Thermochimica Acta, 203 (1992) 289–296
Elsevier Science Publishers B.V., Amsterdam

The effect of water vapour pressure on the kinetics of the thermal dehydration of erbium formate dihydrate

Yoshio Masuda [a,1], Kouichi Hirata [b] and Yoshio Ito [b]

[a] *Department of Chemistry, College of General Education, Niigata University, Niigata 950-21 (Japan)*
[b] *Department of Chemistry, Faculty of Science, Niigata University, Niigata 950-21 (Japan)*

(Received 10 June 1991)

Abstract

The kinetics of the thermal dehydration of erbium formate dihydrate has been studied by means of isothermal gravimetry under various water vapour pressures from 5×10^{-4} to 8 Torr. The kinetics of the dehydration, on the whole, can be described by the contracting volume model, R_3. The rate of dehydration k exhibited an unusual dependence upon the water vapour pressure: with increasing water vapour pressure, the rates increased at first, passed through a maximum, and then decreased gradually to a constant value. These phenomena were analogous to the Smith–Topley effect, and seemed to be correlated to the crystallinity of the dehydrated products. At low water vapour pressure ($\approx 10^{-4}$ Torr), the amorphous dehydrated products cover the surface of the reaction particles and interfere with the escape of the dissociated water molecules. Therefore, the rate of dehydration is slow. The presence of a few water molecules seems to promote recrystallization of the dehydrated products. The recrystallization results in the formation of wide channels between the dehydrated particles, and the dissociated water molecules can easily escape through these channels. Therefore, the dehydration rate seems to increase. At higher vapour pressure, the rate decreased gradually 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

---

Correspondence to: Y. Masuda, Department of Chemistry, College of General Education, Niigata University, Niigata 950 21, Japan.

Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

the Smith–Topley effect and has been observed on the dehydration of several hydrated salts [3–7].

A similar phenomenon is observed on the dehydration of erbium formate dihydrate. In, the present paper, this phenomenon is studied in detail, and the mechanism is discussed on the basis of the crystallinity of the dehydrated product phase.

EXPERIMENTAL

Reagent

Erbium formate dihydrate was prepared by the reaction of formic acid and erbium oxide. The purity of the erbium oxide used was 99.9% (purchased from Shin-Etsu Chemical Co. Ltd., Japan). The oxide was combined with a large excess of aqueous formic acid solution, and the mixture was held at a temperature just below its boiling point, with stirring, until the oxide had dissolved. The crystals were obtained by slow evaporation of the solution and kept in a desiccator. The specimen was pulverized with a mortar and pestle, and sieved to a narrow fraction of 80–100 mesh size.

Apparatus

The isothermal dehydration was followed with a Shinku–Riko TGD-5000 RH microbalance equipped with an infrared gold image furnace. The temperature of the specimen was coordinated so as to arrive at a constant value within 30 s in order to achieve total acquisition of the data for the initial stage of the dehydration [7–11]. The specimen, about 5 mg, was weighed into a platinum crucible and placed in the microbalance. The furnace was controlled at given temperatures between 95 and 140°C, and maintained within ± 0.5°C until the dehydration was complete.

The water vapour pressure of the reaction system was regulated from 5×10^{-4} to 8.0 Torr according to the following procedure [7]. The reaction system was degassed to below 5×10^{-4} Torr for 3 h before the experiment. Water vapour was admitted from a water bulb maintained at a constant temperature to provide a constant vapour pressure. The pressures were measured using a vacuum MKS Baratoron Gauge (Type 122A) and maintained within $\pm 3\%$.

The TG output voltages were amplified and acquired on a micro-computer (Epson QC-10II) via an A/D converter (Datel–Intersil 7109 modified to 13 bit) [7–11]. About 1000 data points were collected at a given time interval for each dehydration process. The fraction of dehydration α was calculated from these data.

The X-ray powder diffraction patterns were obtained with Rigaku

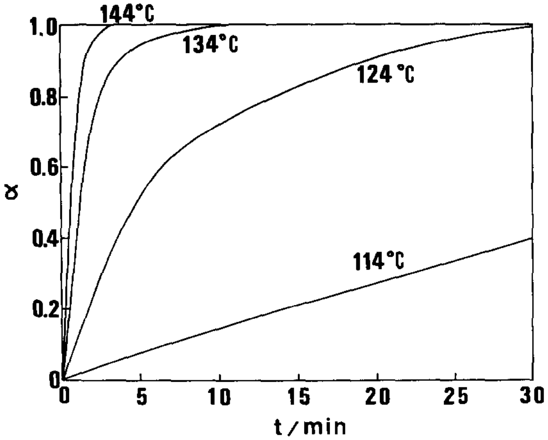

Fig. 1. Typical α vs. t plots for the dehydration of $Er(HCO_2)_3 \cdot 2H_2O$ at a water vapour pressure of 1.0 Torr.

Geigerflex RAD-γA and RAD-3C diffractometers equipped with a standard high-temperature sample holder. Cu Kα radiation, a nickel filter and a graphite monochromator were used for all the measurements. The diffraction data were collected at 0.02° steps.

RESULTS

Figure 1 shows the plots of dehydration function α against the reaction time t at various temperatures.

The dehydration kinetics was analysed by the integral method, according to the following procedure. The kinetics of solid-state reactions can be expressed by the general equation

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

where k is the rate constant, t is the reaction time and $G(\alpha)$ is a function depending on the reaction mechanism. Many theoretical model functions have been proposed for $G(\alpha)$. Typical $G(\alpha)$ functions are shown in Table 1 [12–14]. The kinetic mechanism of the present dehydrations, i.e. the model function, was determined by the linearity of the plots of various $G(\alpha)$ functions versus t, in accordance with eqn. (1).

Figure 2 shows typical $G(\alpha)$ versus t plots for the present dehydrations. The $G(\alpha)$ function selected tends to vary with atmospheric water vapour pressure, as shown in Table 2. At low vapour pressure ($\approx 5 \times 10^{-4}$ Torr) and especially at low temperatures, the initial stage of the dehydration seems to be described by the rate equation A_2, which is referred to as an Avrami–Erofe'ev-type reaction [15,16]. However, in the great majority of cases, the dehydrations are described by a three-dimensional phase-

TABLE 1

Commonly used $G(\alpha)$ 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
$[-\ln(1-\alpha)]^{1/m}$	A_m	Avrami–Erofe'ev equation, $m = 1, 2, 2.5, 3, \ldots$

boundary-controlled reaction R_3, i.e.

$$1-(1-\alpha)^{1/3}=kt \tag{2}$$

This indicates that the present dehydration, as a whole, takes place as a reaction of contracting volume kinetic model.

Figure 3 shows the relation between the rate of dehydration, k and the water vapour pressure at particular temperatures. The value of k increases with increasing water vapour pressure, reaches a maximum value, and thereafter decreases gradually to a constant value. This phenomenon is analogous to the Smith–Topley effect, and was also observed in the case of the thermal dehydration of zinc formate dihydrate [7].

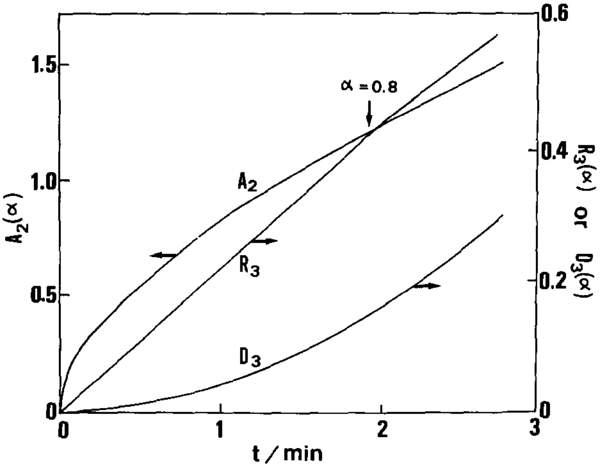

Fig. 2. Typical $G(\alpha)$ vs. t plots for the dehydration of $Er(HCO_2)_3 \cdot 2H_2O$ at 134°C and 8.0 Torr of water vapour pressure.

TABLE 2

Variation of $G(\alpha)$ with atmospheric water vapour pressure P_{H_2O}

P_{H_2O} (Torr)	Temp (°C)	$G(\alpha)$	Range of α	C [a]	ln k
5×10^{-4}	104	R_3	0.289–0.885	0.9995	−9.50
		A_2	0.061–0.802	0.9996	−8.71
	114	R_3	0.373–0.966	0.9996	−8.26
		A_2	0.008–0.531	0.9994	−7.98
	124	R_3	0.368–0.818	0.9985	−7.35
		A_2	0.011–0.541	0.9977	−7.55
	144	R_3	0.197–0.528	0.9955	−6.76
		A_2	0.083–0.533	0.9989	−5.80
0.5	114	R_3	0.189–0.881	0.9996	−8.58
		A_2	0.029–0.551	0.9997	−7.81
	119	R_3	0.095–0.561	0.9996	−6.82
		A_2	0.058–0.355	0.9977	−6.31
	124	R_3	0.020–0.776	0.9998	−5.96
		A_2	0.195–0.690	0.9997	−5.12
	134	R_3	0.190–0.910	0.9996	−5.34
1.0	114	R_3	0.268–0.923	0.9999	−8.71
		A_2	0.031–0.343	0.9963	−6.85
	124	R_3	0.158–0.706	0.9944	−6.60
		A_2	0.028–0.290	0.9987	−5.08
	134	R_3	0.191–0.803	0.9987	−5.24
	143	R_3	0.063–0.925	0.9990	−4.78
8.0	119	R_3	0.101–0.635	0.9995	−8.07
	124	R_3	0.094–0.705	0.9999	−7.06
	134	R_3	0.081–0.735	0.9998	−5.73
	144	R_3	0.081–0.925	0.9999	−5.17

[a] Correlation coefficient.

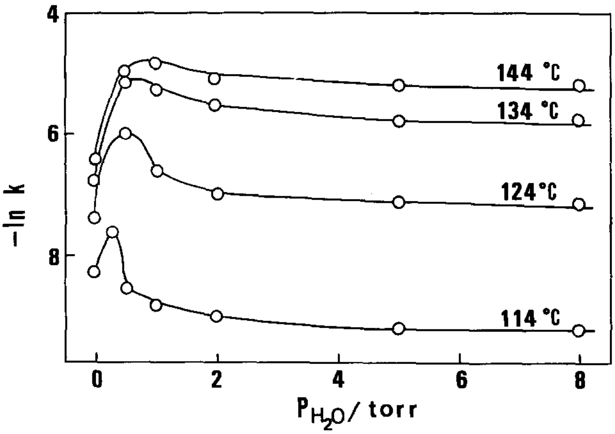

Fig. 3. Variation of dehydration rate with water vapour pressure.

DISCUSSION

It is known that R_3 reactions are characterized by the initial production of a complete reactant–product interface at the surface of the reactant particle, and that the rates of reaction are dependent on the advance of the reaction interface towards the centre of the reacting particle [17].

The X-ray diffraction profile (Fig. 4) shows that the anhydrous formate formed in vacuum was amorphous, while that formed in the auto-evolved atmosphere was crystalline. The critical temperatures for the formation of crystalline anhydrous formates in the presence of water vapour are shown in Fig. 5; they decrease linearly with increasing critical water vapour

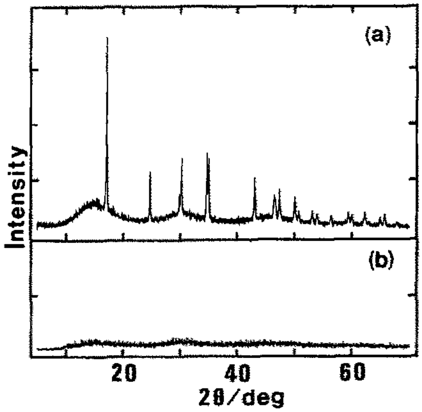

Fig. 4. Powder X-ray diffraction profiles of $Er(HCO_2)_3 \cdot 2H_2O$: (a) dehydrated at 115°C and 15 Torr of water vapour pressure; (b) dehydrated at 115°C in vacuo ($\approx 5 \times 10^{-4}$ Torr).

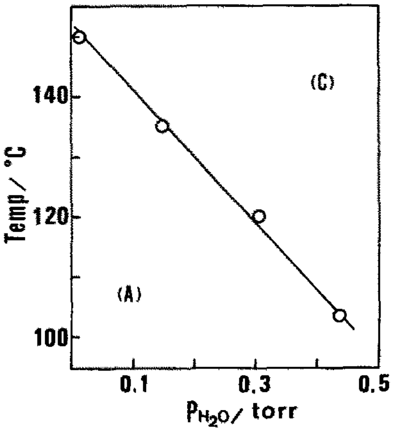

Fig. 5. Relation between the critical temperature and critical water vapour pressure at which crystalline erbium formate is formed: (C) shows the region of crystalline product of erbium formate; (A) shows the region of amorphous product of erbium formate.

pressure. This indicates that atmospheric water molecules are available to form a crystalline anhydrous formate.

The unusual phenomenon shown in Fig. 3 seems to be related to the crystallinity of the dehydrated product, as in the case of the thermal dehydration of zinc formate dihydrate: at low water vapour pressure ($\approx 10^{-4}$ Torr), the amorphous dehydrated product covers the reaction particles and may adsorb the dissociated water molecules onto the narrow walls of their molecular-dimension capillaries. This would interfere with the escape of further water molecules, and the rate of dehydration would be slow as a result of this interference. Therefore, the rate must be controlled by the diffusion of the dissociated water molecules through the amorphous product phase.

This opinion is also supported by the fact that at low water vapour pressure ($\approx 10^{-4}$ Torr) the dehydration seems to be described by an Avrami–Erofe'ev-type reaction A_2

$$[-\ln(1-\alpha)]^{1/2} = k_A t \tag{3}$$

where k_A is the rate constant. It is known that the A_2 equation is the kinetic expression for the model on the basis of random nucleation and diffusion-controlled growth of the nuclei in the form of thin sheets; k_A is given by

$$k_A = (\pi h I D/2)^{1/2} \tag{4}$$

where I is the nucleation rate per unit volume, h is the thickness of the sheet and D is the diffusion coefficient of the migrating species [17]. Consequently, at low water vapour pressure, the rate of the present dehydration would be proportional to the square root of the product of the rate of the nucleation, and the growth rate of the nuclei would be controlled by the diffusion process of the dissociated water molecules.

In the water vapour pressure range of 10^{-4}–0.5 Torr, a few water vapour molecules promote the crystallization of the anhydrous products. In this range, crystallization may bring about the formation of wide channels between the dehydrated particles, through which the dissociated water molecules are easily able to escape. Therefore, the value of k would increase.

At vapour pressures higher than 1 Torr, the apparent rate of dehydration decreases gradually because of the reverse reaction caused by atmospheric water molecules.

ACKNOWLEDGEMENT

The authors thank Mr Hitoshi Minagawa of the Analytical Instrument Laboratory of Niigata University, for the X-ray diffraction measurements at high temperatures.

REFERENCES

1 M.L. Smith and B. Topley, Proc. R. Soc. London Ser. A, 134 (1931) 224.
2 B. Topley and M.L. Smith, J. Chem. Soc., (1935) 321.
3 W.E. Garner and M.G. Tanner, J. Chem. Soc., (1930) 40.
4 W.E. Garner and T.S. Jennings, Proc. R. Soc. London Ser. A, 224 (1954) 460.
5 D. Dollimore, T.E. Jones and P. Spooner, J. Chem. Soc. Ser.A, (1970) 2809.
6 D. Dollimore, G.R. Heal and J. Mason, Thermochim. Acta, 24 (1978) 307.
7 Y. Masuda and K. Nagagata, Thermochim. Acta, 155 (1989) 255.
8 Y. Masuda, Y. Ito, R. Ito and K. Iwata, Thermochim. Acta, 99 (1986) 159.
9 Y. Masuda, Y. Ito, R. Ito and K. Iwata, Thermochim. Acta, 102 (1986) 263.
10 Y. Masuda, K. Iwata, R. Ito and Y. Ito, J. Phys. Chem., 91 (1987) 6543.
11 Y. Masuda and K. Nagagata, Thermochim. Acta, 161 (1990) 55.
12 J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
13 W.E. Brown, D. Dollimore and A.K. Gallway, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Reactions in Solid State, Elsevier, Amsterdam, 1980, p. 90.
14 K. Heide, W. Holand, H. Golker, K. Seyfarth, B. Muller and R. Sauer, Thermochim. Acta, 13 (1975) 365.
15 M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
16 C.R. Erofe'ev, Dokl. Acad. Sci. URSS, 52 (1946) 511.
17 S.F. Hulbert, J. Br. Ceram. Soc., 6 (1969) 11.