Thermochimica Acta, 43 (1981) 289—295
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL STABILITIES AND ENTHALPY CHANGES IN THE THERMAL DEHYDRATION STAGES OF $CuSO_4 \cdot 5\ H_2O$ AND $CuSO_4 \cdot 5\ D_2O$

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(Received 28 July 1980)

ABSTRACT

Deuterium isotope effects in thermal stabilities and enthalpy changes in three stages of thermal dehydration of copper sulfate pentahydrate were examined by means of differential scanning calorimetry (DSC) The dehydration temperatures of hydrated copper sulfates for the first and third stages were found to be lower than those of deuterated copper sulfates, whereas the reverse was found for the second stage. The enthalpy changes of hydrated copper sulfates proved to be smaller than those of their deuterium analogs for all stages of thermal dehydration. The observed isotope effects were compared with those reported earlier. The origin of the deuterium isotope effect in $CuSO_4$ 5 H_2O is briefly discussed.

INTRODUCTION

Although a great number of studies have been carried out on the thermal dehydration of copper sulfate pentahydrate $CuSO_4 \cdot 5\ H_2O$, only a few papers on deuterium isotope effects in the thermal dehydration stages of the hydrate have been reported [1,2]. It seems that some questions of the isotope effects in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ still remain unsolved [3,4]. Oki et al. [1] reported that the thermal stabilities of hydrated copper sulfates are lower than those of their deuterium analogs in three stages of dehydration and that the activation energies of the former are considerably smaller than those of the latter except in the second stage of dehydration. On the contrary, Garn [2] reported that copper sulfate pentahydrate is more stable thermally than its deuterium analog.

In these respects, it seems worthwhile to reinvestigate such an isotope effect in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ under strictly controlled conditions. In the present study, effects of various measuring conditions such as heating rate and atmosphere on the dehydration temperature and enthalpy change in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ were examined, before the determination of deuterium isotope effects in the thermal stabilities and enthalpy changes. The thermal dehydration run was carried out exclusively in a sufficient flow of dry nitrogen to prevent possible reverse reactions [5].

EXPERIMENTAL

Copper sulfate pentahydrate of reagent grade was twice recrystallized from distilled water. The purity of the pentahydrate was found to be quite satisfactory by means of iodometry with a standard solution of $Na_2S_2O_3$. The pentahydrate was ground and sieved to a size fraction of 170—200 mesh. The sample of trihydrate was also prepared by placing the pentahydrate in a small chamber in which the vapor pressure of water was maintained at about 12 mm Hg at 308 K, besides the preparation through the thermal dehydration of the pentahydrate in a flow of dry nitrogen.

TG—DSC measurements were done using a Rigaku Thermoflex TG—DSC 8085E1 type instrument in a flow of dry nitrogen. About 15.0 mg of sample placed in a platinum crucible of 2.5 × 5 mm diameter was used with α-alumina as a reference material. The area of DSC peak was determined using a precision planimeter, which was then converted to the enthalpy change through calibration data for the heat of transition of KNO_3 and the heat of fusion of $AgNO_3$.

The deuterium isotope effects in the thermal dehydration stages of $CuSO_4 \cdot 5\,H_2O$ were determined in the following way. About 30.0 mg of $CuSO_4 \cdot 5\,H_2O$ were dehydrated thermally to give the anhydrous salt by slowly heating up to ca. 500 K in a flow of dry nitrogen at a flow rate of ca. 100 ml min^{-1}, preventing the possible formation of basic salt. Two halves of the anhydrous product were rehydrated with H_2O and D_2O vapors in sealed small bottles at about 280 K to give $CuSO_4 \cdot 5\,H_2O$ and $CuSO_4 \cdot 5\,D_2O$, respectively. The identification of each sample was made by IR spectrophotometry and thermogravimetry. Infrared spectra were recorded on a Hitachi Model EP1-G_2 IR spectrophotometer in the range 4000—400 cm^{-1} by the nujol mull technique.

The measuring conditions of DSC for the determination of deuterium isotope effects were as follows: sample weight, ca. 15.0 mg; heating rate, ca. 2.0 K min^{-1}; crucible, platinum pans of 2.5 × 5 mm diameter; atmosphere, dry nitrogen at a flow rate of 55 ml min^{-1}; and reference material, ca. 10 mg of α-alumina.

RESULTS AND DISCUSSION

The thermal dehydration of copper sulfate pentahydrate can be expressed as [6,7]

$$\tfrac{1}{2}\,CuSO_4 \cdot 5\,H_2O \rightarrow \tfrac{1}{2}\,CuSO_4 \cdot 3\,H_2O + H_2O,\ \Delta H_1 \tag{1}$$

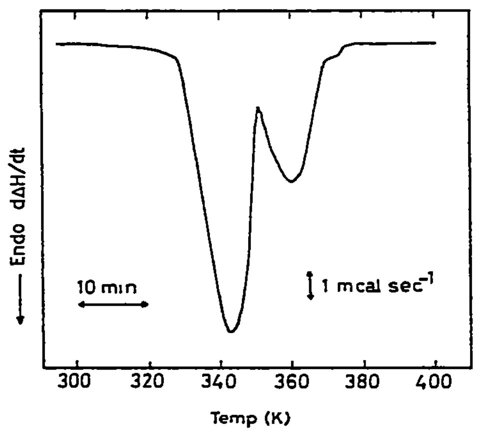
$$\tfrac{1}{2}\,CuSO_4 \cdot 3\,H_2O \rightarrow \tfrac{1}{2}\,CuSO_4 \cdot H_2O + H_2O,\ \Delta H_2 \tag{2}$$

$$CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O,\ \Delta H_3 \tag{3}$$

and for the overall process

$$\tfrac{1}{5}\,CuSO_4 \cdot 5\,H_2O \rightarrow \tfrac{1}{5}\,CuSO_4 + H_2O,\ \Delta H \tag{4}$$

In the present run, however, any distinction between processes (1) and (2)



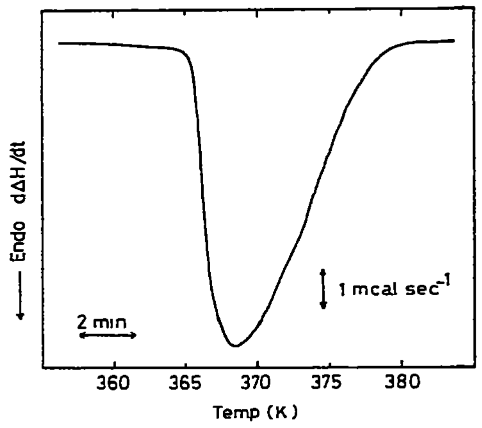


Fig. 1. Typical DSC trace for the thermal dehydration from $CuSO_4 \cdot 5\ H_2O$ to $CuSO_4 \cdot H_2O$ in a flow of N_2 at a flow rate of 55 ml min^{-1}.

Fig. 2. Typical DSC trace for the thermal dehydration from $CuSO_4 \cdot 3\ H_2O$ to $CuSO_4 \cdot H_2O$ in a flow of N_2 at a flow rate of 55 ml min^{-1}, the sample of which was prepared at a water vapor pressure of 12 mm Hg and a temperature of 308 K.

was not found to result, as pointed out by Paulik [6]. The DSC trace for the thermal dehydration of $CuSO_4 \cdot 5\ H_2O$ is shown in Fig. 1. Another measurement is required in order to obtain the ΔH_1 and ΔH_2 values. The DSC trace is given in Fig. 2 for the thermal dehydration of trihydrate which was prepared at a vapor pressure of about 12 mm Hg and a temperature of 308 K. The enthalpy change, ΔH_2, was determined from the area of DSC peak in Fig. 2. The value of ΔH_1 was then obtained by subtracting the peak area in Fig. 2 from the overlapped peak areas in Fig. 1.

The observed dehydration temperatures and enthalpy changes are shown

TABLE 1

Dehydration temperatures and enthalpy changes in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ [a]

Stage	Dehydration temp. (K)		Enthalpy change (kcal mole^{-1}) [c]	
	Intersection [b]	Peak	Obsd	Calcd. [d]
(1)	329.2 ± 0.9	344.5 ± 0.9	13.3 ± 0.5	13.35
(2)	365.8 ± 0.9	368.8 ± 0.9	13.7 ± 0.2	13.72
(3)	455.7 ± 0.8	482.7 ± 0.8	15.4 ± 0.8	17.36
Overall			13.8 ± 0.6	14.30

[a] Measuring conditions: sample weight, ca. 15 mg; heating rate, ca. 2.0 K min^{-1}; atmosphere, N_2 flow of 55 ml min^{-1}.

[b] Temperature at which the baseline of the DSC curve intersects with the tangent of maximum slope of the peak.

[c] Value per mole of $H_2O_{(g)}$ evolved.

[d] Calculated from standard heats of formation at 25°C [8].

in Table 1. It is seen that the enthalpy changes are in good agreement with those calculated using standard heats of formation [8] except that the ΔH_3 value is a little smaller than the calculated one. In the determination of enthalpy changes, the effects of flow rate of dry nitrogen and heating rate on the DSC peak area were examined in the ranges 0—55 ml min^{-1} and 0.5—8.0 K min^{-1}, respectively. Comparison of the resulting peak areas revealed little differences. Comparison of dehydration temperatures was not made since these temperatures are known to be very sensitive to the dehydration conditions.

Deuterium isotope effects

In order to determine the deuterium isotope effects in hydrated copper sulfate, the pentahydrate which was obtained by rehydrating the anhydrous salt with water vapor was used as the sample. This was a simple way of preparing copper sulfate pentahydrate and its deuterium analog under identical conditions. Figure 3 gives TG—DSC curves obtained simultaneously for the thermal dehydration of copper sulfate pentahydrate. The clear distinction between the first two peaks in Fig. 3 was unexpected, since the dehydration conditions are the same as those given in Fig. 1. The same was true for the dehydration of the deuterated sample. The good splitting of two peaks is probably due to the fact that nucleations of the trihydrate may be accelerated by the foregoing treatment of dehydration and subsequent rehydration.

Deuterium isotope effects in thermal stabilities for the thermal dehydration stages of copper sulfate pentahydrate are given in Table 2 which were obtained from analysis of the DSC curve. It is seen that copper sulfate pentahydrate and monohydrate are less stable thermally than their deuterium analogs, whereas the trihydrate is more stable than its deuterium analog. The present isotopic difference in thermal stability seems to be in keeping with that of Oki et al. [1] except in the second dehydration stage.

It can be assumed that the thermal stability of a hydrate should be related

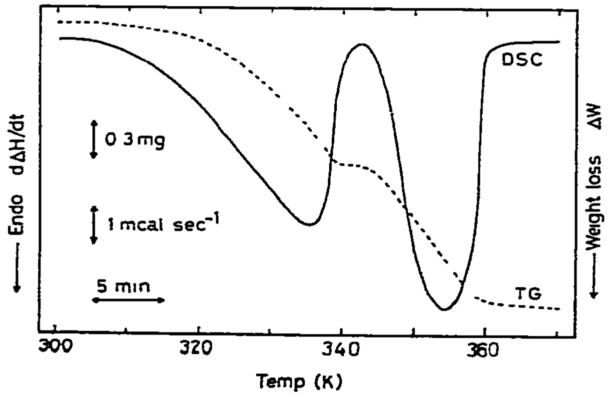


Fig. 3. Typical TG—DSC traces obtained simultaneously for the thermal dehydration from $CuSO_4 \cdot 5H_2O$ to $CuSO_4 \cdot H_2O$ in a flow of N_2 at a flow rate of 55 ml min^{-1}, the sample of which was prepared by rehydrating the anhydrous salt with water vapor.

TABLE 2

Dehydation temperatures (K) in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ and $CuSO_4 \cdot 5\ D_2O$ [a]

Stage	Intersection		Peak	
	Hydrate	Deuterate	Hydrate	Deuterate
(1)	314.6 ± 0.5	318.2 ± 0.5	336.3 ± 0.3	338.0 ± 0.4
(2)	346.3 ± 0.3	344.9 ± 0.3	354.3 ± 0.3	352.9 ± 0.3
(3)	460.1 ± 0.4	462.5 ± 0.6	484.2 ± 0.4	485.4 ± 0.4

[a] Mean of 10 observed values and its probable error

to the rate constant of dehydration. It is interesting that the activation energy in each stage of dehydration reported earlier [1] seems to explain the present isotopic difference in the thermal stability of hydrated copper sulfates, if the effect of frequency factor could be negligible. Further investigations on the deuterium kinetic isotope effects in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ may be required [3,5]. Such an investigation is in progress, using both isothermal and non-isothermal methods.

The isotopic difference in enthalpy change $\delta\Delta H$ in each dehydration stage of $CuSO_4 \cdot 5\ H_2O$ is given in Table 3. It is clear that the enthalpy change in each stage of dehydration of copper sulfate pentahydrate is smaller than that of its deuterium analog. The decreasing tendency of the $\delta\Delta H$ value in going from stage (1) to (3) should be ascribed, in part at least, to increasing temperatures at which the dehydration occurs.

The size of $\delta\Delta H$ could be evaluated if fundamental vibrational frequency shifts upon deuteration of the hydrate were known [4]. In the present study, however, the calculation was not made owing to an incomplete assignment of observed spectra and lack of data of the frequency shifts by deuteration except copper sulfate pentahydrate [9].

TABLE 3

Deuterium isotope effects in enthalpy changes in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ [a]

Stage	ΔH (kcal $mole^{-1}$) [b]		$\delta\Delta H$ (kcal $mole^{-1}$) [c]
	Hydrate	Deuterate	
(1)	13.33 ± 0.13	13.89 ± 0.07	0.56 ± 0.15
(2)	13.26 ± 0.09	13.54 ± 0.07	0.28 ± 0.12
(3)	14.95 ± 0.12	15.14 ± 0.12	0.19 ± 0.17
Overall	13.63 ± 0.08	14.00 ± 0.05	0.37 ± 0.10

[a] Mean of 10 observed values and its probable error.

[b] Enthalpy change per mole of water dehydrated.

[c] Isotopic difference in ΔH between the hydrate and its deuterium analog.

TABLE 4

The isotopic difference in heat of dissociation of the hydrated copper sulfate $\delta\Delta H_{diss}$ (kcal mole^{-1})

Stage	$\delta\Delta H$ [a]	$\delta\Delta H_{vap}$ [b]	$\delta\Delta H_{diss}$ [c]
(1)	0.56 ± 0.15	0.28	0.28 ± 0.15
(2)	0.28 ± 0.12	0.23	0.05 ± 0.12
(3)	0 19 ± 0.17	0.11	0.08 ± 0.17
Overall	0 37 ± 0.10	0.23	0.14 ± 0.10

[a] Value observed.

[b] Value estimated at the temperature where half of the water is evaporated in each stage, by interpolating values from the literature [10].

[c] $\delta\Delta H_{diss} = \delta\Delta H - \delta\Delta H_{vap}$, where $\delta\Delta H_{vap}$ is the isotopic difference in heat of vaporization of water

The isotopic difference in enthalpy change for the thermal dehydration of a salt hydrate $\delta\Delta H$ can be considered as consisting of the following quantities

$$\delta\Delta H = \delta\Delta H_{diss} + \delta\Delta H_{vap} \qquad (5)$$

where $\delta\Delta H_{diss}$ is the isotopic difference in heat of dissociation of a salt hydrate into the lower hydrate or anhydrous salt and water, and $\delta\Delta H_{vap}$ is the isotopic difference in heat of vaporization of water [4]. It is clear from the simultaneous TG and DSC traces given in Fig. 3 that the $\delta\Delta H$ values in Table 3 should consist of $\delta\Delta H_{diss}$ and $\delta\Delta H_{vap}$ values. It can thus be possible to estimate the contribution of $\delta\Delta H_{diss}$ to the $\delta\Delta H$ value, using $\delta\Delta H_{vap}$ values from the literature [10] or those calculated in terms of the Van Hook equation [11]. Table 4 lists the $\delta\Delta H_{diss}$ value in each stage of dehydration. Although no significant isotopic difference for stages (2) and (3) can be seen, the $\delta\Delta H_{diss}$ values for stage (1) and the overall process are larger than zero. The magnitude of $\delta\Delta H_{diss}$ seems to be reasonable, being in keeping with those reported earlier [3,5].

The observed deuterium isotope effects in enthalpy change and thermal stability in the thermal dehydration stages of $CuSO_4 \cdot 5\,H_2O$ could also be discussed in connection with structural isotope effects [12] in hydrated copper sulfates. Unfortunately, only the structural isotope effect in the pentahydrate seems to have been reported [13], so any explanation in the light of structural data was not made. It would be possible to understand such a thermodynamic isotope effect more completely if various data relevant to the subject were accumulated.

ACKNOWLEDGEMENT

The author wishes to thank N. Ikeda for her assistance in the experimental part of this work.

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