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DECOMPOSITION OF *cis*- AND *trans*- POTASSIUM DIAQUOBIS(OXALATO)CHROMATE(III)

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ABSTRACT

The decomposition of *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ has been studied using differential scanning calorimetry. Dehydration occurs as the first step with activation energies being 27.5 and 13.9 kcal mol^{-1}, respectively, for the *cis* and *trans* complexes. After dehydration, continued heating results in loss of CO and CO_2. For the *trans* complex, an additional endothermic peak is seen and the mass loss indicates that CO has been lost in a single step. In both cases, the final product indicated by mass loss data is $KCrO_2$.

INTRODUCTION

Thermal studies on simple metal oxalates are numerous and isothermal kinetic studies on these materials have been carried out by many workers[1,2]. In general, the first step in the decomposition of the simple metal oxalates is the disproportionation of oxalate to give carbonate with the loss of carbon monoxide.

The decomposition of oxalate complexes has been studied by several workers. Wendlandt and Simmons[3–5] have studied the decomposition of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$, $K_3[Co(C_2O_4)_3] \cdot 3H_2O$, and $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$. The manganese and cobalt complexes were found to undergo a reduction of the metal to +2 as water is evolved, but no reduction occurred in the chromium complex. Intermediate products produced are $K_2[Co(C_2O_4)_2]$ and $K_2[Mn(C_2O_4)_2]$. Hydrated oxalate complexes of nickel(II), cobalt(II), and copper(II) have also been studied[6]. When heated in air, $K_2[Ni(C_2O_4)_2] \cdot 6H_2O$ first loses water and is then converted to NiO and K_2CO_3. In a nitrogen atmosphere, the products are Ni and K_2CO_3. The $K_2[Co(C_2O_4)_2] \cdot 6H_2O$ is converted to Co_3O_4 and K_2CO_3 in air and to Co and K_2CO_3 in nitrogen. Similar studies[6] were reported for the copper complex, $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$.

Other studies have been carried out on complex oxalates. For example, hydrated $K_3[Al(C_2O_4)_3]$ has been investigated[7]. Decomposition of $Cu(C_2O_4)(NH_3)_2$ has also been studied[8] as well as the mixed oxalate ethylenediamine complexes of Zn and Cd[9]. The latter complexes lose ethylenediamine before the oxalate group is ruptured. From the results cited here, it is apparent that oxalate complexes decompose by several different means.

We have studied the decomposition of *cis*- and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ to determine the characteristics of these materials under dynamic heating in a differential scanning calorimeter. The main factors of interest in this study were the characteristics of the dehydration of the *cis* and *trans* diaquo complexes and the mode of decomposition of coordinated oxalate. The results of these studies are presented here.

EXPERIMENTAL

The *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]$ and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ used in this work were prepared by adaptations[10] of standard methods[11]. The products were precipitated by addition of ethanol and cooling on ice. After filtration, the products were washed with acetone and dried in air at room temperature.

DSC studies were carried out using procedures similar to those previously described[12]. Weight losses attendant to thermal transitions were obtained by reweighing the sample immediately after scanning to the desired temperature. Activation energies were determined by the procedure of Thomas and Clarke[13]. Enthalpy changes were determined by integration of peak areas after the instrument was calibrated using the fusion of metallic tin.

RESULTS AND DISCUSSION

Decomposition of *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]$ results in a DSC curve which shows two rather large endotherms. The first is well defined and is found in the temperature range where dehydration occurs. The mass loss corresponds closely to that expected for dehydration. The second peak is not as well defined and the mass loss does not correspond to a clean decomposition of oxalate to yield carbonate. It was expected that peaks corresponding to dehydration and loss of CO would be This result will be discussed later.

Decomposition of *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ results in several endothermic peaks. Details of the curves are shown in Fig. 1. Data obtained from the DSC curves are shown in Table 1.

The data shown in Table 1 indicate that both *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]$ and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ are initially dehydrated giving a product having a composition of $KCr(C_2O_4)_2$ in each case. In order to achieve a coordination number of six, some of the oxalate groups probably function as bridging groups producing different structures for the material after dehydration. The activation energy for dehydration of the *cis* complex is apparently about twice that for the *trans* complex. Owing to the indistinct shape of the endotherm as dehydration progresses, the ΔH value could not be determined in the case of the *cis* complex. For both the *cis* and *trans* complexes the mass losses are very close to those expected for the loss of the two coordinated molecules of H_2O. The complexes contain no other hydrate water. Before the dehydration of the *trans* complex is complete, a small sharp endothermic peak results. The peak corresponds to a ΔH value of 0.29 ± 0.03 kcal mol^{-1} and may

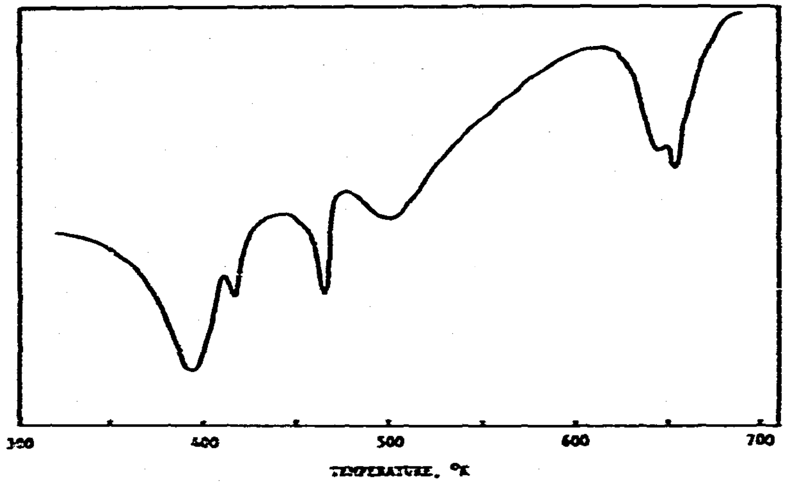

Fig. 1. DSC curve for decomposition of *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$.

TABLE I

MASS LOSSES AND THERMAL DATA FOR DECOMPOSITION OF *cis*- AND *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$

Peak (K)	*% Mass loss*[a]		ΔH *(kcal mol^{-1})*	E_a *(kcal mol^{-1})*	*Product*
	Expt.	*Calc.*			
cis-$K[Cr(C_2O_4)_2(H_2O)_2]$					
358–420	10.9±0.4[b]	11.9	—	27.5±0.3	$KCr(C_2O_4)_2$
615–710	59.0±0.4[c]	59.3	54.2	98	$KCrO_2$
trans-$K[Cr(C_2O_4)_2(H_2O)_2]$					
340–415	12.1±0.75[d]	11.9	11.11±0.16	13.9±0.79	$KCr(C_2O_4)_2$
455–470	—	—	1.44±0.36	—	$KCr(C_2O_4)_{2(l)}$
470–580	28.5±2.1	30.4	—	—	$K_2CO_3 + Cr(CO_3)_3$
610–710	58.5±2.3[c,b]	59.3	12.38	—	$KCrO_2$

[a] Shown as mean value±average deviation from the mean. [b] Based on eight determinations. [c] Mass loss at 750 K. [d] Based on 23 determinations.

be associated with a phase transition. The nature of the transition giving rise to this peak is uncertain, but it is unlikely that it involves loss of any volatile product since the mass loss is so close to that expected for dehydration alone.

If the product having the composition $KCr(C_2O_4)_2$ obtained after dehydration of the *cis* and *trans* complexes is the same in both cases, further decomposition would follow the same pattern regardless of whether the starting complex were *cis* or *trans*. As can be seen from Table 1 and Fig. 1, this was not observed. In either instance, further decomposition must represent rupture of oxalate groups.

In the case of the *cis* complex, further heating produces an additional indistinct endothermic peak from which only an estimated ΔH value could be determined. The indistinct peaks permitted the baseline for the early part of the peak to be determined with reasonable certainty. Using that baseline, an activation energy of about 98 kcal mol^{-1} was obtained. Since the decomposition of oxalate presumably begins with the rupture of a C–O bond, the value of 98 kcal mol^{-1} is reasonable given that the C–O single bond energy is 85.5 kcal mol^{-1} while that of the double C=O bond[14] is 191 kcal mol^{-1}. The C–O bond in $C_2O_4^{2-}$ should be intermediate between single and double bond in character. It appears that the decomposition of the *cis* complex by loss of CO according to the equation

$$2KCr(C_2O_4)_{2(s)} \rightarrow K_2CO_{3(s)} + Cr_2(CO_3)_{3(s)} + 4CO_{(g)}$$

does not occur in a well-defined step. Instead, there is some loss of CO_2 also. Eventually, when the sample is heated to 750 K, a composition of $KCrO_2$ is reached however.

In an effort to determine the conditions under which a product having the composition $KCrO_2$ is obtained from *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]$ several runs were made in which mass loss was the primary measurement. Although no distinct peaks were obtained after dehydration was complete, there was a gradual shift of the curve in the endothermic direction. For example, samples heated at 10 K min^{-1} up to 655 K were found to lose 41.4±1.1% in weight. A sample heated to 700 K was found to lose 50.5±3.0% while scanning to 750 K produced a weight loss of 59.0±0.4%. A similar result (58.4% mass loss) was obtained by holding a sample at 675 K for 5 min after scanning to that temperature. Decomposition of the complex to $KCrO_2$ would require a 59.3% mass loss, and the results show that this is achieved although it does not produce a well-defined peak in the DSC curve.

After dehydration of the *trans* complex, continued heating produces three endothermic peaks with the attendant mass losses and thermal data shown in Table 1. The first of these peaks is in the range 455–465 K. Visual examination of the sample shows that this peak corresponds to melting of the sample with gas evolution beginning as soon as a liquid phase is present. Therefore, a precise value for the heat of fusion is not found, but it is approximately 1.44±0.36 kcal mol^{-1}. The broad endotherm seen between 470–580 K corresponds to decomposition of oxalate and the observed mass loss agrees with that decomposition representing loss of CO. From these data, it can be seen that the results are in agreement with the second step of the decomposition being

$$2KCr(C_2O_4)_{2(s)} \rightarrow K_2CO_{3(s)} + Cr_2(CO_3)_{3(s)} + 4CO_{(g)}$$

The indistinct nature of the broad endothermic peak does not permit an accurate determination of the activation energy or ΔH.

The final endothermic peak in the decomposition of the *trans* complex occurs at 610–710 K and corresponds to a ΔH value of 12.4 kcal mol^{-1}. After this peak, the weight loss corresponds to about 48.4% of the mass of the original sample and heating to 750 K results in a product having the composition $KCrO_2$.

Dehydration of *cis*-$K[Cr(C_2O_4)_2(H_2O)_2]$ and *trans*-$K[Cr(C_2O_4)_2(H_2O)_2]$ occurs cleanly in one step to give products having the composition $KCr(C_2O_4)_2$ in each case.

Subsequently, the decomposition is different owing to different structures in the two cases. The overall decomposition reaction in both cases is

$$K[Cr(C_2O_4)_2(H_2O)_2]_{(s)} \rightarrow KCrO_{2(s)} + 2CO_{(g)} + 2CO_{2(g)} + 2H_2O_{(g)}$$

but in the case of the *trans* complex, an intermediate product is obtained in which only H_2O and CO are lost.

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