Journal of Thermal Analysis, Vol. 24 (1982) 207—213

EFFECT OF DEUTERATION ON THE THERMAL DEHYDRATION OF LITHIUM SULFATE MONOHYDRATE

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(Received December 8, 1981)

Effects of deuteration on the thermal stability, enthalpy change and kinetic parameters for the thermal dehydration of $Li_2SO_4 \cdot H_2O$ were examined by means of TG and DSC. The enthalpy change for the monohydrate was smaller by 1.63 ± 0.75 kJ/mol than that for the monodeuterate. The rate constant for the monohydrate was a little larger than that for the monodeuterate. However, the thermal stability, activation energy and frequency factor were practically unaffected by deuteration of the hydrate. It is suggested that the activation entropy as well as the activation energy should be considered in explaining the kinetic deuterium isotope effect in the thermal dehydration of $Li_2SO_4 \cdot H_2O$.

Recently, we have determined effects of deuteration on the thermal dehydration processes of $CaC_2O_4 \cdot H_2O$ [1], H_3BO_3 [2, 3] and $CuSO_4 \cdot 5\,H_2O$ [4, 5] by means of TG and DSC. It was found from these studies that the size or direction of such an isotope effect varies from sample to sample. In addition, these results proved to be useful for the better understanding of the dehydration processes.

It thus seems of interest to study the dehydration process of various hydrates extensively by means of TG and DSC. The present paper deals with both thermodynamic and kinetic isotope effects of deuterium in the thermal dehydration of $Li_2SO_4 \cdot H_2O$ by means of TG-DSC recorded simultaneously, the kinetics [6, 7] and thermodynamics [8] having been examined earlier.

Experimental

Reagent grade $Li_2SO_4 \cdot H_2O$ was ground and sieved to the size fraction of 170—200 mesh. The monohydrate was dehydrated thermally and the anhydrous product was rehydrated with water vapour in a small sealed bottle to give $Li_2SO_4 \cdot H_2O$. The deuterium analog was prepared with 99.8% deuterium oxide vapour under identical conditions. The identification was made by means of IR and TG.

About $1.56 \cdot 10^{-4}$ mol of the sample was weighed into a platinum crucible 5 mm in diameter and 2.5 mm in depth. α-Alumina was used as a reference material. TG-DSC traces were recorded simultaneously at a heating rate of 1.04 K/min

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in a flow of N_2 at a rate of 50 ml/min, using a TG-DSC (8085 E1) apparatus of Rigaku Denki Co. The measurements were repeated 8 and 5 times for $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$, respectively. The calibration of the enthalpy change and temperature was made on the basis of the transition of KNO_3 at 401 K.

TG traces for the isothermal dehydration of $Li_2SO_4 \cdot H_2O$ at various temperatures were also recorded under the same measuring conditions as in the dynamic run.

The computation of the kinetic parameters was made using a micro-computer. Graphical plots were obtained with a plotter connected to the computer.

Results and discussion

Thermodynamic deuterium isotope effects

Typical TG-DSC traces obtained simultaneously are shown in Fig. 1. Table 1 ists the inception temperature T_i, the extrapolated onset temperature T_{eo}, and the peak temperature T_p for the dehydrations of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ by means of DSC. Table 2 shows the temperature as a function of the fraction dehydrated α by means of TG. It is deduced from Table 2 that the thermal stability

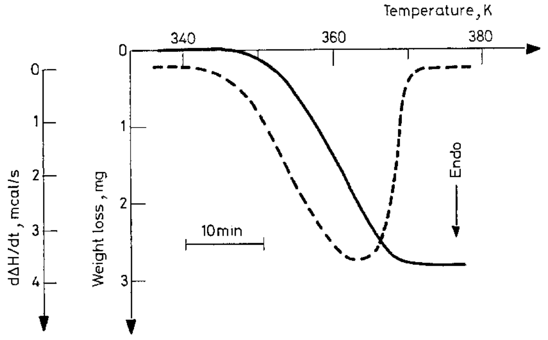

Fig. 1. Typical traces of TG (solid line) and DSC (broken line) recorded simultaneously for the dehydration of $Li_2SO_4 \cdot H_2O$

Table 1

Dehydration temperatures (K) for $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ by means of DSC

Salt	T_i	T_{eo}	T_p
$Li_2SO_4 \cdot H_2O$	341.6 ± 0.6	347.7 ± 0.6	363.7 ± 0.5
$Li_2SO_4 \cdot D_2O$	341.7 ± 0.5	347.0 ± 0.4	364.3 ± 0.4

Table 2

The temperature (K) as a function of the fraction dehydrated α by means of TG for the dynamic dehydrations of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$

Salt	α				
	0.1	0.3	0.5	0.7	0.9
$Li_2SO_4 \cdot H_2O$	351.9 ± 0.5	357.1 ± 0.4	360.5 ± 0.4	363.6 ± 0.4	366.7 ± 0.4
$Li_2SO_4 \cdot D_2O$	352.0 ± 0.5	357.3 ± 0.4	360.9 ± 0.4	363.9 ± 0.4	367.1 ± 0.4

of $Li_2SO_4 \cdot D_2O$, if any difference exists at all, is slightly higher than that of $Li_2SO_4 \cdot H_2O$.

The enthalpy changes for the monohydrate and monodeuterate, ΔH_h and ΔH_d, were determined by means of DSC to be 50.50 ± 0.63 and 52.13 ± 0.38 kJ/mol, respectively. The isotopic difference $\delta\Delta H$ is derived:

$$\delta\Delta H = \Delta H_d - \Delta H_h = 52.13 \pm 0.38 - 50.50 \pm 0.63 = 1.63 \pm 0.75 \text{ kJ/mol}$$

The observed value of $\delta\Delta H$ is compatible with a previous value of 1.15 kJ/mol over the temperature range 290–320 K obtained using a tensimetric technique [8]. The quantity $\delta\Delta H$ can be assumed to consist of the following two terms [1]:

$$\delta\Delta H = \delta\Delta_{\text{diss}} + \delta\Delta H_{\text{vap}}$$

where $\delta\Delta H_{\text{diss}}$ and $\delta\Delta H_{\text{vap}}$ are the isotopic differences in ΔH of dissociation from $Li_2SO_4 \cdot H_2O(s)$ to $Li_2SO_4(s)$ and $H_2O(l)$, and in ΔH of vaporization of $H_2O(l)$, respectively. Using ΔH_{vap} values for $H_2O(l)$ and $D_2O(l)$ given in the literature [9], the $\delta\Delta H_{\text{vap}}$ value is derived as ca. 0.92 kJ/mol at the mean temperature of 360.7 K, where α is 0.5 according to TG. $\delta\Delta H_{\text{diss}}$ is now estimated as:

$$\delta\Delta H_{\text{diss}} = \delta\Delta H - \delta\Delta H_{\text{vap}} = 1.63 \pm 0.75 - 0.92 = 0.71 \pm 0.75 \text{ kJ/mol}$$

It is seen that ΔH_{diss} of the monohydrate does not differ much from that of the monodeuterate, if any difference exists.

Kinetic deuterium isotope effects

The mechanistic functions $F(\alpha)$ examined in the present study are listed in Table 3. From the conventional isothermal analysis by means of TG [10], a random nucleation and subsequent growth mechanism, A_m, was selected for the dehydration of $Li_2SO_4 \cdot H_2O$. Table 4 shows the correlation coefficient r and error δ in the least square fitting of $F(\alpha)$ *vs.* t plot.

The mean value of the exponent m over the temperature range 350.5–355.5 K was 3.1 ± 0.2. Table 5 shows the rate constants k at various temperatures, derived in terms of the mean function $A_{3.1}$. From the Arrhenius plot, the activation energy,

Table 3

Mechanistic functions F(α) used in the analysis of kinetic model for the dehydration of $Li_2SO_4 \cdot H_2O$

$F(\alpha)$	Symbol	Rate controlling process
α^2	D_1	One-dimensional diffusion
$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling-Broushtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	Autocatalytic reaction (Prout-Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase-boundary reaction; $n = 1$, 2, and 3 (one-, two-, and three dimensional, respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	Random nucleation; $m = 1$ Random nucleation and subsequent growth; $m = 2$, 3, and 4 (Avrami-Erofeyev functions)

E, and $\log_{10}$ of the frequency factor, A, were obtained as 95.4 ± 2.1 kJ/mol and 10.8 ± 0.3 s^{-1}, with the r value of -0.9915.

Further, the kinetic parameters seem to be derived rather easily from the analysis of TG traces at a very slowly increasing temperature in terms of $F(\alpha)$ determined isothermally [10]:

$$\ln[F(\alpha)/T^2] = \ln\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \qquad (1)$$

where T is the absolute temperature, R is the gas constant and a is the linear heating rate. Table 6 lists the kinetic parameters for the dehydration of $Li_2SO_4 \cdot H_2O$ in terms of $A_{3.1}$. In this Table, the parameters in terms of A_2 and $A_{2.5}$ functions are also listed, since the agreement between the parameters in terms of $A_{3.1}$ and those from the isothermal run is not necessarily fair. This disagreement may, at least in part, be ascribed to the change in the dehydration temperatures between the dynamic and isothermal runs.

Table 4

Coefficients as a measure of the linearity for

Coefficient*	$F(\alpha)$					
	D_1	D_2	D_3	D_4	A_u	R_1
r	0.9848	0.9651	0.9251	0.9532	0.9968	0.9974
$\delta \times 10^2$	4.884	5.979	3.633	1.887	11.01	1.959

Table 5

The rate constants k at various temperatures in terms of an $A_{3,1}$ function by means of TG

Temp., K	$k \times 10^4$, s^{-1}
350.5	3.97 ± 0.02
351.4	4.10 ± 0.03
352.1	4.60 ± 0.03
354.9	6.01 ± 0.06
355.5	6.06 ± 0.06

Table 6

The kinetic parameters for the non-isothermal dehydration of $Li_2SO_4 \cdot H_2O$ in terms of A_m functions by means of TG

A_m	E, kJ/mol	log A, 1/s	$-r$
$A_{2.0}$	102.5 ± 1.7	12.0 ± 0.2	0.9988
$A_{2.5}$	80.8 ± 1.3	8.8 ± 0.2	0.9988
$A_{3.1}$	63.6 ± 0.9	6.2 ± 0.2	0.9989

It seems that the dynamic parameters in terms of $A_{2.5}$ are in keeping with the isothermal ones, taking into account of slightly larger values at a zero heating rate [10]. It is thus likely that the dynamic dehydration of $Li_2SO_4 \cdot H_2O$ should be regulated by the $A_{2.5}$ law. This can also be inferred from the dynamic analysis alone to some extent. Table 7 lists the values of E and A for all the $F(\alpha)$ except A_u, together with the value of r using Eq. (1). An A_m law with the m value of 2–3 is probable in view of the reasonable order of magnitude of the kinetic parameters and the linearity of ln $[F(\alpha)/T^2]$ *vs.* $1/T$ plot.

he least square fitting of $F(\alpha)$ *vs.* t plot

Coefficient*	$F(\alpha)$					
	R_2	R_3	A_1	A_2	A_3	A_4
r	0.9964	0.9912	0.9722	0.9990	0.9989	0.9967
$\delta \times 10^2$	1.792	2.206	16.84	1.738	1.265	1.726

* r and δ refer to the usual correlation coefficient and the error given by $[\Sigma\varepsilon_i^2/(N-1)]^{1/2}$, where ε_i is the deviation from the straight line, respectively

Table 7

Kinetic parameters for the dynamic dehydration of $Li_2SO_4 \cdot H_2O$ in terms of various $F(\alpha)$

$F(\alpha)$	E, kJ mol^{-1}	log A, s^{-1}	$-r$
D_1	306.3	41.4	0.9837
D_2	339.7	46.1	0.9906
D_3	382.4	51.8	0.9963
D_4	353.5	47.5	0.9929
R_1	150.2	18.8	0.9830
R_2	177.8	22.7	0.9938
R_3	188.3	24.1	0.9962
A_1	211.3	28.0	0.9989
A_2	102.5	12.0	0.9988
A_3	66.40	6.64	0.9987
A_4	48.24	3.91	0.9986

Now that the mechanistic function is estimated for the dynamic run, a comparison of the kinetic parameters can be made in terms of Eq. (1). Table 8 shows the kinetic parameters, together with the corresponding r value, assuming the same $F(\alpha)$ for the dehydrations of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$.

It is seen that the values of E and A are practically unaffected by deuteration of the monohydrate. It is interesting, however, that the k value of the monohydrate is a little larger than that for the monodeuterate. The some 5% smaller k value for the deuterate is not entirely unexpected in connection with the foregoing deuteration effects, if they exist, on the thermal stability and enthalpy change. This may be due to the fact that the activation entropy for the deuterate is smaller than that for the hydrate, as is deduced from the trend of the compensating effect in Table 8. This suggests that the deuterium kinetic isotope effect in the dehydration of $Li_2SO_4 \cdot H_2O$ should not necessarily be discussed in terms of the apparent activation energy E only, as pointed out by Manche and Carroll [11]. In other words, it is important that such an isotope effect should be explained by the activation free energy term of the rate constant k.

Table 8

Kinetic parameters for the non-isothermal dehydrations of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ in terms of $A_{2.5}$

Salt	E, kJ/mol^{-1}	log A, s^{-1}	$k \times 10^3$ (s^{-1})*
$Li_2SO_4 \cdot H_2O$	80.83 ± 1.26	8.80 ± 0.18	1.24 ± 0.01
$Li_2SO_4 \cdot D_2O$	79.33 ± 0.92	8.56 ± 0.13	1.18 ± 0.01

* The values at a mean temperature of 360.7 K, where α is 0.5 according to TG.

In conclusion, it is interesting that the degree of thermodynamic deuterium isotope effect in the dehydration of $Li_2SO_4 \cdot H_2O$, if it exists, is in keeping with that of the kinetic one. The normal isotope effect of ca. 5% in the rate constant k is compatible with that for $CaC_2O_4 \cdot H_2O$ [12]. However, the dehydration mechanism for $Li_2SO_4 \cdot H_2O$ seems difficult to discuss in view of the observed kinetic isotope effect. The dehydration mechanism estimated from the conventional thermal analyses, i.e. an Avrami-Erofeyev law, is supported preferably by the fact that the dehydration was carried out with a small amount of sample, which was finely pulverized in a mortar, at a very low heating rate in an atmosphere of flowing nitrogen [10].

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Zusammenfassung — Die Wirkung der Deuterisierung auf die Thermostabilität, die Enthalpie-Änderungen und kinetischen Parameter der thermischen Dehydratisierung von $Li_2SO_4 \cdot H_2O$ wurden durch TG und DSC untersucht. Die Enthalpie-Änderung für das Monohydrat wurde um 1.63 ± 0.75 kJ/mol niedriger gefunden als für das Monodeuterat. Die Geschwindigkeitskonstante für das Monohydrat war etwas größer als für das Monodeuterat. Die Thermostabilität, die Aktivierungsenergie und der Frequenzfaktor wurden jedoch von der Deuterisierung des Hydrats praktisch nicht beeinflußt. Es wird vorgeschlagen, daß bei der Erklärung des kinetischen Deuterium-Isotop-Effekts bei der thermischen Dehydratisierung von $Li_2SO_4 \cdot H_2O$ sowohl die Aktivierungsentropie als auch die Aktivierungsenergie berücksichtigt werden müssen.

Резюме — С помощью ТГ и ДСК изучено влияние дейтерирования на термоустойчивость, изменение энтальпии и кинетические параметры реакции термической дегидратации $Li_2SO_4 \cdot H_2O$. Значение изменения энтальпии для моногидрата было меньше по сравнению с дейтеропроизводным на величину 1.63 + 0.75 кдж/моль. Константа скорости для моногидрата была немного больше, чем для монодейтеропроизводного. Однако, термоустойчивость, энергия активации и частотный множитель практически не изменялись при дейтерировании. Предложено, что энтропия и энергия активации должны приниматься во внимание при огъяснении кинетики изотопного обмена при термической дегидратации $Li_2SO_4 \cdot H_2O$.