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Mechanisms and Kinetics of the Decomposition of Trioxalatocobaltate(III) in Aqueous Sulfuric Acid

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The kinetics of the thermal decomposition of the trioxalatocobaltate(III) complex were studied in a sulfuric acid solution in the absence and in the presence of oxygen from 25 to 40°C. The decomposition of trioxalatocobaltate(III) was described by the equation: $-d[Co(C_2O_4)_3{}^{3-}]/dt=(k_1+k_2[H^+])[Co(C_2O_4)_3{}^{3-}]$. The values of k_1 and k_2 were 6×10^{-6} sec^{-1} and 1.8×10^{-5} M^{-1} sec^{-1} respectively at 25°C. The values of the activation enthalpy change, $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$, were 29.7 and 30.0 kcal mol^{-1} respectively. The values of the activation entropy change, $\Delta S_1^{\ddagger}$ and $\Delta S_2^{\ddagger}$, were 17.4 and 20.9 eu respectively at 40°C. Although hydrogen peroxide was formed in the presence of oxygen, and although a white precipitate of the polymerized products of acrylonitrile was found in the presence of acrylonitrile, neither oxygen nor acrylonitrile affected the kinetics of the decomposition of trioxalatocobaltate(III). The decomposition of peroxodisulfate was induced by the decompossition of trioxalatocobaltate(III). However, the rate of the decomposition of trioxalatocobaltate(III) was not affected by peroxodisulfate. On the other hand, both copper(II) and iron(III) ions were accelerators of the decompsition of trioxalatocobaltate(III). An anion radical of $CO_2{}^-$ was predicted as an intermediate. The reaction mechanisms will be presented to account for these facts.

It has been known for many years[1] that trioxalatocobaltate(III) decomposes photochemically and thermochemically with internal redox to produce cobalt(II), carbon dioxide and oxalate. Recently, Kolthoff *et al.*[2] have found that hydrogen peroxide is formed upon the decomposition of trioxalatocobaltate(III) in the presence of oxygen in an acidic medium. The initial reaction is:

$$Co(C_2O_4)_3{}^{3-} \rightarrow Co(C_2O_4)_n{}^{(2-2n)} + (2-n)\,C_2O_4{}^{2-} + CO_2 + CO_2{}^- \qquad (1)$$

The anion radical in Reaction (1) may be either $C_2O_4{}^-$ or $CO_2{}^-$. However, the two forms do not appear to be distinguishable on the basis of kinetic or spectroscopic evidence.[3] Following the consensus of previous workers, we will write CO_2 in the present paper.

It would be interesting to know if the $CO_2{}^-$ radical would not reduce $Co(C_2O_4)_3{}^{3-}$, but the two would combine with each other to produce $C_2O_4{}^{2-}$. With the purpose of interpreting the reaction mechanisms, the rate of the decomposition of trioxalatocobaltate(III) was measured in the presence of oxygen, acrylonitrile, copper(II) ion, iron(III) ion, or peroxodisulfate, all of which may be able to react rapidly with the $CO_2{}^-$.

Experimental

Chemicals. The potassium trioxalatocobaltate(III) complex was synthesized following the directions of Sörensen.[4] A guaranteed-reagent-grade potassium peroxodisulfate of the Kanto Kagaku Co., Inc., was recrystallized twice from redistilled water and dried at 40°C in a vacuum desiccator. Extra pure acrylonitrile of the Kanto Chemical Co., Inc., was used without further purification. Cupric sulfate, ferric ammonium sulfate, sulfuric acid, oxalic acid and cobaltous sulfate, all of a guaranteed reagent grade were used without further purification. The water was purified by distillation from an alkaline permanganate solution. Pure

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[1] *a*) T. B. Copestake and N. Uri, *Proc. Roy. Soc.*, *Ser. A*, **228**, 252 (1955); *b*) A. W. Adamson, H. Ogata, J. Grossman and R. Newbry, *J. Inorg. Nucl. Chem.*, **6**, 319 (1958).

[2] I. M. Kolthoff, E. J. Meehan and M. Kimura, *J. Phys. Chem.*, **75**, 3343 (1971).

[3] G. D. Cooper and B. A. de Graff, *ibid.*, **75**, 2897 (1971).

[4] S. P. L. Sörensen, *Z. Anorg. Allg. Chem.*, **11**, 1 (1896).

nitrogen and oxygen were used for the experiments in the absence and in the presence of oxygen respectively.

Technique. A reaction was started by adding a given ammount of the trioxalatocobaltate(III) complex to the reaction mixture. The reaction mixture was saturated with either nitrogen or oxygen, which was bubbled through the reaction mixture. Aliquot samples were withdrawn at appropriate times and mixed with cold water to slow the decomposition of trioxalatocobaltate(III). The decomposition of trioxalatocobaltate(III) during under the analytical run at 20°C was practically negligible. The trioxalatocobaltate(III) concentration was measured at 600 nm in the visible spectrum in a solution of 0.05 M sulfuric acid at 20°C. The cobaltous(II) ion produced in the course of the decomposition of trioxalatocobaltate(III) does not interfere with the absorbance of trioxalatocobaltate(III) at 600 nm. In a few experiments in the presence of copper(II), the concentration of trioxalatocobaltate(III) was determined polarographically at +0.2 V *vs.* SCE. In an experiment in presence of peroxodisulfate, the sum of the concentrations of peroxodisulfate and trioxalatocobaltate(III) was determined by using the polarographic diffusion current at +0.2 V *vs.* SCE. Peroxodisulfate did not interfere with the visible spectrum of trioxalatocobaltate(III). The concentration of the cobaltous(II) ion was determined polarographically. The concentration of oxalic acid or the sum of oxalic acid and hydrogen peroxide was determined by titration with permanganate at 50°C.

Results and Discussion

Kinetics. As is shown in Figs. 1 and 2, the rate of the decomposition of trioxalatocobaltate(III) is of the first order with respect to trioxalatocobaltate(III) in any given reaction mixture; i. e., the kinetics are described by the equation:

$$-d[Co(C_2O_4)_3^{3-}]/dt = k_0[Co(C_2O_4)_3^{3-}] \qquad (2)$$

Figure 3 indicates that the overall rate constant (k_0) of the reaction is given by:

$$k_0 = k_1 + k_2[H^+] \qquad (3)$$

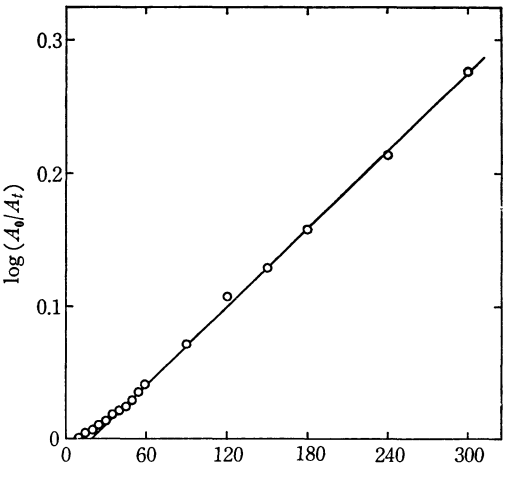


Fig. 1. First order plot for the decomposition of 4.0×10^{-3} M sulfuric acid at 25°C in dark and in nitrogen saturated. Absorbances measured at 600 nm.
A indicates the optical absorbance, subscripts 0 and t refer, respectively, to zero-time and to any other time-t.

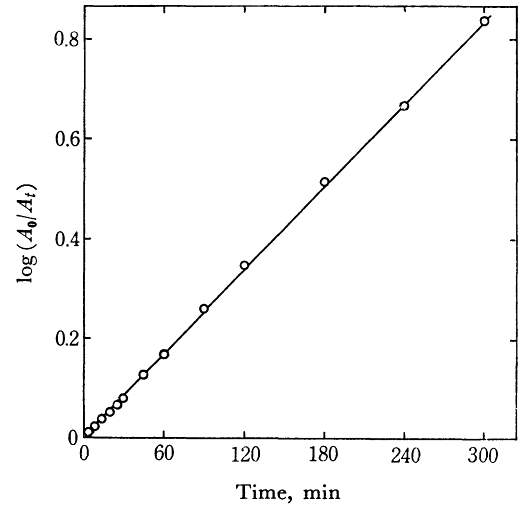
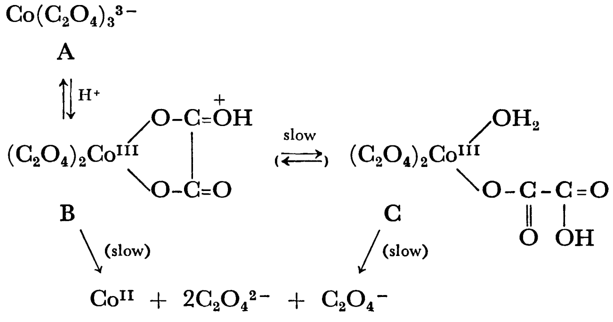


Fig. 2. First order plot for the decomposition of 4.0×10^{-3} M $K_3Co(C_2O_4)_3$ in nitrogen saturated 0.1 M sulfuric acid at 40°C.
Absorbances measured at 600 nm. A is the optical absorbance, subscripts 0 and t refer, respectively, to zero-time and to any other time-t.

where k_1 and k_2 are the rate constants of Reactions (8) and (8′) respectively.

Figure 1 indicates that there is an induction period in the initial stage of the reaction. However, the induction period disappears completely at 40°C, as can be seen in Figure 2. Recently Kruszyna and Milburn[5] have found a similar induction period at 25°C in a 1 M sulfuric acid solution. It will be necessary here to present a brief review from their discussion.[5] The existence of the induction period requires that there are two or more consecutive slow steps in a reaction sequence leading to cobalt(II); they predicted the following reaction mechanisms:



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

Their major points are that, during the very early stages of reaction, A and B will compete with C in the quenching of $C_2O_4^-$ radical, but for the middle and later stages of reaction, no significant amounts of A and B will remain, and $C_2O_4^-$ (or CO_2^-) will be quenched by C only.

The above assumption that the C_2O_4 radical reduces Co^{III} oxalato complex rapidly, is entirely inconsistent with our results. However, it appears that the induction

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[5] H. G. Kruszyna and R. M. Milburn, *Inorg. Chem.*, **10**, 1578 (1971).

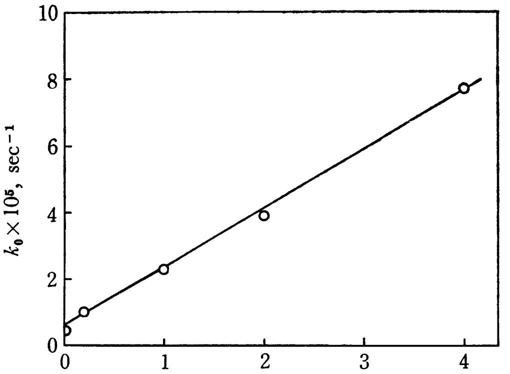

Fig. 3. Sulfuric acid dependence on the rate constant k_0. Condition: 4.0×10^{-3} M $K_3Co(C_2O_4)_3$; Dark; 25°C; N_2 sat. k_0 is the rate constant of the overall reaction (7).

period can be due to the slow steps, from A to C. Such slow steps would be accelerated by the elevated temperature, and the induction period must disappear under such conditions. This prediction is consistent with the fact that the induction period seems to disappear at 40°C.

Enthalpy and Entropy of Activation. The rate constants were determined at several temperatures. The logarithms of the rate constants were in a linear relation to $1/T$. The rate constants for the decomposition of trioxalatocobaltate(III) in 0.1 and 1.0 M sulfuric acid solutions, together with the enthalpy and entropy of activation, are given in Table 1.

TABLE 1. TEMPERATURE DEPENDENCE ON THE RATE OF DECOMPOSITION OF TRIOXALATOCOBALTATE(III). N_2 SATURATED; DARK

Temp. °C	k_0 (sec^{-1})		k_2 (sec^{-1} M^{-1})
	in 0.1 M H_2SO_4	in 1.0 M H_2SO_4	
25	1.0×10^{-5}	3.9×10^{-5}	1.8×10^{-5}
30	2.2×10^{-5}	8.8×10^{-5}	3.7×10^{-5}
35	5.2×10^{-5}	20.7×10^{-5}	9.6×10^{-5}
40	10.8×10^{-5}	46.5×10^{-5}	19.8×10^{-5}

$\Delta H_1^{\ne} = 29.7$ kcal; $\Delta H_2^{\ne} = 30.2$ kcal.

$\Delta S_1^{\ne} = 17.4$ eu; $\Delta S_2^{\ne} = 20.9$ eu at 40°C.

where $\Delta H_1^{\ne}$ and $\Delta S_2^{\ne}$ are the activation enthalpy and the entropy of Reaction (8), and where $\Delta H_2^{\ne}$ and $\Delta S_2^{\ne}$, those of Reaction (8′).

A number of workers[1,5–12] have proposed the monodentate oxalato species as an intermediate in the decomposition of the trioxalato metal complexes, $M(C_2O_4)_3^{3-}$; *e. g.*, in the case of trioxalatocobaltate(III), the following reactions are offered:

$$Co(C_2O_4)_3^{3-} + H_2O \rightarrow Co(C_2O_4)_2(OC_2O_3)(H_2O)^{3-} \quad (4)$$

$$Oo(C_2O_4)_3^{3-} + H_3O^+ \rightarrow Co(C_2O_4)_2(OC_2O_3H)(H_2O)^{2-} \quad (5)$$

In the present study, the enthalpy of the activation of the [H+]-dependent reaction was almost equal to that of [H+]-independent one. This may indicate that the decomposition of trioxalatocobaltate(III) occurs through two reactions (4) and (5). However, there have been many contradictory discussions: Kruszyna and Milburn[5] have emphasized that the protonated intermediate offers the major path for the decomposition and that the direct decomposition of $Co(C_2O_4)_3^{3-}$ occurs at a finite rate[13]. On the contrary, Aggett and Odell[9b] have suggested that the thermal decomposition of trioxalatocobaltate(III) proceeds through the unprotonated $Co(C_2O_4)_2(OC_2O_3)(H_2O)^{3-}$.

Partially-released monodentate oxalato intermediates may lead to a larger positive entropy change. This assumption is in agreement with the present results. Copestake and Uri[1a] have suggested that the hydrolysis reaction:

$$Co(C_2O_4)_3^{3-} + H_2O \rightarrow HCo(C_2O_4)_3^{2-} + OH^- \quad (6)$$

is improbable, since (a) solution of $K_3Co(C_2O_4)_3$ are neutral than alkaline, and (b) pH of a 10^{-2} M solution of $H_3Co(C_2O_4)_3$ is such that all the three hydrogen atoms are completely dissociated. That is, $H_3Co(C_2O_4)_3$ is a very strong acid. In view of these facts, the positive entropy change can hardly be expected to be due to the dehydration by the hydrogen ion.

Stoichiometry. To verify the stoichiometry of the reaction, 4.2×10^{-3} M trioxalatocobaltate(III) was kept in 0.1 M sulfuric acid solutions for 15 hr at 40°C. The solution was saturated with nitrogen or oxygen gas in a closed glass-stoppered vessel sealed with wax. Under these conditions, a green solution of trioxalatocobaltate(III) turns completely pink due to the formation of cobalt(II) ion. No trioxalatocobaltate(III) is left in the solution after 15 hours, and the cobalt(II) ion and oxalic acid are formed in the absence of oxygen as the decomposition products. Hydrogen peroxide is formed in the presence of oxygen. The amount of peroxide formed is equimolar to the amount of oxalic acid which disappears.[14] Therefore,

TABLE 2. ANALYSIS OF THE DECOMPOSITION PRODUCTS OF 4.2×10^{-3} M $Co(C_2O_4)_3^{3-}$ IN 0.1 M H_2SO_4

Cobaltous(II) ion M×10³	Oxalic acid M×10³	Conditions
4.24	10.2	N_2 sat. in Dark
4.17	10.3	N_2 sat. in Room light
4.20	10.1[a)]	O_2 sat. in Room light

a) Sum of oxalic acid and hydrogen peroxide.

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[6] F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).

[7] I. G. Murgulescu and T. Oncescu, *Z. Phys. Chem.* (Leipzig), **214**, 238 (1960).

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

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

[10] L. Hin-Fat and W. C. E. Higginson, *ibid.*, *A*, **1967**, 298.

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

[12] 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).

[13] Only one experiment in a 1 M sulfuric acid solution at 25°C has been made in the work of Kruszyna and Milburn.[5]

[14] The details were reported previously (see Ref. 2).

the sum of oxalic acid and hydrogen peroxide should be equal to the amount of oxalic acid formed in the absence of oxygen. The reaction products were analyzed. The results are listed in Table 2. Table 2 indicates that one mol/l of trioxalatocobaltate(III) produces 2.5 mol/l of oxalic acid in the absence of oxygen, or 2.5 mol/l of a total of oxalic acid and hydrogen peroxide in the presence of oxygen.

That is, in the case of the absence of oxygen the overall reaction is:

$$Co(C_2O_4)_3{}^{3-} \xrightarrow{k_0} Co(C_2O_4)_n{}^{(2-2n)} + (2.5-n)C_2O_4{}^{2-} \quad (7)$$

where n is 0, 1, and/or 2.

The Influence of Other Substances on the Decomposition Rate. Various substances were added to the reaction mixture of 4×10^{-3} M $K_3Co(C_2O_4)_3$ and 0.1 M H_2SO_4.

TABLE 3. INFLUENCE OF OTHER SUBSTANCES ON THE DECOMPOSITION RATE. SOLUTIONS OF 4.0×10^{-3} M $Co(C_2O_4)_3$, 0.1 M H_2SO_4, AND THE GIVEN SUBSTANCES. N_2-SATURATED UNLESS OTHERWISE STATED; IN THE DARK UNLESS OTHERWISE STATED; AT 40°C

Substances added[a]	Rate constant, $k_0\times10^4$, sec^{-1}
None	1.1
None	1.0 (in O_2 sat.)
None	1.3 (in light[b])
0.5% Acrylonitrile	1.0
1.0% Acrylonitrile	1.0
0.004 M $K_2S_2O_8$	1.0
0.002 M Fe(III)	1.1
0.01 M Fe(III)	2.2
0.002 M Cu(II)	1.1
0.015 M Cu(II)	1.7
0.01 M Co(II)	1.1
0.01 M $H_2C_2O_4$	1.0

a) The sulfate salts of Fe(III), Cu(II), and Co(II) were used.

b) A 100-watt tungsten lamp was placed at a distance of 15 cm from the reaction mixture.

(*a*) The decomposition rate in the solution in the presence of oxygen was almost equal to that in the absence of oxygen. In the presence of oxygen, hydrogen peroxide was formed in the course of the decomposition of trioxalatocobaltate(III).

(*b*) Though photochemistry is outside the scope of the present investigation, the decomposition rate in light exposed by a tungsten lamp was compared to that in the dark. As can be seen in Table 3, light accelerates the decomposition of trioxalatocobaltate(III). This appears reasonable, since trioxalatocobaltate(III) has been known to be photochemically active and to be used as a chemical actinometer.[1a)]

(*c*) Acrylonitrile did not affect the decomposition rate of trioxalatocobaltate(III), although its polymerized products were found in the reacting solution.

(*d*) The decomposition rate of trioxalatocobaltate(III) was not affected by the presence of peroxodisulfate. However, the decomposition of peroxodisulfate was induced by the decomposition of trioxalatocobaltate(III). This fact indicates that the CO_2^- radical formed by the decomposition of trioxalatocobaltate(III) reacts with peroxodisulfate as follows:

$$Co(C_2O_4)_3{}^{3-} \rightarrow Co(C_2O_4)_n{}^{(2-2n)} + (2-n)C_2O_4{}^{2-} + CO_2 + CO_2{}^- \quad (8)$$

$$Co(C_2O_4)_3{}^{3-} + H^+ \rightarrow Co(C_2O_4)_n{}^{(2-2n)} + (2-n)C_2O_4{}^{2-} + CO_2 + CO_2{}^- + H^+ \quad (8')$$

$$S_2O_8{}^{2-} + CO_2{}^- \rightarrow SO_4{}^- + SO_4{}^{2-} + CO_2 \quad (9)$$

(*e*) Both iron(III) and copper(II) ions accelerated the decomposition rate of trioxalatocobaltate(III). This can be accounted for by following reactions (8) and (8').

$$\text{Fe(III) or Cu(II)} + CO_2{}^- \rightarrow CO_2 + \text{Fe(II) or Cu(I)} \quad (10)$$

$$Co(C_2O_4)_3{}^{3-} + \text{Fe(II) or Cu(I)} \xrightarrow{\text{fast}} \text{Fe(III) or Cu(II)} + Co(C_2O_4)_n{}^{(2-2n)} + (3-n)C_2O_4{}^{2-} \quad (11)$$

Reactions (10) and (11) constitute a chain reaction.

Mechanisms. The radicals of CO_2^- and HO_2 are apt to be considered to be oxidized by trioxalatocobaltate(III), since both radicals are generally reductants; *e. g.*, in the present study, iron(III), copper (II), and peroxodisulfate were reduced by the radicals. However, none of our results supported the reaction between trioxalatocobaltate(III) and CO_2^- or HO_2 radical; rather, they supported the combination reaction of CO_2^- or HO_2 with each other to make the $C_2O_4^{2-}$ ion, or H_2O_2, respectively. Consequently, the following reaction mechanisms of the thermochemical decomposition of trioxalatocobaltate(III) are presented to account for these results:

$$Co(C_2O_4)_3{}^{3-} \xrightarrow{k_1} Co(C_2O_4)_n{}^{(2-2n)} + (2-n)C_2O_4{}^{2-} + CO_2{}^- + CO_2 \quad (8)$$

$$Co(C_2O_4)_3{}^{3-} + H^+ \xrightarrow{k_2} Co(C_2O_4)_n{}^{(2-2n)} + (2-n)C_2O_4{}^{2-} + CO_2 + CO_2{}^- + H^+ \quad (8')$$

$$2CO_2{}^- \xrightarrow{\text{fast}} C_2O_4{}^{2-} \text{ (in the absence of oxygen)} \quad (12)$$

$$CO_2{}^- + O_2 \xrightarrow{\text{fast}} O_2CO_2{}^- \text{ (in the presence of oxygen)} \quad (13)$$

$$O_2CO_2{}^- + H^+ \rightarrow HO_2 + CO_2 \quad (14)$$

$$2HO_2 \xrightarrow{\text{fast}} H_2O_2 + O_2 \quad (15)$$

The overall reaction corresponds to Reaction (7) and is consistent with the results of stoichiometry listed in Table 2.

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