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THE EFFECT OF WATER VAPOUR PRESSURE ON THE KINETICS OF THE THERMAL DEHYDRATION OF ZINC FORMATE DIHYDRATE

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ABSTRACT

The isothermal dehydration of zinc formate dihydrate has been studied thermogravimetrically under various water vapour pressures from 5×10^{-4} to 6 Torr. The rate of dehydration exhibited an unusual dependence upon the water vapour pressure: with increasing water vapour pressure, the rate of dehydration increased at first, passed through a maximum, and then decreased gradually to a constant value. X-ray diffraction analysis indicated that the crystallinity of the dehydrated product, $Zn(HCO_2)_2$, is affected by the experimental temperature and the water vapour pressure. The presence of a few water molecules seems to promote recrystallization of the dehydrated product. As recrystallization is accompanied by the formation of wide channels between the dehydrated particles, through which the dissociated water molecules can easily escape, so the dehydration rate seems to increase at first. At higher vapour pressure, the rate of dehydration decreases because of the reverse reaction, caused by atmospheric water molecules.

INTRODUCTION

The thermal dehydration of hydrated salts is known to be influenced by the water vapour pressure of the reaction atmosphere. Smith and Topley [1,2] have reported that the rate constants for dehydration of manganese oxalate dihydrate and copper sulphate pentahydrate vary unusually with the partial pressure of atmospheric water vapour. When water vapour pressure is increased, the rate constant for dehydration decreases sharply at first, passes through a minimum, then increases strongly to a maximum, and finally decreases more slowly. This unusual phenomenon is known as the Smith–Topley effect. Garner and Tannar [3] have made similar studies of copper sulphate pentahydrate and potassium ammonium chrome alums.

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Recently, similar phenomena have also been observed by Dollimore et al. [4] on dehydration of calcium oxalate monohydrate and magnesium oxalate dihydrate.

We have discovered that a similar phenomenon occurs on the dehydration of zinc formate dihydrate [5]. The present paper reports on a detailed investigation of this phenomenon.

EXPERIMENTAL

Reagents

Zinc formate dihydrate was obtained commercially and recrystallized from a 1×10^{-4} M solution of formic acid. The crystals, of the hexagonal flat plate form, were air-dried at room temperature and sieved to a narrow fraction of mesh size 100–150.

Apparatus

The isothermal dehydration was followed using a Shinku Riko TGD-5000 RH differential microbalance. A sample of about 5 mg was weighed into a platinum crucible and placed in the microbalance. The dehydration was performed at a constant temperature, from 70 ° C to 100 ° C. The temperature of the furnace was controlled to achieve a given temperature within 30 s for the initial acquisition of dehydration data, and maintained at that temperature within ±0.5 ° C until dehydration was completed. The water vapour pressure of the reaction system was regulated from 5×10^{-4} to 6.0 Torr according to the following procedure. The reaction system was degassed for 3 h before the experiment, to below 5×10^{-4} Torr. Water vapour was then admitted from a water bulb. The water bulb was maintained at a constant temperature to provide a constant vapour pressure. The pressures were measured using an MKS Baratoron vacuum gauge, type 122A, and maintained within ±3%.

The output voltages for weight loss from the microbalance were amplified and recorded on a microcomputer (MZ-80C) via an AD converter (ILC 7109, modified in 13 bit) [6–8].

About 800 data points were collected at given time intervals for each dehydration process. The fraction of dehydration α was calculated from these data.

X-ray powder diffraction profiles were obtained at various temperatures using a Rigaku Geigerflex RAD-rA diffractometer equipped with a standard high-temperature sample holder. The measurements were carried out at controlled water vapour pressures. Cu $K\alpha$ radiation, a nickel filter and a graphite monochrometer were used for all the measurements. The diffraction data were taken at steps of width 0.02°.

RESULTS AND DISCUSSION

Figure 1 shows thermogravimetric (TG) and differential thermal analysis (DTA) curves for the dehydration of zinc formate dihydrate. The smoothness of each curve shows that the dehydration proceeds directly, without an intermediate such as the monohydrate.

The dehydration kinetics were analysed by the integral method, according to the following procedure. The kinetics of a solid state reaction of the type $A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gaseous}}$ can be expressed in the form

$$G(\alpha) = kt \tag{1}$$

where k is the rate constant, t is the reaction time, and $G(\alpha)$ is a function of the macroscopic reaction mechanism. Typical $G(\alpha)$ functions are shown in Table 1 [9]. The dehydration mechanism can be determined by the linearity of the plots of various $G(\alpha)$ functions against t, in accordance with eqn. (1). The $G(\alpha)$ function for the present dehydration tends to vary with atmospheric water vapour pressure, i.e. at low vapour pressure (5×10^{-4}–0.12 Torr) the dehydration corresponds to an Avrami–Erofe'ev type reaction (A_2), but at vapour pressure greater than 0.39 Torr, it conforms with a two-dimensional phase boundary controlled reaction (R_2). Typical α vs. t and $G(\alpha)$ vs. t plots are shown in Fig. 2. The values of the activation energy E and the pre-exponential factor A for both the functions are shown in Table 2. However, the plot of $1-(1-\alpha)^{1/2}$ vs. t (i.e. the plot of the R_2 function vs. t) gave a relatively straight line over the wide range of the water

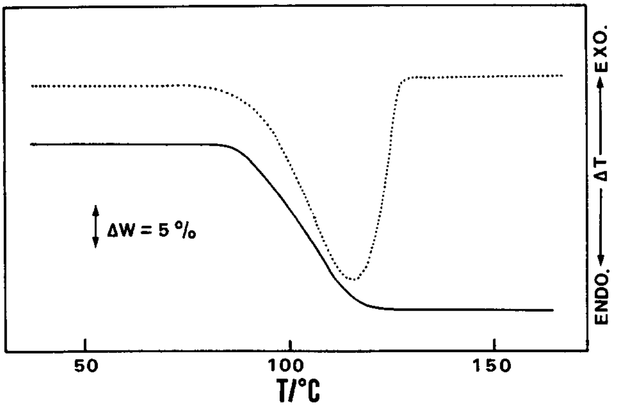

Fig. 1. TG (solid line) and DTA (broken line) curves for the dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$ in a self-generated atmosphere. Heating rate, 10 °C min^{-1}.

TABLE 1

Commonly used $G(\alpha)$ functions for solid-phase reactions

$G(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion: Jander equation
$1-2\alpha/3-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion: Ginstring–Brounshtein equation
$1-(1-\alpha)^{1/2}$	R_2	Two-dimensional phase boundary reaction
$1-(1-\alpha)^{1/3}$	R_3	Three-dimensional phase boundary reaction
$-\ln(1-\alpha)$	F_1	First-order reaction
$[-\ln(1-\alpha)]^{1/n}$	A_n	Random nucleation: Avrami–Erofe'ev equation ($n=1, 2, 3, 4$)

vapour pressures. An R_2 reaction is characterized by rapid initial production of a complete reactant–product interface at the edge of the preferred crystallographic surface, and its rate is dependent upon the advances of this reaction interface [10].

The R_2 mechanism for the present dehydration reaction is supported by consideration of the crystal structure of $Zn(HCO_2)_2 \cdot 2H_2O$. The reported

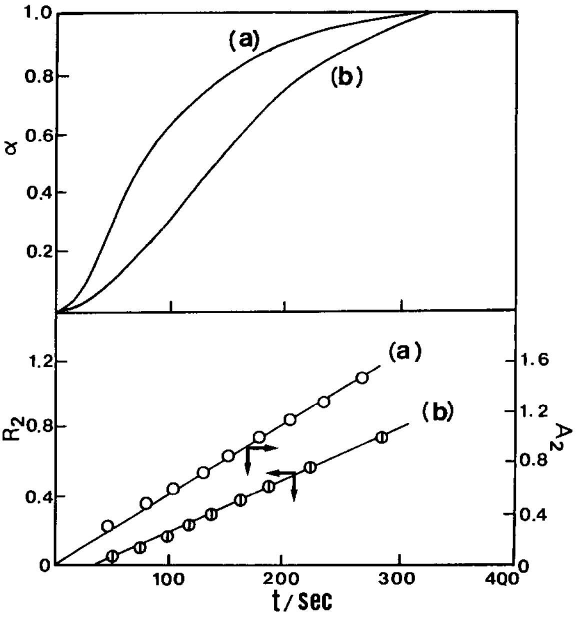

Fig. 2. Typical α vs. t and $G(\alpha)$ vs. t plots for the dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$: (a) at 100 °C, 0.12 Torr of water vapour pressure; (b) at 100 °C, 4 Torr of water vapour pressure.

TABLE 2

Values of activation energy E and pre-exponential factor A (s^{-1}) for the dehydration of $Zn(HCO)_2 \cdot 2H_2O$

Water vapour pressure (Torr)	$G(\alpha)$ function	E (kJ mol^{-1})	ln A
5×10^{-4}	A_2	29.73	3.30
0.12	A_2	44.55	9.03
0.64	R_2	72.97	17.90
2.4	R_2	71.66	17.10
6.0	R_2	63.14	13.94

crystal structure [11] is monoclinic with space group $P2_1/c$. In this structure, the unit cell includes two metallic ions. One of these metallic ions is surrounded by six carbonyl oxygen atoms, the other by two carboxyl oxygen atoms and four water molecules. Both are in a regular octahedral form, with the water molecules lying on a plane parallel to the (100) planes.

Figure 3 shows the relations between the rate of dehydration k and the water vapour pressure at particular temperatures. The value of ln k increases with increasing vapour pressure, reaches a maximum value, and thereafter decreases gradually to a constant value.

X-ray diffraction profiles (Fig. 4) indicate that the anhydrous zinc formate formed in vacuum was amorphous, while that formed above a critical water vapour pressure was crystalline. The critical temperatures for the formation of crystalline zinc formate in the presence of water vapour are illustrated in Fig. 5. The critical temperatures decreased linearly with increasing critical water vapour pressure. These findings indicate the availability of atmospheric water molecules to form a crystalline zinc formate.

It should be noted that the dehydration takes place as an A_2 reaction at below-critical water vapour pressures and temperatures, but as an R_2 reaction at above-critical values. The unusual phenomena shown in Fig. 3 may also be related to the crystallinity of the dehydrated product, as follows.

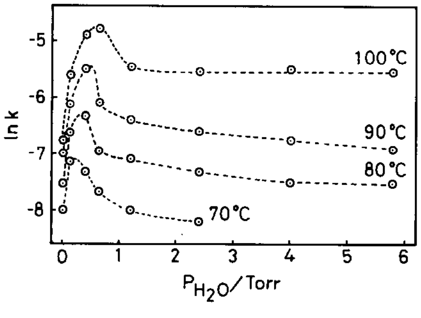

Fig. 3. Variation of dehydration rate k with water vapour pressure.

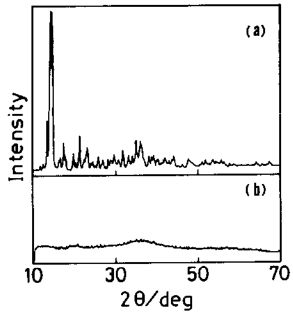

Fig. 4. Powder X-ray diffraction profiles of $Zn(HCO_2)_2 \cdot H_2O$: (a) dehydrated at 95 ° C, 0.7 Torr of water vapour pressure; (b) dehydrated at 95 ° C in vacuum.

At low water vapour pressures, the amorphous products of the zinc formate may adsorb the dissociated water molecules onto the narrow walls of their molecular dimension capillaries [12]. This would interfere with the escape of further water molecules, and the rate of dehydration would therefore be slow. The presence of a few water vapour molecules stimulates recrystallization of the dehydrated zinc formate. The initial increase in the value of *k* suggests that recrystallization may bring about the formation of wide channels between the dehydrated particles, through which the dissociated water molecules are able to escape. The value of *k* would therefore seem to increase at first. At high vapour pressure, however, the apparent rate of dehydration decreases gradually because of the reverse reaction, caused by atmospheric water molecules.

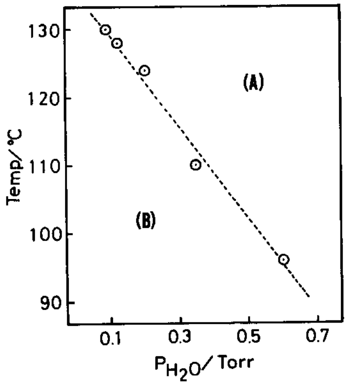

Fig. 5. Relation between the critical temperature and the critical water vapour pressure at which crystalline zinc formate is formed: (A) shows the region of crystalline product of zinc formate; (B) shows the region of amorphous product of zinc formate.

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