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THE KINETIC DEUTERIUM ISOTOPE EFFECT IN THE THERMAL DEHYDRATION OF BORIC ACID

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ABSTRACT

The kinetic deuterium isotope effect in the thermal dehydration process from H_3BO_3 to $HBO_2(III)$ was determined using simultaneous TG and DSC. The rate constant ratio of H_3BO_3 to D_3BO_3 obtained by the analysis of isothermal TG and DSC curves was found to be smaller than unity. Both activation energy, E, and frequency factor, A, for the dehydration of H_3BO_3 proved to be larger than those of D_3BO_3, using non-isothermal TG and DSC. The origin of the deuterium kinetic isotope effect in the thermal dehydration of boric acid is also briefly discussed.

INTRODUCTION

Recently, we have studied the deuterium isotope effects in enthalpy change and thermal stability in the thermal dehydration stages of boric acid [1]. It has been found that the enthalpy change of H_3BO_3 is appreciably smaller than that of D_3BO_3 and H_3BO_3 seems to be thermally more stable (if any isotope effect in the thermal stability could exist) than D_3BO_3. The difference in the thermal stability may lead to the expectation that the rate of thermal dehydration of D_3BO_3 should be slightly larger than that of H_3BO_3 [1].

On the other hand, enormous kinetic deuterium isotope effects in the thermal dehydration of copper sulfate pentahydrate [2] and calcium oxalate monohydrate [3] were reported. Contrary to their results, Manche and Carroll [4,5] have reported that no significant kinetic isotope effect is apparent when the activation energies for $CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot D_2O$ are compared at the same degree of conversion. In these respects, it seems to be worthwhile to examine such a kinetic isotope effect extensively.

The present paper deals with the investigation of the kinetic deuterium isotope effect in the thermal dehydration from boric acid to metaboric acid

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by means of simultaneous TG and DSC at programmed increasing temperatures and also at constant temperatures. Since the dehydration appears to be reversible, it was examined under a flow of dry air. The kinetic isotope effect in the thermal dehydration from metaboric acid to boric oxide was not examined, because the reproducibility of TG and DSC curves was not satisfactory.

EXPERIMENTAL

Purified crystalline boric acid was ground and sieved to a size fraction of 280—350 mesh. Crystalline boric oxide B_2O_3 obtained through the thermal dehydration of boric acid in a stream of dry air was rehydrated with H_2O and D_2O vapours to give H_3BO_3 and D_3BO_3 under identical conditions. The identification of the sample was made from IR spectra as well as by thermogravimetry.

TG and DSC measurements were done simultaneously in a stream of dry air with a flow rate of 25 ml min^{-1} at a heating rate of ca. 1 K min^{-1} using a Rigaku Thermoflex TG—DSC 8085E1 type instrument. About 20 mg of sample were weighed into a platinum crucible of 5 mm diameter and 2.5 mm depth and α-alumina was used as reference material. Isothermal TG and DSC measurements for the dehydration of boric acid were also done in a stream of dry air at various temperatures.

A precision planimeter of Koizumi Sokki Seisakusho (KP-46) was used in the evaluation of fraction of reactant decomposed in the case of DSC. The transition temperature of KNO_3 at 401 K and melting points of Sn and In were used as a standard for the calibration of temperature.

RESULTS AND DISCUSSION

Isothermal method

It is generally accepted that the following kinetic equation holds for reactions of the type

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α is the fraction of reactant decomposed, t is the time, and k is the rate constant. Since the same function $f(\alpha)$ can be expected for the isothermal dehydration of H_3BO_3 and D_3BO_3, we obtain

$$\frac{d\alpha_H/dt}{d\alpha_D/dt} = \frac{k_H f(\alpha)_H}{k_D f(\alpha)_D} = \frac{k_H}{k_D} \tag{2}$$

where the subscripts H and D stand for H_3BO_3 and D_3BO_3, respectively. From eqn. (2), it can be suggested that the rate constant ratio, k_H/k_D, can

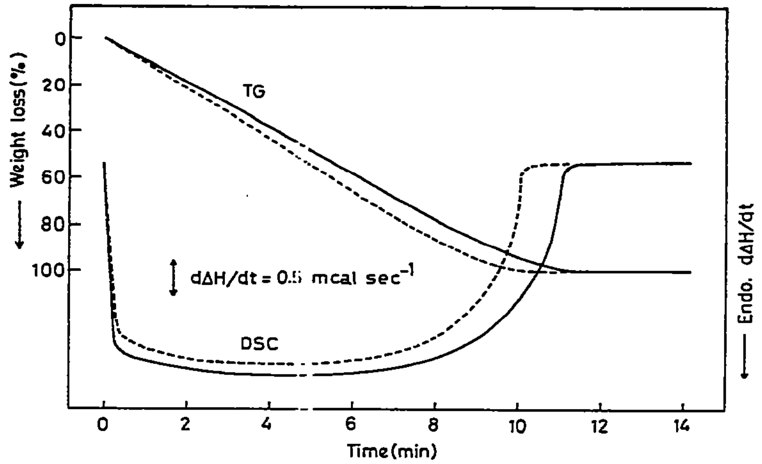

Fig. 1. Typical isothermal TG—DSC traces obtained simultaneously for the dehydration. $H_3BO_3 \rightarrow HBO_2 + H_2O$ (———) and $D_3BO_3 \rightarrow DBO_2 + D_2O$ (- - - - - -).

be obtained from the analysis of the TG or DSC curve. The typical isothermal TG—DSC traces obtained simultaneously are shown in Fig. 1. The ratios k_H/k_D obtained from the isothermal TG—DSC are listed in Tables 1 and 2.

From the fact that the ratio k_H/k_D is considerably smaller than unity, H_3BO_3 is more stable than D_3BO_3 in the light of the kinetic aspect. It is interesting to note here that such a result has been expected from the isotope effect in the thermal stability [1]. The decreasing trend of the ratio k_H/k_D with increasing α probably means that, with increasing α, the activation energy E increases and then the difference between E_H and E_D becomes larger and/or the ratio of frequency factor, A_H/A_D, becomes smaller.

Now integrating eqn. (1), we obtain

$$F(\alpha) \equiv \int \frac{d\alpha}{f(\alpha)} = kt \tag{3}$$

The function F(α) for the thermal dehydration of boric acid was determined, by plotting various theoretical functions against t, as one of Avrami—

TABLE 1

The rate constant ratio, k_H/k_D, obtained from isothermal TG for the dehydration from boric acid to metaboric acid

α	k_H/k_D	
	353.5 ± 0.2 K	359.3 ± 0.6 K
0.2	0.739	0.839
0.3	0.779	0.901
0.4	0.677	0.983
0.5	0.776	0.989
0.6	0.770	0.852
0.7	0.684	0.772
0.8	0.546	0.832

TABLE 2

The rate constant ratio, k_H/k_D, obtained from isothermal DSC for the dehydration from boric acid to metaboric acid

α	k_H/k_D	
	353.5 ± 0.2 K	359.3 ± 0.6 K
0.2	0.841	0.903
0.3	0.828	0.895
0.4	0.809	0.889
0.5	0.784	0.886
0.6	0.756	0.884
0.7	0.719	0.881
0.8	0.632	0.867

Erofeyev expressions [6,7]

$$F(\alpha) = [-\ln(1-\alpha)]^{1/2} \tag{4}$$

which means that the dehydration should obey the mechanism of random nucleation and subsequent growth. The straight line obtained by plotting expression (4) vs. t is shown in Fig. 2. The method of Sharp et al. [8] also gave the same expression for the dehydration mechanism.

Non-isothermal method

Combining eqns. (3) and (4), and differentiating, we obtain

$$\frac{d\alpha}{dt} = 2k(1-\alpha)[-\ln(1-\alpha)]^{1/2}$$

or

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad \text{and } f(\alpha) = 2(1-\alpha)[-\ln(1-\alpha)]^{1/2} \tag{5}$$

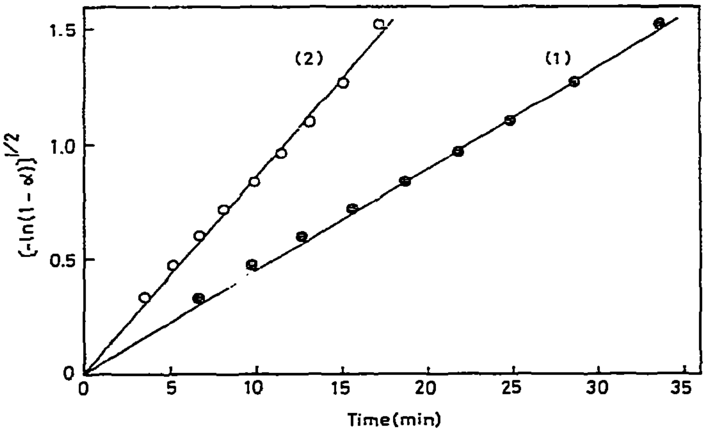

Fig. 2. Plots of $[-\ln(1-\alpha)]^{1/2}$ against time. (1) 353.3 K; (2) 358.8 K.

Now that the function $f(\alpha)$ is known, it should be reasonable to apply eqn. (5) to the non-isothermal method of Coats and Redfern [9] in order to obtain the values of E and A. Then, we obtain

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

where a is the linear heating rate. Accordingly, plots of the left-hand side of eqn. (6) vs. the reciprocal of absolute temperature should give a straight line with a slope of $-E/R$, since the first term on the right-hand side of eqn. (6) seems to be sensibly constant in a narrow range of temperature [9]. Figure 3 shows the typical plot.

Kinetic parameters obtained from the simultaneous non-isothermal TG and DSC data using a micro-computer are shown in Table 3 for the thermal dehydrations of boric acid and its deuterium analog. It is seen from Table 3 that both the activation energy and frequency factor of H_3BO_3 are slightly larger than those of D_3BO_3. The non-isothermal result seems to be compatible with the isothermal one. It is interesting that the deuterium kinetic isotope effect can be detected by means of non-isothermal TG and DSC, although our observed kinetic parameters are averaged ones over the whole range of α in a given temperature range. It can be pointed out here that rather reliable kinetic parameters should be obtained by the repetition of run, since these parameters are very sensitive to the various experimental factors such as particle size, packing of the sample, and geometry of the sample pan, and so on.

It can be concluded from Tables 1—3 that an inverse isotope effect [10] results; the rate constant of H_3BO_3 is smaller than that of D_3BO_3. Such an isotope effect suggests that the isotopic difference in zero-point energy at the transition state is larger than that of reactant. It is noted here that a normal kinetic isotope effect of deuterium was found in the thermal dehydration of calcium oxalate monohydrate [5].

The process of thermal dehydration of boric acid, which is an intramolecular removal of water from the hydrogen-bonded structure [11], is different from that of salt hydrates [4]. The intramolecular dehydration of boric acid

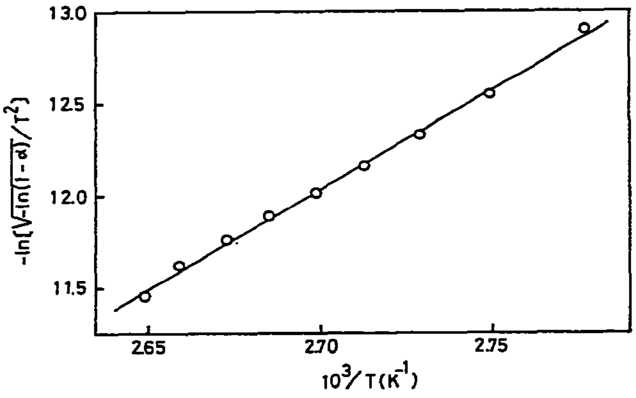

Fig. 3. A typical plot of $-\ln[\sqrt{-\ln(1-\alpha)}/T^2]$ vs. $1/T$.

TABLE 3

Kinetic parameters obtained from non-isothermal TG and DSC for the dehydration from boric acid to metaboric acid *

Method	E(kcal $mole^{-1}$)		A(s^{-1})	
	H_3BO_3	D_3BO_3	H_3BO_3	D_3BO_3
TG	23.1 ± 0.5	22.3 ± 0.5	$(2.1 \pm 1.1) \times 10^{11}$	$(1.4 \pm 0.9) \times 10^{11}$
DSC	22.7 ± 0.6	21.3 ± 0.5	$(1.3 \pm 0.5) \times 10^{11}$	$(2.0 \pm 1.1) \times 10^{10}$

* Mean of five observed values and its probable error.

is assumed to consist of bond cleavage, formation of water, diffusion of water, and the desorption of water, being accompanied by a considerable structural change of the acid [12]. The inverse isotope effect in boric acid might be related to the isotopic difference in the bond cleavage and subsequent crystallization of the product during the course of dehydration. An understanding of the situation of the transition state is required for further explanation of the isotope effect in boric acid.

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