Journal of Thermal Analysis, Vol. 44 (1995) 1013-1020

THE EFFECT OF THE WATER VAPOR PRESSURE ON THE KINETICS OF THERMAL DEHYDRATION OF MANGANESE(II) FORMATE DIHYDRATE

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(Received February 11, 1994)

Abstract

The effect of the water vapor pressure on the thermal dehydration of manganese(II) formate dihydrate was studied by means of isothermal gravimetry under various water vapor pressures, ranging from 4.6 to 24.4 torr.

The kinetics of dehydration was described by a two-dimensional phase-boundary model, R_2. The rate of dehydration decreased with increasing atmospheric water vapor pressure, but the Smith-Topley phenomenon was not observed for the present dehydration. The activation energy and the frequency factor for the dehydration were 110–170 $kJ\cdot mol^{-1}$ and 10^{10}–10^{16} $cm\cdot s^{-1}$, respectively. These values increased with increasing water vapor pressure, and were much larger than those reported for the dehydration in vacuum.

Keywords: kinetics, manganese(II) formate dihydrate, thermal dehydration

Introduction

Although the kinetics of dehydration of solid hydrates has been the subject of considerable study, may features of the reactions have not yet been completely elucidated. It is known that the thermal dehydration of hydrated crystals is influenced by the water vapor pressure of the reaction atmosphere. Smith and Topley [1, 2] reported that the rate constants for the dehydration of manganese(II) oxalate dihydrate and copper(II) sulfate pentahydrate varied unusually with the partial pressure of atmospheric water vapor. As the water vapor pressure increased, the rate of dehydration initially decreased, then passed through

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a minimum, increased strongly to a maximum, and finally decreased more slowly. This unusual phenomenon is known as the Smith-Topley effect [1, 2] and has been observed in the dehydration of other hydrates [3–6].

Recently, we detected similar phenomena and pointed out that they seemed to be related to the crystallinity of the dehydrated products [7–9]. In order to confirm the relation, the influence of the water vapor pressure on the kinetics of thermal dehydration of manganese(II) formate dihydrate was investigated in the work reported in the present paper, by means of isothermal gravimetry.

Experimental

Manganese(II) formate dihydrate was purchased from Wako Pure Chemical Ind. Ltd., Osaka. The reagent was dissolved in distilled water and the solution was filtered. The filtrate was evaporated at 45°C and a polycrystalline specimen was obtained. The polycrystals were washed with ethanol and ethyl ether, dried at 45°C, pulverized with a pestle in a mortar, and sieved to narrow fractions of 60–100 and 150–200 mesh sizes.

The isothermal dehydration was followed with a Shinku-Riko TGD-5000RH differential microbalance equipped with a gold image furnace [7–10]. A specimen of 6.5 mg was weighed into a platinum crucible and set in the microbalance. The furnace was maintained at a constant temperature within ±0.5 deg until the dehydration was completed. The output voltages for mass loss from the microbalance were amplified and acquired on a microcomputer (MZ-80C) via an AD converter (ICL 7109 modified in 13 bits). For each dehydration process, about 700 data relating to the mass loss were collected at given time intervals, and the fraction of dehydration, α, was calculated from these data.

All reactions were carried out at atmospheric pressure under controlled partial pressures of water vapor. The partial water vapor pressure of the reaction system was controlled as follows. Nitrogen was bubbled into boiling water and the gas was passed through a condenser controlled at constant temperatures to obtain a constant vapor pressure. The gas (flow rate 60 $\mathrm{cm^3 \cdot min^{-1}}$) was then admitted to the microbalance.

The enthalpy change for the dehydration was determined from the DSC curve recorded in a Shinku-Riko DSC-1500 M/L. About 10 mg of specimen was placed in an aluminum crucible and α-alumina was used as a reference material. This instrument was calibrated via the heat of transition of potassium nitrate (ΔH=5.4 $\mathrm{kJ \cdot mol^{-1}}$, 400.9 K) [11].

The X-ray powder diffraction patterns were obtained with Rigaku Geigerflex RAD-γA and RAD-C diffractometers with the use of $\mathrm{CuK_\alpha}$ radiation and a nickel filter. Infrared absorption spectra were measured from 250 to 4000 $\mathrm{cm^{-1}}$ in a KBr disk with a Hitachi 295 spectrophotometer.

Results and discussion

Figure 1 shows TG and DTA curves of $Mn(HCO_2)_2{\cdot}2H_2O$. There is no evidence of an intermediate monohydrate because the curve is smooth.

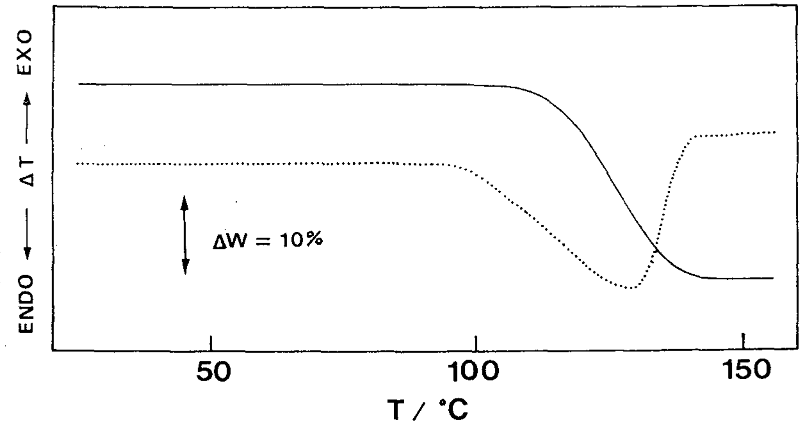

Fig. 1 TG (solid line) and DTA (broken line) curves for the dehydration of $Mn(HCO_2)_2{\cdot}H_2O$ in a self-generated atmosphere (heating rate 5 deg·min^{-1})

The kinetics of solid-state reactions is 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 $G(\alpha)$ [12–15]. The kinetic mechanism (i.e. the model function $G(\alpha)$) was determined via the linearity of the plots of various $G(\alpha)$ functions *vs.* t, in accordance with Eq. (1).

In a dry nitrogen flow, especially at low temperatures, the $\alpha(t)$ curve seems to have an accelerative period, which extends to the maximum rate, and thereafter a decelerative period continues until the completion of dehydration (Fig. 2a). However, the dehydration seems to have the nature of a two-dimensional phase-boundary reaction model, $R_2(\alpha)$, in the region $0.15 < \alpha < 0.85$ (Fig. 2b). In the range of water vapor pressure from 4.6 to 24.4 torr, $\alpha(t)$ seemed to be decelerative (Fig. 3a) and the dehydration was described by the $R_2(\alpha)$ function over nearly the whole range of the process (Fig. 3b). Eckhardt and Flanagan [16] and Clark and Thomas [17] reported that the dehydration in vacuum was also described by the $R_2(\alpha)$ function. The rate constant, k, was determined from the slope of the $R_2(\alpha)$ *vs.* t plot at various temperature.

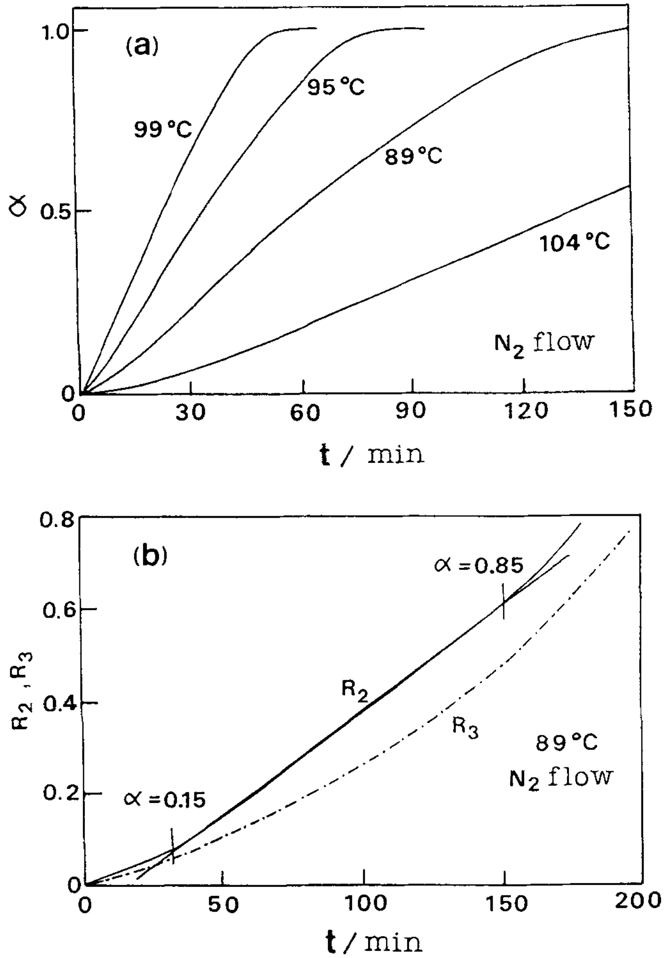

Fig. 2 (a) Typical α *vs.* t plots for the dehydration of $Mn(HCO_2)_2 \cdot 2H_2O$ in dry nitrogen flow atmosphere. (b) Typical $G(\alpha)$ *vs.* t plots for the dehydration in dry nitrogen flow atmosphere. Where $R_n = 1-(1-\alpha)^{1/n}$

The $R_2(\alpha)$ model reaction is characterized by a rapid initial production of a complete reactant-product interface at the edge of preferred crystallographic surfaces, and the rate is determined by the advance of the reaction interface [13]. The $R_2(\alpha)$ mechanism for the present dehydration is supportable by considering the crystal structure of $Mn(HCO_2)_2 \cdot H_2O$ reported by Osaki *et al.* [18]. The reported crystal structure is monoclinic, with space group $P2_1/c$. In this structure, water molecules lie parallel to the (100) planes. Thus, it is reasonable to consider that the dehydration takes place on the planes as a phase-boundary reaction.

The rate constant for the $R_2(\alpha)$ reaction model is known to be represented by

$$k = \frac{k_j}{r_o} \tag{2}$$

where k_j is the velocity of the advancing interface and r_o is the initial radius of the particles of the specimen [13, 19]. r_o was measured as an average radius of 100–150 particles. The values were 0.013±0.004 and 0.006±0.002 cm for the specimens of 60–100 and 150–200 mesh, respectively. Here, the k_j values determined for the two specimens according to Eq. (2) agreed with each other within the experimental error (Fig. 4). The values of k_j decreased with increas-

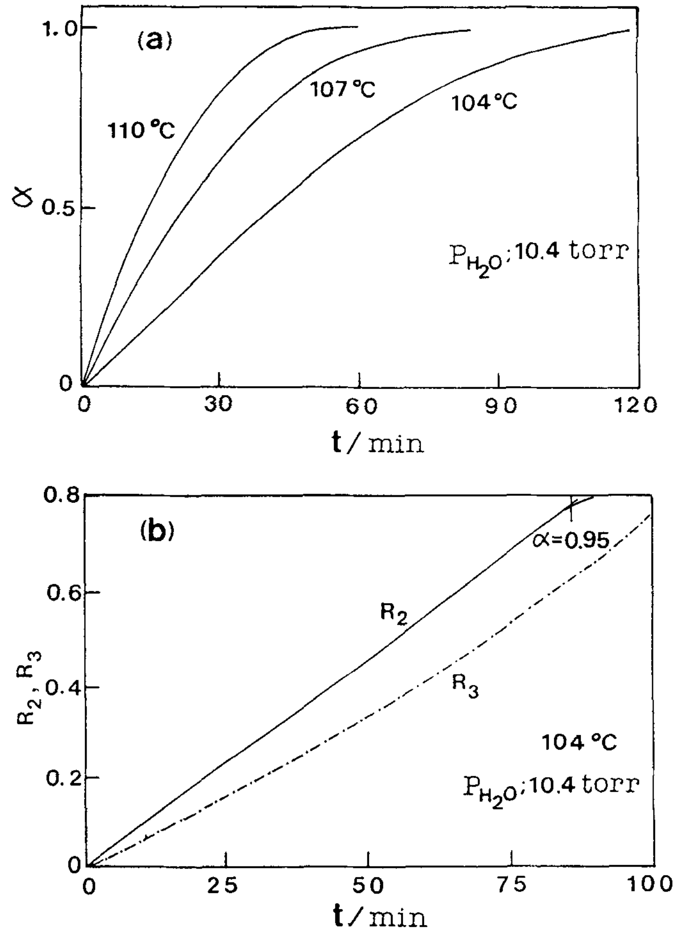

Fig. 3 (a) Typical α vs. t plots for the dehydration of $Mn(HCO_2)_2{\cdot}2H_2O$ at a water vapor pressure of 10.4 torr. (b) Typical $G(\alpha)$ vs. t plots for the dehydration at a water vapor pressure of 10.4 torr. Where $R_n = 1-(1-\alpha)^{1/n}$

ing atmospheric water vapor pressure (Table 1), but the Smith-Topley effect was not observed for the present dehydration.

From the Arrhenius plots for k_j, activation energies, E, and pre-exponential factors, A, were determined. Table 2 shows the values of E and A obtained at various water vapor pressures, together with those reported by Eckhardt and Flanagan [16] and Clarke and Thomas [17]. The values of E (74–71 kJ·mol^{-1}) for the dehydration in vacuum were comparable to that of the enthalpy change for the dehydration (59 kJ·mol^{-1}). Eckhardt and Flanagan compared A with the

Table 1 The velocity of the interface advancing, k_j

P_{H_2O} /	k_j / cm·s^{-1}			
	Temperature / °C			
Torr	95	100	105	110
4.6	0.98	1.83	3.36	6.09
6.7	0.66	1.26	2.37	4.39
10.4	0.61	1.18	2.24	4.18
19.3	0.53	1.03	1.97	3.72
24.4	0.41	0.85	1.73	3.47
Dry N$_2$ flow	3.36	5.70	9.68	–

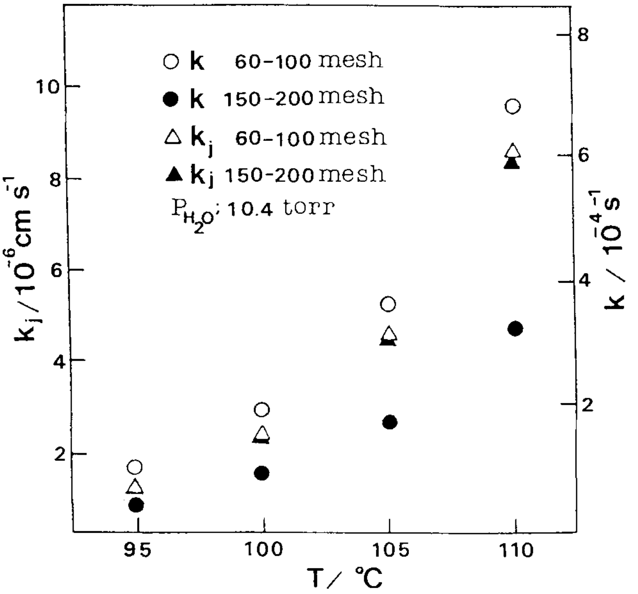

Fig. 4 Relations between temperature and rate constant, k and velocity of interface advancing, k_j ($= k \cdot r_o$)

Polany-Wigner equation [20] and obtained a reasonable frequency ($1.15 \cdot 10^{13}$ s^{-1}) with which an activated complex passes to the product side for dehydration [21]. On the other hand, the *E* and *A* obtained in this study were considerably larger than those reported for the dehydration in vacuum, and the values increased with increasing water vapor pressure. These findings indicate that the presence of atmospheric water molecules has an enormous influence on the rate of the dehydration.

Table 2 Activation energy, *E* and frequency factor, *A* under various water vapor pressure, P_{H_2O}

P_{H_2O} / Torr	*E* / kJ·mol^{-1}	*A* / cm·s^{-1}
4.6	143±3	$1.99 \cdot 10^{14}$
6.7	149±11	$7.94 \cdot 10^{14}$
10.4	150±1	$1.26 \cdot 10^{15}$
19.3	153±10	$2.51 \cdot 10^{15}$
24.1	168±13	$2.51 \cdot 10^{17}$
Dry N_2 flow	112±8	$2.00 \cdot 10^{10}$
in vacuum[a]	74±3	$1.00 \cdot 10^{5}$
in vacuum[b]	71±1	$1.58 \cdot 10^{5}$

a) R.C. Eckhardt and T. B. Flanagan, Trans. Faraday Soc., 60 (1964) 1289.
b) T. A. Clarke and J. M. Thomas, J. Chem. Soc., Ser. A, (1969) 2227.

In general [21–23], the magnitude of *A* for the thermal decomposition of a solid is expected to be ~10^{13} s^{-1}, which is comparable to a frequency of vibration in the crystal lattice. The values of *A* for the present dehydration are larger than those expected by factors of about 10~10^3. Shamonn [24] has discussed the values of *A* for several reactions, and pointed out that the large value of *A* for hydrate dehydration was attributable to the mobile water molecules adsorbed on the reaction interface. Therefore, it is likely for the present dehydration that the dissociated mobile water molecules are adsorbed on the reaction interface and influence the rate of dehydration. Although the equilibrium water vapor pressure for the present dehydration has not been measured, a reverse reaction may be possible at high water vapor pressures and the apparent rate is hindered by atmospheric water molecules.

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Zusammenfassung — Mittels isothermer Gravimetrie wurde bei verschiedenen Wasserdampfdrücken zwischen 4.6 und 24.4 Torr der Einfluß von Wasserdampfdruck auf die thermische Dehydratation von Mangan(II)formiat-Dihydrat untersucht.

Die Kinetik der Dehydratation wurde mittels eines zweidimensionalen Phasengrenzmodelles R_2 beschrieben. Die Dehydratationsgeschwindigkeit sinkt mit zunehmendem atmosphärischen Wassergasdruck, jedoch wird das Smith-Topley-Phänomen für die vorliegende Dehydratation nicht beobachtet. Aktivierungsenergie und Frequenzfaktor der Dehydratation betrugen 110–170 kJ/mol bzw. 10^{10}–10^{16} cm/s. Diese Werte steigen mit zunehmendem Wassergasdruck und sind wesentlich größer als die für die Dehydratation in Vakuum beschriebenen Werte.