 3—5. In each case where $k(R + \text{complex}) \geqslant 1 \times 10^6$ dm³ mol⁻¹ s⁻¹, $G[Co^{2+}(aq)]$ 6.2 ± 0.5. In some cases the rates of reduction were too low to be measured by the pulse-radiolytic technique due to the competition between reactions (18) and (19). In these cases the effect of the complex

$$[Co^{III}(NH_3)_5X] + \dot{R}H \xrightarrow{k_{18}} Co^{2+}(aq) + 5NH_3 + X + R \quad (18)$$

$$2\dot{R}H \xrightarrow{k_{19}} RH_2 + R \text{ (or HRRH)} \quad (19)$$

concentration on $G[Co^{2+}(aq)]$ was examined using the low-dose-rate ^{60}Co γ-source, thus decreasing the concentration of $\dot{R}H$. Under these conditions expression (20) is applicable. Therefore, k_{18} can be calculated from the dose rate of the ^{60}Co γ-source, the measured $Co^{2+}(aq)$ yield, the maximum possible yield of $Co^{2+}(aq)$, $G[Co^{2+}(aq)] = G(\dot{R}H) = G[e^-(aq)] + G(OH) + G(H) \simeq 6.2$, the concentration of the complex, and k_{19}.* These results are summarized in Table 6.

The rates of reduction of several cobalt(III) and ruthenium(III) complexes by a series of aliphatic radicals were

$$G[Co^{2+}(aq)] = \frac{k_{18}[Co^{III}(NH_3)_5X]\,G[\dot{R}H]}{k_{18}[Co^{III}(NH_3)_5X] + k_{19}(\dot{R}H)} \quad (20)$$

measured. Two common features are evident from the results in Tables 3—5. (*a*) For a given complex, excluding $[Co(NH_3)_6]^{3+}$, the order of reactivity is $Me_2\dot{C}OH > Me\dot{C}HOH \sim Me\dot{C}HOEt > \dot{C}H_2OH > \overline{O{-}\dot{C}H{-}CH_2{-}O{-}CH_2{-}CH_2} > \dot{C}H_2CO_2{}^-$. The latter radical reacts only with two of the complexes studied,

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* The observation that $k_{obs.}$ in the buffered solution at pH 5.5 is considerably lower than that in an unbuffered solution at pH 4.5 indicates that the buffer takes part in the reduction mechanism beyond its role as a buffer. We decided therefore not to use buffers in the other experiments, and preferred to use small pulses which have little effect on the pH (see text).

[14] A. L. Buley, R. O. C. Norman, and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1966, 849; C. G. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794; C. E. B. Burchill and K. M. Perron, *Canad. J. Chem.*, 1971, **49**, 2382; C. V. Sonntag and E. Thoms, *Z. Naturforsch.* 1970, **B25**, 1405; F. Seidler and C. V. Sonntag, *ibid.*, 1969, **B24**, 780; A. Samuni and P. Neta, *J. Phys. Chem.*, 1973, **77**, 2425.

[15] K. M. Bansal, M. Gatzel, A. Henglein, and E. Janata, *J. Phys. Chem.*, 1973, **77**, 16.

$[RuCl(NH_3)_5]^{2+}$ and $[RuBr(NH_3)_5]^{2+}$. This order is in accord with the reported irreversible polarographic half-wave redox potential[9f] and with the order of reactivity towards $PhNO_2$ and similar organic oxidants.[16,*] (*b*) At pH 3.5—4.0 the rate of reduction of $[Co^{III}(NH_3)_5X]$ complexes by a given radical increases along the series $X = NH_3 \leqslant F^- < H_2O < Cl^- < Br^-$. This order was found also for the fewer $[Co^{III}(en)_2XY]$ and $[Ru^{III}(NH_3)_5X]$ complexes studied.

TABLE 4

Rates of reaction ($dm^3\ mol^{-1}\ s^{-1}$) of some aliphatic radicals with $[Co^{III}(en)_2XY]$ complexes *

Complex / Radical	*cis*-$[CoCl(en)_2(NH_3)]^{2+}$	*cis*-$[CoCl(en)_2(OH_2)]^{2+}$	*cis*-$[CoCl_2(en)_2]^+$	*trans*-$[CoCl_2(en)_2]^+$	*cis*-$[CoBrF(en)_2]^+$	*trans*-$[CoBr_2(en)_2]^+$
$\dot{C}H_2OH$	$\leqslant 2 \times 10^6$	$(1.8 \pm 0.5) \times 10^6$	$\leqslant 5 \times 10^6$	$(8 \pm 2) \times 10^6$	$\leqslant 2 \times 10^6$	2.6×10^8
$Me\dot{C}HOH$	4.2×10^6	2.0×10^7	3.8×10^7	1.5×10^8	2.8×10^7	5.7×10^8
$Me_2\dot{C}OH$	2.2×10^7	8.2×10^7	1.0×10^8	3.8×10^8	1.1×10^8	6.8×10^8
$Me\dot{C}HOEt$	4.6×10^6	3.5×10^7		1.5×10^8	4.9×10^7	6.5×10^8
$\overline{O-\dot{C}H-CH_2-O-CH_2-}CH_2$				3.5×10^7		4.4×10^8

* All the solutions contained 0.5—1 mol dm^{-3} of the organic solute and were saturated with N_2O; pH 3.5—4.0. The standard deviation of the rate constants is ±15%. No reaction was observed (for all the radicals studied) with $[Co(en)_3]^{3+}$ and *trans*-$[CoF_2(en)_2]^+$.

Several plausible mechanisms for the reduction of complexes by aliphatic radicals have been proposed. (*i*) Attack of the radical on the ligand X.[3] (*ii*) Attack of the radicals on one of the ammine groups (see above). (*iii*) An outer-sphere mechanism. (*iv*) The formation of a seven-co-ordinate complex as an intermediate.[4,13] (*v*) Hydrogen abstraction from one of the ammine groups.[7]

TABLE 5

Rates of reaction ($dm^3\ mol^{-1}\ s^{-1}$) of some aliphatic radicals with $[Ru^{III}(NH_3)_5X]$ complexes [a]

Complex / Radical	$[Ru(NH_3)_6]^{3+}$	$[RuCl(NH_3)_5]^{2+}$	$[RuBr(NH_3)_5]^{2+}$
$\dot{C}H_2OH$	4.1×10^7 [b]	1.2×10^8	
$Me\dot{C}HOH$	5.5×10^8 [b]	8.0×10^8	
$Me_2\dot{C}OH$	9.2×10^8 [b]	1.3×10^9	
$Me\dot{C}HOEt$	1.0×10^8	2.6×10^8	5.8×10^8
$\overline{O-\dot{C}H-CH_2-O-CH_2-}CH_2$	5.0×10^6	8.3×10^7	2.7×10^8
$\dot{C}H_2CO_2H$	$\leqslant 5 \times 10^6$ [c]	4.0×10^7 [c]	4.6×10^8 [c]

[a] All the solutions contained 0.5—1 mol dm^{-3} of the organic solute and were saturated with N_2O; pH 3.5—4.0. The standard deviation of the rate constants is ±15%. [b] From ref. 2. [c] pH 3.9.

The last two mechanisms have been ruled out for $[Co(NH_3)_6]^{3+}$ (see above discussion).[2] It is difficult to envisage an increase in the rates of reduction *via* these mechanisms by replacing a co-ordinated ammine group by a halide. We now discuss the other three plausible mechanisms in terms of the experimental results.

(*i*) Several oxidizing radicals were shown to reduce $[CoI(NH_3)_5]^{2+}$ and $[CoBr(NH_3)_5]^{2+}$ *via* an atom-transfer mechanism.[17] The observation that the $\dot{C}H_2CO_2^-$ radical reduces $[RuBr(NH_3)_5]^{2+}$ and $[RuCl(NH_3)_5]^{2+}$ can be explained by the same mechanism, as this radical is a strong oxidizing agent and a weak reducing agent.[2,18] The large effect of changing one of the ligands on the reactivity of the complexes towards the different radicals is in accord with a mechanism involving the formation of $[M^{III}(NH_3)_5(XCR^1R^2OH)]$ as an ' intermediate ' or transition state. The observation that the rates of reaction increase with the redox potential of the radical suggests that the ' intermediate ' decomposes into $[M^{II}(NH_3)_5X] + R^1R^2CO$ and not into $[M^{II}(NH_3)_5]^{2+} + R^1R^2C(OH)X$. (The final products in both cases are identical.) It is of interest to note that the radicals $\dot{C}H_2OH$, $Me\dot{C}HOH$, $Me_2\dot{C}OH$, and $Me\dot{C}HOEt$ react with $[Co(CN)(NH_3)_5]^{2+}$ yielding intermediates with an absorption spectrum between 250 and 550 nm. The mechanism of decomposition of these intermediates as well as their identification is under study. However, it is clear that the cyanide group is attacked in these reactions.

(*ii*) The rate of reaction of $\dot{C}H_2OH$ radicals with $[Co(NH_3)_6]^{3+}$ at pH *ca.* 6 is higher than that with all the other $[Co^{III}(NH_3)_5X]$ complexes studied (Tables 2 and 6). Thus the results seem to indicate that substitution of an ammine by a halide decreases the rate of reaction *via* the mechanism by which $[Co(NH_3)_6]^{3+}$ is reduced by $\dot{C}H_2OH$ radicals at pH *ca.* 6 (see above). On the other hand, at pH 3.5, $[Co(NH_3)_6]^{3+}$ is less reactive than all the other complexes. It therefore seems that the increase in the rate of reduction along the series $X = NH_3, F^-, H_2O, Cl^-, Br^-$ at pH 3.5 is due to another mechanism. Furthermore, the order of reactivity of the different radicals towards $[Co(NH_3)_6]^{3+}$ at pH 6 is the reverse of that found for any of the $[Co^{III}(NH_3)_5X]$ complexes at pH 3.5.

(*iii*) The correlation of the rates of reduction with the redox potentials might also be explained by the outer-

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[*] The rates of reduction of nitrobenzene by the $Me\dot{C}HOEt$ and $\overline{O-H\dot{C}-CH_2-O-CH_2-}CH_2$ radicals were not reported and were therefore measured by us as $k = 2.5 \times 10^8$ and $2.5 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$.

[16] K. D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsenges-ellschaft Phys. Chem.*, 1966, **70**, 862.

[17] A. Haim and H. Taube, *J. Amer. Chem. Soc.*, 1963, **95**, 495.

[18] T. S. Roche and J. F. Endicott, *Inorg. Chem.*, 1974, **13**, 1575.

sphere mechanism. However, the observation that atom transfer occurs at least in the reaction of the $\dot{\mathrm{C}}\mathrm{H_2}$-$\mathrm{CO_2^-}$ radicals with the $[\mathrm{Ru^{III}(NH_3)_5X}]$ complexes, and that $\mathrm{R^1R^2\dot{C}OH}$ radicals attack the cyano-group in $[\mathrm{Co(CN)(NH_3)_5}]^{2+}$, supports the 'bridged mechanism'. We cannot exclude the possibility that part of the reactions occur *via* the outer-sphere mechanism, although we feel that this is not the case.

TABLE 6

Rates of reaction of $\dot{\mathrm{C}}\mathrm{H_2OH}$ radicals with $[\mathrm{Co^{III}(NH_3)_5X}]$ complexes obtained by steady-state radiolysis *

	Concentration		$k(\dot{\mathrm{C}}\mathrm{H_2OH}$ + complex)
Complex	mol $\mathrm{dm^{-3}}$	$G(\mathrm{Co^{2+}})$	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$[\mathrm{CoF(NH_3)_5}]^{2+}$	2×10^{-4}	1.5	8×10^5
	1×10^{-3}	3.5	3×10^5
$[\mathrm{CoCl(NH_3)_5}]^{2+}$	1×10^{-4}	4.8	3×10^6
$[\mathrm{Co(NH_3)_5(OH_2)}]^{3+}$	1×10^{-4}	1.7	2×10^6
	1×10^{-3}	4.9	1×10^6

* All the solutions contained 1.0 mol $\mathrm{dm^{-3}}$ MeOH at pH 3.5—4.0 and were saturated with $\mathrm{N_2O}$. The standard deviation of the rate constants is ±30%. The large error limit is due to the error in the determination of $G[\mathrm{Co^{2+}(aq)}]$, ±0.3, and to the fact that part of the $\mathrm{Co^{2+}(aq)}$ is formed by reaction (5). Thus k was determined from the difference between two values of similar magnitude with a relatively large error.

Conclusions.—We would like to emphasize the following points. The results clearly indicate that there is a basic difference between the mechanisms of reduction of $[\mathrm{M^{III}(NH_3)_5X}]$ complexes by aliphatic radicals and by low-valent transition-metal complexes. These differences stem from: (*a*) the free radicals do not have an empty low-lying orbital capable of co-ordinating to the ligand X (furthermore, in any written structure of the 'intermediate' or transition state an unpaired electron has to be considered); (*b*) most of the free radicals studied are considerably stronger reducing agents than most of the low-valent transition-metal complexes used in aqueous solutions;[9c] and (*c*) although strong reducing agents, the free radicals studied are also very strong oxidizing agents.[18] These features of the aliphatic free radicals permit mechanisms of reduction like those suggested above for the reduction of $[\mathrm{Co(NH_3)_6}]^{3+}$ by $\dot{\mathrm{C}}\mathrm{H_2OH}$ radicals.

The study of the rates of reaction of aliphatic radicals with transition-metal complexes including oxidation reactions[6a] indicates the effects of different substituents on the reactivity. In interpreting the results one has to remember that most of these reactions are within three orders of magnitude of the diffusion-controlled limit, thus diminishing and masking different effects. The results also enable the study of the pK values of the radicals, and, in some cases, where the radical undergoes a first-order reaction, the rate of this reaction, from the change in the reactivity towards the complex [*e.g.* water elimination from the $\mathrm{CH_2(OH)\dot{C}HOH}$ and $\mathrm{HO_2C\dot{C}(OH)}$-$\mathrm{CH(OH)CO_2H}$ radicals].

The results suggest that the mechanisms of reduction of $[\mathrm{Co(NH_3)_6}]^{3+}$ and $[\mathrm{Ru(NH_3)_6}]^{3+}$ differ significantly (see above and ref. 2). The study of the kinetics of reaction of aliphatic radicals with similar complexes of other transition metals might help in elucidating the sources of these differences.

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