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Measurement of equilibrium water vapor pressures for the thermal dehydrations of some formate dihydrates by means of the transpiration method[1]

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Abstract

The equilibrium water vapor pressures, P_{H_2O} for the thermal dehydrations of some formate dihydrates, $M(HCO_2)_2{\cdot}2H_2O$, where M is Mg, Mn, Co, Ni and Zn, were measured by means of the transpiration method using a laboratory-made apparatus. These hydrates have a monoclinic isomorphous crystal structure with a space group, $P2_1/C$. The thermodynamic data such as ΔG, ΔH and ΔS for the dehydration were derived from the P_{H_2O} and correlated to the crystal structures of these hydrates.

Although the values of ΔH were expected to increase in the order of the hydrates of Mn<Zn<Mg<Co<Ni from the interatomic distance of M^{2+}–OH_2 bond, they increased in the order of Mn<Co<Ni<Mg<Zn. The large values of ΔH for $Mg(HCO_2)_2{\cdot}2H_2O$ and $Zn(HCO_2)_2{\cdot}2H_2O$ seemed to be due to the relatively strong hydrogen bond between the water molecules and the formate ions. The values of ΔG obtained at 373 K, $\Delta G(373)$ showed a good correlation with the beginning temperatures of the dehydrations, *Ti*. © 1998 Elsevier Science B.V.

Keywords: Equilibrium water vapor pressure; Hydrates; Thermal dehydration; Transpiration method

1. Introduction

Thermal dehydrations of solid hydrates have been studied extensively by means of thermal analyses such as the thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). It has been known that the dehydration of the hydrates is generally reversible reaction and the rate of the dehydration is affected by the atmospheric water vapor pressure [1–10]. However, the equilibrium water vapor pressure for the dehydration of hydrate has scarcely been measured.

From the equilibrium water vapor pressure (P_{H_2O}), the fundamental thermodynamic data such as the Gibbs energy change, ΔG, the enthalpy change, ΔH and the entropy change, ΔS for the dehydration can be determined [11–15]. It is also significant to discuss the relationship between these fundamental thermodynamic data and the crystal structure of the hydrates.

It is known that there are two kinds of methods to determine the P_{H_2O} [14]. One is a static method which directly measures the P_{H_2O} using a manometer or a pressure gauge. The other is a dynamic method such as a transpiration method [14–16], in which carrier gas is passed over the sample hydrate, saturated with the water molecules generated from the hydrate and then the P_{H_2O} is determined from the mass of the water absorbed by an absorber in a given time interval.

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In this study, the equilibrium water vapor pressures for the dehydrations of the formate dihydrates such as $M(HCO_2)_2{\cdot}2H_2O$, where M is Mg, Mn, Ni, Co and Zn, were measured by means of the transpiration method using a laboratory-made apparatus, and the ΔG, ΔH and ΔS for the dehydration were determined from the P_{H_2O}. These hydrates are known to form an isomorphous monoclinic crystal with a space groups, $P2_1/C$ [17–20] and the water molecules lie in the plane parallel to the (100) planes. It is interesting to study the relationship between the fundamental thermodynamic data and the structures of these hydrates.

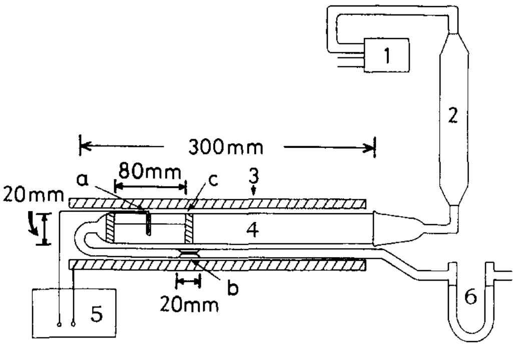

Fig. 1. The transpiration apparatus for the measurement of P_{H_2O}. (1) Flow control bulb, (2) Dry column, (3) Electric furnace, (4) Reaction vessel, (5) Temperature controller, (6) Absorption vessel, (a) Thermocouple, (b) Capillary, (c) Glass wool.

2. Experimental

2.1. Materials

The formate dihydrates, $M(HCO_2)_2{\cdot}2H_2O$, where M is Mg, Mn, Ni, Co and Zn, were purchased from Wako and recrystallized from a 10^{-4} M solution of formic acid. The crystals were air-dried at room temperature and pulverized in a mortar with pestle. These hydrates were identified by means of TG and IR spectrum.

2.2. Measurements of P_{H_2O}

The equilibrium water vapor pressures for the dehydrations were measured using a handmade apparatus shown in Fig. 1 [13–15]. The apparatus consisted of a flow control valve, a dry collum (Nikka Seiko), an electric furnace, a reaction vessel, a temperature controller (EC5600 Ohkura) and an absorption U-tube.

About 5 g powdered sample was packed into the reaction vessel and both the ends of the sample were sealed with glass wool. Extra pure (99.9999%) nitrogen gas was used as a carrier gas and a small amount of water contained in the carrier gas was removed using the dry column. The flow rate of the carrier gas was controlled by the flow control valve, and the rate was measured using a soap-film flow meter.

Then the temperature of the furnace was raised up to a given temperature, and maintained at the temperature within ±0.5 K by means of the temperature controller. The water molecules evolved from the sample at the temperature were carried to the absorption tube with the carrier gas. The capillary zone of the reaction vessel served to satisfactorily saturate the carrier gas with the water molecules evolved [13–16].

The P_{H_2O} was determined from the mass of water absorbed by the absorber, magnesium perchlorate, packed in the U-tube in accordance with the Eq. (1) [13],

$$P_{H_2O} = P \times [n_{H_2O}/(n_{H_2O} + n_{N_2})] \tag{1}$$

where P is atmospheric pressure (1 atm), n_{H_2O} the number of moles of the water molecules absorbed by the absorber in a given time interval, and n_{N_2} the number of moles of carrier nitrogen flowing in a given time interval.

2.3. Instruments

The TG and DTA were performed by means of a RIGAKU TAS 200 Thermoflex TG8101D system with a heating rate of 5 K min^{-1}. About 10 mg of sample was weighed into platinum cell, and α-alumina was used as a reference material. The ΔH for dehydration was determined from the DSC curve recorded on a RIGAKU TAS 200 Thermoflex DSC8230D using α-alumina as a reference material. About 3 to 4 mg specimen was weighed into an aluminum open cell, and heated with a heating rate 0.5 K min^{-1}.

The DSC measurement was calibrated with the heat of transition of potassium nitrate (400.9 K, ΔH=5.4 kJ mol^{-1}) and the heats of fusion of gallium, indium, tin, lead and zinc (Ga: 309.94 K, ΔH= 5.59 kJ mol^{-1}; In: 430 K, ΔH=3.3 kJ mol^{-1}; Sn: 505 K, ΔH=7.07 kJ mol^{-1}; Pb: 600.6 K, ΔH=4.77 kJ mol^{-1}; and Zn: 692.7 K, ΔH=6.57 kJ mol^{-1}) [21].

IR spectrum was measured from 400 to 4400 cm^{-1} by means of a diffuse reflectance method with a Horiba FT-300 spectrophotometer. The X-ray powder diffraction patterns were obtained with a Rigaku Geigerflex RAD 3R diffractometer equipped with a standard high temperature sample holder. A MoK_α radiation and a graphite monochrometer were used for all measurements. The diffraction data were collected at 0.02° intervals.

3. Results and discussion

The dehydrations of these hydrates

$$M(HCO_2)_2 \cdot 2H_2O \rightarrow M(HCO_2)_2 + 2H_2O \qquad (2)$$

took place at temperatures ranging from 350 to 475 K, where M is Mg, Mn, Co, Ni and Zn (Fig. 2). The TG, DTA and DSC curves show that the dehydrations apparently take place as an one step reaction for all the hydrates.

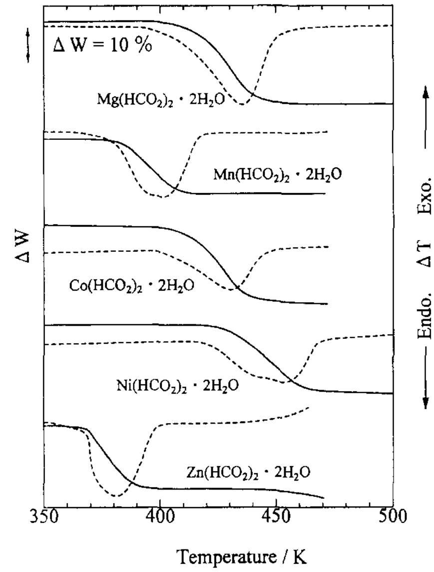

Fig. 2. The TG (solid line) and DTA (dotted line) curves of magnesium, manganese, cobalt, nickel and zinc formate dihydrates.

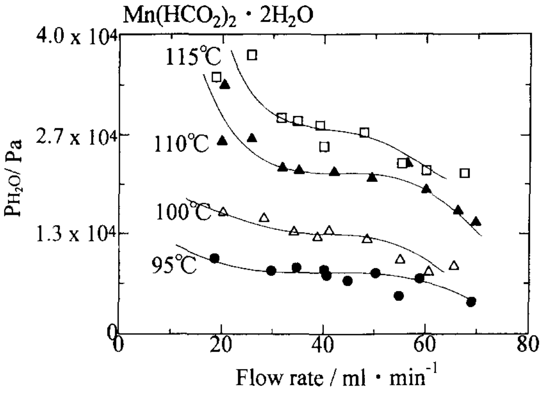

Fig. 3. The relationship between the flow rate of carrier gas and the P_{H_2O} for the thermal dehydration of $Mn(HCO_2)_2{\cdot}2H_2O$.

The P_{H_2O} were measured at around the temperatures of the endothermic peaks of DTA curves and at various flow rates of the carrier gas. The P_{H_2O} are affected on the flow rates of carrier nitrogen as shown in Fig. 3 [13–16]. When the flow rate increased, the value of P_{H_2O} first decreased, passed through a constant value and then decreased. A similar tendency was recognized for the other hydrates, and is explained as follows. At a slow-flow rate, the water molecules produced appear to self-diffuse the absorption U-tube, so the value of P_{H_2O} shows an apparently high value, and at a higher-flow rate the carrier gas cannot be saturated with the produced water molecules. An average of approximately constant values obtained during the medium flow rate region was adopted as the equilibrium water vapor pressure for a given temperature.

The P_{H_2O} values were determined for various temperatures and listed with the standard deviations in Table 1. The temperature dependency of P_{H_2O} is shown in equation:

$$\ln P_{H_2O} = -\Delta H/RT + \Delta S/R \qquad (3)$$

Fig. 4 shows the plot of the natural logarithm of the P_{H_2O} for the dehydration of $Mn(HCO_2)_2{\cdot}2H_2O$ against the reciprocal of the absolute temperature, $1/T$ in accordance with the Eq. (3). By means of the linear least-squares method, the value of ΔH for the dehydration was determined from the slope of the line, and the ΔS was determined from the intercept. The values of ΔH and ΔS for the dehydrations of other hydrates were also obtained in the same way. The ΔG for the

Table 1
The P_{H_2O} for the dehydrations of magnesium, manganese, cobalt, nickel and zinc formate dihydrates

Sample	Temperature/ K	P_{H_2O}/ k Pa
$Mg(HCO_2)_2{\cdot}2H_2O$	408	3.29±0.144
	413	4.48±0.102
	418	6.43±0.047
	428	11.6±0.400
	433	16.1±0.515
$Mn(HCO_2)_2{\cdot}2H_2O$	368	8.28±0.399
	373	13.2±0.565
	383	21.9±0.727
	388	28.1±0.860
$Co(HCO_2)_2{\cdot}2H_2O$	403	4.49±0.253
	413	8.11±0.092
	418	11.0±0.567
	423	14.1±0.173
$Ni(HCO_2)_2{\cdot}2H_2O$	423	6.49±0.177
	428	8.39±0.308
	438	15.5±0.488
$Zn(HCO_2)_2{\cdot}2H_2O$	363	5.43±0.284
	368	7.79±0.209
	373	13.5±0.663
	378	18.5±0.540

dehydration was obtained from the equation [11–14],

$$\Delta G = -2 \times RT \ln P_{H_2O} \qquad (4)$$

The values of ΔG at 373 K, ΔG (373) were shown in Table 2 together with the beginning temperatures (*Ti*) of the dehydrations obtained from the TG–DTA curves.

These dihydrates are known to form an isomorphous crystal in which there are two kinds of metallic ions. Both the metallic ions are located in the centers of octahedrons formed by six oxygen atoms, i.e. one of them is coordinated by the six oxygen atoms of formate ions, and the other is coordinated by the four oxygen atoms of water molecules and two oxygen atoms of formate ions. The water molecules lie on the plane parallel to the (100) planes (Fig. 5), and the crystal data are shown in Table 3 [22,23].

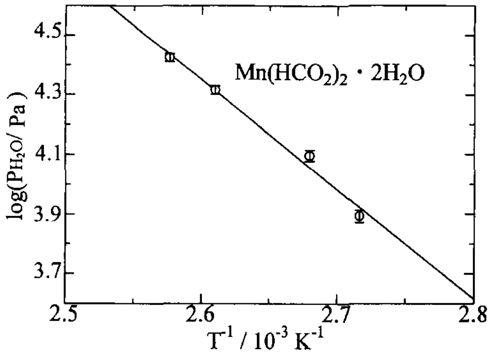

Fig. 4. The plots of ln P_{H_2O} vs. 1/T of $Mn(HCO_2)_2{\cdot}2H_2O$.

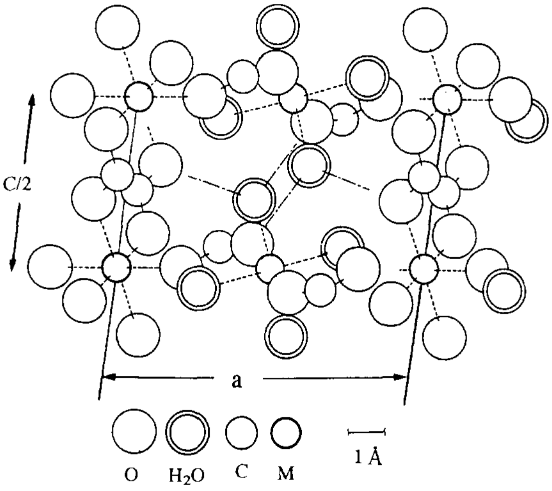

Fig. 5. The crystal structure of $M(HCO_2)_2{\cdot}2H_2O$.

Table 2
The thermodynamic data derived from P_{H_2O}

Sample	ΔH/kJ mol^{-1}	ΔH(DSC)/kJ mol^{-1}	ΔG(373)/kJ mol^{-1}	ΔS/J mol^{-1}	*Ti*^{a}/K
$Mg(HCO_2)_2{\cdot}2H_2O$	186±2.74	149±1.79	−3.90	509	392
$Mn(HCO_2)_2{\cdot}2H_2O$	140±12.4	112±1.58	−27.9	451	367
$Co(HCO_2)_2{\cdot}2H_2O$	163±2.72	115±2.72	−9.70	463	390
$Ni(HCO_2)_2{\cdot}2H_2O$	180±9.42	119±2.09	−2.68	490	414
$Zn(HCO_2)_2{\cdot}2H_2O$	193±13.7	124±4.91	−28.2	593	356

[a] *Ti* means beginning temperature of the thermal dehydration.

Table 3
The crystal data of magnesium, manganese, cobalt, nickel and zinc formate dihydrates

Sample	a/Å	b/Å	c/Å	β/°	rM^{2+}/Å [a]	Interatomic distance [b]/Å	
						M–OH_2(1)	M–OH_2(2)
$Mg(HCO_2)_2 \cdot 2H_2O$	8.69	7.18	9.39	97.6	0.86	2.08 (1.01)	2.06
$Mn(HCO_2)_2 \cdot 2H_2O$	8.86	7.29	9.60	97.7	0.97	2.22 (1.02_3)	2.17
$Co(HCO_2)_2 \cdot 2H_2O$	8.63	7.06	9.21	96.0	0.79	2.07 (1.00)	2.06
$Ni(HCO_2)_2 \cdot 2H_2O$	8.60	7.06	9.21	96.5	0.83	2.06 (1.01)	2.04
$Zn(HCO_2)_2 \cdot 2H_2O$	8.69	7.16	9.32	97.6	0.88	2.10 (1.02_4)	2.05

[a] rM^{2+} means a ionic radius of metallic ion.
[b] Figures in parentheses mean the ratio of M–OH_2(1) to M–OH_2(2).

The anhydride products obtained immediately after the dehydration were amorphous, so the ΔH obtained above seems to correspond to the reaction

$$M(HCO_2)_2 \cdot 2H_2O \rightleftarrows M(HCO_2)_2(\text{amorphous}) + 2H_2O(\text{gas}) \qquad (5)$$

The ΔH is mainly due to the bond energy between the metallic ion and the coordinated water molecules. It is reasonable that the values of ΔH decrease with increasing of the interatomic distances of M^{2+}–OH_2 and the smallest value of ΔH for $Mn(HCO_2)_2 \cdot 2H_2O$ is compatible with the largest bond length of the Mn^{2+}–OH_2. Although the ΔH are expected to increase gradually in the order of the hydrates of Zn<Mg<Co<Ni by considering the bond length of the M^{2+}–H_2O, they increase in the order of Co< Ni<Mg<Zn. The ΔH for the dehydrations of $Zn(HCO_2)_2 \cdot 2H_2O$ and $Mg(HCO_2)_2 \cdot 2H_2O$ are considerably larger than those expected from the bond lengths of the Zn^{2+}–OH_2 and Mg^{2+}–OH_2. These findings suggest that there would be other components to contribute the values of ΔH.

It is known that the coordinated water molecules interact with the neighbor formate ions by hydrogen bonds [17–20], and these interactions should contribute to the ΔH. The strength of the hydrogen bond depends on the interatomic distance of the OH_2–OCO bond, but the distances cannot be determined at present because the positions of hydrogen atoms in the crystal have not been yet determined. The interaction on the basis of hydrogen bond for $Zn(HCO_2)_2 \cdot 2H_2O$ and $Mg(HCO_2)_2 \cdot 2H_2O$ may be larger than those of others.

It is reasonable to consider that the hydrogen bond between the water molecules and the neighbor formate ions causes warp to the octahedron and then two kinds of the interatomic distances, M^{2+}–OH_2(1) and M^{2+}–OH_2(2) appear. In order to estimate the degree of distortion of the octahedrons from these interatomic distances, the ratios of interatomic distances to the smallest one are shown in Table 3. The degree of the distortion for $Zn(HCO_2)_2 \cdot 2H_2O$ is larger than those of the other hydrates, so the hydrogen bonds is stronger than those of the other hydrates, and the large value of ΔH for $Zn(HCO_2)_2 \cdot 2H_2O$ seems to be due to the relatively strong hydrogen bonds. Comparatively strong hydrogen bonds are also expected for both the crystals of $Mn(HCO_2)_2 \cdot 2H_2O$ and $Mg(HCO_2)_2 \cdot 2H_2O$, however, the largest interatomic distances of Mn^{2+}+(1)–OH_2 and Mn^{2+}(2)–OH_2 weaken the coordination bonds between Mn^{2+} and water molecules, so the ΔH seems to be small value, on the whole.

The values of ΔS for dehydrations are corresponded to the entropy changes between the free water molecule and the water molecule restrained in the crystal. The largest value of ΔS for the dehydration of $Zn(HCO_2)_2 \cdot 2H_2O$ would be explained on the basis of the strongest hydrogen bonds.

It is noteworthy that the values of ΔG (373) and *Ti* give a good correlation, i.e. the *Ti* increases with decreasing the value of ΔG (373). The *Ti* determined from TG curve may be corresponded to the temperature at which the coordination bond of Zn^{2+}–OH_2 is dissociated and the water molecules evaporate. The lowest *Ti* of $Zn(HCO_2)_2 \cdot 2H_2O$ seems to reflect the weakest coordination bond, Zn^{2+}–OH_2, but the largest values of ΔH of $Zn(HCO_2)_2 \cdot 2H_2O$ seems to be ascribable to the strongest hydrogen bonds.

The enthalpy change for the dehydration can also be measured directly by means of the DSC measurement

(Table 2). The enthalpy change obtained from the DSC measurement, ΔH(DSC) is smaller than that obtained from the P_{H_2O}. The values of ΔH obtained from the P_{H_2O} are corresponded to those measured at a equilibrium condition, but it is very difficult to measure directly the enthalpy change for the dehydration on the equilibrium condition by means of DSC. As shown in the previous section, the ΔH values determined from P_{H_2O} correspond to the enthalpy change of reaction (5), while the values of ΔH (DSC) to the reaction

$$\mathrm{M(HCO_2)_2 \cdot 2H_2O \rightarrow M(HCO_2)_2(crystal) + 2H_2O(gas)} \quad (6)$$

because the $M(HCO_2)_2$ obtained after DSC measuring is a crystal. So the values of ΔH (DSC) contain the exothermic crystallization energy of the dehydrated salts together with the endothermic energy to break the M^{2+}–OH_2 bonds. Therefore it is irrelevant to compare directly both the values of ΔH and ΔH(DSC).

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