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THERMAL STUDIES ON OXALATE COMPLEXES. II. COMPLEXES OF IRON(III) AND CHROMIUM(III) *

J.E. HOUSE, JR. and THOMAS G. BLUMTHAL

Department of Chemistry, Illinois State University, Normal, IL 61761 (U.S.A.)

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ABSTRACT

The decomposition of solid $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$ and $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ has been studied using TGA and DSC. After dehydration, the chromium compound was found to decompose by the loss of CO in two steps, the loss of CO_2 and additional CO, and finally the loss of CO_2. The final product appears to be either K_3CrO_3 or the mixed oxides of chromium and potassium. Kinetic parameters and enthalpy data are presented for these reactions. In the case of $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$, dehydration is followed by the loss of CO_2 and CO, CO_2 alone, and finally CO. The final product appears to be a basic carbonate of the type $K_3[Fe(O)_2(CO_3)]$. Kinetic and thermal data are presented for most of these decomposition reactions.

INTRODUCTION

The first step in the decomposition of solid oxalates is the loss of carbon monoxide to produce a carbonate, and simple oxalates have been the subject of numerous studies by a variety of thermal techniques [1—3]. Studies on oxalate complexes have also received some attention [4—7]. The potassium salts of complex anions of oxalate with Cr(III), Mn(III), Co(III), Co(II), Ni(II), and Cu(II) have been studied [8]. From these studies, it appears that when the transition metal is easily reduced, a variety of redox reactions takes place during decomposition. This occurs for complexes of Mn(III), Co(III), Ni(II), and Cu(II). No reduction of the transition metal occurs when the transition metal is Fe(III) or Cr(III).

In a previous report, we described the behavior of *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ and the products obtained after dehydration of the starting material [9]. While both the *cis* and *trans* diaquo compounds lose water in the initial stages of decomposition, there are significant differences in the decomposition taking place after dehydration. In both cases, the final product is $KCrO_2$.

It is apparent from the studies on oxalate complexes that these compounds undergo several interesting reactions during decomposition. We have consequently continued our study of oxalate complexes, and this report

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* For Part I, see ref. 9.

presents results obtained for the decomposition of $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ and $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$.

EXPERIMENTAL

The $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ and $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$ were obtained from Apache Chemical Co., and were used without further treatment. The degree of hydration of these compounds was established by both TG and isothermal mass loss studies.

TG studies were carried out using a Perkin—Elmer thermogravimetric system, TGS-2. The compounds were heated in a nitrogen atmosphere and the procedures employed were similar to those described previously [10].

Isothermal kinetic studies on the dehydration reactions were carried out as described previously [11,12].

RESULTS AND DISCUSSION

As expected, the TG curves show that dehydration occurs prior to decomposition of the compounds. In addition to the DSC and TG studies to be described later, the dehydration processes were studied isothermally. The fraction dehydrated, α, was found to obey the equation

$$-\ln(1-\alpha) = kt \qquad (1)$$

which is characteristic of first-order processes. The linear plots of $-\ln(1-\alpha)$ vs. time were used to calculate the rate constants at various temperatures by means of a linear regression analysis. Table 1 shows the values of the rate constants for the dehydration of $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ and $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$.

For both $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$ and $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ the dehydration processes are adequately described by a first-order rate law. Analysis of the variation in rate constant with temperature according to the Arrhenius equation leads to an activation energy of 86.1 kJ mole^{-1} and a frequency factor of 1.1×10^9 sec^{-1} in the case of $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$. For $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$, these parameters have values of 64.1 kJ mole^{-1} and

TABLE 1

Rate constants for the dehydration of oxalate complexes

Temp. (°C)	$K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$		$K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$	
	k (sec^{-1})	Corr. coeff.	k (sec^{-1})	Corr. coeff.
75	1.11×10^{-4}	0.994	—	—
85	4.32×10^{-4}	0.980	—	—
90	4.68×10^{-4}	0.974	1.20×10^{-4}	0.991
100	8.55×10^{-4}	0.986	2.60×10^{-4}	0.992
110	—	—	3.64×10^{-4}	0.998

2.1×10^5 sec^{-1}, respectively. The activation energies are estimated to be accurate to about ±5%.

The TG, DTG, and DSC curves for $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ and $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$ are shown in Figs. 1 and 2, respectively. In the case of $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$, the dehydration in the TG results in a mass-loss curve having the appearance of a two-step dehydration. Consequently, a kinetic analysis of this process was not possible. However, for $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ it was possible to study the dehydration from the TG curves using the Coats and Redfern equation for a first-order process [13]

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

where α is the fraction dehydrated, E is the activation energy, T is the absolute temperature, R is the gas constant, β is the heating rate, and A is the frequency factor. For four separate samples, the results for the activation energy and the correlation coefficients calculated from the linear regression analysis fitting the data to eqn. (2) are as follows: 42.6 kJ $mole^{-1}$, 0.997; 45.3 kJ $mole^{-1}$, 0.997; 43.2 kJ $mole^{-1}$, 0.995; 46.5 kJ $mole^{-1}$, 0.994. These results yield a mean value of 44.4 kJ $mole^{-1}$ for the activation energy, with a standard deviation of 1.6 kJ $mole^{-1}$. A first-order equation fits the data well, and reproducible values for the activation energy are obtained. However, the activation energy from isothermal studies is about 64.1 kJ $mole^{-1}$. No explanation for this difference is readily available.

The DSC curve for $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$ shows that the dehydration

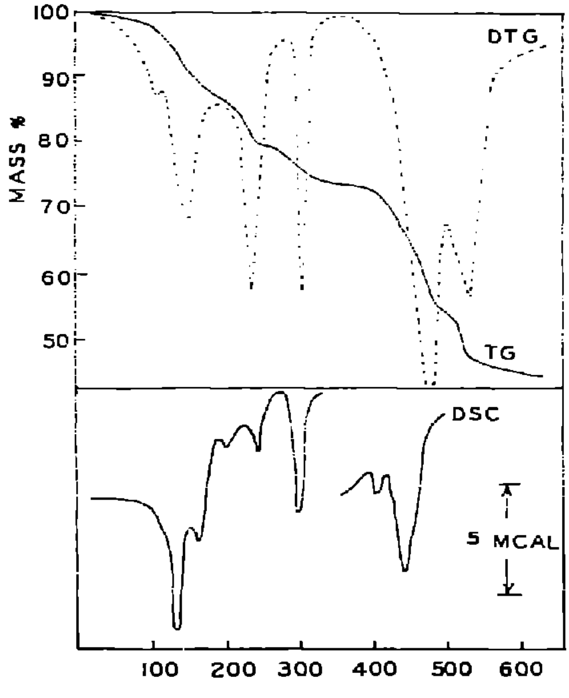

Fig. 1. TG, DTG, and DSC curves for the decomposition of $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$.

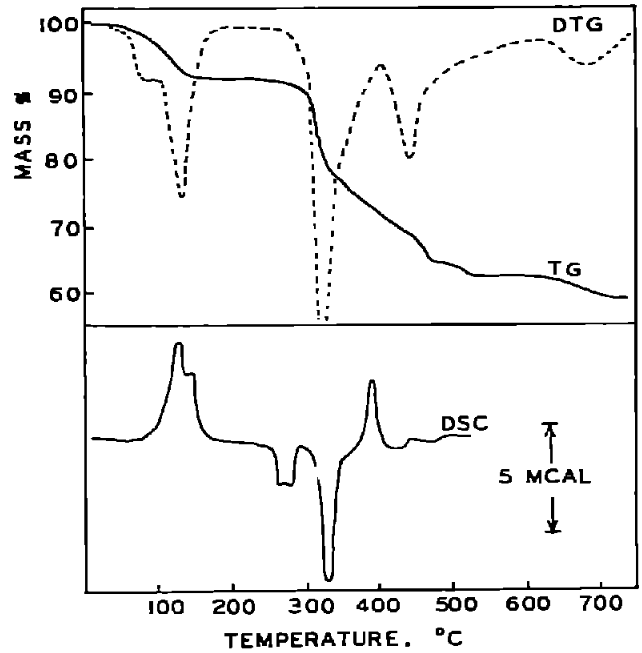

Fig. 2. TG, DTG, and DSC curves for the decomposition of $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$.

does not take place completely in one step. The total ΔH of 125.5 kJ $mole^{-1}$ corresponds to 41.8 kJ $mole^{-1}$ of water removed. These results are in good agreement with those previously published for this complex [4]. For $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$, a well-defined endothermic peak is seen in the dehydration region. A ΔH value of 60.8 kJ $mole^{-1}$ is obtained, which is equivalent to 30.4 kJ $mole^{-1}$ of water removed.

Analysis of the TG curves shows that the decomposition of $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$ takes place according to eqns. (3)—(6).

$$K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O(s) \rightarrow K_3[Fe(C_2O_4)_3](s) + 2\ H_2O(g) \quad (3)$$

$$K_3[Fe(C_2O_4)_3](s) \rightarrow K_3[Fe(C_2O_4)(CO_3)(O)](s) + 2\ CO(g) + CO_2(g) \quad (4)$$

$$K_3[Fe(C_2O_4)(CO_3)(O)](s) \rightarrow K_3[Fe(C_2O_4)(O)_2](s) + CO_2(g) \quad (5)$$

$$K_3[Fe(C_2O_4)(O)_2](s) \rightarrow K_3[Fe(CO_3)(O)_2](s) + CO(g) \quad (6)$$

The final product stable at 750°C is written as a basic carbonate, but it is also possible that the product is an equimolar mixture of K_2CO_3 and $KFeO_2$.

Following the dehydration of $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$ in the DSC, an exotherm is observed from 280—295°C. This peak does not appear to be associated with any of the processes involving mass loss, except perhaps in the initial stages, and may represent a structural rearrangement in the dehydrated material. At 315—330°C, a second exotherm is seen, which corresponds to the reaction represented by eqn. (4). Because an endotherm follows immediately, it is not possible to resolve the peaks and obtain ΔH values for the separate steps in the decomposition. Table 2 shows the thermal parameters for the decomposition of $K_3[Fe(C_2O_4)_3] \cdot 2\ H_2O$. The activa-

TABLE 2

Thermal parameters for the decomposition of $K_3[Fe(C_2O_4)_3]\cdot 2\,H_2O$

Eqn.	Temp. range (°C)	% Mass loss		ΔH (kJ mole^{-1})	E_a (kJ mole^{-1})
		Calc.	Obs.		
3	100—145	7.6	7.5	60.8 [a]	173.6
4	285—385	21.2	20.5	—	24.8
5	405—525	9.2	10.2	—	38.3
6	625—725	6.0	4.5	—	94.6
Total	100—725	44.0	42.7	—	—

[a] 30.4 kJ mole^{-1} of H_2O released.

tion energies were obtained by fitting the TG data to eqn. (2), and a good linear fit was obtained in each case.

For $K_3[Cr(C_2O_4)_3]\cdot 3\,H_2O$, the analysis of the TG curves shows that the decomposition takes place in five steps according to eqns. (7)—(11).

$$K_3[Cr(C_2O_4)_3]\cdot 3\,H_2O(s) \rightarrow K_3[Cr(C_2O_4)_3](s) + 3\,H_2O(g) \tag{7}$$

$$K_3[Cr(C_2O_4)_3](s) \rightarrow K_3[Cr(C_2O_4)_{3/2}(CO_3)_{3/2}](s) + 3/2\,CO(g) \tag{8}$$

$$K_3[Cr(C_2O_4)_{3/2}(CO_3)_{3/2}](s) \rightarrow K_3[Cr(C_2O_4)_{1/2}(CO_3)_{5/2}](s) + CO(g) \tag{9}$$

$$\begin{aligned} K_3[Cr(C_2O_4)_{1/2}(CO_3)_{5/2}](s) \rightarrow {} & K_3[Cr(CO_3)(O)_2](s) + 1/2\,CO(g) \\ & + 2\,CO_2(g) \end{aligned} \tag{10}$$

$$K_3[Cr(CO_3)(O)_2](s) \rightarrow K_3CrO_3(s) + CO_2(g) \tag{11}$$

The final product is written as potassium chromite, although it could also be considered as a mixture of the metal oxides. The steps in the decomposition were sufficiently separated that kinetic and thermal parameters could be determined from the TG and DSC curves. In each case, the first-order Coats and Redfern equation provided the best fit to the TGA data. In general, correlation coefficients in the range 0.992—0.999 were obtained from the

TABLE 3

Thermal parameters for the decomposition of $K_3[Cr(C_2O_4)_3]\cdot 3\,H_2O$

Eqn.	Temp. range (°C)	% Mass loss		ΔH (kJ mole^{-1})	E_a (kJ mole^{-1})
		Calc.	Found		
7	100—165	11.1	10.5	125.5 [a]	44.4
8	185—265	8.6	9.5	22.3	174.9
9	285—310	5.7	5.0	20.9	—
10	345—485	20.9	20.9	89.7	163.1
11	485—545	9.0	9.6	—	—
Total	100—545	55.4	54.6	—	—

[a] 41.8 kJ mole^{-1} of H_2O released.

curves for several runs. Table 3 shows the thermal parameters for the decomposition of $K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$.

The results of this work show that decomposition of $K_3[Fe(C_2O_4)_3]$ and $K_3[Cr(C_2O_4)_3]$ takes place in somewhat different ways. For the chromium compound, only CO is lost in the first two steps as oxalate is converted to carbonate. For the iron compound, this is not the case, CO and CO_2 being lost in the initial step. However, equivalent products, $K_3[Fe(CO_3)(O)_2]$ and $K_3[Cr(CO_3)(O)_2]$, are obtained during the processes [eqns. (6) and (10)]. It has not been possible to determine the kinetics of all the steps, but the decomposition patterns appear to be reproducible and reliable.

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