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Note

THERMAL STUDIES ON OXALATE COMPLEXES. V. POTASSIUM TRIS(OXALATO)ALUMINATE(III) TRIHYDRATE

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A large number of thermal studies on oxalate complexes have been reported [1]. Our previous studies [1–4] have shown that oxalate complexes of transition metals decompose to yield basic carbonates in most cases. In general, the reactions are well defined and kinetic and thermodynamic parameters have been evaluated. We present here the results of TG studies on $K_3[Al(C_2O_4)_3] \cdot 3\ H_2O$.

EXPERIMENTAL

The preparation of $K_3[Al(C_2O_4)_3] \cdot 3\ H_2O$ was carried out by the method of Yost and Simons [5]. TG data were obtained using a Perkin-Elmer thermogravimetric system Model TGS-2. Procedures employed were similar to those previously reported [6]. Kinetic parameters were obtained from the TG data using the method of Reich and Stivala [7], which was carried out by means of the program previously reported [8].

RESULTS AND DISCUSSION

The TG and DTG curves for $K_3[Al(C_2O_4)_3] \cdot 3\ H_2O$ are shown in Fig. 1. Mass losses obtained from the curves show that dehydration occurs in three steps according to the reactions

$$K_3[Al(C_2O_4)_3] \cdot 3\ H_2O(s) \xrightarrow{50-70^\circ C} K_3[Al(C_2O_4)_3] \cdot 7/3\ H_2O(s) + 2/3\ H_2O(g) \tag{1}$$

$$K_3[Al(C_2O_4)_3] \cdot 7/3\ H_2O(s) \xrightarrow{80-130^\circ C} K_3[Al(C_2O_4)_3] \cdot 1/3\ H_2O(s) + 2\ H_2O(g) \tag{2}$$

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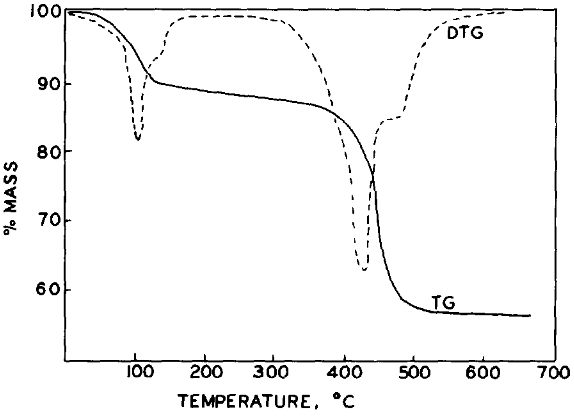

Fig. 1. TG and DTG curves for $K_3[Al(C_2O_4)_3]\cdot 3\ H_2O$.

$$K_3[Al(C_2O_4)_3]\cdot 1/3\ H_2O(s) \xrightarrow{130-170°C} K_3[Al(C_2O_4)_3](s) + 1/3\ H_2O(g) \quad (3)$$

The reactions represented by eqns. (1) and (3) take place so gradually and with such small mass losses that it was not possible to obtain reproducible kinetic parameters. Consequently, kinetic parameters are shown only for the reaction represented by eqn. (2).

Decomposition of the anhydrous $K_3[Al(C_2O_4)_3]$ occurs in two well-defined steps. These can be written as

$$K_3[Al(C_2O_4)_3](s) \xrightarrow{380-480°C} K_3[Al(CO_3)_2O](s) + 3\ CO(g) + CO_2(g) \quad (4)$$

$$2\ K_3[Al(CO_3)_2O](s) \xrightarrow{490-525°C} K_6Al_2(CO_3)_3O_3(s) + CO_2(g) \quad (5)$$

Kinetic parameters for these and one dehydration reaction are shown in Table 1.

TABLE 1

Reaction parameters for decomposition reactions

Reaction	Temp. range (°C)	Calcd.	Observed	Best n [a]	E [a] (kJ mole^{-1})
2	80–130	7.8	7.5	1.40 ± 0.22	116.1 ± 12.2
4	390–480	27.7	27.8	0.96 ± 0.33	202.1 ± 15.6
5	490–525	4.8	5.4	3.07 ± 0.25	979.4 ± 9.6

[a] Calculated by Reich and Stivala method. Shown as mean value ± standard deviation.

The two decomposition reactions are identical with two of those observed for $K_3[Co(C_2O_4)_3]$ [3]. However, the cobalt complex was found to undergo further decomposition by loss of CO_2. The reaction represented by eqn. (4) was found to have an activation energy of 237 kJ mole^{-1} for the cobalt complex [3] and 202 kJ mole^{-1} for the aluminum complex. However, the reaction orders for the processes represented in eqns. (4) and (5) do not appear to be the same as those for similar reactions of the cobalt complex [3]. It can not be ascertained whether this indicates a different mechanism of decomposition of the aluminum and cobalt complexes or whether other factors are involved. Also, the solid product of reaction (5) was stable to 700°C. Thus, while there are some differences, the present work indicates that intermediates of the basic carbonate type are obtained in the decomposition of oxalate complexes of both transition and non-transition metals.

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