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DEUTERIUM ISOTOPE EFFECTS IN THE THERMAL DEHYDRATION OF BORIC ACID

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ABSTRACT

The thermal dehydration of boric acid, H_3BO_3, was studied systematically by means of TG and DSC. Deuterium isotope effects in enthalpy change and dehydration temperature in the thermal dehydration stages of H_3BO_3 were examined by means of DSC. The enthalpy change of D_3BO_3 was found to be appreciably larger than that of H_3BO_3, whereas the thermal stability was little affected by deuteration. The isotopic difference in enthalpy change calculated from vibrational frequency shifts upon deuteration of H_3BO_3 was compared with the experimental value.

INTRODUCTION

A number of papers have been published on the thermal dehydration of boric acid [1—3]. It appears, however, that no systematic study on the dehydration of boric acid has been carried out. Moreover, as far as we are concerned, deuterium isotope effects on kinetic and calorimetric parameters during the dehydration of boric acid have not been reported, although those of various salt hydrates have been reported by several workers [4—7]. It seems interesting to examine such an isotope effect in boric acid in that the dehydration mechanism of boric acid is different from that of a salt hydrate.

The present paper deals with the effects of various factors and measuring conditions on the thermal dehydration process of boric acid as well as the evaluation of enthalpy changes in the dehydration by means of differential scanning calorimetry (DSC). Studies were also performed on deuterium isotope effects in the enthalpy changes and the temperatures of dehydration stages of boric acid from the analysis of DSC curves.

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EXPERIMENTAL

Reagent grade boric acid was recrystallized twice from distilled water. The crystalline sample was ground to powder in a mortar with pestle, and sieved to several size fractions: 170—200, 200—280, 280—350, and 350—400 meshes.

TG and DSC measurements were made simultaneously using a Rigaku Thermoflex TG—DSC 8085E1 type instrument in a stream of dry air. The sample was weighed into a platinum crucible of 2.5 × 5 mm diameter and α-alumina was used as reference material.

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 samples was made from IR spectra [8] taken on a Hitachi IR spectrophotometer EP1-G_2 as well as by thermogravimetry. The enthalpy changes in the thermal dehydration of H_3BO_3 and D_3BO_3 were determined from the peak area of the DSC curve. The measuring conditions were as follows: sample weight, ca. 20 mg; particle size, 280—350 meshes; heating rate, ca. 1 K min^{-1}; atmosphere, dry air at a flow rate of 25 ml min^{-1}; crucible, platinum pans of 2.5 × 5 mm diameter; and reference material, ca. 10 mg of α-alumina. The heat of transition of KNO_3 at 401 K and melting points of In and Sn were used as standards for the calibrations of enthalpy change and temperature, respectively.

RESULTS AND DISCUSSION

It is well known that boric acid is subjected to stepwise thermal dehydration

$$H_3BO_3 \rightarrow HBO_2 + H_2O \tag{1}$$

$$HBO_2 \rightarrow \tfrac{1}{2}\,B_2O_3 + \tfrac{1}{2}\,H_2O \tag{2}$$

and for the overall process

$$H_3BO_3 \rightarrow \tfrac{1}{2}\,B_2O_3 + \tfrac{3}{2}\,H_2O \tag{3}$$

The typical TG—DSC curves are shown in Fig. 1. Metaboric acid is known to have three modifications: HBO_2 (I), HBO_2 (II), and HBO_2 (III). The present metaboric acid was identified as HBO_2 (III) from IR spectra [9] and X-ray diffraction patterns [10].

Recently, it was reported that tetraboric acid was obtained during the thermal dehydration of boric acid [1]. As seen from Fig. 1, however, no stable tetraboric acid was recognized in the present study. Instead, from the TG—DSC curves, an unidentified compound seems to have resulted at about 400 K. The composition of the compound may be formulated tentatively as $H_{10}B_{12}O_{23}$ from TG analysis. To confirm the composition, further investigation is required.

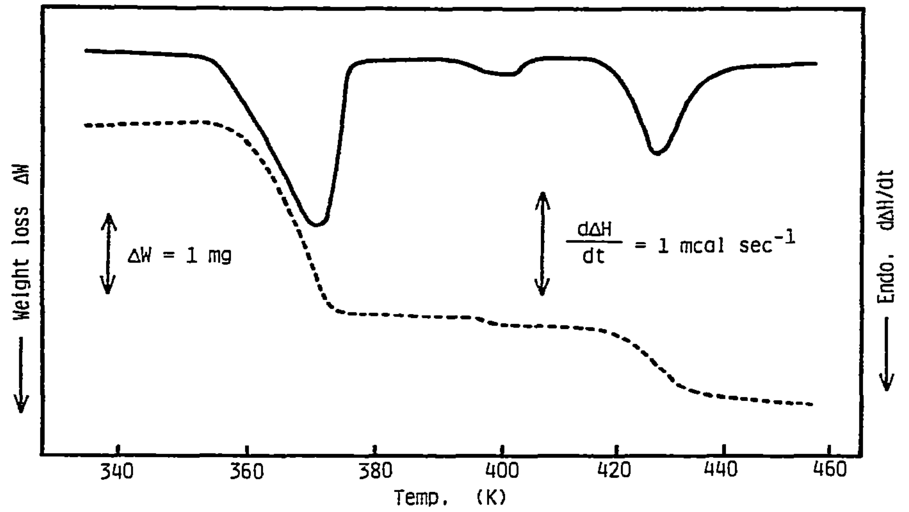

Fig. 1. Typical TG (broken line) and DSC (solid line) curves for the thermal dehydration of boric acid.

Boric oxide obtained in the thermal dehydration was not vitreous but well crystalline, since the water vapour from the product was effectively removed with a sufficient flow of dry air [11]. The particle size of the sample and sample weight were not so effective on the TG—DSC curves in the range 170—400 meshes and 5—20 mg, respectively, under the conditions; heating rate, 1 K min^{-1}; atmosphere, dry air at a flow rate of 25 ml min^{-1}. The heating rate, however, proved to be effective on the dehydration temperature of boric acid, as shown in Table 1.

It should be noted that the thermal dehydration of boric acid can be affected greatly by various measuring conditions such as heating rate and atmosphere. The enthalpy changes in the dehydration stages of boric acid, ΔH_1, ΔH_2, and ΔH_3 in eqns. (1), (2), and (3), respectively, which were determined from the DSC peak area are listed in Table 2. It is seen from Table 2 that the observed value of ΔH_3 is in good agreement with that calcu-

TABLE 1

The effect of heating rate on the dehydration temperature of boric acid

Heating rate (K min^{-1})	Dehydration temperature (K) [a]		
	A	B	C
1.0	349.8	352.8	368.8
1.9	350.7	358.8	376.1
3.9	352.4	360.2	384.2
7.8	354.9	368.2	395.0

[a] A, B, and C correspond to the temperature where the DSC curve departs from the base line and the temperature where the base line intersects with the tangent of maximum slope of peak, and the peak temperature, respectively.

TABLE 2

Enthalpy changes in the thermal dehydration of H_3BO_3

	Enthalphy change (kcal mole^{-1})		
	ΔH_1	ΔH_2	ΔH_3
Obsd. [a]	15.0 ± 0.3	7.5 ± 0.6	22.5 ± 0.3
Calcd. [b]	13.40	9.10	22.50

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

[b] Calculated from standard heats of formation ΔH_f^0 at 25°C. ΔH_f^0 values adopted were −260.2 [12], −189.02 [13],−302.0 [12], and −57.80 [13] kcal mole^{-1} for H_3BO_3, HBO_2(III), B_2O_3(c), and H_2O(g), respectively.

lated, whereas the agreements in ΔH_1 and ΔH_2 are not so good. The cause of deviation is equivocal at the moment.

Deuterium isotope effects in the enthalpy changes during the thermal dehydration of boric acid are given in Table 3. It can be seen that the enthalpy change of D_3BO_3 is larger than that of H_3BO_3, although the isotopic difference in ΔH_2 is ambiguous.

It is interesting to calculate the isotope effect in ΔH_3 from vibrational frequencies [14] and compare the value with that observed. The enthalpy difference between a protium compound and its deuterium analogue, δH, is given by the equation [14]

$$\delta H = RT\sum^{n}\left\{\frac{u'}{\exp(u')-1}+\frac{u'}{2}\right\} - RT\sum^{n}\left\{\frac{u}{\exp(u)-1}+\frac{u}{2}\right\} \qquad (4)$$

and

$u = hc\omega/kT$

where R is the gas constant, T is the absolute temperature, n is the number of fundamental vibrations affected by deuteration, h is Planck's constant, c

TABLE 3

The isotope effect in enthalpy changes for the dehydration of boric acid

	Enthalpy change (kcal mole^{-1})		
	ΔH_1	ΔH_2	ΔH_3
Deuterium [a]	15.7 ± 0.3	7.7 ± 0.6	22.5 ± 0.3
Protium	15.0 ± 0.3	7.5 ± 0.6	23.5 ± 0.3
Difference ($\delta\Delta H_i$) [b]	0.7 ± 0.4	0.2 ± 0.9	1.0 ± 0.4

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

[b] The difference between the enthalpy change of the protium compound and that of the deuterium analogue.

TABLE 4

The calculated values of δH(kcal mole^{-1}) for H_3BO_3 and H_2O, and their difference

Temp. (K)	$\delta H(H_3BO_3)$	$\delta H(H_2O)$ [a]	$\delta H(H_3BO_3) - \delta H(H_2O)$
298	4.62	3.38	1.24
355 [b]	4.52	3.37	1.15
417 [b]	4.42	3.35	1.07

[a] Calculated using vibrational frequencies of water vapour in ref. 15.

[b] The temperatures where the base line intersects with the tangent of maximum slope of the first and second peak in Fig. 1, respectively.

is the velocity of light, w is the fundamental vibrational frequencies, and the prime refers to the deuterium analogue.

The calculated values of δH for boric acid and water vapour, together with their differences, are given in Table 4. It was assumed in the calculation that the internal vibration is a harmonic oscillation and that the frequency is invariable in a temperature range of 298—417 K. For the internal vibration of boric acid, the value given in Table 5 is used. Contributions from the librational and translational modes are neglected, assuming that a planar molecule of boric acid belongs to the symmetry point group C_{3h}.

It is evident that the quantity $\delta H(H_3BO_3) - \delta H(H_2O)$ refers to the isotopic difference in enthalpy change in the dehydration of boric acid, $\delta\Delta H_3$. If we adopt the values 1.15 and 1.07 at 355 and 417 K, respectively, in Table 4 for $\delta H(H_3BO_3) - \delta H(H_2O)$, and 22.5 for ΔH_3 in Table 2, the calculated enthalpy change for the deuterium analogue, $\Delta H_3'$ is in the range 23.57—23.65 kcal mole^{-1}. The calculated value is in fair agreement with that ob-

TABLE 5

Fundamental vibrational frequencies, ω, of boric acid [a]

Assignment	Symmetry type	ω (cm^{-1})	
		H_3BO_3	D_3BO_3
OH stretch	A'	3250	(2466)
BO stretch	A'	1060	(1057)
BOH bending	A'	881	(686)
BO_3 bending	A''	648	541
OH torsion	A''	824	709
OH stretch	E'	3150	2390
BO stretch	E'	1428	1424
OBO bending	E'	544	504
BOH bending	E'	1183	921
OH torsion	E''	209	(180)

[a] Taken from ref. 16 and the values in parentheses are estimated assuming that the ratios ω'/ω are equal to those which belong to the same assignment.

TABLE 6

Dehydration temperatures for boric acid and its deuterium analogue

	Dehydration temperature (K) [a]	
	Boric acid → Metaboric acid	Metaboric acid → Boric oxide
Protium [b]	354.9 ± 0.7	417.0 ± 0.7
Deuterium [b]	354.0 ± 1.0	416.2 ± 0.5

[a] The temperature where the base line intersects with the tangent of maximum slope of the DSC peak.

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

served. Accordingly, we can assume that the value of $\delta \Delta H_3$ is at least ca. 1.0 kcal mole^{-1}.

It is quite interesting to notice that the magnitude of $\delta \Delta H_3$ is large in comparison with that of salt hydrates [5]. The isotope effect, $\delta \Delta H_3$, during the dehydration of boric acid is assumed to originate from the bond cleavage and subsequent vaporization of water. From the literature [17], the contribution from the latter may be estimated as ca. 0.2 kcal mole^{-1} in the dehydration temperature range 355—417 K. The deuterium isotope effect in bond cleavage of boric acid during the thermal dehydration should thus amount to about 0.8 kcal mole^{-1}. It can be concluded that D_3BO_3 should be more stable than H_3BO_3 in the light of enthalpy change.

Calculations of the isotope effects, $\delta \Delta H_1$ and $\delta \Delta H_2$, could not be done owing to a lack of available data of vibrational frequencies for metaboric acid, HBO_2 (III).

Detection of the deuterium isotope effect in the dehydration temperature of boric acid from the DSC curve has been tried and the result is shown in Table 6. As is expected from the limit of accuracy of the DSC temperature, the isotopic difference proved to be difficult to detect. However, it is interesting to notice that the result might suggest that the thermal stabilities of H_3BO_3 and HBO_2 (III) are slightly higher than those of D_3BO_3 and DBO_2 (III). This can be related to the assumption that the rate of thermal dehydration of D_3BO_3 should be larger than that of H_3BO_3. Deuterium isotope effects in the rate of thermal dehydration of boric acid will be reported elsewhere.

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