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DEUTERIUM ISOTOPE EFFECTS IN THE THERMAL DEHYDRATION OF $K_2Mg(SO_4)_2 \cdot 6\,H_2O$

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ABSTRACT

Deuterium isotope effects in the thermal stability, enthalpy change, and kinetic parameters were examined by means of TG–DSC recorded simultaneously for the dehydration stages of $K_2Mg(SO_4)_2 \cdot 6\,H_2O$

$$K_2Mg(SO_4)_2 \cdot 6\,H_2O \xrightarrow{(1)} K_2Mg(SO_4)_2 \cdot 4\,H_2O \xrightarrow{(2)} K_2Mg(SO_4)_2 \cdot 2\,H_2O \xrightarrow{(3)} K_2Mg(SO_4)_2$$

The thermal stability and enthalpy change for the hydrate were smaller than those for its deuterium analog in stage (1). In addition, the rate constant for the hydrate was larger than that for the deuterate in this stage. As for stages (2) and (3), any isotope effect in these parameters was not recognized in practice. The correlation of these isotope effects observed in stage (1) is briefly discussed.

INTRODUCTION

Deuterium isotope effects in the thermal dehydration of various compounds have been studied by several workers. Some of them revealed that the size of such an isotope effect may be within a few percent [1–4]. However for the thermal dehydration of double salt hydrates of the type $K_2M(SO_4)_2 \cdot 6\,H_2O$, where M is a divalent cation, it was reported that the dehydration behavior of $K_2Mg(SO_4)_2 \cdot 6\,H_2O$ is abnormally different from that of its deuterium analog [5]. It is worth re-examining the dehydration of

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the hydrate and its deuterium analog under strictly identical experimental conditions in order to investigate such an isotope effect, since the kinetics of nucleation of the solid product in such a multi-stage dehydration are easily affected by the experimental conditions [6,7].

The present article deals with the dehydration behavior of $K_2Mg(SO_4)_2 \cdot 6\,H_2O$ under various measuring conditions as well as the deuterium isotope effects in the dynamic dehydration. The isotope effect was examined with regard to the activation energy, frequency factor, enthalpy change, and thermal stability for the three dehydration stages of the hexahydrate.

EXPERIMENTAL

The hexahydrate was prepared from reagent-grade K_2SO_4 and $MgSO_4 \cdot 7\,H_2O$ according to the standard procedure. It was ground and sieved to 170–200 mesh. Some tens of mg of the sample were thermally dehydrated. The anhydrous salt was then rehydrated with H_2O and D_2O vapors under identical conditions to give $K_2Mg(SO_4)_2 \cdot 6\,H_2O$ and its deuterium analog, respectively. Identification was made by means of IR and TG.

TG and DSC measurements were performed simultaneously using a Rigaku Thermoflex TG–DSC 8085E1 type instrument. Other experimental procedures were the same as those described previously [8].

RESULTS AND DISCUSSION

Preliminary examination of the dehydration process

It is known that $K_2Mg(SO_4)_2 \cdot 6\,H_2O$ is subject to stepwise dehydration under certain measuring conditions [5,9].

$$K_2Mg(SO_4)_2 \cdot 6\,H_2O \xrightarrow{(1)} K_2Mg(SO_4)_2 \cdot 4\,H_2O \xrightarrow{(2)}$$

$$K_2Mg(SO_4)_2 \cdot 2\,H_2O \xrightarrow{(3)} K_2Mg(SO_4)_2$$

In the present examination, the following results were obtained.

(a) The original hexahydrate is dehydrated to the anhydrous salt in a single step under the conditions of sample size, ca. 19.0 mg; heating rate range, ca. 1.0–4.0 K min^{-1}; atmosphere, dry N_2 at a flow rate of 50 ml min^{-1}.

(b) The rehydrated hexahydrate is dehydrated to the anhydrous salt via the stable tetrahydrate and unstable dihydrate under the same measuring conditions as (a).

(c) The dihydrate is easily obtained from the rehydrated hexahydrate with decreasing N_2 flow rate and with increasing heating rate and sample size in an atmosphere of static dry N_2.

It follows that the tetrahydrate is obtained rather easily from the rehydrated hexahydrate, whereas the stable dihydrate seems to result under limited conditions in which the nuclei of the dihydrate are formed. This condition is realized by a relatively higher partial pressure of water [10] and an introduction of various defects through the pretreatment in the rehydration process [11].

Estimation of the kinetic model

Stage (1) of the dehydration from the rehydrated hexahydrate to the tetrahydrate was examined isothermally with a sample size of 19.0 mg in a stream of dry N_2 with a flow rate of 50 ml min^{-1} in order to estimate the kinetic model. Twelve theoretical kinetic functions $F(\alpha)$ for solid decompositions were tested by plotting them vs. time, t, assuming the equation

$$F(\alpha) = kt$$

where α is the fraction dehydrated at time t and k is the rate constant. Table 1 gives the kinetic functions $F(\alpha)$.

Figure 1 shows the typical plot of various $F(\alpha)$ vs. t. It is seen in view of the linearity that an A_m mechanism should regulate dehydration stage (1). Table 2 shows the best values of m at various temperatures. It is interesting that the m value increases with increasing temperature. This may be due to a possible change in nucleation rate with temperature in the bulk of the decomposing solid. It is reasonable to assume that the m value ranges between ca. 3.0 and 3.5, noting that the average dehydration temperature by means of TG is around 351 K, as will be seen later.

TABLE 1

The mechanistic functions $F(\alpha)$ examined in the isothermal dehydration stages of $K_2Mg(SO_4)_2 \cdot 6\,H_2O$

Symbol	$F(\alpha)$
D_1	α^2
D_2	$\alpha+(1-\alpha)\ln(1-\alpha)$
D_3	$[1-(1-\alpha)^{1/3}]^2$
D_4	$1-2\alpha/3-(1-\alpha)^{2/3}$
A_u	$\ln[\alpha/(1-\alpha)]$
A_m	$[-\ln(1-\alpha)]^{1/m}$; $m=1, 2, 3, 4$
R_n	$1-(1-\alpha)^{1/n}$; $n=1, 2, 3$

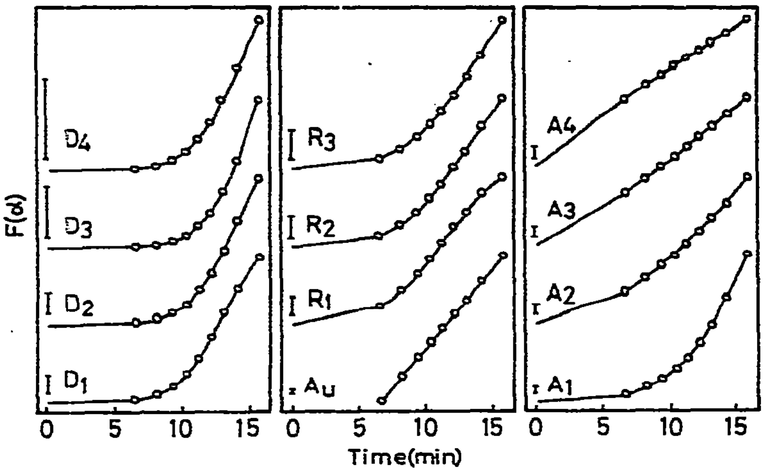

Fig. 1. Typical plots of F(α) vs. *t* for dehydration stage (1) of $K_2Mg(SO_4)_2 \cdot 6\ H_2O$ at 354.0 K by means of TG. The segment on the lower left-hand side of each F(α)–*t* plot refers to an ordinate scale of 0.1.

Dehydration stage (2) was examined isothermally with a sample size of 27.5 mg in an atmosphere of static N_2. An A_m law was found to be adequate when the *m* value was 2.33 in the α range 0.1–0.9 between 403.2 and 413.2 K. The temperature dependence of the *m* value was not recognized in dehydration stage (2).

Dehydration stage (3) was examined dynamically because the isothermal trace was not obtained satisfactorily in the present study. It was observed with a sample size of 27.3 mg in an atmosphere of static N_2 at a heating rate of 4.76 K min^{-1} and analyzed in a similar manner to a previous study [8]. Table 3 shows the activation energy, *E*, and the frequency factor, *A*, for various F(α). In view of the reasonable order of magnitude for the kinetic parameters in Table 3, an A_m law is also assumed to regulate dehydration stage (3). It seems that an A_m law with the *m* value of around 4 is adequate,

TABLE 2

The values of exponent *m* in A_m in the α range 0.1–0.9 for stage (1) by means of TG at constant temperatures

Temp. (K)	*m*	*r*
339.6	1.67	0.9992
341.1	1.82	0.9986
342.8	2.27	0.9999
348.0	2.50	0.9999
354.0	3.57	0.9999

TABLE 3

The activation energy, E, and frequency factor, A, for stage (3) in the α range 0.1–0.9 by means of dynamic TG

F(α)	E (kJ mole^{-1})	log$A$ (1/s)
D_1	684	76
D_2	767	86
D_3	874	97
D_4	802	89
R_1	338	37
R_2	407	44
R_3	433	47
A_1	492	55
A_2	242	26
A_3	159	16
A_4	117	11

noting that the parameters and their reliabilities increase with decreasing heating rate.

Deuterium isotope effects

Using the mechanistic functions F(α) estimated above, the kinetic parameters for the dynamic dehydration stages of $K_2Mg(SO_4)_2 \cdot 6H_2O$ and $K_2Mg(SO_4)_2 \cdot 6D_2O$ can be obtained [4]. Table 4 summarizes the kinetic parameters for the three stages of dehydration which were derived according to the so-called integral method [8,12].

TABLE 4

Kinetic parameters for the dynamic dehydration stages of $K_2Mg(SO_4)_2 \cdot 6H_2O$ and $K_2Mg(SO_4)_2 \cdot 6D_2O$ in the α range 0.1–0.9 by means of TG [a]

Stage	F(α)	Hydrate	E (kJ mole^{-1})	log$A$ (1/s)	$k \times 10^3$ (1/s) [b]
1	$A_{3.5}$	H_2O	124.7±3.4	15.9±0.5	2.37±0.07
		D_2O	114.2±2.5	14.2±0.4	1.71±0.04
2	A_2	H_2O	115.9±5.1	12.9±0.7	10.2±0.3
		D_2O	110.5±2.5	12.2±0.3	10.0±0.2
3	A_4	H_2O	117.2±1.7	11.2±0.3	5.60±0.07
		D_2O	126.8±2.1	12.3±0.3	5.58±0.10

[a] The accuracy is denoted by a probable error.

[b] Values at the temperatures of 351.6, 406.5 and 455.1 K for stages (1), (2) and (3), respectively.

It is seen in stage (1) that the k value for the hydrate is considerably larger than that of the deuterate, whereas the reverse is the case with the E value. The observed magnitude of the isotope effect in k seems to be too large in view of the theoretical estimation [1]. The large kinetic isotope effect may be explained by invoking the observed smaller value of A for the hexadeuterate than that for the hexahydrate: the smaller value of activation entropy for the former than that for the latter. Our magnitude is obviously smaller than the enormous isotope effects claimed earlier [5], however, which are improbable. This may be attributable to a possible delicate difference in the sample condition, as can be expected from the preceding preliminary examination. Such a difference may easily affect the nucleation kinetics, particularly in such a multi-stage dehydration [6,7].

It is also worth estimating the thermodynamic deuterium isotope effect in the dehydration stages of the hexahydrate. Table 5 shows the extrapolated onset temperature, T_{eo}, peak temperature, T_p, the enthalpy change, ΔH, from DSC, and the mean temperature, $T_{0.5}$, which refers to the temperature where α is 0.5 according to TG. It is seen that the value of ΔH for the hexahydrate is smaller than that of its deuterium analog in stage (1), whereas the values are equal within experimental error in stages (2) and (3). The decreasing tendency of the isotopic difference in ΔH, $\delta\Delta H$, in going from stage (1) to (3) is ascribed, at least in part, to the increasing temperature at which the dehydration occurs.

The observed $\delta\Delta H$ for stage (1) is assumed to consist of the following two terms

$$\delta\Delta H = \delta\Delta H_{\mathrm{diss}} + \delta\Delta H_{\mathrm{vap}} = 1.53 \pm 0.28 \text{ kJ mole}^{-1}$$

where $\delta\Delta H_{\mathrm{diss}}$ is the isotopic difference in heat of dissociation of the hexahydrate to the tetrahydrate and water, and $\delta\Delta H_{\mathrm{vap}}$ is the isotopic

TABLE 5

The thermal stabilities and enthalpy changes for the dynamic dehydration stages of $K_2Mg(SO_4)_2 \cdot 6\ H_2O$ and $K_2Mg(SO_4)_2 \cdot 6\ D_2O$ by means of TG–DSC [a]

Stage	Hydrate	T_{eo}(K)	T_p(K)	$T_{0.5}$(K)	ΔH(kJ mole^{-1}) [b]
1	H_2O	350.0±0.2	355.3±0.3	350.5±0.4	51.53±0.13
	D_2O	352.6±0.4	357.9±0.4	352.7±0.3	53.06±0.25
2	H_2O	393.8±1.2	409.1±0.6	407.6±0.7	51.0±1.1
	D_2O	390.7±0.7	407.2±0.4	405.4±0.5	51.5±0.7
3	H_2O	449.2±0.1	454.1±0.2	454.9±0.2	51.0±0.7
	D_2O	449.8±0.2	454.8±0.2	455.2±0.2	51.3±1.1

[a] The accuracy is denoted by a probable error.

[b] Value per mole of water dehydrated.

difference in heat of vaporization of water [1]. The value of $\delta\Delta H_{\mathrm{diss}}$ is thus derived as 0.57 ± 0.28 kJ mole^{-1} using the literature value of $\delta\Delta H_{\mathrm{vap}}$, 0.96 kJ mole^{-1}, at the mean temperature of ca. 352 K [13]. Such a $\delta\Delta H_{\mathrm{diss}}$ may be partly correlated to the deuterium isotope effect in the thermal stability of the hexahydrate. The positive value of $\delta\Delta H_{\mathrm{diss}}$ seems to be incompatible with the foregoing inverse isotope effect in E, if the bond cleavage of water molecules is a rate determining step in the dehydration of the hexahydrate. It may be considered that this is another argument for the estimated kinetic model; a random nucleation of the solid product and subsequent growth mechanism (an A_m law). The detail is ambiguous at this stage.

The isotopic difference in the thermal stability may also be correlated, in part, to the kinetics [3,4], because the dehydration temperature estimated by means of dynamic thermal analyses is likely to be far from the value at equilibrium. For this purpose, the rate constant, k, rather than the activation energy, E, should be properly used, since the value of A of the hexahydrate is not equal to that of the hexadeuterate. It is interesting that the higher thermal stability of the hexadeuterate than that of the hexahydrate might be, at least in part, explained by the smaller value of k for the hexadeuterate than that for hexahydrate. With regard to dehydration stages (2) and (3), such a discussion could not be made due to the larger experimental errors in the dehydration temperature, enthalpy change, and rate constant.

In conclusion, an Avrami–Erofeyev law is adequate for the thermal dehydration process of $K_2Mg(SO_4)_2 \cdot 6\,H_2O$ by means of thermal analyses. A phase boundary law is also improbable in view of the fact that the original hexahydrate was pulverized to a fine powder in which the number of various lattice defects is multiplied and the dehydration can take place inside the crystal grain quite randomly [8,14]. The isotope effect in the thermal stability seems to be in keeping with those in the enthalpy change and/or rate constant for dehydration stage (1). It is important that the kinetic deuterium isotope effect in the dehydration of solid hydrates should be discussed in terms of both E and A, since the values of A are likely to be different between the hydrate and its deuterium analog.

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