

THERMAL STUDIES ON OXALATE COMPLEXES. IV. POTASSIUM BIS(OXALATO)CUPRATE(II) DIHYDRATE

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ABSTRACT

The dehydration and decomposition of $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ have been studied using TG. The dehydration reaction gave the best fit to a second-order rate equation and has an activation energy of 411.5 ± 41.1 kJ mole⁻¹. Three distinct decomposition patterns were observed for the anhydrous complex. In the first case, $K_2[Cu(C_2O_4)_2]$ decomposes to K_2CO_3 and CuO by loss of CO_2 and 2 CO. In the second case, decomposition leads to $K_2C_2O_4$ and Cu by loss of 2 CO_2 . In the third case, the basic carbonate $K_2[Cu(CO_3)_{3/2}O_{1/2}]$ is produced by loss of 2 CO and 0.5 CO_2 . In the last case, additional loss of CO_2 leads to the formation of K_2CO_3 and CuO in a separate reaction. Kinetic parameters are reported and discussed for all these reactions.

INTRODUCTION

It is often the practice that TG experiments are carried out on some material, and the data obtained are analyzed according to one of the growing number of mathematical techniques to provide kinetic parameters [1–12]. Additionally, it is increasingly the practice to use several methods of data analysis and compare the results in an attempt to show the superiority of some particular method [13–15]. However, the sample-to-sample differences are rarely considered even though those variations may give rise to larger uncertainties in derived kinetic parameters than are introduced by different numerical methods [16]. In a previous study it was shown that even for the decomposition of simple salts this situation exists [16]. Further, certain reactions of more complicated materials are known to depend on other variables, such as sample size, even in stoichiometry [17]. Thus, derived kinetic parameters are also greatly influenced. Therefore, a great deal of data must be at hand for reliable kinetic parameters to be determined for complex reactions.

Metal oxalate complexes have been studied by numerous workers. In our previous studies, the thermal decomposition of oxalate complexes of Fe(III) and Cr(III) [18] and Co(II) and Co(III) [19] have been studied. We have also studied the decomposition of *cis*- and *trans*- $K[Cr(C_2O_4)_2(H_2O)_2]$ [20] and a sizeable number of other studies have been reported on oxalate complexes of Mn(III), Ni(II), Cu(II), and other metals [21–27]. In most of these studies,

it is shown that decomposition leads to basic carbonates, at least as intermediates. Depending on the metal, reduction may also occur during the decomposition. Also, the nature of the decomposition reactions appears to depend on the experimental conditions. For example, the decomposition of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$ in air is reported to give K_2CO_3 and CuO , but it produces $K_2C_2O_4$ and Cu in nitrogen [24]. No kinetic data were reported for the reactions. The present study was undertaken to elucidate the dehydration and decomposition reactions of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$. Additionally, the study was undertaken to study the effects of sample-to-sample variations on the derived kinetic parameters for these reactions.

EXPERIMENTAL

The preparation of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$ was carried out by the method of Kirschner [28]. The decomposition in a dynamic nitrogen atmosphere was studied using a Perkin-Elmer thermogravimetric system Model TGS-2. Procedures used were similar to those previously reported [29]. Kinetic data were obtained by means of the Coats and Redfern equations [4]

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

when $n = 1$ and, when $n \neq 1$

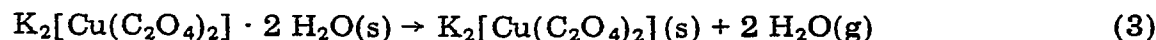
$$\ln \left[\frac{1 - (1-\alpha)^{1-n}}{(1-n) T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (2)$$

The data were analyzed using a Texas Instruments TI-59 programmable calculator program [30]. The most appropriate value of the reaction order was determined as that giving the highest value for the correlation coefficient.

RESULTS AND DISCUSSION

Dehydration

The dehydration of $CaC_2O_4 \cdot H_2O$ has been the model reaction most often used to test kinetic methods by TG [4,31]. This reaction has an activation energy of about 90 kJ mole⁻¹ and gives the best fit with an n value of about 2/3 in the Coats and Redfern equation. Dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$ provides an interesting comparison so this process was studied in detail. The dehydration reaction



occurs in a single step from 110 to 130°C. The average observed mass loss was 10.1% compared to a theoretical value of 10.2%. Figure 1 shows the TG and DTG curves in the dehydration region. Analysis of 12 samples provided

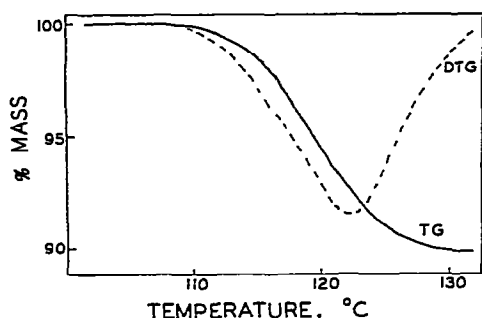


Fig. 1. TG and DTG curves for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$.

the data shown in Tables 1–3. It is readily apparent that there are significant differences in the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$ and $CaC_2O_4 \cdot H_2O$. In the case of the former, the highest correlation coefficient is obtained when the second-order Coats and Redfern equation is used. Some runs gave results that were about equal when first-order and second-order equations were compared, and one run (sample 2) gave a better fit to the first-order equation. However, when the average of 12 runs is considered, the fit of the second-order equation clearly gave the highest correlation coefficient. Assuming that the highest correlation coefficient indicates the correct order, the activation energy is thus determined as $411.5 \pm 41.1 \text{ kJ mole}^{-1}$ in contrast to the $80\text{--}110 \text{ kJ mole}^{-1}$ reported for $CaC_2O_4 \cdot H_2O$ [4,31]. Thus, not only is the order of the reaction different in the two cases, but also the activation energies differ substantially. The data shown in Tables 1–3 also show that while the correlation coefficients may differ little, the derived kinetic parameters may differ by a much greater amount [16].

TABLE 1

Correlation coefficients for fitting $f(\alpha)$ to the Coats and Redfern equation for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$

Sample	Correlation coefficient				
	$n = 0$	$n = 1/3$	$n = 2/3$	$n = 1$	$n = 2$
1	0.9767	0.9850	0.9916	0.9962	0.9986
2	0.9836	0.9909	0.9961	0.9991	0.9959
3	0.9613	0.9730	0.9829	0.9906	0.9998
4	0.9718	0.9808	0.9881	0.9936	0.9994
5	0.9737	0.9822	0.9892	0.9944	0.9992
6	0.9755	0.9834	0.9899	0.9948	0.9995
7	0.9722	0.9815	0.9887	0.9936	0.9952
8	0.9754	0.9838	0.9905	0.9954	0.9998
9	0.9761	0.9851	0.9921	0.9969	0.9987
10	0.9670	0.9767	0.9849	0.9912	0.9998
11	0.9701	0.9793	0.9869	0.9926	0.9997
12	0.9685	0.9786	0.9869	0.9931	0.9997
\bar{r}	0.9727	0.9817	0.9890	0.9943	0.9988
σ	0.0056	0.0046	0.0035	0.0024	0.0016

TABLE 2

Apparent activation energies for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$ assuming different orders of reaction

Sample	Apparent activation energy (kJ mole ⁻¹)				
	$n = 0$	$n = 1/3$	$n = 2/3$	$n = 1$	$n = 2$
1	215.0	241.6	272.1	306.7	435.1
2	185.2	210.2	238.9	271.6	393.8
3	229.8	258.1	290.7	328.2	469.5
4	210.2	234.1	261.3	291.7	402.9
5	209.9	231.4	255.7	283.0	382.3
6	210.1	231.3	255.1	281.7	378.3
7	189.3	210.8	235.2	262.6	363.7
8	216.2	243.2	274.0	308.7	436.5
9	219.7	248.6	282.1	320.4	464.1
10	243.4	271.2	302.9	338.5	469.4
11	185.8	208.3	233.7	262.2	366.5
12	195.1	217.3	242.6	271.1	375.9
\bar{E}_a	209.1	233.8	262.0	293.9	411.5
σ	17.9	20.0	22.7	26.2	41.1

Decomposition

Figure 2 shows the TG and DTG curves for the decomposition of $K_2[Cu(C_2O_4)_2]$. From the TG curves and by comparison of the data from several samples, it became quite obvious that different samples decomposed

TABLE 3

Values of $\ln A$ for the dehydration of $K_2[Cu(C_2O_4)_2] \cdot 2 H_2O$ assuming different orders of reaction

Sample	$\ln A$				
	$n = 0$	$n = 1/3$	$n = 2/3$	$n = 1$	$n = 2$
1	63.72	71.89	81.23	91.81	130.90
2	56.36	64.21	73.23	83.49	121.71
3	69.94	78.80	89.05	100.78	144.88
4	63.91	71.45	79.97	89.52	124.31
5	63.52	70.31	77.96	86.51	117.58
6	63.57	70.25	77.75	86.11	116.33
7	56.74	63.44	71.03	79.57	110.87
8	67.40	76.09	85.97	97.08	137.89
9	69.24	78.64	89.47	101.84	148.17
10	76.26	85.25	95.44	106.91	148.91
11	57.72	64.96	73.13	82.29	115.63
12	60.62	67.80	75.94	85.10	118.65
$\ln A$	64.08	71.92	80.85	90.92	127.99
σ	5.93	6.67	7.61	8.78	13.71

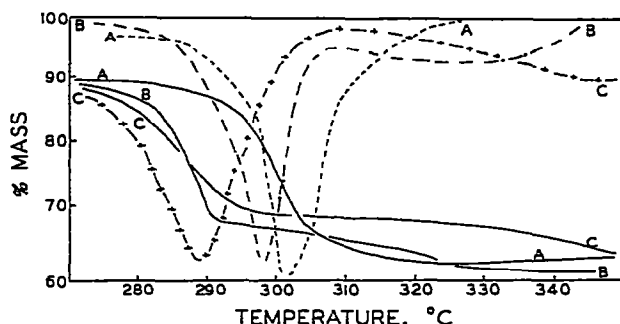
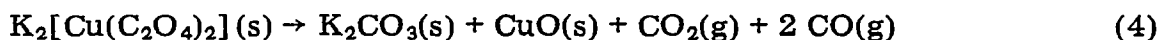


Fig. 2. TG (solid lines) and DTG (dashed lines) curves for the decomposition of $K_2[Cu(C_2O_4)_2]$. A, Decomposition according to eqn. (4); B, decomposition according to eqn. (5); C, decomposition according to eqn. (7).

differently. Three distinct decomposition patterns were observed. No relationship was found between sample mass or any other observable and the decomposition pattern. The behavior appeared to be entirely random.

In the first case, samples were found to lose an average of 28.7% mass in the range 260–330°C. This corresponds closely to the reaction



which represents a 28.1% mass loss. Data for this process are shown in Table 4.

In the second case, samples of $K_2[Cu(C_2O_4)_2]$ were found to lose an average of 23.9% mass in a single step from 275 to 315°C. This corresponds closely to the reaction

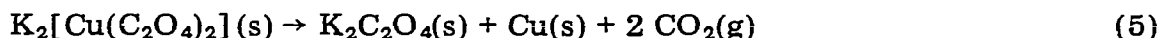


TABLE 4

Reaction parameters for the decomposition of $K_2[Cu(C_2O_4)_2]$ according to eqn. (4)

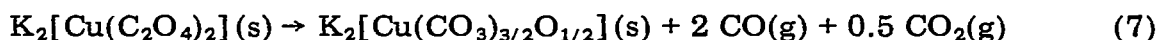
Sample	$n = 0$	$n = 1/3$	$n = 2/3$	$n = 1$	$n = 2$
<i>Correlation coefficients</i>					
1	0.9883	0.9877	0.9861	0.9834	0.9704
4	0.9964	0.9965	0.9962	0.9954	0.9906
6	0.9977	0.9979	0.9974	0.9960	0.9875
\bar{r}	0.9941	0.9940	0.9932	0.9916	0.9828
σ	0.0051	0.0055	0.0062	0.0071	0.0109
<i>Apparent activation energies ($kJ\ mole^{-1}$)</i>					
1	362.5	396.9	435.5	478.3	632.3
4	456.3	482.7	511.0	541.1	642.6
6	418.5	446.8	477.6	511.1	627.4
\bar{E}_a	412.4	442.1	474.7	510.2	634.1
σ	20.3	43.1	37.8	31.4	7.8

for which the calculated mass loss is 24.7%. This reaction has been reported earlier for samples of $K_2[Cu(C_2O_4)_2]$ decomposing in a nitrogen atmosphere [24]. The samples showing this behavior also showed a gradual continued mass loss at higher temperatures indicating another indistinct process that appears to be



The observed mass loss is about 7% compared to a calculated value of about 7.9%. Table 5 shows the reaction parameters for samples decomposing according to eqn. (5).

In the third case, still other samples of the dehydrated complex gave mass losses averaging about 21.6%, which indicates that the reaction is



This reaction represents a mass loss of 21.9%. Table 6 shows the reaction parameters for samples exhibiting this behavior. Samples exhibiting this type of behavior gave a third mass loss of 6.6% which indicates continued loss of CO_2 according to



This process has a corresponding mass loss of 6.2% and the solid products can also be formulated as K_2CO_3 and CuO as in eqn. (4). Owing to the limited number of samples exhibiting this behavior and the indistinct nature

TABLE 5

Reaction parameters for the decomposition of $K_2[Cu(C_2O_4)_2]$ according to eqn. (5)

Sample	$n = 0$	$n = 1/3$	$n = 2/3$	$n = 1$	$n = 2$
	<i>Correlation coefficients</i>				
2	0.9968	0.9957	0.9943	0.9927	0.9867
7	0.9961	0.9978	0.9988	0.9990	0.9955
9	0.9902	0.9951	0.9983	0.9997	0.9932
10	0.9990	0.9990	0.9985	0.9972	0.9902
11	0.9974	0.9987	0.9990	0.9983	0.9910
12	0.9972	0.9962	0.9936	0.9893	0.9674
\bar{r}	0.9961	0.9971	0.9971	0.9960	0.9873
σ	0.0031	0.0016	0.0024	0.0041	0.0102
	<i>Apparent activation energies (kJ mole⁻¹)</i>				
2	514.9	542.2	570.8	600.9	699.5
7	590.2	637.2	688.3	743.6	935.1
9	468.5	520.0	579.0	645.7	893.1
10	472.6	506.4	542.8	582.0	716.2
11	507.9	556.3	609.8	668.7	877.3
12	470.4	506.7	547.3	592.3	754.1
\bar{E}_a	504.1	544.8	589.7	638.9	812.6
σ	46.8	49.4	54.0	61.2	101.2

TABLE 6

Reaction parameters for the decomposition of $K_2[Cu(C_2O_4)_2]$ according to eqn. (7)

Sample	$n = 0$	$n = 1/3$	$n = 2/3$	$n = 1$	$n = 2$
	<i>Correlation coefficients</i>				
3	0.9853	0.9924	0.9973	0.9997	0.9942
5	0.9791	0.9871	0.9930	0.9969	0.9989
\bar{r}	0.9822	0.9898	0.9952	0.9983	0.9966
σ	0.0044	0.0037	0.0030	0.0020	0.0033
	<i>Apparent activation energies (kJ mole⁻¹)</i>				
3	257.4	299.7	348.8	405.0	617.4
5	260.9	297.9	340.9	390.4	577.5
\bar{E}_a	259.2	298.8	344.8	397.7	597.4
σ	2.5	1.3	5.6	10.3	28.2

of the TG curves, reliable kinetic parameters could not be obtained for the reaction represented in eqn. (8).

From the data shown in Tables 4–6, it is evident that $K_2[Cu(C_2O_4)_2]$ decomposes in three different ways. In the first, eqn. (4), the best order appears to be either $n = 0$ or $n = 1/3$ and the apparent activation energy is about 412–442 kJ mole⁻¹. In the second scheme, eqn. (5), the best order appears to be either $n = 1/3$ or $n = 2/3$ and the apparent activation energy is about 544–590 kJ mole⁻¹. This is not totally certain, however, because $n = 0$ and $n = 1$ gave correlation coefficients almost equal to those obtained with $n = 1/3$ and $n = 2/3$. In the third case, eqn. (7), the best results were obtained with $n = 1$ which yields an apparent activation energy of 398 kJ mole⁻¹. Clearly, quite different kinetic parameters result when $K_2[Cu(C_2O_4)_2]$ decomposes in these three different ways.

It has been reported that $K_2[Cu(C_2O_4)_2]$ decomposes to CuO and K_2CO_3 in air and to $K_2C_2O_4$ and Cu in nitrogen [24]. The results obtained in this work indicate that even in a nitrogen atmosphere the decomposition is considerably more complex than previously reported. Thus, it appears that some of the samples decompose to $K_2C_2O_4$ and Cu [eqn. (5)] as previously reported while others decompose to K_2CO_3 and CuO in either a single step [eqn. (4)] or in two steps [eqns. (7) and (8)]. It also appears that in some cases, as represented in eqn. (7), a basic carbonate is found as an intermediate as is the case in the decomposition of most other oxalate complexes [18–20].

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