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THE EFFECT OF WATER VAPOUR PRESSURE ON THE THERMAL DEHYDRATION OF YTTRIUM FORMATE DIHYDRATE

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The kinetics of the thermal dehydration of yttrium formate dihydrate was studied by means of isothermal gravimetry under various water vapour pressures from 5×10^{-4} to 8 torr. On the whole, the dehydration was described as the three dimensional phase boundary reaction, R_3. An unusual dependence of the rate of dehydration on the atmospheric water vapour pressure was observed: with increasing water vapour pressure, the rate increased at first, passed through a maximum, and then decreased gradually to a constant value. These phenomena were similar to the Smith-Topley effect. The mechanism of the phenomena can be described on the basis of the crystallinity of the dehydrated product phase.

Keywords: hydrated salts, kinetics, thermal dehydration, yttrium formate dihydrate

Introduction

It has been known that the thermal dehydration of hydrated salt is affected by the water vapor pressure of reaction atmosphere. An unusual variation in the dehydration rate with the partial pressure of water vapor was noted by Smith and Topley [1, 2]. They reported that the rate constants for dehydration of manganese oxalate dihydrate and copper sulfate pentahydrate varied unusually with the partial pressure of atmospheric water vapor. When water vapor pressure increased, the rate constant for dehydration decreased sharply at first, passed through a minimum, then increased strongly to a maximum, and finally decreased more slowly. This unusual phenomenon is known as the Smith-Topley effect. Similar phenomena have also been observed on the dehydration of other hydrates [3–7].

Recently, we have discovered that similar phenomena occur on the dehydration of zinc formate dihydrate and erbium formate dihydrate [7, 12]. We pointed

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out that the phenomena seemed to be correlated to the crystallinity of the dehydrated products.

A similar phenomenon is also discovered on the dehydration of yttrium formate dihydrate. In this paper, the mechanism of the phenomenon is discussed briefly on the basis of the crystallinity of the dehydrated product phase.

Experimental

Yttrium formate dihydrate (99.0%) was purchased from Kishida Chemical Co., Ltd., Osaka, and recrystallized from distilled water. The specimen was pulverized with a pestle in a mortar and sieved to a narrow fraction of 80–100 mesh size.

The isothermal dehydration was followed with a Shinku-Riko TGD-5000RH differential microbalance equipped with a gold image furnace. The specimen of about 5 mg was weighed into a platinum crucible and placed in the microbalance. The furnace was controlled at given temperatures between 90°–140°C, and maintained within ±0.5°C until the dehydration was completed.

The water vapor pressure of the reaction system was regulated from 5×10^{-4} to 8.0 torr according to the following procedure [7, 12]. The reaction system was degassed for 3 hours before the experiment, below 5×10^{-4} torr. A suitable amount of water vapor was then admitted from a water bulb which was maintained at a constant temperature to provide a constant vapor pressure. The pressure was measured using a vacuum gauge of MKS Baratoron (Type 112A), and maintained within ±3% until the dehydration was completed.

The output voltages from the microbalance were amplified and recorded on a micro-computer (EPSON QC-10 II) via an A/D converter (ILC 7109 modified in 13 bit). About 1000 data points were collected at a given time interval for each dehydration process. From these data, the fraction of dehydration (α) was calculated [7–12].

The X-ray powder diffraction patterns were obtained with a Rigaku Geigerflex RAD-3C and RAD-γA diffractometers equipped with a standard high-temperature sample holder. CuK_{α} radiation, a nickel filter and a graphite monochrometer were used in all measurements. The diffraction data were taken at steps of width 0.02°C.

Results and discussion

Figure 1 shows a typical plot of the dehydration fraction (α) against the reaction time (t) at various temperatures. The dehydration kinetics was analyzed by the integral method. 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 $G(\alpha)$ [13–15, 21]. The kinetic mechanism (i.e. the model function $G(\alpha)$) was determined by the linearity of the plots of various $G(\alpha)$ functions against t in accordance with Eq. (1). The $G(\alpha)$ function determined for the present dehydration tends to vary with atmospheric water vapor pressure.

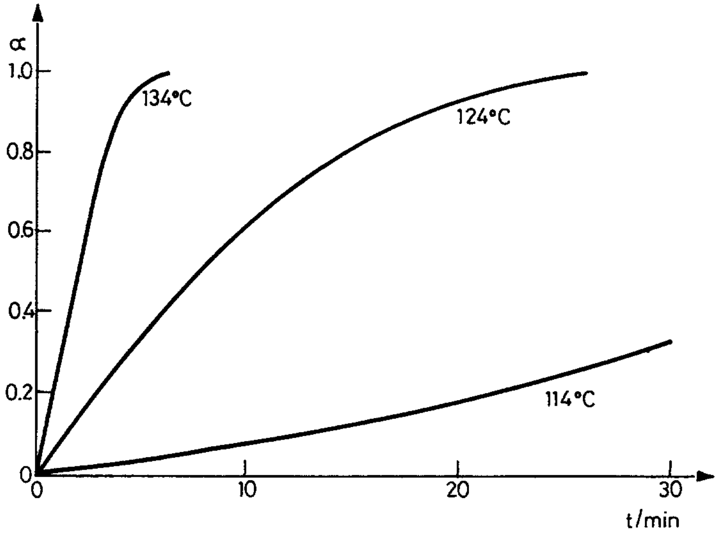

Fig. 1 Typical α *vs.* t plots for the dehydration of $Y(HCO_2)_3 \cdot 2H_2O$ at a water vapor pressure of 1 torr

At low vapor pressure (~5×10^{-4} Torr) and especially at low temperatures, the initial stage of dehydration seems to be described by the rate equation

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

which is referred to as the Avrami-Erofe'ev equation A_2 [17–20].

However, in the main stage the dehydration can be described as three dimensional phase boundary reaction R_3,

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

The R_3 reaction has been characterized by the rapid initial production of a complete reactant-product interface at the surface of reactant particles, and its rate is determined by the advance of the reaction interface.

Figure 2 shows the relation between the rate of dehydration, *k* and the water vapor pressure at particular temperatures. The value of k increased with increasing of water vapor pressure, reached to a maximum, and decreased gradually to a constant value. This phenomena is similar to the Smith-Topley effect and was observed in the cases of the thermal dehydration of zinc and erbium formate dihydrates [7, 12]. This unusual phenomenon seems to depend upon the crystallinity of the dehydrated product phases.

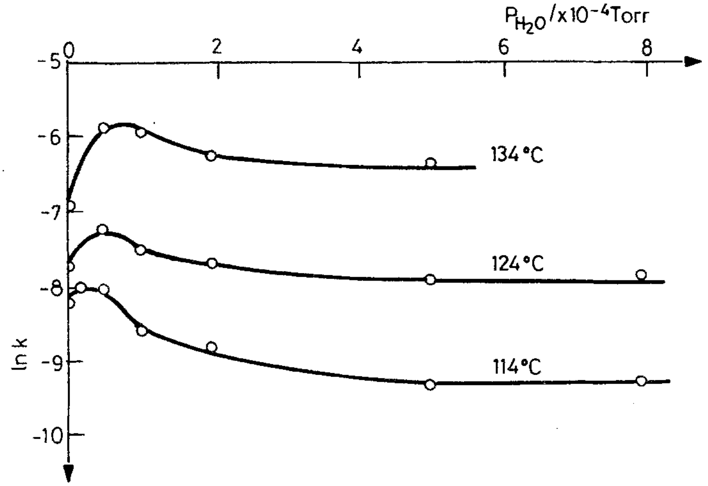

Fig. 2 Variation of dehydration rate with the atmospheric water vapor pressure

In the present experiment (Fig. 3), X-ray diffraction profile showed that the anhydrous yttrium formate formed in vacuum was amorphous, while that formed in the self-generated atmosphere was crystalline. The critical temperatures for the formation of crystalline anhydrous yttrium formate tend to decrease with increasing critical water vapor pressure. This finding supports the previous suggestion [7, 12] on the mechanism of the unusual phenomena; that is, the unusual phenomena seems to be related to the crystallinity of the dehydrated product. Namely, at a low water vapor pressure (~10^{-4} torr), the amorphous product of $Y(HCO_2)_3$ covers the reaction particles and the dissociated water molecules may be adsorbed by the narrow walls of molecular dimensional capillaries in the produced phase. This would interfere with the escape of further water molecules, and the rate of dehydration would be observed as the result of this interference. Therefore, at a low water vapor pressure, the dehydration rate must be controlled by the diffusion of the dissociated water molecules through the amorphous product phase.

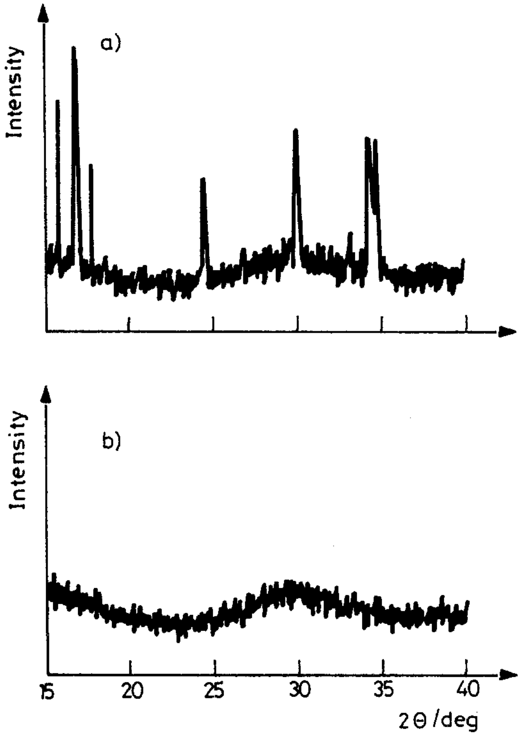

Fig. 3 X-ray powder diffraction profiles at $Y(HCO_2)_3 \cdot 2H_2O$: (*a*) dehydrated at 123°C in the self-generated atmosphere; (*b*) dehydrated at 117°C in vacuum (~10^{-3} torr)

The finding that the present dehydration is described by the Avrami-Erofe'ev equation, Eq. (2) at a low water vapor pressure, seems to support the above suggestion. Although Eq. (2) is the kinetic expression concerning with the random nucleation and the nuclei growth processes, Hulbert pointed out the relationship between the nuclei growth and diffusion process as follows [21]. When (i) the nucleation rate is assumed to be constant, (ii) the nuclei grow two-dimensionally and (iii) the growth is diffusion controlled, Eq. (2) can be derived on the basis of the overall rate constant to be given by Eq. (4) [21].

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

where I is the nucleation rate per unit volume, h is the thickness of the specimen, and D is the diffusion coefficient of the migrating species. On the basis of above opinion, the reaction described by Eq. (2) would be controlled by the diffusion process of the migrating species: in the present dehydration, the rate would be controlled by the diffusion of the dissociated water molecules through the amorphous phase, at a low water vapor pressure.

Table 1 Variation of $G(\alpha)$ with the Atmospheric Water Vapor Pressure

P_{H_2O} / Torr	T/°C	$G(\alpha)$	Range of α	C^*	ln k
5×10^{-4}	114	A_2	0.131 – 0.442	0.9990	–8.30
		R_3	0.550 – 0.980	0.9995	–8.19
	124	A_2	0.014 – 0.263	0.9990	–7.67
		R_3	0.413 – 0.825	0.9991	–7.74
	134	A_2	0.014 – 0.203	0.9964	–7.13
		R_3	0.440 – 0.950	0.9980	–6.93
1.0	114	A_2	0.094 – 0.376	0.9993	–8.50
		R_3	0.452 – 0.927	0.9988	–8.52
	124	R_3	0.058 – 0.925	0.9995	–7.50
	134	R_3	0.020 – 0.987	0.9999	–5.90
5.0	114	R_3	0.025 – 0.895	0.9990	–9.25
	124	R_3	0.015 – 0.971	0.9997	–7.80
	134	R_3	0.010 – 0.905	0.9999	–6.19

* correlation coefficient

At a water vapor pressure ranged from 10^{-4} to 0.5 torr, water molecules promote the crystallization of the yttrium formate. The crystallization forms wide channels between the dehydrated particles, through which the dehydrated water molecules escape easily. The value of rate constant, therefore, would increase.

At vapor pressures higher than 0.5 torr, the apparent rate of dehydration decreases gradually due to the reverse reaction.

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Zusammenfassung — Mittels isothermer Gravimetrie und bei verschiedenen Wasserdampfdrücken zwischen 5×10^{-4} und 8 Torr wurde die Kinetik der thermischen Dehydratation von Yttriumformiat-Dihydrat untersucht. Die Dehydratation wird als dreidimensionale Phasengrenzreaktion R_3 beschrieben. Dabei wurde ein ungewöhnlicher Einfluß des athmosphärischen Wasserdampfdruckes auf die Dehydratationsgeschwindigkeit beobachtet: mit steigendem Wasserdampfdruck wächst die Geschwindigkeit zunächst ebenfalls an, durchquert ein Maximum und sinkt dann nach und nach auf einen konstanten Wert ab. Diese Erscheinung ähnelt dem Smith-Topley-Effekt. Der Mechanismus dieser Erscheinung kann auf der Grundlage der Kristallinität der dehydratierten Produktephase diskutiert werden.