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Note

THE THERMAL DECOMPOSITION OF ZINC(II) GLUTARATE TRIHYDRATE

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Recently, the thermal decomposition of metal carboxylates [1–3] and especially zinc carboxylates [4–6] has attracted the attention of many workers. Since zinc carboxylates and their decomposition products find many applications, it inspired us to study in detail the thermal decomposition of this very important class of compounds. In continuation of our work on the thermal decomposition of zinc carboxylates [1], we report here the thermal decomposition of zinc(II) glutarate trihydrate.

EXPERIMENTAL

Zinc(II) glutarate trihydrate was prepared by dissolving slowly excess zinc oxide (AR) in a hot aqueous solution of glutaric acid (B.D.H.), filtering off the excess solid and concentrating the clear solution. Analysis of the white solid that crystallized out gave Zn = 26.0%, C = 23.9% and H = 4.5% (calcd. for $Zn(II)(CH_2)_3(COO)_2 \cdot 3H_2O$; Zn = 26.2%, C = 24.05% and H = 4.81%).

Simultaneous DTG–DTA–TG curves for the compound (100 mg) in static air and in N_2 were obtained at a heating rate of 10° min^{-1} using a cylindrical platinum crucible on a Paulik–Paulik–Erdey MOM derivatograph (Hungary).

X-Ray diffraction studies have been carried out on an X-ray diffractogram using nickel filtered CuK_α radiation. The scanning speed of the diffractometer was 2.5° min^{-1}.

Isothermal decomposition studies of a known amount of the sample have been carried out on a manually operated thermobalance described earlier [7].

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RESULTS AND DISCUSSION

Non-isothermal studies

Simultaneous DTG–DTA–TG curves of zinc(II) glutarate trihydrate in air and N_2 atmospheres are shown in Fig. 1. The TG curves for the compound reveal that the weight loss is gradual from 391 to 593 K, indicating that the dehydration reaction proceeds gradually over this range. However, a careful examination of Fig. 1 reveals three steps of weight loss indicated by slackening at three stages in the TG and corresponding three peaks in DTA and DTG in both atmospheres. The first weight loss step is abrupt from 391 to 473 K as represented by the steep slope of the TG curve and DTG peak at 443 K. TG data for this dehydration step obeyed the Coats–Redfern equation [8] only with $g(\alpha) = \alpha$ [for the zero-order kinetic model] and yielded an energy of activation of 71.6 kJ mole^{-1}. The weight loss in the second step occurs from 433 to 453 K, whereas the third weight

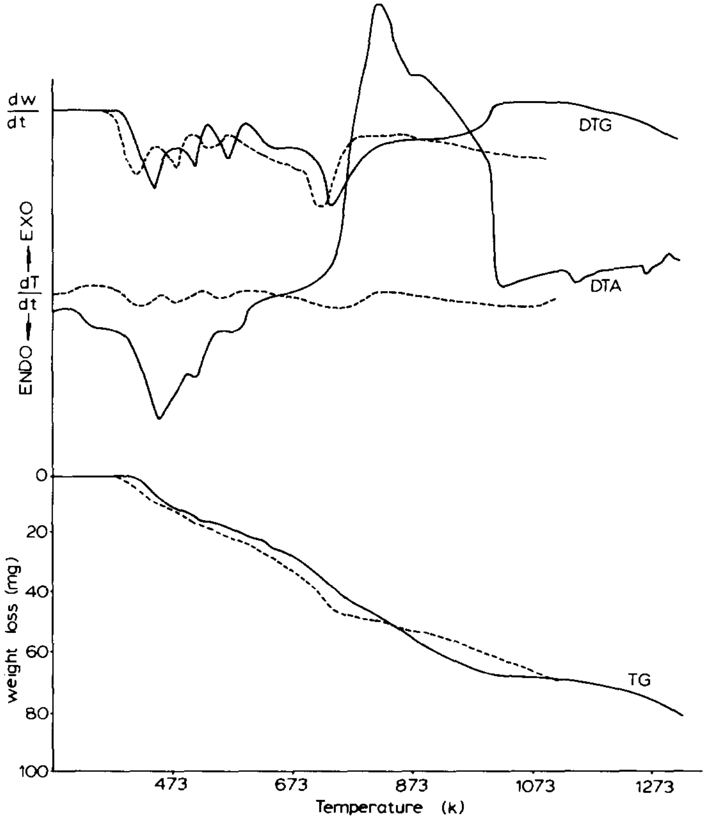

Fig. 1. Simultaneous DTG–DTA–TG curves of zinc(II) glutarate trihydrate in nitrogen (- - - - -) and air (————).

loss step occurs from 533 to 593 K. These three steps account for the elimination of one, two and three water molecules in succession. The corresponding DTA curve shows a strong endothermic peak having a maximum at 453 K and two small endothermic effects at 513 and 573 K, respectively. TG curves in both atmospheres have three narrow plateau regions showing the lesser stability of intermediate hydrates. Immediately after dehydration, DTG shows a broad region terminating at 1000 K. In the corresponding DTA above 673 K, a large exothermic region commences. It is difficult to predict or determine the number and nature of all the intermediates. However, there was definite indication of the formation of $ZnCO_3$ at a loss of 49.0 mg (calcd. loss = 49.2 mg) from the DTG curve both in air and N_2 atmospheres. In N_2, the decomposition effect was endothermic, as evidently it should be, whereas in air, the effect is exothermic because of (a) oxidation of CO to CO_2 and (b) oxidation of the rest of the molecule attached to the central zinc metal. Kinetic analysis for the formation of $ZnCO_3$ from the Horowitz–Metzger equation [9] in the modified form [10] for the first-order kinetic model yielded an activation energy of 43.0 kJ mole^{-1}. At 1003 K, the TG curve represents a weight loss of 69.0 mg in accordance with the formation of zinc oxide (calcd. loss = 67.4 mg). X-Ray diffraction data (Table 1) further confirms the formation of crystalline zinc oxide [11] as the final product.

Isothermal studies

Isothermal kinetic data in the temperature range 363–383 K for the loss of one molecule of water were tried for various kinetic equations. Best fit was found for a zero-order plot, which shows that a large number of nuclei are formed rapidly on the reactant particles. The kinetic plots start from the

TABLE 1

X-Ray diffraction data of the final decomposition product of zinc(II) glutarate trihydrate

Experimental		ASTM data file for ZnO	
d*A*° (obsd.)	Intensities	d*A*°	Intensities
6.324	10		
3.209	10		
2.805	80	2.816	71
2.468	100	2.476	100
2.592	70	2.602	56
2.738	10		
1.910	50	1.911	29
1.625	60	1.626	40

origin, indicating the absence of an induction period. The energy of activation was calculated to be 54.7 kJ mole^{-1} from an Arrhenius plot. A second molecule of water was lost between 433 and 453 K, and this dehydration process obeyed a first-order kinetic equation with an activation energy of 72.5 kJ mole^{-1}.

Anhydrous zinc(II) glutarate was formed only when the isothermal reaction was conducted at 483–503 K. For this third dehydration step, kinetic data followed the Erofeev–Avrami equation [12,13] with an activation energy of 38.0 kJ mole^{-1}. Kinetic analyses for the thermal decomposition process have not been carried out isothermally.

On the basis of these studies, the thermal decomposition of zinc(II) glutarate trihydrate can be expressed as

$$\mathrm{Zn(CH_2)_3(COO)_2 \cdot 3\,H_2O \rightarrow Zn(CH_2)_3(COO)_2 \cdot 2\,H_2O}$$
$$\mathrm{\rightarrow Zn(CH_2)_3(COO)_2 \cdot H_2O \rightarrow Zn(CH_2)_3(COO)_2 \rightarrow ZnCO_3 \rightarrow ZnO}$$

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