Its infrared spectrum is quite similar to that of the cobalt complex (see Table II) indicating that the two have similar structures. The zinc compound is not as soluble in acetonitrile or tetrahydrofuran as the cobalt analog, suggesting that the zinc complex is more ionic. This conclusion is supported by the fact that the metal–oxygen stretching frequency is lower in the zinc compound than in the cobalt complex. The thermal decomposition of $Ni(NH_3)_6(NO_3)_2$ was also investigated. The product appears to be diamminedinitratonickel(II) on the basis of weight loss measurements; however, this complex was not characterized further.

In conclusion, the thermal decomposition under vacuum of μ-peroxo-bis[pentaamminecobalt(III)] tetranitrate has been shown to produce diamminedinitratocobalt(II) with loss of oxygen and ammonia. A similar decomposition of hexaamminecobalt(II) nitrate was found to yield the same diamminedinitrato complex. Spectroscopic and magnetic data strongly indicate that this complex is six-coordinate containing nitrate ions bound as bidentate ligands. It was found that diammine(iodo)(nitrato)cobalt(II) could be prepared from the dinitrato complex suggesting that diamminedinitratocobalt(II) might be useful in synthesizing new coordination compounds. Finally, the diamminedinitrato(zinc and nickel) complexes were prepared by the thermal decomposition of the ammine nitrate salts of these metals. In general, it appears that complexes of the type $M(NH_3)_2(NO_3)_2$ can be produced in this fashion.

Acknowledgment.—We particularly wish to thank Mr. K. J. Jensen for his advice and assistance and also Mr. A. Venters and other members of the analytical chemistry staffs of Argonne National Laboratory and of the University of Illinois for their help. G. L. M. wishes to acknowledge receipt of a predoctoral fellowship from the National Science Foundation.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS 02215

Acid-Promoted Redox Decomposition and Cerium(IV) Oxidation of Tris(oxalato)cobaltate(III) Ion in Aqueous Sulfuric Acid[1]

BY HARRIET G. KRUSZYNA AND RONALD M. MILBURN*

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In aqueous 1 *M* sulfuric acid, cerium(IV) reacts directly with $Co(C_2O_4)_3{}^{3-}$ as well as with oxalate species produced by acid-promoted decomposition of the tris-oxalato complex. The one-electron redox reaction between $Co(C_2O_4)_3{}^{3-}$ and cerium(IV) proceeds with a second-order rate constant of 1.2×10^{-3} M^{-1} sec^{-1} at 25°. An induction period exhibited in the acid-promoted decomposition of $Co(C_2O_4)_3{}^{3-}$ is ascribed to slow formation of a monodentate oxalato species which then provides the major path for decomposition.

For some time we have been interested in the factors which influence the redox reactivities of metal–oxalato complexes.[2] In this connection we have undertaken studies on the cerium(IV) oxidations of $Cr(C_2O_4)_3{}^{3-}$, $Co(C_2O_4)_3{}^{3-}$, $Rh(C_2O_4)_3{}^{3-}$, and $Ir(C_2O_4)_3{}^{3-}$. A summary of this work has been presented,[3] and more recently a full report on the $Cr(C_2O_4)_3{}^{3-}$–Ce(IV) and $Rh(C_2O_4)_3{}^{3-}$–Ce(IV) systems has been given.[4] The purpose of the present paper is to provide a detailed account of results obtained for the $Co(C_2O_4)_3{}^{3-}$–Ce(IV) system.

In acidic sulfate media, addition of cerium(IV) to $Cr(C_2O_4)_3{}^{3-}$ or $Rh(C_2O_4)_3{}^{3-}$ results in stepwise oxidation of coordinated oxalate. While oxalate remains attached to the chromium or rhodium, there is no evidence for the oxidation of these metal centers.[4] On the other hand, cerium(IV) rapidly and quantitatively oxidizes[3] $Ir(C_2O_4)_3{}^{3-}$ to the corresponding iridium(IV) complex, $Ir(C_2O_4)_3{}^{2-}$. A further contrast is found in the behavior of $Co(C_2O_4)_3{}^{3-}$ toward cerium(IV).

It is well known[5-10] that $Co(C_2O_4)_3{}^{3-}$ in aqueous acidic solution undergoes internal redox decomposition to produce cobalt(II), carbon dioxide, and oxalic acid.[11] In the 1 *M* sulfuric acid medium used for the present studies, this internal redox decomposition exhibits an induction period which appears to have gone unnoticed by others who have investigated this reaction. The significance of this induction period is examined herein.

Addition of the *oxidant* cerium(IV) to solutions containing $Co(C_2O_4)_3{}^{3-}$ results in an *accelerated reduction* of the cobalt(III) center. Such behavior toward cerium(IV) is in marked contrast to the reaction patterns exhibited by the tris-oxalato complexes of chromium(III), rhodium(III), and iridium(III). This reactivity of $Co(C_2O_4)_3{}^{3-}$ toward cerium(IV) is analogous, however, to the type of behavior often observed when a

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[1] Supported by the National Science Foundation.

[2] J. E. Teggins, M. T. Wang, and R. M. Milburn, *Advan. Chem. Ser.*, **No. 37**, 226–242 (1963).

[3] H. G. Kruszyna, M. W. Hsu, and R. M. Milburn, *Proc. Int. Conf. Coord. Chem., 10th, 1967*, 302 (1967).

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[9] W. Schneider, *Helv. Chim. Acta*, **46**, 1863 (1963).

[10] (a) C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4622 (1964); (b) J. Aggett and A. L. Odell, *ibid.*, *A*, 1415 (1968).

[11] The rate-determining step is not necessarily a redox process. See Discussion.

ligand L in complexes of type $(NH_3)_5Co^{III}$–L is oxidized by external one-electron oxidants.[12,13]

Experimental Section

Materials.—Potassium tris(oxalato)cobaltate(III) was prepared as described by Bailar and Jones.[14] *Anal.* Calcd for $K_3Co(C_2O_4)_3 \cdot 3H_2O$: C, 14.6; H, 1.21; K, 23.9. Found: C, 14.6; H, 1.37; K, 23.9.[15]

The preparation of standard solutions of cerium(IV) and cerium(III) and analytical methods for cerium(IV) and cerium(III) have been described earlier.[2,4] Other materials were of reagent grade quality. The solvent used throughout this investigation was aqueous 1.00 *M* sulfuric acid. Water, used for all solutions involved in the kinetic studies, was obtained by heating ordinary distilled water with potassium permanganate and sodium hydroxide and redistilling in a Barnstead S-1 apparatus.

Preparation of Reaction Solutions.—Measured volumes of solutions of all reaction components, with the exception of the tris-oxalato complex, were introduced into a 50-ml "low actinic" flask which was then immersed in a thermostat bath. A freshly prepared aqueous solution of the potassium tris(oxalato)cobaltate(III) was also immersed in the bath. After the flasks and their contents had reached the thermostat temperature, reaction was initiated by introducing an aliquot of the tris(oxalato)cobaltate(III) solution into the flask containing the other components.

Acid-Promoted Decomposition of $Co(C_2O_4)_3^{3-}$.—In the absence of light and at room temperature, neutral aqueous solutions of $Co(C_2O_4)_3^{3-}$ remain unchanged in visible absorbances over at least a 6-hr period. Over similar time periods, the complex in 1 *M* sulfuric acid decomposes significantly, as observed by changes in the visible spectrum. This acid-promoted decomposition proceeds at rates which are comparable to those observed for the reaction between $Co(C_2O_4)_3^{3-}$ and Ce(IV), and it thus must be taken into account.

The decomposition in acid proceeds according to the stoichiometry[5−10,16,17]

$$2Co(C_2O_4)_3^{3-} + 10H^+ \longrightarrow 2Co(II) + 5H_2C_2O_4 + 2CO_2 \quad (1)$$

The progress of this reaction in 1.00 *M* sulfuric acid and 25.0° was followed for solutions which were $\sim 4 \times 10^{-3}$ *M* in $Co(C_2O_4)_3^{3-}$ by measuring absorbance changes at 596 and 420 nm. At these wavelengths the absorbance of product species is negligible in comparison to the $Co(C_2O_4)_3^{3-}$ ion. In Figure 1 we show a simple first-order rate plot of log (A_0/A_t) against time. The plot provides evidence for an induction period, after which the reaction clearly follows first-order behavior. From the straight-line portion of the graph one obtains a first-order rate constant, k_d, of 4.30 (±0.15) × 10^{-5} sec^{-1}. The induction period of some 20–30 min is unaffected by the presence or absence of oxygen or cobalt(II). Also, no significant change in reaction *rate* results when cobalt(II), in as high a concentration as $Co(C_2O_4)_3^{3-}$, is initially present in the reaction mixture.[18]

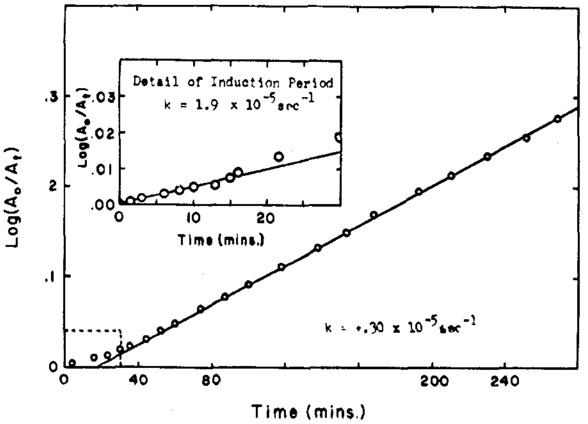

Figure 1.—First-order plot for decomposition of 3.17×10^{-3} *M* $Co(C_2O_4)_3^{3-}$ in 1.00 *M* sulfuric acid at 25.0°. Absorbances measured at 410 nm.

Oxidation of $Co(C_2O_4)_3^{3-}$ by Ce(IV).—The reaction between $Co(C_2O_4)_3^{3-}$ and Ce(IV) was studied in 1 *M* sulfuric acid. Earlier the stoichiometry was determined[16] to be

$$5Ce(IV) + Co(C_2O_4)_3^{3-} \longrightarrow 5Ce(III) + Co(II) + 6CO_2 \quad (2)$$

The stoichiometry was checked in the present study by allowing a slight excess of Ce(IV) to react with $Co(C_2O_4)_3^{3-}$ over several weeks, in 1 *M* sulfuric acid at ~25°, and then analyzing for residual Ce(IV) as described below.

Cerium(IV) concentrations throughout the course of the reaction were measured by two methods. In one method, absorbances of solutions in thermostated 1-cm cells were measured directly at 480 nm. In the second method, aliquots of the reaction mixture were removed from the reaction flask and were quenched by dilution to 1 l. with 1 *M* sulfuric acid.[4] The absorbances at 320 nm were then measured. For the range of concentrations used, Beer's law was followed at 320 and 480 nm by each absorbing reactant and product species in the 1 *M* sulfuric acid medium. For either wavelength, concentrations of cerium(IV) could be calculated for the various reaction times from the relation

$$[Ce(IV)]_t = [Ce(IV)]_0 - (A_0 - A_t)/q \quad (3)$$

where *A* is the optical absorbance, subscripts "0" and "*t*" refer, respectively, to "zero time" and to any other "time *t*," and *q* is related to the absorbancy coefficients "*a*" by[19]

$$q = a_{Ce(IV)} + \{a_{Co(C_2O_4)_3^{3-}} - a_{Co(II)}\}/5 \quad (4)$$

Values of $[Co(C_2O_4)_3^{3-}]_t$ were obtained from values of $[Ce(IV)]_t$ and the stoichiometry (eq 2).

Several reaction series were run, each series consisting of a number of kinetic runs at constant $[Co(C_2O_4)_3^{3-}]_0$ with varying $[Ce(IV)]_0$.

Based on knowledge that the related Ce(IV)–$Cr(C_2O_4)_3^{3-}$ reaction is first order in each reactant[2−4] and that the acid-promoted decomposition of $Co(C_2O_4)_3^{3-}$ closely approximates pseudo-first-order behavior (see above), it seemed likely that the Ce(IV)–$Co(C_2O_4)_3^{3-}$ reaction in the 1 *M* sulfuric acid would follow, at least in first approximation, a rate law of the form

$$\frac{-d[Co(C_2O_4)_3^{3-}]}{dt} = k_1[Co(C_2O_4)_3^{3-}] + k_2[Ce(IV)][Co(C_2O_4)_3^{3-}] \quad (5)$$

Equation 5 may also be written

$$\frac{-d \ln [Co(C_2O_4)_3^{3-}]}{dt} = k_1 + k_2[Ce(IV)] \quad (6)$$

For such a rate law, plots of $-d \ln [Co(C_2O_4)_3^{3-}]/dt$ *vs.* [Ce(IV)] should be linear, and one should obtain consistent values of k_1 and k_2 for various initial concentrations of reactants.

Values for the left-hand side of eq 6 were determined from the *initial* slopes of plots of ln $[Co(C_2O_4)_3^{3-}]$ *vs.* time. For each series of runs in which $[Co(C_2O_4)_3^{3-}]_0$ was held constant, a second plot was made of these d ln $[Co(C_2O_4)_3^{3-}]/dt$ values against $[Ce(IV)]_0$. Data for three series are presented in Table I and in Figure 2. The average values for k_1 and k_2, with least-squares deviations, are k_1 = 2.0 (±0.3) × 10^{-5} sec^{-1} and k_2 = 1.23 (±0.07) × 10^{-3} M^{-1} sec^{-1}. The excellent consistency of the k_2 values and reasonable consistency of the k_1 values (see Discussion) provide support for the proposed rate law (eq 5). Further support for this rate law comes by substituting the average values

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[12] (a) P. Saffir and H. Taube, *J. Amer. Chem. Soc.*, **82**, 13 (1960); (b) R. T. M. Fraser and H. Taube, *ibid.*, **82**, 4152 (1960); (c) R. Robson and H. Taube, *ibid.*, **89**, 6487 (1967); (d) J. E. French and H. Taube, *ibid.*, **91**, 6951 (1969).

[13] J. P. Candlin and J. Halpern, *ibid.*, **85**, 2518 (1963).

[14] J. C. Bailar, Jr., and E. M. Jones, *Inorg. Syn.*, **1**, 37 (1939).

[15] Analysis by Schwarzkopf Microanalytical Laboratory.

[16] A. Gertzman, A.M. Thesis, Boston University, 1962.

[17] The cobalt(II) will exist in equilibrium between various complexed forms; the oxalic acid will be partially dissociated.

[18] The first-order rate constant reported by Bunton, *et al.*,[10a] for the same conditions (1 *M* H_2SO_4, 25°, H_0 = −0.26) is k_1 = 3.39 × 10^{-5} sec^{-1}. These authors make no mention of an induction period.

[19] In a comparison to other species the absorbance due to Ce(III) is negligible.

TABLE I

RESULTS FOR THE $Co(C_2O_4)_3^{3-}$–Ce(IV) REACTION IN 1.00 *M* SULFURIC ACID AT 25.0°[a]

Kinetic run	$10^2[Ce^{IV}]_0$, *M*	$-d \ln [Co(C_2O_4)_3^{3-}] \times 10^5/dt$, sec^{-1}	Rate constants (from least-squares line)
A1	6.52	9.72	$k_1 = 2.2\ (\pm 0.2) \times 10^{-5}$ sec^{-1}
A2	6.52	10.4	$k_2 = 1.20\ (\pm 0.07) \times 10^{-3}\ M^{-1}$ sec^{-1}
A3	4.34	7.18	
A4	2.17	4.95	
A5	1.30	4.00	
A6	0.434	2.42	
B1	6.52	10.2	$k_1 = 1.5\ (\pm 0.3) \times 10^{-5}$ sec^{-1}
B2	6.52	10.1	$k_2 = 1.27\ (\pm 0.10) \times 10^{-3}\ M^{-1}$ sec^{-1}
B3	4.34	6.28	
B4	4.34	6.22	
B5	2.17	4.25	
B6	2.17	4.63	
B7	1.30	3.27	
B8	0.434	2.25	
C1	6.52	10.0	$k_1 = 2.3\ (\pm 0.4) \times 10^{-5}$ sec^{-1}
C2	4.34	8.40	$k_2 = 1.23\ (\pm 0.10) \times 10^{-3}\ M^{-1}$ sec^{-1}
C3	3.04	5.63	
C4	2.17	5.20	
C5	1.30	4.12	
C6	0.434	2.45	

[a] $[Co(C_2O_4)_3^{3-}]_0$: series A, 4.80×10^{-3} *M;* series B, 1.00×10^{-2} *M;* series C, 3.20×10^{-3} *M.*

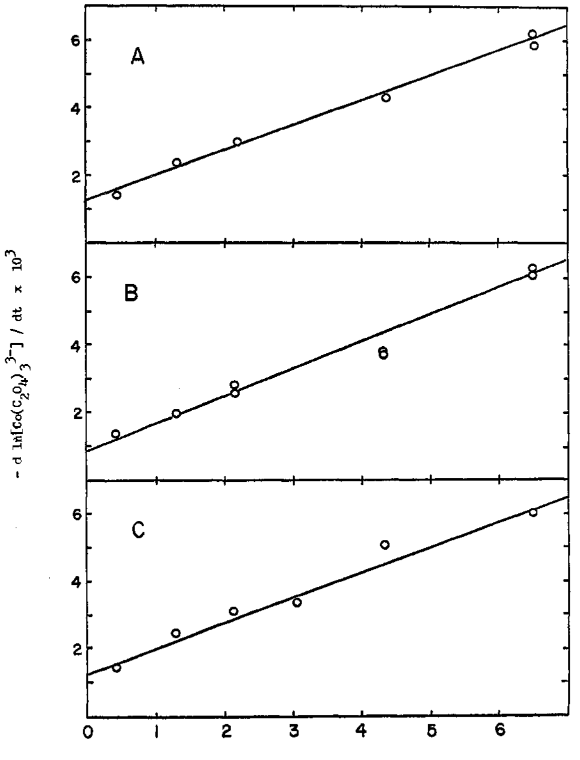

Figure 2.—Plots used in the evaluation of k_1 and k_2. $[Co(C_2O_4)_3^{3-}]$: A, 4.80×10^{-3} *M;* B, 1.00×10^{-2} *M;* C, 3.20×10^{-3} *M.* Units for ordinate in min^{-1}.

of k_1 and k_2 obtained into the integrated form of the rate law[20]

$$\ln \frac{[Co(C_2O_4)_3^{3-}]_0\{k_1 + k_2[Ce(IV)]_t\}}{[Co(C_2O_4)_3^{3-}]_t\{k_1 + k_2[Ce(IV)]_0\}} = \{k_1 + k_2([Ce(IV)]_0] - [Co(C_2O_4)_3^{3-}]_0)\}t \quad (7)$$

A plot of the left-hand side against the right-hand side of this equation yields straight-line behavior with a slope of unity for more than 60% of the reaction (Figure 3).

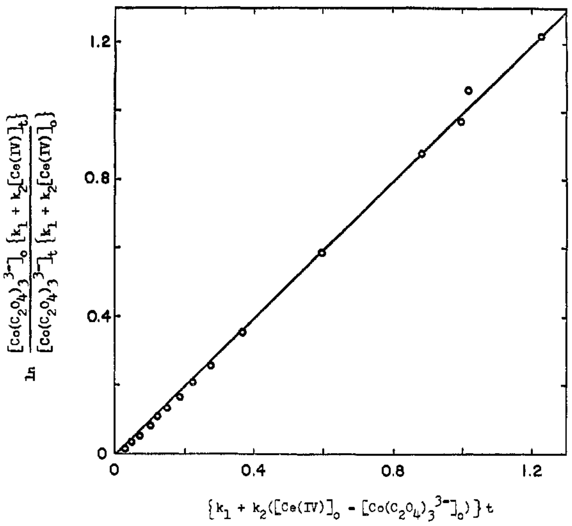

Figure 3.—A test of the rate law for the $Co(C_2O_4)_3^{3-}$–Ce(IV) reaction.

Discussion

The acid-promoted decomposition clearly exhibits first-order behavior after 30 min or so (at 25°, in 1 *M* sulfuric acid), but an obvious induction period precedes this region. Existence of the induction period requires that there be two or more consecutive slow steps in a reaction sequence leading to cobalt(II). We interpret our results with the view that the induction period is associated with buildup of a monodentate oxalato species, which, through consecutive reaction, offers the major path for the decomposition

$$Co(C_2O_4)_3^{3-} + H_3O^+ \rightleftarrows Co(C_2O_4)_2(OC_2O_3H)(H_2O)^{2-} \quad (8)$$

$$Co(C_2O_4)_2(OC_2O_3H)(H_2O)^{2-} \longrightarrow \text{products} \quad (9)$$

Considerable evidence exists for the importance of such monodentate oxalato species as intermediates during the acid-catalyzed aquation of various $M(C_2O_4)_3^{3-}$ ions.[6-10,21-23] Contrary to some expressed views,[10b,21] however, we do not believe that equilibration between closed and ring-opened species in the case of $Co(C_2O_4)_3^{3-}$ can be a rapid process. Direct support for the slowness of Co^{III}–oxygen bond cleavage is provided by recent results on acid-catalyzed oxygen exchange between $Co(C_2O_4)_3^{3-}$ and solvent water in which only half of the oxygens are found to undergo rapid exchange.[24,25]

As a test for our proposed explanation of the induction period, the general reaction scheme 10 has been considered. In the specific instance I represents the fully chelated tris-oxalato complex, II the monodentate oxalato intermediate, III the cobalt(II), and X a reactive intermediate (such as $C_2O_4^-$) which will be rapidly

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[20] Reactant concentrations are here in units of "normality" as defined by reaction 2.

[21] L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc. A*, 298 (1967).

[22] (a) D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962); (b) K. V. Krishnamurty, *ibid.*, **1**, 422 (1962); (c) H. Kelm and G. M. Harris, *ibid.*, **6**, 1743 (1967).

[23] (a) L. Damrauer and R. M. Milburn, *J. Amer. Chem. Soc.*, **90**, 3884 (1968); (b) L. Damrauer and R. M. Milburn, *Proc. Int. Conf. Coord. Chem., 12th, 1969*, 38 (1969).

[24] (a) J. A. Broomhead, I. Lauder, and P. Nimmo, *Chem. Commun.*, 652 (1969); (b) J. A. Broomhead, I. Lauder, and P. Nimmo, *Proc. Int. Conf. Coord. Chem., 12th, 1969*, 149 and Suppl (1969).

[25] A slow exchange between inner oxygens and solvent water has now been observed: J. A. Broomhead, I. Lauder, and P. Nimmo, *J. Chem. Soc. A*, 645 (1971).

consumed in converting II or I to III. Our experi-

$$\begin{tikzcd} \mathrm{I} \arrow[r, shift left, "k_{12}"] \arrow[d, "(k_{13})"'] & \mathrm{II} \arrow[l, shift left, "(k_{21})"] \arrow[dl, "k_{23}"] \\ \mathrm{III} + \mathrm{X} & \end{tikzcd} \tag{10}$$

$$\mathrm{X} + \mathrm{II}\ (\text{or I}) \xrightarrow[\text{fast}]{k_{2\mathrm{x}}\ (\text{or } k_{1\mathrm{x}})} \mathrm{III}$$

mental results on the decomposition may be accommodated most simply by considering only the steps corresponding to the rate constants k_{12}, k_{23}, and k_{2x} (*i.e.*, the steps in the reaction scheme 10 which are not in parentheses). Kinetic treatment of this system allows one to calculate values of C_1, C_2, and C_3, the concentrations of I, II, and III, as a function of time for various k_{12} and k_{23} values.[26-28] Plots of log $[C^0_1/(C^0_1 - C_3)]$ against time for various assumed values of the rate constants show induction periods followed by regions of first-order behavior, thus exhibiting the same pattern as that observed experimentally.[29] By systematic variation of the rate constants we have been able to obtain quite a good fit of the experimental data with $k_{12} = 1.25 \times 10^{-3}$ sec^{-1} and $k_{23} = 2.08 \times 10^{-5}$ sec^{-1} (Figure 4). The "fit" in the region of the induction period may be improved, and agreement may be obtained over the entire range, by allowing k_{13} to have a small but finite value ($\sim 0.7 \times 10^{-5}$ sec^{-1}) and by very slightly lowering the value of k_{23}. It is, of course, likely that, during the very early stages of reaction, I will compete with II in the quenching of X, but this situation could not be maintained for long since the required magnitude of k_{12} implies a moderately rapid increase in the concentration of II and decrease in the concentration of I (also, the removal of I would be accelerated if this species reacts with X). Certainly for the middle and later stages of reaction no significant amounts of I will remain, and we must require that X be quenched by II. While exact solutions for the differential equations are not obtainable in the case where II and I compete for X, one here still expects an induction period and time-dependent behavior for III similar to the case where II is the sole quenching reagent. It may be added that some re-formation of I from II would also be consistent with our experimental results (*i.e.*, k_{21} is not necessarily 0).[30] The major point to be emphasized here, however, is that the observed induction period can be simply explained in a quantitative way by the view that, in acid, $Co(C_2O_4)_3{}^{3-}$ is removed largely through its conversion to $Co(C_2O_4)_2(OC_2O_3H)(H_2O)^{2-}$ which then offers the major path for the decomposition.

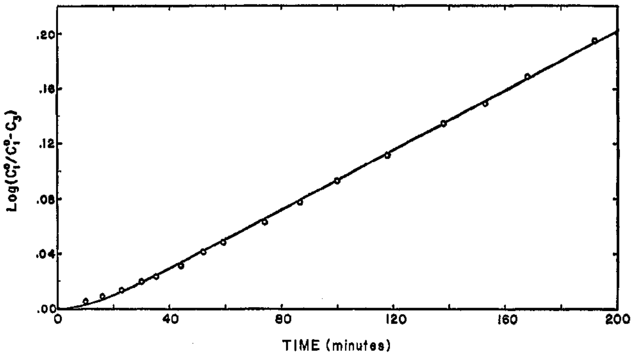

Figure 4.—Decomposition of $Co(C_2O_4)_3{}^{3-}$ in 1 *M* H_2SO_4 at 25°. Points are experimental. Curve is calculated for $k_{12} = 1.25 \times 10^{-3}$ sec^{-1}; $k_{23} = 2.08 \times 10^{-5}$ sec^{-1}; $k_{21} = k_{13} = 0$.

A point we have not commented on is whether the rate-determining step in the conversion II → III is a redox reaction or a substitution reaction. Most workers have favored the view that the reduction accompanies the complete release of the first oxalato group.[5-9] On the other hand, Aggett and Odell have observed a repression of the decomposition rate by added oxalate and have concluded that a reversible dissociation to yield $Co(C_2O_4)_2(H_2O)_2{}^-$ and $HC_2O_4{}^-$ precedes the electron-transfer step.[10b] In contrast, working in the pH range 6–9, Graziano and Harris[7] found that the $Co(C_2O_4)_3{}^{3-}$–$C_2O_4{}^{2-}$ exchange proceeds at negligible rates compared to the redox decomposition and that the rates for the latter process are independent of the concentration of added free oxalate. On this basis, the latter workers concluded that the redox decomposition proceeds by a mechanism which does *not* involve appreciable reversible equilibration with oxalate radicals or ions. The apparently different effects of added oxalate are possibly a function of the different pH ranges and different added oxalate concentrations studied. Quite possibly acidic conditions favor the production of $Co(C_2O_4)_2(OC_2O_3H)(H_2O)^{2-}$ which undergoes oxalate dissociation in preference to redox decomposition, whereas in the neutral pH range aquation of $Co(C_2O_4)_3{}^{3-}$ is not found, and the redox decomposition of $Co(C_2O_4)_3{}^{3-}$ becomes the preferred process. Our own results give some suggestion that direct decomposition of $Co(C_2O_4)_3{}^{3-}$ occurs at a finite rate (*i.e.*, $k_{13} \neq 0$).

We may summarize our conclusions on the acid-promoted decomposition by reiterating that all our data are consistent with the interpretation that reaction starts with $Co(C_2O_4)_3{}^{3-}$, that hydrogen ion converts this into $Co(C_2O_4)_2(OC_2O_3H)(H_2O)^{2-}$, and that the latter species undergoes decomposition much more rapidly than $Co(C_2O_4)_3{}^{3-}$.

The following mechanistic outline is consistent with the various observations and summarizes our views on the essential features of the reactions. It should be understood that the Co^{II} will be variously complexed and that released oxalate, written below as $C_2O_4{}^{2-}$, will be variously protonated or complexed. The acid-

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(26) On the assumption that X will be maintained at very low concentrations (steady-state conditions) the kinetic treatment reduces to a consideration of coupled first-order reactions, as discussed for example by Benson.[27]

(27) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 39.

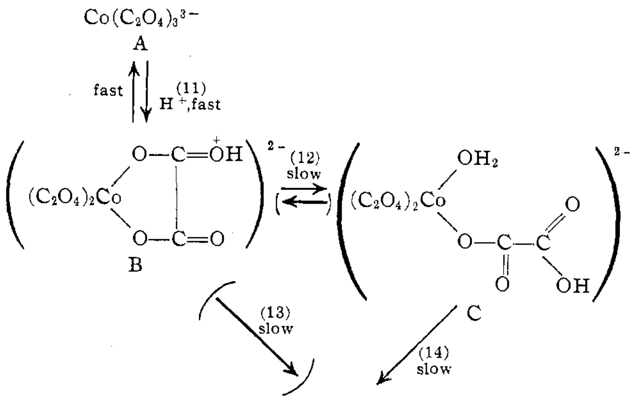
(28) The resulting expression for C_3, where C^0_1 is the concentration of *I* at $t = 0$, is

$$C_3 = C^0_1 + \left(\frac{2k_{23}}{k_{12} - 2k_{23}}\right)C^0_1 e^{-k_{12}t} - \left(\frac{k_{12}}{k_{12} - 2k_{23}}\right)C^0_1 e^{-2k_{23}t}$$

(29) It may be noted that $C^0_1/(C^0_1 - C_3)$ becomes equal to A_0/A_t in the event that the absorbancy coefficients of I and II are the same at the chosen wavelength. Preliminary indications are that this is approximately the case, although the matter is now under more detailed study.

(30) Through pH measurements, Hin-Fat and Higginson[21] have estimated that the equilibrium constant for reaction 8 has a value of 2.8 (25°; 0.100 *M* $K_3Co(C_2O_4)_3$, 0.10 *M* hydrochloric acid, and 0.20 *M* potassium chloride). Their estimate is based upon the questionable premise that equilibrium will be established rapidly. It may be noted that their suggestion that the thermal decomposition occurs through the unprotonated $Co(C_2O_4)_2(OC_2O_3)(H_2O)^{3-}$ cannot account for the acid dependence of the decomposition.[10b]

promoted decomposition is written as



$$Co^{II} + 2C_2O_4^{2-} + C_2O_4^-$$

$$C_2O_4^- + Co^{III}(A, B, or C) \xrightarrow{fast} Co^{II} + 3C_2O_4^{2-} + 2CO_2 \quad (15)$$

Also, in the presence of cerium(IV) we have the reactions

$$Co^{III}(A, B, or C) + Ce^{IV} \xrightarrow{slow} Co^{II} + Ce^{III} + 2C_2O_4^{2-} + 2CO_2 \quad (16)$$

$$C_2O_4^{2-} + Ce^{IV} \xrightarrow{fast} C_2O_4^- + Ce^{III} \quad (17)$$

$$C_2O_4^- + Ce^{IV} \xrightarrow{fast} 2CO_2 + Ce^{III} \quad (18)$$

For the system under study, as for the $Cr(C_2O_4)_3^{3-}$–Ce(IV) and $Rh(C_2O_4)_3^{3-}$–Ce(IV) systems,[4] there are slight inequalities between the sums of the absorbances due to the individual reactants and corresponding absorbances of reactant solutions on first mixing. In accord with our previous views, these inequalities suggest preequilibrium formation of binuclear intermediates which can subsequently undergo internal electron transfer with reduction of the cerium(IV). On this basis, together with arguments previously presented,[4] it seems probable that reactions of types 15 and 16 will in fact occur in several steps, as in the example

$$Co^{III}(C_2O_4)_3^{3-} + Ce^{IV} \underset{}{\overset{fast}{\rightleftarrows}} Co^{III}(C_2O_4)_3^{3-}\text{-}Ce^{IV} \quad (16a)$$

$$Co^{III}(C_2O_4)_3^{3-}\text{-}Ce^{IV} \overset{slow}{\rightleftarrows} Co(C_2O_4)_3^{2-}\text{-}Ce^{III} \quad (16b)$$

$$Co(C_2O_4)_3^{2-}\text{-}Ce^{III} \overset{fast}{\rightleftarrows} Co(C_2O_4)_3^{2-} + Ce^{III} \quad (16c)$$

$$Co(C_2O_4)_3^{2-}\text{-}Ce^{III} \xrightarrow{fast} Co^{II} + 2C_2O_4^{2-} + 2CO_2 + Ce^{III} \quad (16d)$$

$$Co(C_2O_4)_3^{2-} \xrightarrow{fast} Co^{II} + 2C_2O_4^{2-} + 2CO_2 \quad (16e)$$

Reactions 16a–16c are analogous to the steps proposed for $Cr(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_3^{3-}$. The subsequent step in the present case is reduction of the cobalt(III) center, however, rather than attack by further Ce^{IV} as in the case of the chromium(III) and rhodium(III) systems.

The straight-line portion of Figure 1 corresponds to a value for the pseudo-first-order decomposition rate constant (k_d) of 4.30 (±0.3) × 10^{-5} sec^{-1}, while in the presence of cerium(IV) the apparent values for the first-order decomposition rate constants (k_1) are in the range 1.5 × 10^{-5} to 2.3 × 10^{-5} sec^{-1}. These observed k_d and k_1 values are consistent with our proposed mechanism. One certainly expects Ce(IV) will be competitive with Co(III) in the consumption of $C_2O_4^-$ (compare reactions 18 and 15). If reaction 18 is much faster than reaction 15, the Co(III) would be reduced by apparent first-order processes at half the rate in the presence of cerium(IV) compared to the rate in its absence. Superimposed on this effect is the consideration that k_d has been calculated using data obtained *after* the induction period, while k_1 was evaluated with use of initial rates. For comparison, the value one estimates for the first-order rate constant with use of the portion of Figure 1 which corresponds to the induction period (see Figure 1, "Detail of Induction Period") is 1.9 × 10^{-5} sec^{-1}. Consistent with the importance of the induction period are the trends in the values of k_1 obtained when one evaluates d log $[Co(C_2O_4)_3^{3-}]/dt$ for $t = 0$ and for $t > 0$. For example, whereas for series B with data extrapolated to $t = 0$ we find k_1 = 1.5 (±0.3) × 10^{-5} sec^{-1} and k_2 = 1.27 (±0.10) × 10^{-3} M^{-1} sec^{-1}, the data corresponding to consumption of 20% of the cobalt(III) results in the values k_1 = 2.6 (±0.4) × 10^{-5} sec^{-1} and k_2 = 1.13 (±0.10) × 10^{-3} M^{-1} sec^{-1}.

In certain of the reaction runs where $[Ce(IV)]_0$ was very low (*e.g.*, A6 and C6) short induction periods were observed. An explanation similar to that proposed for the acid-promoted decomposition reaction can be advanced. Where $[Ce(IV)]_0$ is low, opportunity exists for the buildup of appreciable concentrations of $Co(C_2O_4)_2(OC_2O_3H)(H_2O)^{2-}$ during the early stages of reaction. If cerium(IV) reacts more rapidly with $Co(C_2O_4)_2(C_2O_4H)(H_2O)^{2-}$ than with $Co(C_2O_4)_3^{3-}$, an induction of the type observed would be apparent at low $[Ce(IV)]_0$.

For comparison, Table II gives the rate constants at 25° for the cerium(IV) *one-electron* oxidations of $Co(C_2O_4)_3^{3-}$, $Rh(C_2O_4)_3^{3-}$, and $Cr(C_2O_4)_3^{3-}$. There are difficulties in trying to arrive at specific reasons for the differing rates, as we have discussed in detail in relation to the rhodium(III) and chromium(III) complexes.[4] For the latter complexes there is in fact evidence that the transition states for the reactions with cerium(IV) do not have identical compositions with respect to sulfate and hydrogen ions. As we have suggested, it seems likely that at least for the early stages of reaction all three oxalates in $Rh(C_2O_4)_3^{3-}$ will be fully chelated to the rhodium as this complex combines with cerium(IV) to produce the transition state. This condition is much less likely to be maintained for $Cr(C_2O_4)_3^{3-}$, and this may well be the reason that the rhodium(III) and chromium(III) complexes exhibit different sensitivities to various acidic sulfate media. On the other hand, $Co(C_2O_4)_3^{3-}$, because of its general inertness, should behave much like $Rh(C_2O_4)_3^{3-}$ for the *early* stages of reaction. The fairly close similarity in rates for the cobalt(III) and rhodium(III) complexes is consistent

TABLE II

SECOND-ORDER RATE CONSTANTS FOR Ce(IV) *One-Electron* OXIDATIONS IN 1.00 *M* SULFURIC ACID AT 25.0°

Complex	k_2, M^{-1} sec^{-1}
$Cr(C_2O_4)_3^{3-}$	4.0 (±0.5) × 10^{-2}
$Co(C_2O_4)_3^{3-}$	1.2 (±0.1) × 10^{-3}
$Rh(C_2O_4)_3^{3-}$	6.1 (±1.0) × 10^{-4}

with the expectations that the binuclear complexes of type $M(C_2O_4)_3^{3-}$–Ce(IV) will be of similar stability that the remaining details of coordination about the cerium(IV) will be similar for such complexes and for the transition state and that the rhodium and cobalt centers will influence similarly the capacity of oxalate to transfer an electron to cerium(IV).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CANTERBURY, CHRISTCHURCH, NEW ZEALAND

Enthalpy Data as Evidence for a Dissociative Mechanism in the Base Hydrolysis of Some Acidopentaamminecobalt(III) Complexes

BY D. A. HOUSE AND H. K. J. POWELL*

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The enthalpy changes for the reactions $Co(NH_3)_5X^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^-$ (X = Cl, Br, I, NO_3) have been measured in 0.097 *F* NaOH at 25° as −6.1 ± 0.25, −5.7 ± 0.15, −3.65 ± 0.05, and −3.85 ± 0.05 kcal mol^{-1}, respectively. These numerical data, when subtracted from the enthalpies of activation for these reactions, give a constant value of 32.0 ± 0.9 kcal mol^{-1} for the "transition enthalpy." This experimental result and other calculated data are discussed in support of a transition state in which the leaving group is essentially dissociated. The heats of formation of the complexes $Co(NH_3)_5X^{n+}$ (X = OH^-, H_2O, I^-) were determined as −172.0 ± 0.8, −180.8 ± 0.9, and −126.6 ± 1.0 kcal mol^{-1}, respectively.

Introduction

The mechanism of the base hydrolysis of octahedral cobalt(III) complexes has been the subject of much discussion.[1] Both bimolecular (associative) (SN2,[2] SN2IP,[3] and SN2CB[4]) and unimolecular (dissociative) (SN1CB[1,5] and SN1IP[3]) displacement mechanisms (CB, conjugate base; IP, ion pair) have been proposed and recently Gillard[6] has postulated a bimolecular mechanism involving electron transfer.

For the reaction

$$Co(NH_3)_5X^{2+} + OH^- \longrightarrow Co(NH_3)_5OH^{2+} + X^- \qquad (1)$$

the rate law rate = $k_2[\text{complex}][OH^-]$ indicates that the nucleophile is involved in the approach to the transition state. However, the nucleophile may or may not be a part of the metal coordination sphere in the transition state. By considering the involvement of OH^- in the rate expression alone, it is not possible to distinguish between the associative or dissociative mechanisms.[7]

To focus attention on the leaving group in the transition state, we have measured the enthalpy changes for the base hydrolysis reactions $Co(NH_3)_5X^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^-$ (X = Cl, Br, I, NO_3). We find that the heat content of the transition state species, with respect to the products X^- and $Co(NH_3)_5OH^{2+}$, is essentially constant and independent of the leaving group. These results are discussed in support of a dissociative[7] mechanism for this type of reaction.

Experimental Section

Complex Salts and Analyses.—The perchlorate salts of the acidopentaamminecobalt(III) cations were prepared from solutions of the halide or nitrate salts in 0.1 *F* $HClO_4$ by the addition of excess $NaClO_4 \cdot H_2O$. These salts were recrystallized twice from 0.1 *F* $HClO_4$ by the addition of $NaClO_4 \cdot H_2O$. $[Co(NH_3)_5NO_3](NO_3)_2$ was prepared using the method of Schlessinger.[8] Ammonia was determined using a micro Kjeldahl apparatus. The complexes were decomposed with hot NaOH solution (7 *F*) and the released NH_3 was steam distilled into 2% boric acid and titrated with standard HCl solution. *Anal.* Calcd for $[Co(NH_3)_5Cl](ClO_4)_2$:[8] NH_3, 22.5. Found: NH_3, 22.3. Calcd for $[Co(NH_3)_5Br](ClO_4)_2$:[8] NH_3, 20.1. Found: NH_3, 20.0. Calcd for $[Co(NH_3)_5I](ClO_4)_2$:[9] NH_3, 18.1. Found: NH_3, 18.3. Calcd for $[Co(NH_3)_5OH_2](ClO_4)_3$:[8] NH_3, 18.5. Found: NH_3, 18.5. Calcd for $[Co(NH_3)_5NO_3](NO_3)_2$: NH_3, 25.8. Found: NH_3, 26.0.

The Calorimeter.—The calorimeter and circuits were essentially the same as described previously.[10] The solid sample container was similar to that described by Arnett, *et al.*[11] Solutions were added as weighed samples from thin-walled glass bulbs. The heat changes associated with container opening or bulb breaking were not detectable (<0.009 cal).

The accuracy and reliability of the calorimeter were tested by measuring the heat of solution of potassium chloride. Analar KCl was recrystallized from hot water, oven dried, ground, and sieved to 100 mesh. For the solution of KCl (1:500), ΔH was determined as 4179 ± 11 cal mol^{-1} (mean of four measurements; ± value is the standard deviation), in satisfactory agreement with the literature value[12] of 4200 cal mol^{-1}.

Enthalpy Changes.—For the complexes $Co(NH_3)_5X^{2+}$ (X = I, NO_3), the enthalpy of base hydrolysis (ΔH_R, reaction 1) was determined by addition of a small sample of concentrated alkali (*ca.* 2 ml of 1 *F* NaOH) to a solution (95 or 100 ml) of $Co(NH_3)_5X^{2+}$ (*ca.* 6 × 10^{-3} *F*) in $NaClO_4$ (0.08 *F*) and $HClO_4$ (*ca.* 5 × 10^{-3}

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[7] Here we define an associative mechanism as one involving a seven-coordinate transition state with the OH^- and X^- groups associated with the metal ion. Conversely, a dissociative mechanism is one involving a six-coordinate transition state with the X^- group substantially dissociated and the OH^- not directly involved in the coordination sphere. This six-coordinate transition state could subsequently form a five-coordinate intermediate with the X^- group completely dissociated (see Figure 1).

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