Inorg. Chem. **1982**, *21*, 2537–2542 **2537**

81572-49-8; $[(NH_3)_5Co(pyruvato)]^{2+}$, 19306-91-3; $[(NH_3)_5Co(phenylglyoxylato)]^{2+}$, 49861-82-7; $[(NH_3)_5Co((2,4\text{-dimethoxyphenyl})glyoxylato)]^{2+}$, 81572-50-1; $[(NH_3)_5Co((2,4,6\text{-trimethoxyphenyl})glyoxylato)]^{2+}$, 81572-51-2; $[(NH_3)_5Co(4\text{-formylbenzoato})]^{2+}$, 19743-65-8; $[(NH_3)_5Co(2\text{-formylbenzoato})]^{2+}$, 42532-71-8; $[(NH_3)_5Co(glyoxylato)](ClO_4)_2$, 15189-50-1; V, 7440-62-3; Cr, 7440-47-3; Eu, 7440-53-1; $Ru(NH_3)_6^{2+}$, 19052-44-9; U, 7440-61-1; $Rb^{+}\cdot$, 78962-23-6; RbH_2, 13345-95-4.

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Novel Method for the Chemical Generation of Aliphatic Radicals and Its Application to the Kinetics of Reduction of Cobalt(III)–Amine Complexes by 2-Hydroxy-2-propyl Radicals

JAMES H. ESPENSON,* MAKOTO SHIMURA, and ANDREJA BAKAČ

Received February 17, 1982

Homolytic cleavage of the chromium–carbon bond in the complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$ provides a ready source of the carbon-centered radical $\cdot C(CH_3)_2OH$ in strongly acidic solutions, pH 0–3. The kinetics of reaction of the radical with another substrate present in solution can be studied in competition with the recombination reaction between radical and Cr^{2+}. The method was applied to a study of the reduction of several cobalt(III) complexes, with the following pH-independent rate constants at 25.0 °C: $Co(NH_3)_6^{3+}$, 4.1×10^5 M^{-1} s^{-1}; $Co(ND_3)_6^{3+}$, 3.0×10^5; $Co(en)_3^{3+}$, 1.7×10^5; $Co(tn)_3^{3+}$, 1.9×10^6; $Co(chxn)_3^{3+}$, $<1 \times 10^4$. The mechanism of $Co(NH_3)_6^{3+}$ reduction over the entire pH range 0–14 has been reformulated as consisting of three pathways: (1) outer-sphere electron transfer from $\cdot C(CH_3)_2OH$, dominant at pH 0–3; (2) outer-sphere electron transfer from $\cdot C(CH_3)_2O^-$, dominant at pH >10; (3) reversible formation of a covalent intermediate, $(NH_3)_5CoNH_2C(CH_3)_2OH^{2+}$, whose subsequent decomposition is the prevalent reaction at intermediate pH, pH 5–9. The rate constants for the first of these reactions correlate well with λ_{max} and $E°$ values of the Co(III) complexes and with the rate constants for the corresponding reduction by $Cr(bpy)_3^{2+}$, save for $Co(chxn)_3^{3+}$ whose low reactivity with the free radical is attributed to its conformational inflexibility. Several Cr(III) complexes—$Cr(NH_3)_6^{3+}$, $Cr(urea)_6^{3+}$, and $(H_2O)_5CrCl^{2+}$—failed to react with $\cdot C(CH_3)_2OH$.

Introduction

The 2-hydroxy-2-propyl radical (referred to by Chemical Abstracts as 1-hydroxy-1-methylethyl) is a powerful one-electron reducing agent: $(CH_3)_2CO + H^+ + e^- = \cdot C(CH_3)_2OH$, $E° = -1.2$ V[1] vs. NHE. The rates of its reactions and those of related free radicals are often determined by the pulse-radiolysis technique. The competition between the reaction of the substrate of interest with the free radical and its bimolecular disproportionation poses a limit: only the most reactive substrates, typically those with $k > \sim 3 \times 10^6$ M^{-1} s^{-1}, can be studied.

In the course of studying the reversible homolytic cleavage of organochromium cations,[2] including $(H_2O)_5CrC(CH_3)_2OH^{2+}$, it occurred to us that this reaction could be used for the chemical, rather than radiolytic, generation of the free radical in acidic solution. The experimental conditions can easily be controlled to adjust the rate of radical formation to a range suitable for quantitative kinetic studies of the rates of the radical–substrate reaction.

We describe in this paper the development of the technique and its limitations, chief among which is the requirement that the substrate not react rapidly with Cr^{2+}. The reaction of $\cdot C(CH_3)_2OH$ with $Co(NH_3)_6^{3+}$ and related complexes[3–9] provides an important application since the constants in acidic solution fall to values too low for radiolytic determination. The mechanism is, moreover, of considerable interest in view of the change in rate at a pH well below the pK_a value of the free radical, which has been the basis for suggestions that certain chemical intermediates play a key role in the oxidation–reduction reaction.[4,5]

The notation used for the reactions occurring is given in eq 1–3, with $Co(NH_3)_6^{3+}$ as one example of the complexes under consideration. The values of the forward[2] and reverse[10] rate constants for the first step being known, the results permit the evaluation of k_2.

$$CrC(CH_3)_2OH^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{2+} + \cdot C(CH_3)_2OH \qquad (1)$$

$$Co(NH_3)_6^{3+} + \cdot C(CH_3)_2OH \xrightarrow{k_2} Co(NH_3)_6^{2+} + (CH_3)_2CO + H^+ \qquad (2)$$

$$Co(NH_3)_6^{2+} + 6H_3O^+ \xrightarrow{\text{fast}} Co(H_2O)_6^{2+} + 6NH_4^+ \qquad (3)$$

Experimental Section

The cobalt(III) and chromium(III) complexes[11] were prepared by standard methods: $[Co(NH_3)_6](ClO_4)_3$,[12] $[Co(ND_3)_6](ClO_4)_3$,[13] $[Co(en)_3](ClO_4)_3$,[14] $[Co(tn)_3](ClO_4)_3$,[15] $[Co(chxn)_3]Cl_3\cdot H_2O$,[16]

---

(1) The value cited is from the estimate made by: Endicott, J. F. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 90–92. It is probably preferred to the experimental determination of $E_{1/2}$ given by: Lilie, J.; Beck, G.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 458.

(2) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(3) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1972**, *94*, 6944.

(4) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1977**, 1056.

(5) Olson, K. R.; Hoffman, M. Z. *J. Chem. Soc., Chem. Commun.* **1974**, 938.

(6) Hoffman, M. Z.; Simic, M. *J. Am. Chem. Soc.* **1972**, *94*, 1757.

(7) Campano, D. C.; Kantrowitz, E. R.; Hoffman, M. Z.; Weinberg, M. S. *J. Phys. Chem.* **1974**, *78*, 626.

(8) Papaconstantinou, E. *J. Inorg. Chem.* **1978**, *40*, 2071.

(9) Papaconstantinou, E. *J. Inorg. Nucl. Chem.* **1981**, *43*, 115.

(10) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(11) The chelating ligands are abbreviated as follows: en = 1,2-diaminoethane; tn = 1,3-diaminopropane; chxn = *trans*-1,2-diaminocyclohexane; bpy = 2,2′-bipyridine.

(12) Bjerrum, J.; McReynolds, J. P. *Inorg. Synth.* **1946**, *2*, 216.

(13) Anderson, J. S.; Briscoe, H. V. A.; Spoor, N. *J. Chem. Soc.* **1943**, 361.

(14) Work, J. B. *Inorg. Synth.* **1946**, *2*, 221.

(15) Bailar, J. C., Jr.; Work, J. B. *J. Am. Chem. Soc.* **1946**, *68*, 232.

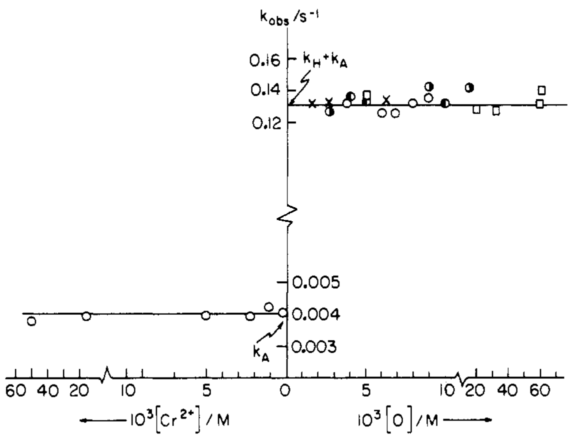


Figure 1. Jump in rate constant for decomposition of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ from solutions containing added Cr^{2+} (left, where only acidolysis is important) to experiments (right) containing various oxidizing scavengers for Cr^{2+} and $\cdot C(CH_3)_2OH$. The latter include points for $Co(NH_3)_5F^{2+}$ (◐), $Co(NH_3)_5Cl^{2+}$ (○), $Co(NH_3)_5Br^{2+}$ (◑), VO^{2+} (□), and H_2O_2 (×).

$[Cr(NH_3)_6](ClO_4)_3$.[17] and $[Cr(urea)_6](ClO_4)_3$.[18] Solutions of $(H_2O)_5CrCl^{2+}$ were prepared from $[CrCl_2(H_2O)_4]Cl$ and isolated by ion-exchange chromatography. Solutions containing $(H_2O)_5Cr(CH_3)_2OH^{2+}$ were prepared as needed under rigorously O_2-free conditions from hydrogen peroxide and a controlled stoichiometric excess of $Cr(H_2O)_6^{2+}$ in the presence of 0.27–0.40 M 2-propanol.[2,19]

The kinetic measurements were made under a nitrogen atmosphere at 25.0 °C. Ionic strength was controlled by addition of lithium perchlorate at 0.10 or 1.00 M. Reactions were initiated by addition of the oxidant with syringe-rubber septum procedures. The reactions were monitored spectrophotometrically by using a Cary Model 219 spectrophotometer to follow the decrease in $[CrC(CH_3)_2OH^{2+}]$ near one of its absorption maxima: 311 nm (ϵ 2500 M^{-1} cm^{-1}) or 407 nm (700 M^{-1} cm^{-1}). The kinetic data followed a first-order rate law in each run and were analyzed by standard methods.

Results

Acidolysis and Homolysis Reactions. The basis of the kinetic method rests on results[2] which show a step-function jump in the rate of decomposition of $CrC(CH_3)_2OH^{2+}$ when certain oxidizing agents are added, as shown in Figure 1. The species which are effective are those which react rapidly with Cr^{2+} and/or $\cdot C(CH_3)_2OH$ but do not react directly with the organochromium complex. Thus $Co(NH_3)_5X^{2+}$ complexes as well as VO^{2+} and H_2O_2 lead to much more rapid decomposition than when the oxidizing agents are absent, although the rate constant is independent of which of the species is added and of its concentration. The principal reaction under these conditions is homolysis (eq 1), as documented earlier.[2]

In the absence of the oxidizing agents, particularly if Cr^{2+} is present, the only mode of decomposition is the much slower acidolysis reaction[19,20] eq 4, for which the apparent rate constant depends upon $[H^+]$ (eq 5).

$$(H_2O)_5CrC(CH_3)_2OH^{2+} + H_3O^+ = Cr(H_2O)_6^{3+} + (CH_3)_2CHOH \qquad (4)$$

$$k_A = k_{1A} + k_{2A}[H_3O^+] \qquad (5)$$

Competitive Kinetics. If the species under study is one which does *not* react rapidly with Cr^{2+}, then the situation depicted by eq 1–3 will prevail. The radical will react competitively with Cr^{2+} ($k_{-1} = 5.1 \times 10^7$ M^{-1} s^{-1})[10] or with the cobalt(III) complex (k_2). The steady-state approximation for $[\cdot C(CH_3)_2OH]$ results in expression 6 for the rate of reaction. The

$$\frac{-d[CrC(CH_3)_2OH^{2+}]}{dt} = \left(k_A + \frac{k_1k_2[Co(III)]}{k_{-1}[Cr^{2+}] + k_2[Co(III)]}\right)[CrC(CH_3)_2OH^{2+}] \qquad (6)$$

experiments have concentrations of Cr^{2+} and the cobalt(III) complex which are sufficiently high relative to the initial value of $[CrC(CH_3)_2OH^{2+}]$ that the reaction follows pseudo-first-order kinetics. The values of k_{obsd} will increase with [Co(III)]; typical runs are shown in Figure 2. The relationship for k_{obsd} can be rearranged to the linearized form

$$\frac{1}{k_{obsd} - k_A} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\frac{[Cr^{2+}]}{[Co(III)]} \qquad (7)$$

The kinetic data for $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $Co(tn)_3^{3+}$ are given in Tables I–III. The plots suggested by eq 7 are

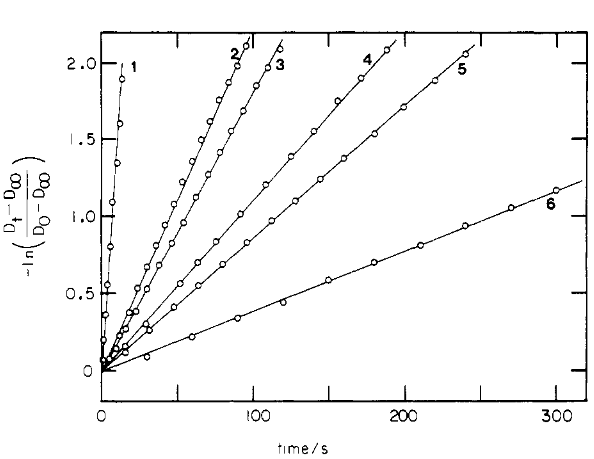


Figure 2. First-order kinetic plots showing the increase in rate from an experiment (6) containing Cr^{2+}, representing acidolysis, to a run (1) with $Co(NH_3)_5Cl^{2+}$ present, representing homolysis. The intervening graphs (2–5) present data from determinations with $[Cr^{2+}]_0$ = 4.40 mM, $[CrC(CH_3)_2OH^{2+}]_0$ = 0.30 mM, and varying $[Co(tn)_3^{3+}]_0$: 21.8 16.7, 7.53, and 5.02 mM, respectively.

Table I. Kinetic Data[a] for the Reduction of $Co(NH_3)_6^{3+}$ by $\cdot C(CH_3)_2OH$

$10^2[H^+]$/M	$[Cr^{2+}]/[Co(NH_3)_6^{3+}]$[b]	10^3k_{obsd}/s^{-1} [c]
0.45	0.524	5.69 (5.79)
0.45	0.465	6.01 (6.03)
0.45	0.418	6.60 (6.26)
0.45	0.362	6.51 (6.63)
0.45	0.313	6.55 (7.05)
1.70	0.588	5.65 (5.60)
1.70	0.482	5.76 (5.97)
1.70	0.407	6.45 (6.35)
1.70	0.312	7.05 (7.07)
1.70	0.270	7.37 (7.55)
6.38	0.670	5.77 (5.58)
6.38	0.501	6.33 (6.08)
6.38	0.398	7.04 (6.58)
6.38	0.331	7.12 (7.08)
6.38	0.293	7.20 (7.45)
6.38	0.264	8.25 (7.82)

[a] At 25.0 °C, 0.10 M ionic strength, with $[CrC(CH_3)_2OH^{2+}]_0 = 1.5 \times 10^{-4}$ M, $[(CH_3)_2CHOH] = 0.403$ M, and $[Cr^{2+}]_0 = 1.37 \times 10^{-3}$ M. [b] At the midpoint of the kinetic run. [c] The values in parentheses were calculated from $k_1 = 0.127$ s^{-1} and the value of k_A appropriate to the value of $[H^+]$ at this ionic strength.

---

(16) Beattie, J. K.; Binstead, R. A.; Broccardo, M. *Inorg. Chem.* **1978**, *17*, 1822.

(17) Mori, M. *Nippon Kagaku Zasshi* **1953**, *74*, 253.

(18) Pfeiffer, P. *Chem. Ber.* **1903**, *36*, 1926.

(19) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

(20) Our values of k_A at 25.0 °C are in reasonably good agreement with those reported earlier.[19] The values found here follow the equations 10^3k_A (s^{-1}) = (3.854 ± 0.015) + (3.50 ± 0.40)$[H^+]$ at μ = 0.100 M and 10^3k_A (s^{-1}) = (3.31 ± 0.10) + (4.91 ± 0.71)$[H^+]$ at μ = 1.00 M.

Table II. Kinetic Data[a] for the Reduction of $Co(en)_3{}^{3+}$ by $\cdot C(CH_3)_2OH$

$10^2[H^+]/M$	$[Cr^{2+}]/[Co(en)_3{}^{3+}]$[b]	$10^3 k_{obsd}/s^{-1}$ [c]
3.94	0.232	5.32 (5.35)
3.94	0.174	5.76 (5.95)
3.94	0.139	6.51 (6.55)
3.98	0.110	7.04 (7.33)
3.98	0.0881	7.28 (8.25)
7.06	0.233	5.55 (5.49)
7.06	0.175	6.40 (6.09)
7.06	0.140	6.52 (6.68)
7.10	0.111	7.13 (7.45)
7.10	0.089	8.36 (8.37)
13.0	0.243	5.68 (5.71)
13.3	0.226	6.01 (5.85)
13.0	0.217	5.75 (5.92)
13.3	0.193	6.30 (6.17)
12.9	0.175	6.52 (6.38)
12.9	0.134	6.75 (7.10)
12.7	0.135	7.07 (7.07)
12.7	0.108	7.82 (7.83)
13.3	0.0895	8.83 (8.63)
12.7	0.0823	8.59 (8.99)
13.4	0.0740	10.5 (9.6)
13.4	0.0635	12.2 (10.4)
32.0	0.228	6.41 (6.76)
32.1	0.0782	11.3 (10.2)
32.1	0.0628	11.9 (11.4)

[a] At 25.0 °C, 1.00 M ionic strength, with $[CrC(CH_3)_2OH^{2+}]_0 = (3.0\text{–}9.0) \times 10^{-4}$ M, $[(CH_3)_2CHOH] = 0.403$ M, $[Cr^{2+}]_0 = (1.90\text{–}5.77) \times 10^{-3}$ M, and $[Co(en)_3{}^{3+}]_0 = (1.95\text{–}3.30) \times 10^{-2}$ M. [b] See footnote *b* in Table I. [c] See footnote *c* in Table I.

Table III. Kinetic Data[a] for the Reduction of $Co(tn)_3{}^{3+}$ by $\cdot C(CH_3)_2OH$

$10^2[H^+]/M$	$[Cr^{2+}]/[Co(tn)^{3+}]$[b]	$10^3 k_{obsd}/s^{-1}$ [c]
1.68	0.760	9.53 (9.21)
1.68	0.536	11.5 (11.5)
1.68	0.407	14.2 (13.8)
1.68	0.268	19.1 (18.6)
6.67	0.900	8.57 (8.58)
6.67	0.773	9.92 (9.36)
6.67	0.674	10.2 (10.2)
6.67	0.597	11.0 (10.9)
6.67	0.539	12.8 (11.7)
6.67	0.448	13.1 (13.2)
6.67	0.382	14.5 (14.7)
6.67	0.268	17.8 (18.8)
6.67	0.206	22.1 (22.7)
19.1	0.887	9.13 (9.26)
19.1	0.664	10.3 (10.9)
19.1	0.481	12.9 (13.2)
19.1	0.263	19.4 (19.7)

[a] At 25.0 °C, 1.00 M ionic strength, with $[CrC(CH_3)_2OH^{2+}]_0 = 3.0 \times 10^{-4}$ M, $[(CH_3)_2CHOH] = 0.347$ M, $[Cr^{2+}] = 4.40 \times 10^{-3}$ M, and $[Co(tn)_3{}^{3+}] = (5.0\text{–}22) \times 10^{-3}$ M. [b] See footnote *b* in Table I. [c] See footnote *c* in Table I.

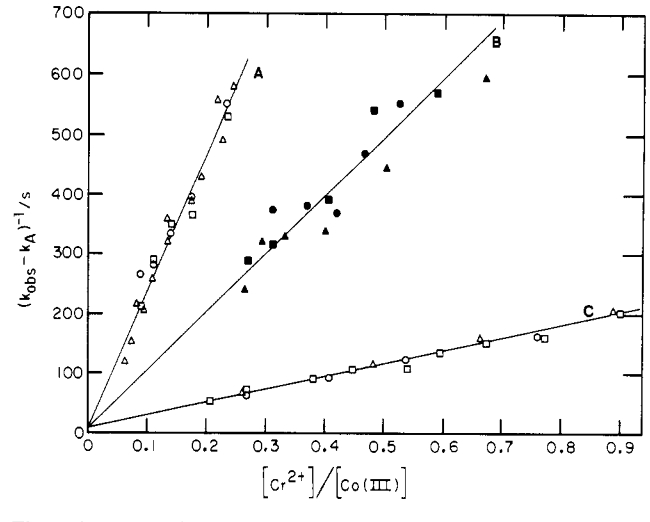


Figure 3. First-order rate constant correlation with the concentrations of the competitive reagents for the free radical such that a plot of $1/(k_{obsd} - k_A)$ varies linearly with the concentration ratio $[Cr^{2+}]/[Co(III)]$ according to eq 7. Data are shown for $Co(en)_3{}^{3+}$ (A), $Co(NH_3)_6{}^{3+}$ (B), and $Co(tn)_3{}^{3+}$ (C); the different symbols represent concentrations of $[H^+]$ (given in Tables I–III) which increase in the order ○, □, △, and ▽.

shown in Figure 3. The numerical fit of the parameters was carried out by using a nonlinear least-squares fit to eq 8 with

$$k_{obsd} = k_{1A} + k_{2A}[H^+] + \frac{k_1}{1 + (k_{-1}/k_2)[Cr^{2+}]/[Co(III)]} \tag{8}$$

k_{1A}, k_{2A} and k_1 fixed at their independently known values.[2,10] This afforded the values of the ratio k_{-1}/k_2 and, since $k_{-1} = 5.1 \times 10^7$ M^{-1} s^{-1},[10] of k_2. (A treatment in which k_1 is also allowed to vary yielded comparable values.) With due allowance for the $[H^+]$ dependence of k_A,[19,20] the ratio k_{-1}/k_2 (and, hence, k_2) was found to be independent of $[H^+]$. The range of $[H^+]$ was from 4.5×10^{-3} to 0.32 M, all three complexes considered together.

As demonstrated previously,[3-9] Co^{2+} is the product of the reaction, and is formed quantitatively. This was checked[21] again with this method for generation of the radical. The yield of Co^{2+} was determined to be 1.70×10^{-4} M (expected, 1.61×10^{-4} M, or 106%) in an experiment using $Co(en)_3{}^{3+}$ at 0.043 M H^+.

Anion Effects. Measurements for the $Co(chxn)_3{}^{3+}$ complex were made in chloride media since its perchlorate salt was practically insoluble. The rate constants observed were independent of $[Co(chxn)_3{}^{3+}]$ up to a ratio of $[Co(chxn)_3{}^{3+}]/[Cr^{2+}] = 13$, the value of k_{obsd} being essentially equal to k_A in this medium. Thus, the reduction of $Co(chxn)_3{}^{3+}$ by $\cdot C(CH_3)_2OH$ has the upper limit, $k_2 < 10^4$ M^{-1} s^{-1}.

So that any possible effects of chloride ions on reactions of $\cdot C(CH_3)_2OH$ could be explored, measurements on the various reactions of $CrC(CH_3)_2OH^{2+}$ by itself and with $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ were also conducted in LiCl–$LiClO_4$ media having $\mu = 0.10$ and 1.0 M, respectively. The data show the following: (1) Acidolysis is slightly faster, $k_A = 4.45 \times 10^{-3}$ s^{-1} at $[Cl^-] = 0.060$ M compared to 3.89×10^{-3} s^{-1} in perchlorate medium (both 5.27×10^{-3} M H^+, $\mu = 0.10$ M), and $k_A = 4.01 \times 10^{-3}$ s^{-1} at $[Cl^-] = 0.60$ M, compared to 3.55×10^{-3} s^{-1} (both at 0.0667 M H^+, $\mu = 1.00$ M). (2) Homolysis (k_1) is completely unaffected by chloride ions up to $[Cl^-] = 0.49$ M. (3) The values of k_{-1}/k_2 are 248 for $Co(NH_3)_6{}^{3+}$ at 0.060 M Cl^- and 605 for $Co(en)_3{}^{3+}$ at 0.60 M Cl^-, each about twice the value (125 and 293, respectively) determined in perchlorate medium.

Deuterium Isotope Effects. Kinetics experiments were conducted with various combinations of isotopic substitution: acidolysis and homolysis in D_2O and reduction of $Co(ND_3)_6{}^{3+}$ in H_2O, $Co(NH_3)_6{}^{3+}$ in D_2O, and $Co(ND_3)_6{}^{3+}$ in D_2O by $\cdot C(CH_3)_2OH/\cdot C(CH_3)_2OD$. In acidic solution coordinated ammonias and solvent water exchange hydrogens negligibly slowly, $k = 1.6 \times 10^{-6}$ s^{-1}.[22]

The acidolysis of $(D_2O)_5CrC(CH_3)_2OD^{2+}$ proceeds with $k_A = 6.43 \times 10^{-4}$ s^{-1} (25.0 °C, 96% D_2O, 0.010 M D_3O^+, 0.10

---

(21) Kitson, R. F. *Anal. Chem.* **1950**, *22*, 664.
(22) Basolo, F.; Palmer, J. W.; Pearson, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 1073.

Table IV. Kinetic Data for the Reduction of $Co(ND_3)_6{}^{3+}$ by $\cdot C(CH_3)_2OH/\cdot C(CH_3)_2OD$ in H_2O and D_2O

in H_2O[a]		in D_2O[b]	
$[Cr^{2+}]/[Co(ND_3)_6{}^{3+}]$	$10^3k_{obsd}/s^{-1}$ [c]	$[Cr^{2+}]/[Co(ND_3)_6{}^{3+}]$	$10^3k_{obsd}/s^{-1}$ [c]
0.531	5.49 (5.29)	0.425	2.09 (2.07)
0.433	5.60 (5.60)	0.387	2.20 (2.21)
0.424	5.55 (5.64)	0.356	2.38 (2.35)
0.384	5.86 (5.82)	0.306	2.94 (2.62)
0.356	6.29 (5.97)	0.286	2.97 (2.89)
0.352	6.13 (5.99)	0.239	3.11 (3.16)
0.301	6.55 (6.34)	0.178	3.64 (4.00)
0.288	6.25 (6.45)		
0.280	6.72 (6.52)		
0.250	6.66 (6.83)		
0.214	6.87 (7.31)		

[a] At $\mu = 0.10$ M, 25.0 °C, with $[CrC(CH_3)_2OH^{2+}]_0 = 9.0 \times 10^{-5}$ M and $[(CH_3)_2CHOH] = 0.403$ M. [b] At $\mu = 0.10$ M, 25.0 °C, in 96% D_2O, with $[CrC(CH_3)_2OD^{2+}]_0 = 9.0 \times 10^{-5}$ M and $[(CH_3)_2CHOH]_0 = 0.347$ M. [c] Calculated values in parentheses.

Table V. Summary of Rate Constants[a] for the Reduction of Cobalt(III)-Amine Complexes by 2-Hydroxy-2-propyl Radicals

complex	k_{-1}/k_2	$k_2/M^{-1}\ s^{-1}$	reaction medium
$Co(NH_3)_6{}^{3+}$	125 ± 3	4.1×10^5	$\mu = 0.10$
$Co(en)_3{}^{3+}$	293 ± 7	1.7×10^5	$\mu = 1.0$
$Co(tn)_3{}^{3+}$	274 ± 0.4	$1.8_6 \times 10^6$	$\mu = 1.0$
$Co(chxn)_3{}^{3+}$	$>5 \times 10^3$	$<1 \times 10^4$	$\mu = 1.0$
$Co(ND_3)_6{}^{3+}$	169 ± 5	3.0×10^5	$\mu = 0.1$, H_2O
$Co(NH_3)_6{}^{3+}$	113 ± 4	4.5×10^5 [b]	$\mu = 0.1$, D_2O
$Co(ND_3)_6{}^{3+}$	210 ± 7	2.4×10^5 [b]	$\mu = 0.1$, D_2O

[a] Values of k_{-1}/k_2 at 25.0 °C; k_2 calculated with $k_{-1} = 5.1 \times 10^7\ M^{-1}\ s^{-1}$ (22 ± 2 °C).[10] The uncertainty in k_2 is thus ±10–15%. [b] Calculated by assuming $k_{-1}(D_2O) = k_{-1}(H_2O)$.

M ionic strength) compared to $(H_2O)_5CrC(CH_3)_2OH^{2+}$ under the same conditions in H_2O/H_3O^+ with $k_A = 4.13 \times 10^{-3}\ s^{-1}$. Although each is a composite of two rate constants (eq 5), the values consist largely of the acid-independent term at this acid concentration. Hence $k_{1A}(H)/k_{1A}(D) \approx 6.3$.

The rate constant for homolysis for $(D_2O)_5CrC(CH_3)_2OD^{2+}$ in D_2O was determined with $Co(NH_3)_5Cl^{2+}$. The value in 96% D_2O ($k_1(D) = 0.129\ s^{-1}$) is essentially the same as the value in H_2O ($0.127\ s^{-1}$).

Reductions of the hexaamminecobalt(III) complexes with 2-hydroxy-2-propyl radicals were examined as in the preceding sections. The effect of solvent on the rate constants for a given complex proved to be small, whereas the change from coordinated ND_3 to NH_3 increased the ratio k_{-1}/k_2 quite appreciably, a factor of 1.35 in H_2O, or 1.86 in D_2O. The data are given in Table IV, and a summary of all the values appears in Table V.

Reactions of $\cdot C(CH_3)_2OH$ with Cr(III) Complexes. It was mentioned in a preceding section that the reaction of $\cdot C(CH_3)_2OH$ with $Co(chxn)_3{}^{3+}$ was too slow for determination by this method. The same is true of the three complexes $Cr(NH_3)_6{}^{3+}$, $Cr(urea)_6{}^{3+}$, and $(H_2O)_5CrCl^{2+}$. In each case, the rate constant was within 10% of the value of k_A even at the lowest ratios $[Cr^{2+}]/[Cr(III)]$ used. On the basis of the concentrations employed and the 10% detection limit, the upper limits of the rate constants for the three are 7×10^4, 7×10^4, and $3 \times 10^4\ M^{-1}\ s^{-1}$, respectively.

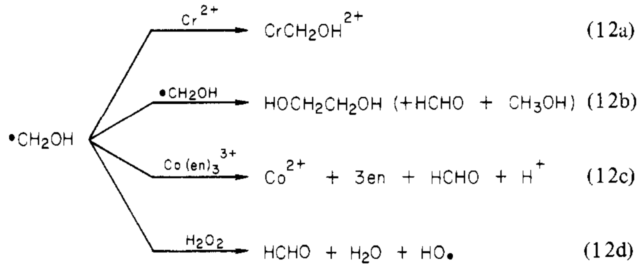
Reaction of $\cdot CH_2OH$ with $Co(en)_3{}^{3+}$. The homolytic cleavage of $(H_2O)_5CrCH_2OH^{2+}$ occurs so slowly relative to its acidolysis that it does not provide a useful source of the hydroxyalkyl radical based on the corresponding techniques. Instead a mixture of $(H_2O)_5CrCH_2Ph^{2+}$ (6.2×10^{-4} M), H_2O_2 (6.4×10^{-4} M), and CH_3OH (0.81–3.5 M) was used to generate $\cdot CH_2OH$ in the presence of $Co(en)_3{}^{3+}$ (7.6×10^{-2} M). The reactions occurring in the generation of the free radical are[19,23] given by eq 9–11. The radical so formed then has

$$CrCH_2Ph^{2+} \rightarrow Cr^{2+} + PhCH_2\cdot \qquad (9)$$

$$Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + HO\cdot \qquad (10)$$

$$HO\cdot + CH_3OH \rightarrow H_2O + \cdot CH_2OH \qquad (11)$$

several possible reactions (eq 12).



The product solutions were analyzed for $[Co^{2+}]$, which was found to be present at an amount very much smaller than it would be were eq 12c an important reaction. Evidently eq 12b predominates. On the basis of values found, an upper limit of $k_{12c} < 10^3\ M^{-1}\ s^{-1}$ may be set in acidic solution (pH 2.5), using $k_{12d} = 4 \times 10^4\ M^{-1}\ s^{-1}$.[24]

Interpretation and Discussion

Kinetic Techniques for Free Radical Rate Constants. The method developed for obtaining quantitative kinetic data for the reactions of $\cdot C(CH_3)_2OH$ and related radicals is applicable for reagents which react with the free radical but not, or not rapidly, with Cr^{2+}. It is advantageous where the self-reaction of the free radical might preclude use of pulse radiolysis. The method is applicable in strongly acidic solution, pH 0–3. Further amplification of the technique itself appears unnecessary.

Mechanism of $Co(NH_3)_6{}^{3+}$ Reduction. The Rate–pH Profile. The particular reaction system of $Co(NH_3)_6{}^{3+} + \cdot C(CH_3)_2OH$ is one which has seemed quite perplexing.[3–9] It, and the related reaction with $\cdot CH_2OH$, have been studied extensively. The troublesome feature is that marked pH effects are seen in a region (pH ~4–6) far removed from the pK_a of the Co(III) complex ($pK_{Co} \approx 15$) or the pK_a of the free radicals ($\cdot C(CH_3)_2OH$, $pK_a = 12.0$; $\cdot CH_2OH$, $pK_a = 10.7$). There are in fact three plateaus in the pH-rate profile, at approximately pH 0–3, 6–8, and >12. The change in rate between pH 0 and 8 is the feature, found for both $\cdot C(CH_3)_2OH$ and $\cdot CH_2OH$ reactions, which is difficult to account for. Closely related to that is the pH dependence of the yield of Co^{2+}; the reaction with $\cdot C(CH_3)_2OH$ produces Co^{2+} quantitatively throughout,[3,4,9] whereas that with $\cdot CH_2OH$ has a yield of Co^{2+} and of HCHO which decreases steadily with $[H^+]$, becoming quite small at pH <4.[4–6,9]

One explanation[9] for this phenomenon suggests the formation of an outer-sphere complex which is more acidic than its constituents (eq 13). A similar but less specific proposal[5]

$$Co(NH_3)_6{}^{3+},\cdot CH_2OH \overset{K_a}{\rightleftharpoons} Co(NH_3)_6{}^{3+},\cdot CH_2O^- + H^+ \qquad (13)$$

was made in terms of the deprotonation of an associated free radical having a pK_a value lower than that of the constituents. The claim was made[5,9] that if pK_a were ~4.2 this would duplicate the observed pH profiles of both rate and product yields provided that the basic form reacted by internal electron transfer to produce Co^{2+} at a rate greater than the acidic form. Further implications of a comparison of the pH dependences of the rate constant and the Co^{2+} yields are that, in the case of $\cdot CH_2OH$, radical self-reaction predominates over Co^{2+}

---

[23] Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.

[24] Burchill, C. E.; Ginns, I. S. *Can. J. Chem.* **1970**, *48*, 2628.

Table VI. Comparisons of the Properties of Cobalt(III)–Amine Complexes with Rate Constants for Their Reactions with the 2-Hydroxy-2-propyl Radical and Tris(bipyridine)chromium(II) Ion

Co(III) complex	log k_{298}		λ_{max}^{Co}/nm	$E°_{Co(III)/Co(II)}$/V vs SCE
	$\cdot C(CH_3)_2OH$	$Cr(bpy)_3^{2+}$		
$Co(tn)_3^{3+}$	6.27	3.46[b]	488	
$Co(NH_3)_6^{3+}$ (H_2O/D_2O)	5.61, 5.65	2.39, 2.40[c]	474	−0.245[d]
$Co(ND_3)_6^{3+}$ (H_2O/D_2O)	5.47, 5.38	2.26[c]	474	
$Co(en)_3^{3+}$	5.24	1.54[e]	466	−0.495[f]
$Co(chxn)_3^{3+}$	<4.0	1.60[e]	470	−0.515[g]

[a] This work. [b] Reference 32. [c] Reference 31. [d] Reference 29. [e] Reference 16. [d] Reference 28. [g] Reference 30.

formation at a pH <4, whereas in the case of $\cdot C(CH_3)_2OH$ only a reduction in rate would be noted, self-reaction remaining unimportant at all pHs.

These mechanisms will not reproduce the rate profile with its plateau at pH 6–8. Instead, they would lead to an apparent rate constant which increases indefinitely with pH.[25]

We wish to suggest a kinetically consistent mechanism to account for the entire range of behavior, a proposal consisting of three concurrent pathways, each prevalent in a particular pH range. Pathway 1 is outer-sphere electron transfer in which the reaction of eq 2 is viewed as an elementary step. Its detailed mechanism is considered in a subsequent section. This would be the predominant reaction at pH 0–3. Pathway 2 is an analogous reaction of the conjugate base from the free radical. This pathway, with rate constant designated k_5, would predominate at pH >10 and, as observed, would be expected to be much more efficient than the first (i.e., $k_5 >> k_2$) since the $\cdot CR_2O^-$ radical anions (R = H, CH_3) are substantially more powerful reducing agents than their $\cdot CR_2OH$ counterparts.[26] Pathway 3 is formation of a covalent intermediate, prevalent at intermediate pH. We suggest[27] $(NH_3)_5CoNH_2CR_2OH^{2+}$ is formed as a steady-state intermediate in a two-step sequence:

$$Co(NH_3)_6^{3+} + \cdot C(CH_3)_2OH \underset{-3}{\overset{3}{\rightleftharpoons}} (NH_3)_5CoNH_2C(CH_3)_2OH^{2+} + H^+ \quad (14)$$

$$(NH_3)_5CoNH_2C(CH_3)_2OH^{2+} \xrightarrow{4} Co(NH_3)_6^{2+} + (CH_3)_2CO \quad (15)$$

When all three pathways are considered together, the apparent second-order rate constant determined in the experiments at any pH will be expected to follow eq 16. The magnitudes

$$k_{app} = \left(k_2 + \frac{k_3k_4}{k_{-3}[H^+] + k_4} + \frac{k_5K_R}{[H^+]} \right) \frac{[H^+]}{[H^+] + K_R} \quad (16)$$

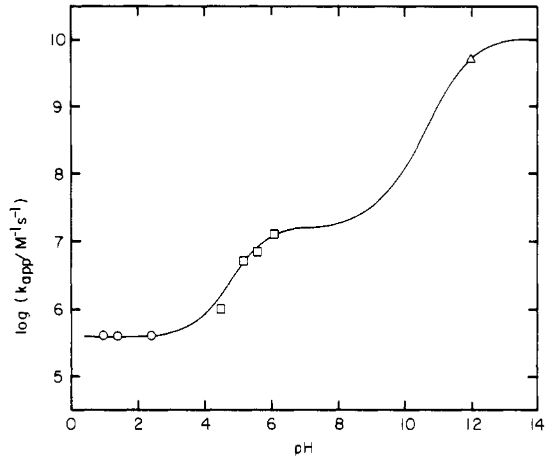


Figure 4. Rate–pH profile for the reaction of $Co(NH_3)_6^{3+}$ with $\cdot C(CH_3)_2OH$ showing the three plateaus corresponding to k_2, k_3, and k_5. The data points refer to determinations based on competitive kinetics (circles, this work) and on pulse radiolysis in neutral (squares, ref 4) and basic (triangle, ref 3) solutions. The solid line is the theoretical result from eq 16 with values of the parameters cited in the text.

of $[H^+]$ and the acid ionization constant of the free radical (K_R) permit simplification without loss of accuracy to the form of eq 17. The three pH plateaus are evident: at $[H^+] >>$

$$k_{app} = k_2 + \frac{k_3k_4}{k_{-3}[H^+] + k_4} + \frac{k_5}{1 + [H^+]/K_R} \quad (17)$$

K_R and $[H^+] >> k_4/k_{-3}$, $k_{app} \approx k_2$ (pH 0–3); at $[H^+] >> K_R$ and $[H^+] << k_4/k_{-3}$, $k_{app} \approx k_3$ (pH ~6–8); at $[H^+] << K_R$ and $[H^+] << k_4/k_{-3}$, $k_{app} \approx k_5$ (at pH >11 or 12, depending on pK_R for the given radical). Figure 4 shows a sketch of the variation of k_{app} with pH for the particular reaction of $Co(NH_3)_6^{3+}$ and $\cdot C(CH_3)_2OH$ with known parameters (pK_R = 12) and rate constants determined here and elsewhere ($k_2 = 4.1 \times 10^5$ M^{-1} s^{-1}, $k_3 = 1.7 \times 10^7$ M^{-1} s^{-1}, $k_4/k_{-3} = 2 \times 10^{-6}$ M, $k_5 = 10^{10}$ M^{-1} s^{-1}) such that there is a reasonable match of the data throughout the entire range.

Reactions of Cobalt(III) Complexes with $\cdot C(CH_3)_2OH$ in Acidic Solutions. The pH-independent reaction in strongly acidic solution we believe to occur by outer-sphere electron transfer. Approach of the free radical to a trigonal face of the metal complex may provide an intermediate (or transition state) suitable for transfer of an electron from the p_z orbital of the π radical to the vacant e_g^* orbital of the metal complex.

In searching for evidence bearing on this formulation, we sought to compare the values of k_2 found for these reactions with such properties of the individual cobalt(III) complexes as their standard reduction potentials[28-30] and d–d absorption maxima. It was also of interest to compare the values of k_2

---

(25) The evident assumption[9] was that the acid–base equilibration of eq 13 would lead to $k_{app} = K_{os}(k_a[H^+] + k_bK_a)/([H^+] + K_a)$, where k_a and k_b represent the rate constants for the respective internal electron transfers of acidic and basic forms, and K_{os} the outer-sphere association constant. A similar but less explicit mechanism[5] has implicit in it a similar rate law. Provided the outer-sphere association processes are "instantaneously" equilibrated and that the concentration of outer-sphere complexes remains much lower than [$\cdot CH_2OH$] or [$\cdot C(CH_3)_2OH$] at any time—the latter proviso is necessary to retain the first-order kinetic dependence on [Co(III)] found in every determination—then the correct rate law for this pH range (0–8; here we neglect any reactions of $\cdot RO^-$ in highly alkaline solution) will *not* show a plateau: $k_{app} = K_{os}k_a + k_bK_{os}K_a/[H^+]$. We should particularly like to call attention to the fact that the latter equation and not the former is the one applicable to the case in which an acidic intermediate, present only at steady-state concentration, reacts by parallel pathways. The reason is that the formation of the deprotonated form of the intermediate does not deplete the concentration of the protonated form, as it would if a bulk reagent were so equilibrated; rather, the concentration of outer-sphere complex $Co(NH_3)_6^{3+},\cdot CH_2OH$ remains at the same value, regardless of the amount of $Co(NH_3)_6^{3+},\cdot CH_2O^-$ formed, because the equilibrium concentrations of its constituents, $Co(NH_3)_6^{3+}$ and $\cdot CH_2OH$, are not altered.

(26) Swallow, A. J. *Prog. React. Kinet.* **1978**, *9*, 195.

(27) This intermediate resembles, but is not identical with, the tripositive species [$(NH_3)_5Co^{III}NH_2CH_2OH^{3+}$] suggested by others.[4]

(28) Bartelt, H.; Skilandat, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *23*, 407.

(29) Laitinen, H. A.; Kivalo, P. *J. Am. Chem. Soc.* **1953**, *75*, 2198.

(30) Bartelt, H. *J. Electroanal. Chem.* **1970**, *25*, 79.

on a more empirical basis with the rate constants[16,31,32] for outer-sphere electron transfer from $Cr^{II}(bpy)_3^{2+}$ to the same family of cobalt(III) complexes (eq 18). The quantities referred to are listed in Table VI.

$$Cr(bpy)_3^{2+} + Co(NH_3)_6^{3+} \xrightarrow{k_{18}} Cr(bpy)_3^{3+} + Co(NH_3)_6^{2+} \qquad (18)$$

The rate constants for eq 18 decrease, as one might expect, with the excitation energy from the t_{2g}^6 ground state ($^1A_{1g}$) to the $t_{2g}^5e_g^*$ excited state ($^1T_{1g}$), as measured by λ_{max}. The standard reduction potentials of the different cobalt(III) complexes[28-30] are also consistent with the observed reactivity order, although the value for $Co(tn)_3^{3+}$ has not been measured.

One might expect a parallel between the values of k_2 and k_{18} if the same outer-sphere mechanism applies to both. Indeed, that is what is seen except for $Co(chxn)_3^{3+}$, whose reduction is >20 times slower than expected from the relationship followed by the other complexes, $\log k_2 = 4.30 + 0.55 \log k_{18}$. The success of the correlation lends support to our formulation of the free radical reductions as proceeding by an outer-sphere mechanism. We would suggest that the failure of $Co(chxn)_3^{3+}$ to react with $\cdot C(CH_3)_2OH$ may signal a conformational (λ, δ) change of the chelate ligands are required to facilitate approach of the planar radical to a trigonal face sufficient to permit facile electron transfer. Such conformational changes are readily experienced by all of the cobalt(III) complexes other than $Co(chxn)_3^{3+}$ whose cyclohexyl ring systems preclude similar steric adaptation. The character of the required conformational change is not, however, clear at this time.

The relative rate constants for the deuterated complex $Co(ND_3)_6^{3+}$ as compared to $Co(NH_3)_6^{3+}$ are not greatly different for $\cdot C(CH_3)_2OH$ ($k_D/k_H = 0.73$) than for $Cr(bpy)_3^{2+}$ (0.74). This supports our contentiopn that, in the strongly acidic medium, both reactions proceed by outer-sphere electron transfer. The failure of the Cr(III) complexes to react with $\cdot C(CH_3)_2OH$, on the other hand, probably arises from the much less favorable reduction potential for Cr(III) → Cr(II).

The substantial deuterium isotope effect in acidolysis of $CrC(CH_3)_2OH^{2+}$ corresponds to $k_{1A}(H)/k_{1A}(D) = 6.3$. It is similar to the corresponding rate constant ratios for $CrCH_2OH^{2+}$ (8.4),[33] $CrCH_3^{2+}$ (6.3),[34] and CrH^{2+} (4.8).[34] The reasons have already been given: the activation process along this pathway contains dominant contributions from the effect of O–H bond breaking, possibly from a water molecule coordinated to Cr(III), cis to the chromium–carbon bond.[34] The contrast between the isotope effect on acidolysis (6.3) and homolysis (1.01) is striking. The latter is consistent with our conclusion that homolytic cleavage is a genuine unimolecular process unassisted by solvent participation.[2]

As reactions of $\cdot C(CH_3)_2OH$ and $\cdot CH_2OH$ go, the reductions of the cobalt(III)–amine complexes are much slower than the reductions of most other metal complexes. On the other hand, these Co(III) complexes are notorious for their high kinetic barriers. The present reactions are, in fact, some of the most rapid reductions of these complexes which have been found. Reduction of $Co(NH_3)_6^{3+}$ by $\cdot C(CH_3)_2OH$ ($E° \approx -1.2$ V)[1] and $\cdot CH_2OH$ ($E° \approx -0.92$ V) are both highly exoergic processes. The former is much faster, $k_2 = 4.1 \times 10^5$ M^{-1} s^{-1} vs. $<1 \times 10^3$ M^{-1} s^{-1}. Observation of only a small extent of reduction of $Co(NH_3)_6^{3+}$ by $\cdot CH_2OH$ in acidic solution is not to be taken to indicate complete failure of reaction 12c but simply that another reaction, radical self-reaction eq 12b, is dominant under the conditions employed.

The effect of Cl^- most deserving of comment is the twofold increase of the k_{-1}/k_2 ratio, at the same time leaving k_1 unaltered. Since Cl^- does not interact appreciably with $Cr(H_2O)_6^{2+}$, and most likely not with $\cdot C(CH_3)_2OH$ either, it is tempting to argue from microscopic reversibility that k_{-1}, like k_1, is Cl^- independent. The consequence of that argument is then that k_2 is *decreased* by a factor of 2.0 for $Co(NH_3)_6^{3+}$ at 0.060 M Cl^- and by the same factor for $Co(en)_3^{3+}$ at 0.60 M Cl^-, each compared to the value in perchlorate medium. Although ion pairing between the cobalt(III) complexes and chloride ions does occur, its extent is inappreciable under these conditions.[35] Thus partial conversion of the reactive Co(III) ions to nonreactive Cl^- ion pairs cannot be invoked to account for this phenomenon, although other plausible explanations are not apparent.

Acknowledgment. This research was supported by the Chemical Sciences Division of the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-82. Discussions with Professors M. Z. Hoffman and D. Meyerstein during the course of this work are gratefully acknowledged.

Registry No. $\cdot C(CH_3)_2OH$, 5131-95-3; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(en)_3^{3+}$, 14878-41-2; $Co(tn)_3^{3+}$, 16786-53-1; $Co(ND_3)_6^{3+}$, 23945-61-1; $Co(chxn)_3^{3+}$, 41970-05-2; $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3.

---

[31] Zwickel, A. M.; Taube, H. *Discuss. Faraday Soc.* **1960**, *29*, 42.
[32] Ulstrup, J. *Trans. Faraday Soc.* **1971**, *67*, 2645.
[33] Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 2452.
[34] Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 704.
[35] King, E. L.; Espenson, J. H.; Visco, R. E. *J. Phys. Chem.* **1959**, *63*, 755.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

S to O and O to S Linkage Isomerization in Sulfoxide Complexes of Pentaammineruthenium

A. YEH, N. SCOTT, and H. TAUBE*

Received November 10, 1981

When $Ru(NH_3)_5Me_2SO^{2+}$ is oxidized to the 3+ state, S → O isomerization takes place at a specific rate of $(7.0 \pm 0.5) \times 10^{-2}$ s^{-1} (24×10^{-2} s^{-1} for the methioninesulfonate complex). Aquation is quite slow, k_{aq} being 7.7×10^{-5} s^{-1} (6.2×10^{-5} s^{-1}). On reduction to the 2+ state, O → S isomerization takes place, the values of k_{ism} being 30 ± 7 s^{-1} (99 ± 7 s^{-1}). Aquation accompanies isomerization in the 2+ species and $k_{aq} \approx 10$ s^{-1} (30 s^{-1}). The shift from the S- to the O-bound form changes the 3+/2+ reduction potential from 1.0 to 0.01 V.

Though a value of E_f for the couple $Ru(NH_3)_5Me_2SO^{3+/2+}$ as obtained by cyclic voltammetry has been reported (E_f = 1.0 V in 0.10 M HCl),[1] it has frequently been observed in our laboratories, and probably also by others, that complications