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KINETIC STUDIES OF THERMAL DEHYDRATION OF ZINC(II) FORMATE DIHYDRATE BY MEANS OF ISOTHERMAL GRAVIMETRIC MEASUREMENTS AND MICROSCOPIC OBSERVATION

YOSHIO MASUDA

General Education Department, Niigata University, Niigata 950-21 (Japan)

KAZUO NAGAGATA

Department of Chemistry, Faculty of Science, Niigata University, Niigata 950-21 (Japan)

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ABSTRACT

The kinetics of the thermal dehydration of zinc formate dihydrate, $Zn(HCO_2)_2 \cdot 2H_2O$, was studied by means of isothermal gravimetry and microscopic observations at atmospheric pressure under controlled water vapour partial pressure at 12.8 Torr. The rates of advancement of the interface established between reactant and product were determined directly by microscopic observation and were compared with those obtained by means of isothermal gravimetry.

INTRODUCTION

A kinetic investigation on the basis of thermogravimetry is an effective method of clarifying the mechanism of solid-state reactions such as thermal decompositions and dehydrations.

In our preceding paper [1], the effect of the presence of water vapour on the thermal dehydration of zinc formate dihydrate was studied using isothermal gravimetry and X-ray diffraction. The dehydration rate was unusually dependent on the water vapour pressure: the rate at first increased with increasing water vapour pressure, passed through a maximum, and then decreased gradually to a constant value.

In the present paper, the kinetics of the thermal dehydration of zinc formate dihydrate, $Zn(HCO_2)_2 \cdot 2H_2O$, are studied by means of isothermal gravimetry and microscopic observations at atmospheric pressure under controlled water vapour partial pressure at 12.8 Torr.

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EXPERIMENTAL

Reagent

Zinc formate dihydrate, $Zn(HCO_2)_2 \cdot 2H_2O$, was commercially obtained and recrystallised from a 10^{-4} M solution of formic acid. The crystals, in the form of flat hexagonal plates, were air-dried at room temperature. The specimen was identified by means of TG, IR spectrophotometry and X-ray diffraction analysis, and sieved to 100–150 mesh.

Apparatus

The isothermal dehydration was followed with a Shinku Riko TGD-5000 RH microbalance which can reach a given furnace temperature within 30 s. The specimen, of about 5 mg, was weighed into a platinum crucible and placed in the microbalance. The temperature of the furnace was controlled at a given temperature between 95 and 115 °C and maintained within ±0.5 °C until the dehydration was complete. The TG output voltages were amplified and acquired on a micro-computer (Sharp MZ80C) via an A/D converter (Datel–Intersil 7109, modified to 13 bit) [2–4].

IR absorption spectra were measured from 250 cm^{-1} to 4000 cm^{-1} in a KBr disc with a Hitachi-295 spectrophotometer.

The X-ray powder diffraction patterns were obtained with a Rigaku Geigerflex RAD-rA diffractometer using Cu $K\alpha$ radiation and a nickel filter.

Optical microscopic studies

The course of the crystal dehydration was followed using a Nikon Model S-P_0 polarising microscope. The crystal was mounted on a heating stage made of brass. The temperature of the stage was regulated in the range between 95 °C and 115 °C by a temperature controller (Ohkura EC1500), within ±0.5 °C. Photographs were taken at appropriate time intervals. The rates of interface advancement were accurately estimated from enlarged micrographs.

Control of water vapour pressure

The isothermal gravimetric experiments and microscopic observation were carried out at atmospheric pressure under a controlled water vapour partial pressure at 12.8 Torr. The water vapour partial pressure was controlled as follows: nitrogen was saturated with water vapour by passing through boiling water at a flow rate of 70 cm^3 min^{-1}, and then transported to a spiral condenser. The temperature of the condenser was held at 15.0 ± 0.1 °C, so that the excess water in the gas was condensed in this condenser. Nitrogen gas contains water vapour of partial pressure 12.8 Torr at this temperature [5]. The wet nitrogen gas was passed through a heated line to prevent condensation of water and carried to the microbalance or to the hot stage of the microscope.

RESULTS AND DISCUSSION

Figure 1 shows plots of the dehydration fraction α against the reaction time (t) at various temperatures. There is no evidence of an intermediate monohydrate because of the smoothness of each curve.

The kinetics of solid-state reactions can be represented by the general equation

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

where k is a rate constant and $F(\alpha)$ is a function depending on the reaction mechanism. Many theoretical model functions have been proposed for $F(\alpha)$ [6,7]. The kinetic mechanism of the present dehydration, i.e. the model function, was judged on the basis of the linearity of the plots of the $F(\alpha)$ functions calculated from α against time for the dehydration, in accordance with eqn. (1). Figure 2 shows the $1-(1-\alpha)^{1/2}$ versus t plots in expectation of the two-dimensional phase boundary reaction (R_2) on the basis of the experimental data obtained at various temperatures. All the plots give straight lines over nearly the whole range of the dehydration process. Thus

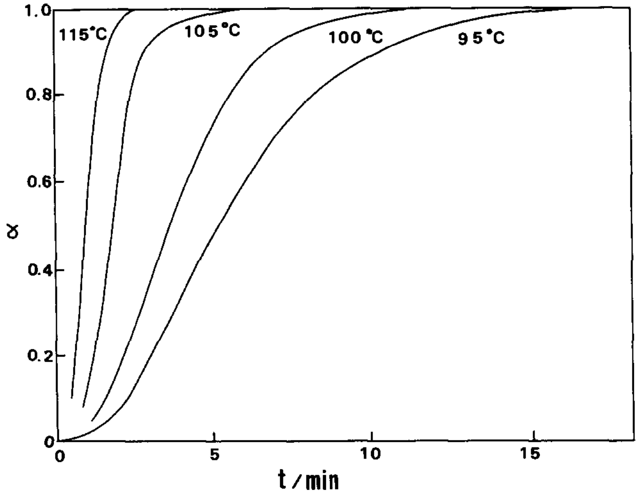

Fig. 1. Isothermal dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$. Plots of dehydration fraction α vs. time t.

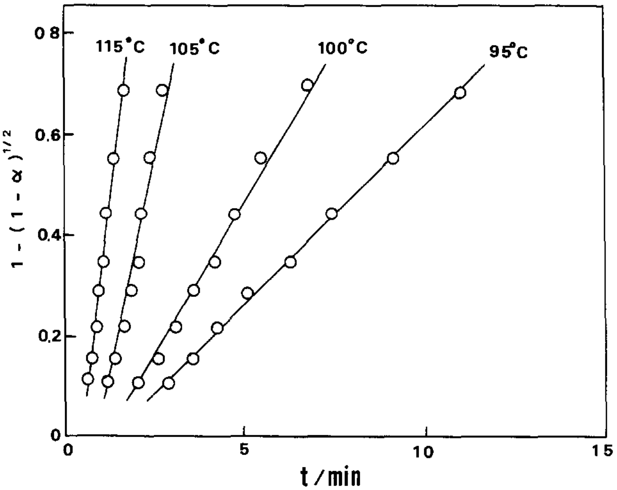

Fig. 2. Plots of $1-(1-\alpha)^{1/2}$ vs. t for the isothermal dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$.

the present dehydration seems be characteristic of a two-dimensional phase boundary reaction

$$R_2(\alpha) = 1 - (1-\alpha)^{1/2} = kt \qquad (2)$$

The R_2 mechanism for this dehydration is also supported by the crystal structure of $Zn(HCO_2)_2 \cdot 2H_2O$ as reported by Osaki et al. [8]. They showed that the crystal structure is monoclinic with space group $P2_{1/c}$. In this structure, the water molecules lie in the plane parallel to the (100) planes. It is, therefore, reasonable to consider that the dehydration takes place on these planes.

Table 1 shows the values of the rate constants k determined from the slopes of the $R_2(\alpha)$ versus plots at various temperatures. The values of activation energy and pre-exponential factor determined from the Arrhenius plot (Fig. 3) were 98.7 kJ mol^{-1} and 1.54×10^{11} s^{-1}, respectively.

It is known that phase boundary reactions are characterised by the rapid initial production of a complete reactant–product interface at the edge of a preferred crystallographic surface, and that the rates of reaction are dependent upon the advance of the reaction interface [3,9]. If the reactant in the form of a circular disc reacts by advancing from the edge of the surface to

TABLE 1

Rate constants k determined by means of isothermal thermogravimetry

T (°C)	95	100	105	115
k (10^{-3} s^{-1})	1.40	2.16	3.56	7.82

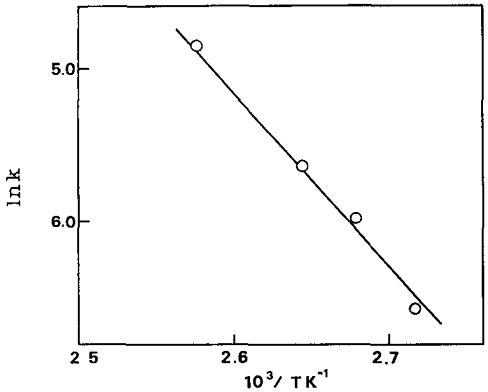

Fig. 3. Arrhenius plot for the isothermal dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$.

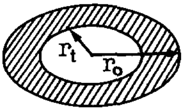

Fig. 4. Schematic expression of the dehydration fraction for the R_2 model $\alpha = h\pi(r_0^2 - r_t^2)/h\pi r_0^2 = [r_0^2 - (r_0 - vt)^2]/r_0^2 = 1 - [1 - (v/r_0)t]^2$ (see text.)

the centre, the fraction of reaction (α) at time t is given by

$$\alpha = h\left(\pi r_0^2 - \pi r_t^2\right)/h\pi r_0^2 \tag{3}$$

$$r_t = r_0 - vt \tag{4}$$

where h is the thickness of the disc, r_0 is the original radius of the disk, r_t is the radius of the unreacted portion at time t and v is the velocity of advance of the reaction interface (Fig. 4). Substituting eqn. (4) in eqn. (3), and rearranging, gives

$$1 - (1 - \alpha)^{1/2} = (v/r_0)t \tag{5}$$

Equation (5) is consistent with eqn. (2). Therefore, the rate constant, k, determined by thermogravimetry is correlated to v/r_0. Figure 5 shows the advance of the interface of the dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$. The

TABLE 2

Rate of advance of the interface between reactant and product

T (°C)	95	105	108
v_{obs} ($\mu m\ s^{-1}$) [a]	0.105	0.252	0.324
v_{cal} ($\mu m\ s^{-1}$) [b]	0.120 ± 0.019	0.281 ± 0.045	0.360 ± 0.058

[a] Determined from microscopic observation.

[b] Calculated in accordance with $kr_0 = A\exp(-E/RT)r_0$ with $E = 98.7$ kJ mol^{-1}, $A = 1.54 \times 10^{11}$ s^{-1} and $r_0 = 78.7 \pm 12.6$ μm.

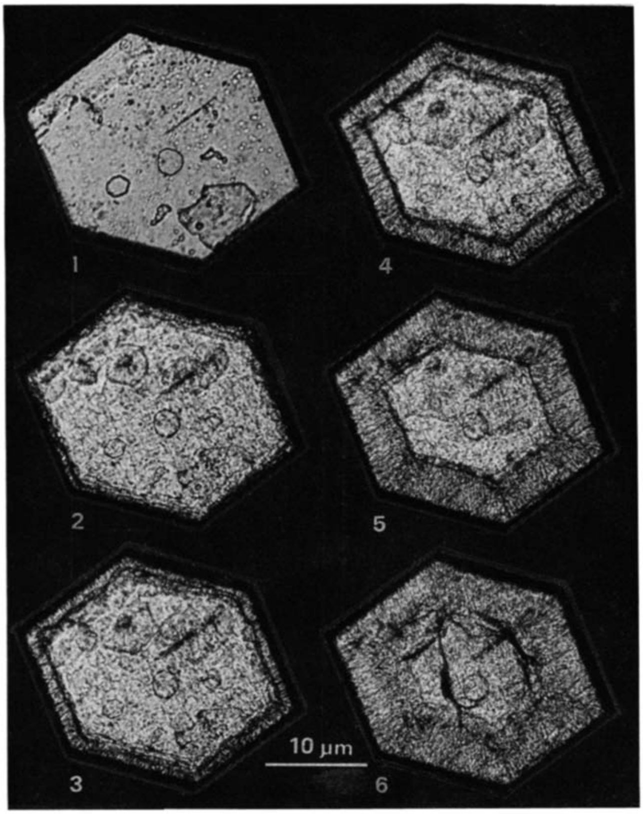

Fig. 5. Optical microscopic observations of the dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$ at 12.8 Torr water vapour partial pressure: 1, crystal of a hydrated specimen; 2, after heating for 2.5 min at 108 ° C; 3, after heating for 3 min at 108 ° C; 4, after heating for 3.5 min at 108 ° C; 5, after heating for 4.5 min at 108 ° C; and 6, after heating for 7 min at 108 ° C.

series of photographs (Fig. 5) shows that an interface is immediately established at the edge of the disc, and then advances into the centre. The rate of advance of the interface, which was directly determined from these micrographs, agreed with that obtained from thermogravimetry within experimental error (Table 2). These findings support the conclusion that the present dehydration proceeds in accordance with a two-dimensional phase boundary reaction (R_2).

CONCLUSIONS

The isothermal gravimetric measurements and microscopic observation were carried out at atmospheric pressure under a controlled partial pressure of water vapour at 12.8 Torr. The dehydration proceeded as a two-dimensional phase boundary reaction, R_2. The rates of advance of the interface between the reactant and the product were directly determined by means of optical microscopic observation. The rates were compatible with those determined by isothermal gravimetry. The values of the activation energy and pre-exponential factor were 98.7 kJ mol^{-1} and 1.54×10^{11} s^{-1}, respectively.

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REFERENCES

1 Y. Masuda and K. Nagagata, Thermochim. Acta, 155 (1989) 255.
2 Y. Masuda, Y. Ito, R. Ito and K. Iwata, Thermochim. Acta, 99 (1986) 205.
3 Y. Masuda, K. Iwata, R. Ito and Y. Ito, J. Phys. Chem., 99 (1987) 6543.
4 Y. Masuda, T. Matsuda, H. Kume and Y. Ihara, Thermochim. Acta, 156 (1989) 137.
5 Kagaku Binran Kisohen II (Handbook of Chemistry), The Chemical Society of Japan, Maruzen, Tokyo, 3rd edn., 1984, p. 117.
6 J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
7 H. Heide, W. Holand, H. Golker, K. Seyfarth, B. Muller and R. Sauer, Thermochim. Acta, 13 (1975) 365.
8 K. Osaki, Y. Nakai and T. Watanabe, J. Phys. Soc. Jpn., 18 (1963) 919.
9 S.F. Hulbert, J. Br. Ceram. Soc., 6 (1969) 11.