A DIFFERENTIAL SCANNING CALORIMETRY STUDY OF SOME TRIS(OXALATO)METAL(III) COMPLEXES

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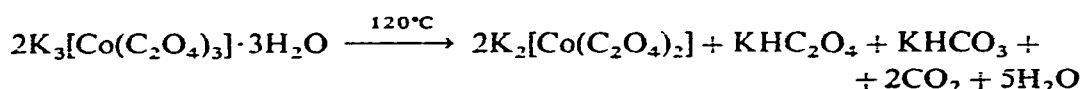
ABSTRACT

The enthalpy and kinetic parameters of the solid-state deaquation reaction of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ were determined from DSC measurements. A sealed-tube DSC technique was employed to determine the enthalpies and to study the kinetics of the solid-state oxidation–reduction reactions of $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$.

INTRODUCTION

The solid-state thermal oxidation–reduction reactions of $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$ have previously been investigated[1-6]. The thermal dissociation reaction stoichiometries are given by the following equations[5,6]:

$$2K_3[Co(C_2O_4)_3] \cdot 3H_2O \xrightarrow{120^\circ C} 2K_2[Co(C_2O_4)_2] + KHC_2O_4 + KHCO_3 + \\ + 2CO_2 + 5H_2O$$

and

$$2K_3[Mn(C_2O_4)_3] \cdot 3H_2O \xrightarrow{85^\circ C} 2K_2[Mn(C_2O_4)_2] + K_2C_2O_4 + 2CO_2 + 6H_2O$$

Possible reaction mechanisms have been postulated[5,6], which in both cases, involve free radical intermediates. Since the evolution of hydrate-bound water is concurrent with the oxidation–reduction reaction, it was not possible to determine the enthalpies of the oxidation–reduction reactions.

In this investigation, an attempt is made to determine the enthalpies of the oxidation–reduction reactions by two different methods involving DSC measurements.

For the first method, the overall enthalpy of the oxidation–reduction reaction and the concurrent evolution of water are determined. The enthalpy of the evolution of water is subtracted from the overall reaction enthalpy to obtain the enthalpy of the oxidation–reduction reaction. The enthalpy of water evolution, in both cases, was assumed to be the same as that of the corresponding chromium compound, $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$, which does not undergo an oxidation–reduction reaction in the temperature range in which water is evolved.

In the second method, DSC measurements are made with the compounds contained in sealed glass tubes, in a manner which has previously been described[7].

The high pressures developed in the sealed tubes suppresses the vaporization of water which, in open tubes, masks the exothermic DSC peaks corresponding to the oxidation–reduction reaction. Enthalpies of reaction can therefore be measured directly.

Since DSC measurements give a direct measure of heat absorbed or released by a sample during reaction, it is probably the most reliable method for studying kinetics of solid-state reactions and has been widely used for this purpose[8-14]. In this investigation, the kinetics of the deaquation reaction of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ and the oxidation–reduction reactions of $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$ were studied using the sealed-tube technique.

EXPERIMENTAL

Preparation and analysis of compounds

The compounds, $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$, were prepared and analyzed for metal ion content as previously described[5,6]. The compound, $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$, was prepared by the method of Bailar and Jones[15] and was analyzed for chromium ion content by pyrolyzing samples at 500°C and weighing the products as K_2CrO_4 and K_2CO_3. All three compounds were analyzed for oxalate ion content by titration with potassium permanganate. The results of the analysis were as follows: $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$: Mn, found, 11.6%, calc., 11.20%; C_2O_4, found, 59.2%, calc., 58.58%; $K_3[Co(C_2O_4)_3] \cdot 3H_2O$: Co, found, 12.1%, calc., 11.92%; C_2O_4, found, 53.6%, calc., 53.41%; $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$: Cr, found, 11.2%, calc., 10.67%; C_2O_4, found, 53.9%, calc., 54.17%.

Reaction enthalpies

The reaction enthalpies were determined using a Perkin–Elmer Model DSC-1B differential scanning calorimeter. From 1–7 mg of sample were employed at a heating rate of 10°C/min. The heat of fusion of indium ($\Delta H_f = 6.8$ cal/g) was used as the standard. Areas under the peaks were measured using a planimeter. Sealed tube DSC measurements were carried out using sample holders which have previously been described[7].

Reaction kinetics

The DSC data were evaluated using a previously described method[12]. The rate constant, k, for the reaction is given by

$$k = \frac{\left(\dfrac{A_v}{N_0}\right)^{z-1} d}{(A-a)^z}$$

where χ is the reaction order, d the deviation from the base line, A the total peak area, a the peak area up to temperature. T, v, the sample volume, and N_0 the number of moles of sample.

RESULTS AND DISCUSSION

The DSC curves for $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$, $K_3[Co(C_2O_4)_3] \cdot 3H_2O$, and $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$, are given in Fig. 1.
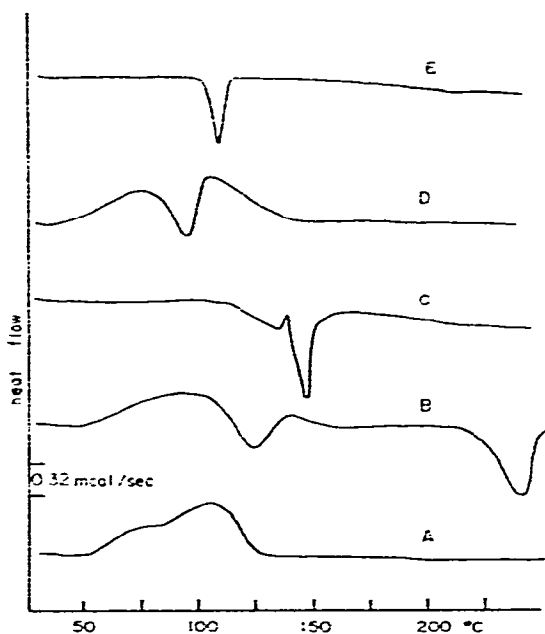

Fig. 1. DSC curves of some tris(oxalato)metal(III) complexes: (A) $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ (open sample container); (B) $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ (open sample container); (C) $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ (sealed tube); (D) $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$ (open sample container); (E) $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$ (sealed tube).

The deaquation of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ appears to occur in two overlapping steps. A single mole of water per mole of complex is apparently evolved in the first step while the remaining two moles are evolved in the second step. This indicates that perhaps the one mole of water is situated in the crystal lattice in a different manner than the other two. The enthalpy of reaction, on the basis of three determinations, was 10.5 ± 0.5 kcal/mole, which is about the value expected for loosely bound hydrate water. This value is also very close to the value previously obtained for dehydration reactions[16].

Besides suppressing the vaporization of hydrate-bound water, the pressure developed in the sealed tubes had other effects on the DSC curves of $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$. First, the temperatures of the oxidation–reduction reactions were increased 24 and 22 °C, respectively, as can be seen from Table I. This indicates that the presence of the hydrate-bound water in the crystal lattice probably stabilizes the complexes toward the oxidation–reduction reaction, a supposition which has previously been made[17]. Secondly, the temperature of the second exothermic reaction of the cobalt compound, which has previously been found to be the

decomposition[5] of $KHCO_3$. was decreased 73°C. Probably, the presence of water in the sealed tube initiated the reaction at a lower temperature.

TABLE I

REACTION ENTHALPIES FOR SOME TRIS(OXALATO)METAL(III) COMPLEXES

Reaction	Peak temperature (°C)	ΔH (kcal/mole)
$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$	~100	10.5 ± 0.5
deaquation		(per mole of H_2O)
$K_3[Co(C_2O_4)_3] \cdot 3H_2O$		
open sample	~120	~16
	220	-9.9 ± 0.5
oxidation–reduction only	~120	~10
sealed tube	144	-12.1 ± 0.6
	147	-8.4 ± 0.5
$K_3[Mn(C_2O_4)_3] \cdot 3H_2O$		
open sample	~85	~20
oxidation–reduction only	~85	~ -11
sealed tube	107	-12.3 ± 0.6

Enthalpies of the combined deaquation and oxidation–reduction reactions were estimated from the DSC curves (B and D) in Fig. 1 and are listed in Table I. Little confidence can be placed in these values, because of the difficulties in determining the baseline of the overlapping exothermic and endothermic peaks which covered a wide temperature range.

From the reaction stoichiometries of the two oxidation–reduction reactions[5,6], it is known that 2.5 moles of water per mole of complex are evolved during the dissociation of the cobalt compound while 3 moles are evolved during the dissociation of the manganese compound. Assuming that the enthalpy of deaquation for each of the two compounds is the same as that of $K_3[Cr(C_2O_4)_3].3H_2O$, estimates of the enthalpies of the oxidation–reduction reactions were made and are listed in Table I.

Enthalpies of the oxidation–reduction reactions from the sealed-tube DSC curves (C and E) are also given in Table I. As can be seen, the values obtained by the two different methods agree reasonably well. The sealed-tube values are probably more reliable for reasons mentioned previously. The sealed tube method is apparently applicable for measuring enthalpies of reactions which are not influenced greatly by pressure, but under normal conditions, are masked by the concurrent evolution of water. The method could find use for several other such reactions.

As expected, the oxidation–reduction reactions of both the maganese and the cobalt compounds are highly exothermic. The divalent oxidation state of the central metal ion is more stable in both cases despite the large stabilization energy of the coordinate ligands in the case of the inner orbital cobalt compound.

The Arrhenius plot for the deaquation of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ is given in Fig. 2. As is the case for most deaquation reactions, the deaquation reaction found
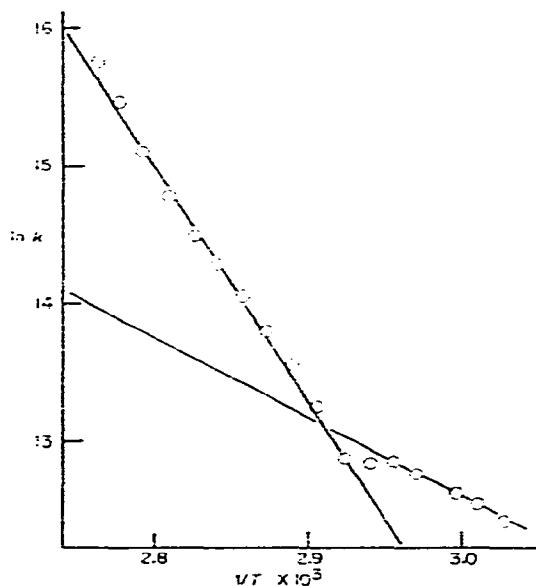
Fig. 2. Arrhenius plot for the deaquation of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$; heating rate of 10 °C/min.

here obeys first order kinetics. It is apparent that two separate reactions occur. The activation energy for the deaquation of one mole of water is apparently lower than that of the other two, again indicating that one is situated differently in the crystal lattice. Activation energies and values of log A for each of the two deaquation steps at three different heating rates are given in Table II. In this case, the heating rate did

TABLE II

ARRHENIUS PARAMETERS FOR THE DEAQUATION OF $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$

Heating rate (°C/min)	Evolution of one water		Evolution of the remaining two waters	
	Ea^a	log A	Ea^a	log A
5	12.5	13.4	31.4	25.4
10	13.3	14.1	32.8	26.3
20	13.3	13.9	28.1	23.3

^{a}kcal/mole.

not seem to influence either the value of Ea or that of log A. The values of the activation energies differ little from those found for the deaquation of other hydrogen-bonded hydrates[16,18]. The activation energy can probably be interpreted as the energy barrier associated with the breaking of hydrogen bonds and the escaping of the crystal lattice by water molecules. The large log A values are not surprising, since the activated complex for the deaquation process is expected to be more disordered than the initial state.

The sealed tube oxidation–reduction reaction of the cobalt and manganese compounds fit no reaction order exactly. Best fits were obtained assuming the reaction of the manganese compound to be second order (a result which has previously been observed[17]) and that of the cobalt compound to be first order. These kinetic plots are illustrated in Fig. 3. Superficially, it is not surprising that the two reactions involve
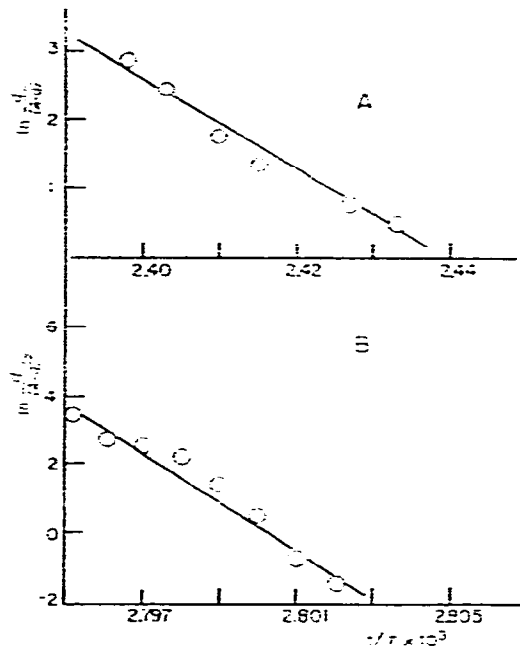

Fig. 3. Arrhenius plots for the oxidation–reduction reactions of: (A) $K_3[Co(C_2O_4)_3] \cdot 3H_2O$; (B) $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$.

different reaction orders since they involve different mechanisms. Most likely, however, neither reaction can be correctly fitted to an Arrhenius type plot. The activation energies are unreasonably high (133 kcal/mole for the manganese compound and 82 kcal/mole for the cobalt compound). As for most highly exothermic solid-state reactions, these occur rapidly over a very narrow temperature range, indicating that as a molecule reacts. it releases a large quantity of energy which is distributed first to neighboring molecules. momentarily raising their temperatures. The neighboring molecules thus react before the excess energy can be dissipated and they in turn release energy to their immediate neighbors. Thus such reactions proceed by the process of nucleus formation and growth, a process which has been well described[19,20]. Such reactions cannot, therefore, be described by the usual kinetic methods. Although the plots in Fig. 3 yield no useful information, they illustrate that kinetic measurements may be made for reactions which are masked by water evolution using the sealed tube method.

ACKNOWLEDGMENT

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