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# THERMAL STUDIES ON OXALATE COMPLEXES. III. COMPLEXES OF COBALT(III) AND COBALT(II)

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## ABSTRACT

The decomposition of $K_2[Co(C_2O_4)_2]$ and $K_3[Co(C_2O_4)_3]$ has been studied using TG. In the case of the latter compound, the first step involves the rupture of all the oxalates and one of the resultant carbonates to liberate $CO_2$ and three molecules of CO. Subsequent steps involve the loss of $CO_2$. In the case of $K_2[Co(C_2O_4)_2]$, four decomposition reactions are observed. The first involves the loss of only CO. Subsequent steps involve loss of $CO_2$, $CO_2$ and CO, and $CO_2$, respectively. Basic carbonates appear to be the intermediate products. Kinetic parameters are presented for most of the reactions.

## INTRODUCTION

Simple metal oxalates and oxalate complexes have been studied by many workers over the last several years using thermal methods. A large number of simple oxalates undergo decomposition by loss of CO and conversion to carbonates [1,2] and these reactions have been studied kinetically [2,3]. Decomposition of oxalate complexes is usually more complicated and occurs in a series of steps. These involve loss of CO and $CO_2$ to yield basic carbonates or oxides, sometimes by means of oxidation—reduction reactions involving the metal. Complexes containing a variety of metals have been investigated [4].

In our previous studies, we have investigated the decomposition of *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ [5] and the trisoxalato complexes of iron(III) and chromium(III) [6]. In the present report we describe the results of studies on $K_2[Co(C_2O_4)_2]$ and $K_3[Co(C_2O_4)_3]$.

## EXPERIMENTAL

The $K_2[Co(C_2O_4)_2]$ and $K_3[Co(C_2O_4)_3]$ were obtained from Apache Chemical Co., and were used without further treatment. TG studies were carried out in a dynamic nitrogen atmosphere using a Perkin-Elmer thermogravimetric system model TGS-2. The procedures employed were similar to those described previously [7].

Kinetic data were analyzed by means of the Coats and Redfern equation [8]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \tag{1}$$

and for the first order case

$$\ln\ln\frac{1}{1-\alpha}-2\ln T = \ln\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \tag{2}$$

where $\alpha$ is the fraction of reaction completed, $\beta$ is the heating rate, $E$ is the apparent activation energy, $T$ is the absolute temperature, $A$ is the frequency factor, and $R$ is the molar gas constant. Calculations were carried out using a previously described program for the Texas Instruments programmable TI-59 calculator [9].

## RESULTS AND DISCUSSION

The TG and DTG curves for the decomposition of $K_2[Co(C_2O_4)_2]$ and $K_3[Co(C_2O_4)_3]$ are shown in Figs. 1 and 2, respectively. The $K_3[Co(C_2O_4)_3]$ was found to contain enough water to actually be formulated as $K_3[Co(C_2O_4)_3] \cdot 0.75\ H_2O$. From the TG curves, it was found that the decomposition of this compound takes place in the following steps.

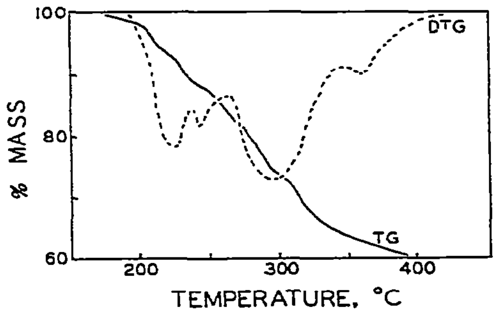
$$K_3[Co(C_2O_4)_3] \cdot 0.75\ H_2O(s) \rightarrow K_3[Co(C_2O_4)_3](s) + 0.75\ H_2O(g) \tag{3}$$

$$K_3[Co(C_2O_4)_3](s) \rightarrow K_3[Co(CO_3)_2O](s) + CO_2(g) + 3\ CO(g) \tag{4}$$

$$K_3[Co(CO_3)_2O](s) \rightarrow K_3[Co(CO_3)_{3/2}O_{3/2}](s) + \tfrac{1}{2}CO_2(g) \tag{5}$$

$$K_3[Co(CO_3)_{3/2}O_{3/2}](s) \rightarrow K_3[Co(CO_3)_{1/2}O_{5/2}](s) + CO_2(g) \tag{6}$$

The first and last steps of the decomposition process were too indistinct to determine reliable kinetic parameters for them. Dehydration appears to



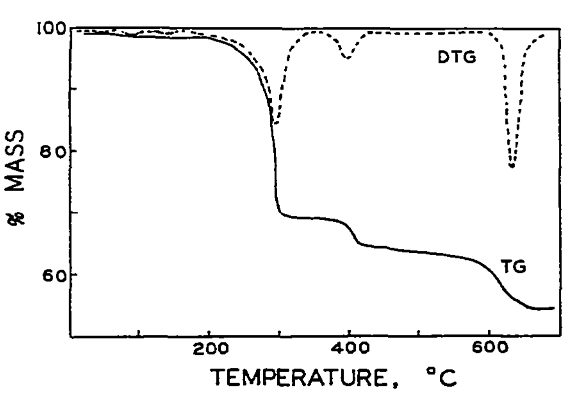


Fig. 1. TG and DTG curves for the decomposition of $K_2[Co(C_2O_4)_2]$.

Fig. 2. TG and DTG curves for the decomposition of $K_3[Co(C_2O_4)_3]$.

occur in three stages that are not separable. These reactions are quite different from those found to describe the process in a static air thermobalance [10].

Decomposition of $K_2[Co(C_2O_4)_2]$ also takes place in a series of steps. These may be written as follows.

$$K_2[Co(C_2O_4)_2](s) \rightarrow K_2[Co(C_2O_4)(CO_3)](s) + CO(g) \tag{7}$$

$$K_2[Co(C_2O_4)(CO_3)](s) \rightarrow K_2[Co(C_2O_4)(CO_3)_{1/2}O_{1/2}](s) + \tfrac{1}{2}CO_2(g) \tag{8}$$

$$K_2[Co(C_2O_4)(CO_3)_{1/2}O_{1/2}](s) \rightarrow K_2[Co(CO_3)O](s) + CO(g) + \tfrac{1}{2}CO_2(g) \tag{9}$$

$$K_2[Co(CO_3)O](s) \rightarrow K_2[Co(CO_3)_{1/2}O_{3/2}](s) + \tfrac{1}{2}CO_2(g) \tag{10}$$

All of these reactions were sufficiently distinct to enable kinetic analysis of the curves. Table 1 shows the reaction parameters for these processes.

Previously, products for the decomposition of $K_2[Co(C_2O_4)_2]$ have been reported as $K_2CO_3$ and $Co_3O_4$ when the decomposition is carried out in air and as Co and $K_2CO_3$ when a nitrogen atmosphere is used [4]. The results obtained in this work appear to be somewhat different.

The decomposition of $K_3[Co(C_2O_4)_3] \cdot 3\,H_2O$ has been studied using a variety of experimental techniques [10]. From that study it was reported that from TG experiments in static air the first step in the decomposition involved the formation of $K_2[Co(C_2O_4)_2]$ according to the reaction

$$2\,K_3[Co(C_2O_4)_3] \cdot 3\,H_2O(s) \rightarrow 2\,K_2[Co(C_2O_4)_2](s) + KHC_2O_4(s) + KHCO_3(s) + CO_2(g) + 5\,H_2O(g) \tag{11}$$

TABLE 1

Reaction parameters for the decomposition of $K_3[Co(C_2O_4)_3] \cdot 0.75\,H_2O$ and $K_2[Co(C_2O_4)_2]$

| Reaction | Temp. range (°C) | % Mass loss. |  | Best order | Corr. Coeff. * | ln $A$ | $E$(kJ mole$^{-1}$) |
|---|---|---|---|---|---|---|---|
|  |  | Calcd. | Found |  |  |  |  |
| *$K_3[Co(C_2O_4)_3] \cdot 0.75\,H_2O$* |  |  |  |  |  |  |  |
| 3 | 25—235 | 3.0 | 3.0 |  |  |  |  |
| 4 | 245—300 | 28.2 | 27.5 | 0 | 0.9980 | 49.50 | 257 |
| 5 | 365—435 | 4.8 | 4.5 | 2/3 | 0.9983 | 81.91 |  |
| 6 | 520—650 | 9.7 | 10.0 |  |  |  |  |
| Overall | 25—650 | 45.7 | 45.0 |  |  |  |  |
| *$K_2[Co(C_2O_4)_2]$* |  |  |  |  |  |  |  |
| 7 | 195—239 | 8.9 | 9.8 | 1 | 0.9997 | 40.76 | 169 |
| 8 | 240—265 | 7.0 | 5.2 | 2 | 0.9989 | 83.77 | 364 |
| 9 | 266—345 | 16.0 | 18.8 | 2 | 0.9996 | 43.37 | 208 |
| 10 | 346—415 | 7.0 | 5.2 | 2 | 0.9921 | 36.94 | 200 |
| Overall | 25—625 | 38.9 | 39.0 |  |  |  |  |

* For linear regression analysis fitting f(α) to the Coats and Redfern equation of the best order.

This process would require 13.56% mass loss. In the present study in a nitrogen atmosphere dehydration is accompanied by a 3.0% mass loss and occurs slowly over a wide range of temperature. This is followed closely by a process representing 27.5% mass loss which closely corresponds to eqn. (4) (calculated 28.2% mass loss). In this instance, the decomposition is similar to that of $K_3[Fe(C_2O_4)_3]$ which first loses two molecules of CO and one of $CO_2$ per molecule of complex [6]. Further, the latter stages of decomposition of $K_3[Co(C_2O_4)_3]$ do not resemble the decomposition pattern of $K_2[Co(C_2O_4)_2]$. Subsequent volatile products from the cobalt(III) complex appear to be only $CO_2$ with the stable product at 650°C being the basic carbonate, $K_3[Co(CO_3)_{1/2}O_{5/2}]$. In the case of $K_2[Co(C_2O_4)_2]$, the first volatile product is CO and that is followed immediately by loss of $CO_2$. Subsequently, additional CO and $CO_2$ are evolved.

It is of interest that the first loss of CO, one molecule per molecule of $K_2[Co(C_2O_4)_2]$, gives the best fit to the first order Coats and Redfern equation and by a considerable amount. All the remaining reactions provided the best fit of the data by the second order equation. In each case the correlation coefficients were considerably higher for $n = 2$ than for any other value of $n$. It is tempting to try to ascribe these observations to some sort of bimolecular process, but it is more likely that they reflect other types of rate controlling influences in the escape of CO and $CO_2$ from the solids.

In the case of $K_3[Co(C_2O_4)_3]$, the first reaction of the anhydrous material is

$$K_3[Co(C_2O_4)_3](s) \rightarrow K_3[Co(CO_3)_2O](s) + 3\,CO(g) + CO_2(g) \tag{4}$$

The correlation coefficient for the zero order fit (0.9980) is only slightly higher than that provided by the $n = 1/3$ and $n = 2/3$ equations (0.9968 and 0.9952, respectively). The second reaction

$$K_3[Co(CO_3)_2\,O](s) \rightarrow K_3[Co(CO_3)_{3/2}O_{3/2}](s) + \tfrac{1}{2}CO_2(g) \tag{5}$$

gave the highest correlation coefficient when $n = 2/3$ but the value was only slightly higher than when $n = 0$ or $n = 1/3$. These results are consistent with some sort of diffusion controlled process for the decomposition, but this is not known with certainty.

The difficulty in interpreting the activation energy for a solid state process is well known [11]. Therefore, it is unlikely that in most cases the activation energy can be ascribed to elementary steps involving bond breaking. The C—O bond energy is about 358 kJ $mole^{-1}$ while for the C—C and C=O bonds the values are 345 and 799 kJ $mole^{-1}$, respectively [12]. In order to rupture an oxalate group to produce CO or $CO_2$ we would expect that rupture of C—C and C—O bonds would be required. Therefore, the activation energy might be about 358 kJ $mole^{-1}$, the higher of the two values, for such a process. Only the processes shown in eqns. (5) and (8) have activation energies of that magnitude. All the others take place with lower activation energies, indicating that processes are available that allow the oxalate and carbonate groups to react without having a direct rupture of bonds or that diffusion control may limit the reaction rates.

In this work we have found that the decomposition of $K_3[Co(C_2O_4)_3]$ and

$K_2[Co(C_2O_4)_2]$ takes place with the formation of basic carbonates by evolving CO and $CO_2$. In that regard, the decompositions are similar to those of Fe(III) and Cr(III) complexes [6]. It has also been possible to measure kinetic parameters for the processes involved. In a nitrogen atmosphere, the decomposition of $K_3[Co(C_2O_4)_3]$ after the first stage does not resemble the decomposition of $K_2[Co(C_2O_4)_2]$, and all of the observed mass losses can be accounted for by reactions in which the only gaseous products are CO and $CO_2$.

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