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KINETIC DEUTERIUM ISOTOPE EFFECTS IN THE THERMAL DEHYDRATION STAGES OF $CuSO_4 \cdot 5\ H_2O$ *

HARUHIKO TANAKA

Chemistry Laboratory, Faculty of School Education, Hiroshima University, Hiroshima (Japan)

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ABSTRACT

The kinetic deuterium isotope effects in three stages of thermal dehydration of $CuSO_4 \cdot 5\ H_2O$ were examined by means of TG. The activation energies and frequency factors of the hydrate for the first and third dehydration stages were practically equal to those of the deuterium analogue, whereas these parameters of the hydrate for the second dehydration stage were a little larger than those of the deuterium analogue. The kinetic deuterium isotope effects in these stages are correlated with deuterium isotope effects in the thermal stabilities of hydrated copper sulfates reported earlier. The reliability of such a kinetic isotope effect is also discussed briefly in connection with ambiguities incidental to the evaluation of kinetic parameters by means of thermal analyses.

INTRODUCTION

Recently, we have studied the kinetic deuterium isotope effect in the thermal dehydration from boric acid to metaboric acid(III) [1]. Both activation energy and frequency factor for the dehydration proved to be slightly larger than those of its deuterium analogue using simultaneous TG and DSC.

On the other hand, enormous kinetic deuterium isotope effects were reported in the thermal dehydration stages of copper sulfate pentahydrate [2] and the thermal dehydration of calcium oxalate monohydrate [3]. Manche and Carroll [4] reinvestigated the kinetic deuterium isotope effect in the thermal dehydration of calcium oxalate monohydrate, and concluded that the magnitude of the isotope effect of $CaC_2O_4 \cdot H_2O$ may be as high as a few percent.

Reinvestigation of the kinetic deuterium isotope effects in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ seems worthwhile. Such an examination is also of interest in connection with the deuterium isotope effects in the thermal stabilities in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ [5], since the thermal stabilities are considered as dependent on the rate of dehydration.

The present paper deals with the kinetic deuterium isotope effects in three

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stages of the thermal dehydration of $CuSO_4 \cdot 5\ H_2O$ by means of TG at programmed increasing temperatures

$$CuSO_4 \cdot 5\ H_2O \rightarrow CuSO_4 \cdot 3\ H_2O + 2\ H_2O \tag{1}$$

$$CuSO_4 \cdot 3\ H_2O \rightarrow CuSO_4 \cdot H_2O + 2\ H_2O \tag{2}$$

$$CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O \tag{3}$$

EXPERIMENTAL

Reagent grade copper sulfate pentahydrate was recrystallized twice from distilled water. The pentahydrate was ground and sieved to the size fraction of 170—200 mesh. About 15.0 mg of the pentahydrate were dehydrated to give the anhydrous salt by heating slowly up to ca. 500 K in a flow of dry nitrogen at a rate of ca. 100 ml min^{-1}, preventing the possible formation of basic salt. The anhydrous salt was converted to the pentahydrate by the back hydration with water vapor at about 280 K in a sealed small bottle. The deuterium analogue of the pentahydrate was prepared with 99.8% deuterium oxide vapor under identical conditions. The identification of each sample was made by means of IR and TG.

TG measurements for the dehydration stages of $CuSO_4 \cdot 5\ H_2O$ and $CuSO_4 \cdot 5\ D_2O$ were made using a Rigaku Thermoflex TG—DSC 8085E1 type instrument at a heating rate of ca. 2.0 K min^{-1} in a flow of dry nitrogen at a rate of 55 ml min^{-1}. About 15.0 mg of sample placed in a platinum crucible of 5 mm diameter and 2.5 mm depth were used, with α-alumina as reference material.

Isothermal TG measurements for the three-stage dehydration of $CuSO_4 \cdot 5\ H_2O$ in a flow of dry nitrogen at a rate of 55 ml min^{-1} were also carried out by maintaining the temperature constant within ±0.5 K.

Computation of kinetic parameters was made using an Apple II micro-computer.

RESULTS AND DISCUSSION

We may assume that the following kinetic equation holds for the thermal dehydration stages of copper sulfate pentahydrate

$$\frac{d\alpha}{dt} = k\mathrm{f}(\alpha) \tag{4}$$

where α is the fraction of reactant dehydrated at time t and k is the rate constant. Integration of eqn. (4) gives

$$\mathrm{F}(\alpha) \equiv \int \frac{d\alpha}{\mathrm{f}(\alpha)} = kt \tag{5}$$

The function $\mathrm{F}(\alpha)$, which describes the mechanism for the isothermal dehydration, can be determined by plotting various theoretical functions

TABLE 1

Mechanistic functions F(α) *

F(α)	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion, cylindrical symmetry
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion, spherical symmetry; Jander function
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion, spherical symmetry; Ginstiling—Broushtein function
$1-(1-\alpha)^{1/2}$	R_2	Phase boundary reaction, cylindrical symmetry
$1-(1-\alpha)^{1/3}$	R_3	Phase boundary reaction, spherical symmetry
$-\ln(1-\alpha)$	F_1	Random nucleation, one nucleus on each particle
$[-\ln(1-\alpha)]^{2/3}$	$A_{1.5}$	Random nucleation and subsequent growth; Avrami—Erofeyev type functions
$[-\ln(1-\alpha)]^{1/2}$	A_2	
$[-\ln(1-\alpha)]^{2/5}$	$A_{2.5}$	
$[-\ln(1-\alpha)]^{1/3}$	A_3	
$[-\ln(1-\alpha)]^{1/4}$	A_4	

* The symbols used are similar to those in ref. 8.

against t; the correct function should give a straight line with slope k [6]. The functions F(α) used in the present study are listed in Table 1 [7,8]. Typical plots of the correct F(α) vs. t in the three-stage dehydration of $CuSO_4 \cdot 5\ H_2O$ are shown in Fig. 1. Table 2 gives the correct function for each stage, together with kinetic parameters obtained in terms of the Arrhenius equation. A typical plot of ln k vs $1/T$ is shown in Fig. 2.

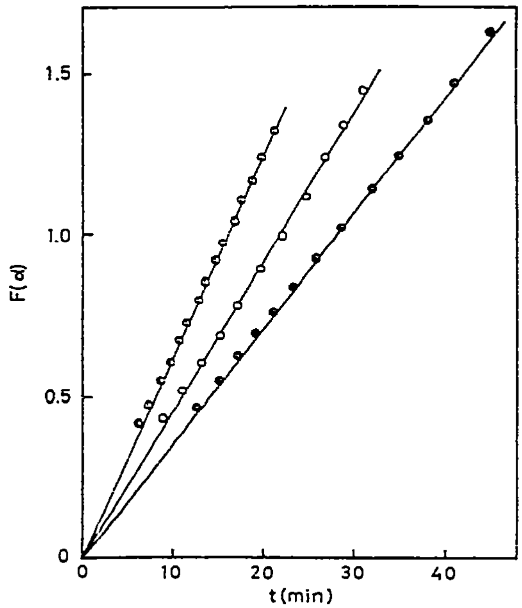
We can obtain, in turn, the kinetic parameters from the analyses of dynamic TG traces at programmed increasing temperatures, by assuming for the moment that the function F(α) estimated by means of the isothermal method is also valid for the non-isothermal run [9]. The typical TG trace for the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ is shown in Fig. 3.

According to the method of Coats and Redfern [10], we obtain [1]

$$\ln \frac{F(\alpha)}{T^2} = \ln \frac{AR}{aE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{R}\frac{1}{T} \tag{6}$$

where T is the absolute temperature, A is the frequency factor, R is the gas constant, a is the linear heating rate, and E is the activation energy. Plots of the left-hand side of eqn. (6) vs. $1/T$ should give a straight line with a slope of $-E/R$, if the correct F(α) is employed. Figure 4 shows the typical plot.

Kinetic parameters thus obtained for the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ are shown in Table 3. It is seen that the kinetic parameters for dehydration stages (1) and (2) in Table 3 seem to be compatible with those given in Table 2, whereas those of Table 3 for stage (3) may not coincide with those of Table 2. We can thus use F(α) estimated by the isothermal method in evaluating the kinetic deuterium isotope effects for stages (1) and (2) by means of the dynamic TG. Such a method of evaluating kinetic



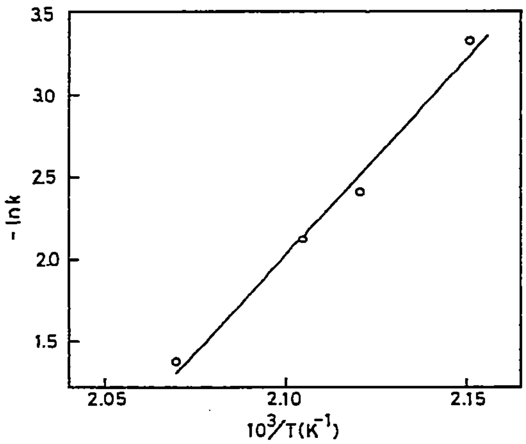


Fig. 1. Plots of F(α) vs. *t* for the isothermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$. The temperatures are 320.4, 340.0, and 464.9 K for stages (1), (2), and (3), respectively. ○, Stage (1) A_2; ⦶, stage (2) $A_{2.5}$; ●, stage (3) F_1.

Fig. 2. The Arrhenius plot for the isothermal dehydration from $CuSO_4 \cdot H_2O$ to $CuSO_4$.

parameters for the thermal decomposition of solids is widely used [1,9].

On the other hand, the need of evaluating the kinetic parameters for stage (3) from the dynamic method alone may arise, since the agreement between the isothermal method and the dynamic one is not fair. Such a disagreement has also been reported for the thermal decomposition of a few other solids [11–13].

Now, we may select tentatively possible mechanisms for the dehydration from $CuSO_4 \cdot H_2O$ to $CuSO_4$ at programmed increasing temperatures by assuming the following, although a single function F(α) can not be specified in general: (1) the mechanistic function which gives an activation energy smaller than the corresponding enthalpy change is ruled out [14]; (2) the correct function gives good linearity in the plot of the left-hand side of eqn. (6) vs. $1/T$; (3) the correct function gives a frequency factor in the range ca.

TABLE 2

The mechanistic functions F(α) and kintic parameters, *E* and *A*, for the dehydration of copper sulfate hydrates by means of isothermal technique

Stage	F(α)	*E*(kcal mole^{-1})	*A*(s^{-1})
(1)	A_2	19.8	2.5×10^{10}
(2)	$A_{2.5}$	22.1	1.6×10^{11}
(3)	F_1	48.4	3.9×10^{19}

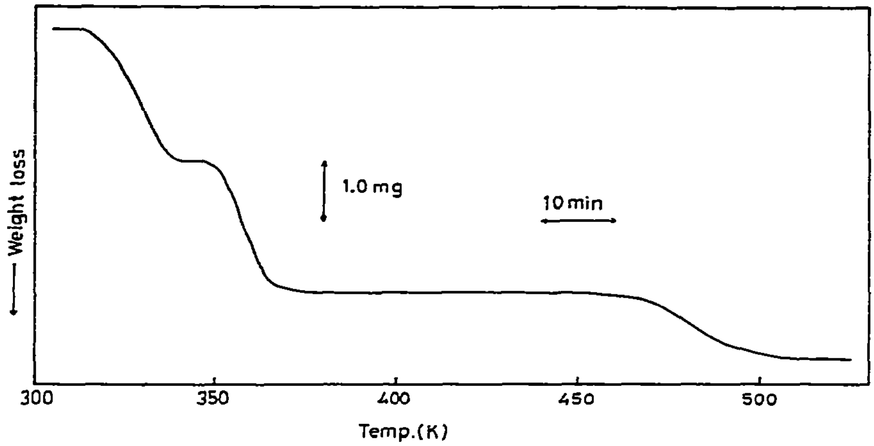


Fig. 3. The typical TG trace for the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$.

10^3—10^{18} s^{-1} [15].

The functions F_1 and $A_{1.5}$ are thus selected for dehydration stage (3) by examining the kinetic parameters calculated in terms of eqn. (6) for all the functions listed in Table 1 using the micro-computer. Table 4 shows the kinetic parameters for the three dehydration stages of $CuSO_4 \cdot 5\ H_2O$, together with those for its deuterium analogue which were obtained by assuming that the functions F(α) for the deuterates are the same as those of the hydrates.

It can be seen from Table 4 that the magnitude of the kinetic deuterium isotope effects in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ is reasonable in the light of those for the other solids [1,4]. It is interesting to note

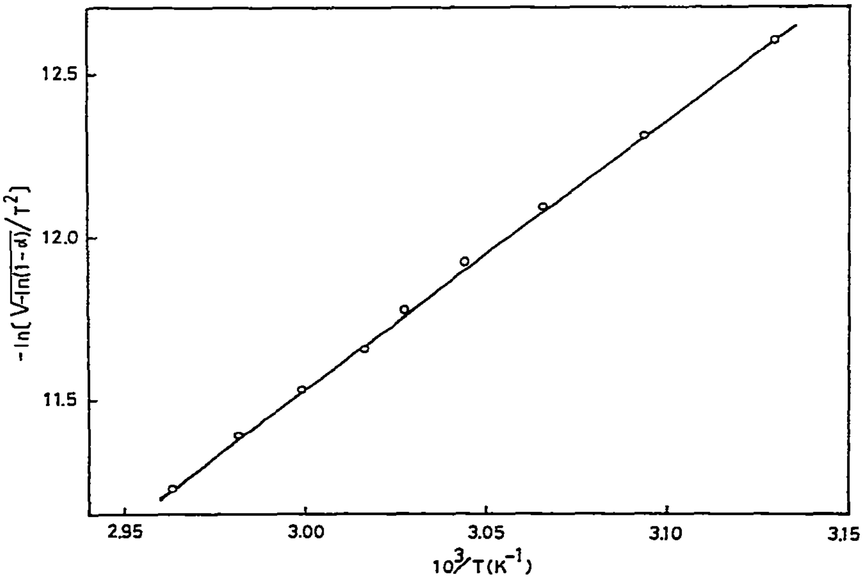


Fig. 4. The plot of $\ln[F(\alpha)/T^2]$ vs. $1/T$ for the thermal dehydration from $CuSO_4 \cdot 5\ H_2O$ to $CuSO_4 \cdot 3\ H_2O$.

TABLE 3

Kinetic parameters, E and A, in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ obtained by means of dynamic TG in terms of F(α) estimated from the isothermal technique

Stage	F(α)	E(kcal mole^{-1})	A(s^{-1})
(1)	A_2	17.42 ± 0.28	$(8.0 \pm 3.3) \times 10^8$
(2)	$A_{2.5}$	25.43 ± 0.34	$(1.8 \pm 0.9) \times 10^{13}$
(3)	F_1	37.53 ± 0.85	$(2.4 \pm 1.7) \times 10^{14}$

that the direction of the isotope effect can be detected in stage (2); an inverse isotope effect resulted, whereas the situation is ambiguous in stages (1) and (3) owing to experimental errors. The result of Table 4 seems, qualitatively, to be in keeping with that of Oki et al. [2] and to explain the deuterium isotope effects in the thermal stabilities in the step-wise dehydration of $CuSO_4 \cdot 5\ H_2O$ reported earlier [5]. The deuterium isotope effects in the thermal stabilities are reproduced in Table 5. Such an inverse isotope effect was also recognized in the thermal dehydration from H_3BO_3 to HBO_2(III) [1]. The cause of the inverse isotope effect is not known at this stage but will be understood to some extent if the situation of transition states during the thermal dehydration is clarified.

In conclusion, the determination of the mechanistic function F(α) for the thermal dehydration at programmed increasing temperatures from the dynamic method alone seems to be required in order to evaluate the kinetic parameters unequivocally, although these parameters from the thermal analyses cannot be overestimated in general. It is probable that these kinetic values could vary according to the measuring condition and should depend on the fraction dehydrated, α [4]. It is also probable that the mechanism regulating the course of dehydration may vary depending on temperatures and water vapor pressures, etc. These factors affecting the kinetic parameters, however, may not diminish the reliability of the present kinetic deuterium isotope effects since the measuring conditions and the method of kinetic analysis for the hydrate are identical to those of its deuterium analogue.

TABLE 4

Kinetic parameters for the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ and $CuSO_4 \cdot 5\ D_2O$ by means of dynamic TG *

Stage	F(α)	E(kcal mole^{-1})		A(s^{-1})	
		Hydrate	Deuterate	Hydrate	Deuterate
(1)	A_2	17.42 ± 0.28	17.50 ± 0.29	$(8.0 \pm 3.3) \times 10^8$	$(8.3 \pm 3.7) \times 10^8$
(2)	$A_{2.5}$	25.43 ± 0.34	24.03 ± 0.24	$(1.8 \pm 0.9) \times 10^{13}$	$(2.5 \pm 0.8) \times 10^{12}$
(3)	F_1	37.53 ± 0.85	38.05 ± 1.07	$(2.4 \pm 1.7) \times 10^{14}$	$(4.3 \pm 3.4) \times 10^{14}$
	$A_{1.5}$	24.27 ± 0.51	24.65 ± 0.72	$(1.5 \pm 0.8) \times 10^8$	$(2.3 \pm 1.5) \times 10^8$

* Mean of six observed values and its probable error.

TABLE 5

Dehydration temperatures (K) in the thermal dehydration stages of $CuSO_4 \cdot 5\ H_2O$ and $CuSO_4 \cdot 5\ D_2O$

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

In addition, it should be pointed out here that the various functions $F(\alpha)$ used in the present study are based on the theoretical model; experimentally, the exponent in Avrami—Erofeyev type functions can vary continuously from unity to 1/4 [7]. It is thus reasonable to consider that the function given in Table 4 is approximate for each stage of dehydration, which in turn gives the approximate kinetic parameters. The best function and kinetic parameters could be determined by "scanning" the exponent by, say, 0.1 from 1/4 to unity in the case of Avrami—Erofeyev type functions. Nevertheless, it can be seen that the direction and magnitude (%) of the kinetic deuterium isotope effect are almost invariable for any mechanism assumed in a given dehydration, as can be substantiated, for example, by comparing the values for F_1 with those for $A_{1.5}$ in stage (3).

Although a number of methods have been so far reported for the determination of reaction mechanism and/or the kinetic parameters for the non-isothermal solid decompositions [16], each method gives more or less a different result for a given trace of TG or DSC, with the merits or demerits of each. We are at present investigating the most reliable method for the estimation of dehydration mechanism and kinetic parameters during the thermal dehydration of solids by means of simultaneous TG—DSC at programmed increasing temperatures.

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