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Short communication

Thermochemistry of hexamethylenetetramine pentaborate

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Abstract

The crystalline hexamethylenetetramine pentaborate $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ has been prepared and identified by XRD, FT-IR, DTA-TG, elemental analysis and chemical analysis. The molar enthalpy of solution of $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ in $(HCl\cdot 54.554H_2O)$ and of $(CH_2)_6N_4$ in $(HCl + H_3BO_3)(aq)$ were determined. With the incorporation of the enthalpies of solution of H_3BO_3 in HCl(aq), and the standard molar enthalpies of formation of $(CH_2)_6N_4(s)$, $H_3BO_3(s)$, and $H_2O(l)$, the standard molar enthalpy of formation of $-(4042.7 \pm 4.1)\ \mathrm{kJ\,mol^{-1}}$ of $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ was obtained.

Keywords: $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$; Standard molar enthalpy of formation; Solution calorimetry

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1. Introduction

Boron exists as polyborate anions composed of BO_3 and BO_4 groups and can form a large variety of compounds because of the complexity of the structures involved. Batsanov et al. [1] synthesized a hexamethylenetetramine pentaborate $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ by reaction of boric acid and hexamethylenetetramine. As part of the continuing study [2] of the thermochemistry of organic borates, this paper reports the thermochemistry of $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$.

2. Experimental

2.1. Preparation of $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ sample

$[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ was prepared by the literature [1] method. To a solution of 2.66 g $(CH_2)_6N_4$ in 10 cm^3 of water was added 1.23 g of boric acid. The mixture was heated to 353 K and maintained with stirring for 1 h, cooled to room temperature. The crystalline solid was separated, washed thoroughly with ethanol and diethyl ether, and finally, dried at 313 K to constant mass. The sample was identified by X-ray powder diffraction (recorded on a Rigaku D/MAX-ШC with Cu target at 8° min^{-1}), FT-IR (determined on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature) and simultaneous DTA-TG (determined on a Universal V4.1D TA Thermal Analyzer at a heating rate of 10 K min^{-1} in flowing air). The chemical composition was determined by C, H, N elemental analysis and B by titration with NaOH standard solution in the presence of mannitol.

HCl(aq) (1 mol dm^{-3}) was prepared from analytical grade hydrochloric acid and deionized water, and its concentration, 0.9996 mol dm^{-3}, determined by titration with standard sodium carbonate. The density, 1.018 g cm^{-3}, was taken from [3].

2.2. Calorimetric experiment

$[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ can be regarded as the product of the following reaction:

$$(CH_2)_6N_4(s) + 5H_3BO_3(s) \rightarrow [(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O](s) + 4.5H_2O(l)$$

HCl(aq) (1 mol dm^{-3}) rapidly dissolves all components of the reaction. The thermochemical cycle is given in Table 1. Applying Hess's law, $\Delta_r H_m^o(5)$ is calculated according to the following expression:

$$\Delta_r H_m^o(5) = \Delta_r H_m^o(1) + \Delta_r H_m^o(2) - \Delta_r H_m^o(3) - \Delta_r H_m^o(4)$$

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Table 1
Thermochemical cycle for the derivation of $\Delta_f H_m^o$ ([$(CH_2)_6N_4H$][$B_5O_6(OH)_4$]·$0.5H_2O$, 298.15 K)

	Reaction	$\Delta_r H_m^o$ (kJ mol^{-1})
$\Delta_r H_m^o(1)$	$5H_3BO_3$(s)+ 93.435 ($HCl\cdot54.506H_2O$) = 5 H_3BO_3(aq) + 93.435 ($HCl\cdot54.506H_2O$)	109.2 ± 0.4
$\Delta_r H_m^o(2)$	$(CH_2)_6N_4$(s) + 5 H_3BO_3(aq) + 93.435 ($HCl\cdot54.506H_2O$) = $(CH_2)_6N_4H^+Cl^-$(aq) + $5H_3BO_3$(aq) + 92.435 ($HCl\cdot55.096H_2O$)	−22.86 ± 0.16
$\Delta_r H_m^o(3)$	93.435 ($HCl\cdot54.506H_2O$) + $4.5H_2O$ (l) = 93.435 ($HCl\cdot54.554H_2O$)	−0.09 ± 0.01
$\Delta_r H_m^o(4)$	[$(CH_2)_6N_4H$][$B_5O_6(OH)_4$]·$0.5H_2O$(s) + 93.435 ($HCl\cdot54.554H_2O$) = $(CH_2)_6N_4H^+Cl^-$(aq) + $5H_3BO_3$(aq) + 92.435 ($HCl\cdot55.096H_2O$)	65.40 ± 0.35
$\Delta_r H_m^o(5)$	$5H_3BO_3$(s) + $(CH_2)_6N_4$(s) = [$(CH_2)_6N_4H$][$B_5O_6(OH)_4$]·$0.5H_2O$(s)+$4.5H_2O$(l)	21.0 ± 0.6

The molar enthalpy of formation of [$(CH_2)_6N_4H$][$B_5O_6(OH)_4$]·$0.5H_2O$ is obtained from the value of $\Delta_r H_m^o(5)$ in combination with the molar enthalpies of formation of H_3BO_3(s), $(CH_2)_6N_4$(s), and H_2O(l).

The RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) has been described in detail previously [4,5]. The temperature of the calorimetric experiment was 298.15 K. Total time required for the complete reaction was about 0.5 h. No solid residues were observed after the reactions.

3. Results and discussion

3.1. Identification of synthetic sample

Anal. calc. for [$(CH_2)_6N_4H$][$B_5O_6(OH)_4$]·$0.5H_2O$: C, 19.57%; H, 4.93%; N, 15.21%; B, 14.68%. Found: C, 19.96%; H, 4.74%; N, 15.65%; B, 14.30%.

Fig. 1 shows the powder XRD pattern of synthetic sample. The characteristic d values of the synthetic sample are 0.9420, 0.7468, 0.6197, 0.5726, 0.5329, 0.4721, 0.4599, 0.3883, 0.3785, 0.3671, 0.3584, 0.2972, 0.2776 nm. No peaks from H_3BO_3 or $(CH_2)_6N_4$ were observed.

The FT-IR spectrum absorptions of synthetic sample are assigned as follows: the band at 3259 cm^{-1} is the O–H stretching mode. The strong bands at 1413, 909 cm^{-1} and 1009, 777 cm^{-1} are in agreement with the existence of BO_3 and BO_4 group, respectively. The strong band at 529 cm^{-1} is the characteristic peak of the pentaborate anion, [$B_5O_6(OH)_4$]$^-$.

Simultaneous DTA-TG curves (Fig. 2) of synthetic sample indicate that there exist a total weight loss 52.80% from 50 to 950 °C. The total residue of 47.20% corresponds to the mass of $2.5B_2O_3$ with a calculated value of 47.25%. In the DTA curve, there are two peaks. The first endothermic peak appearing at 237.50 °C is related to the dehydration of crystal water and OH groups. The exothermic peak at 390.38 °C is related to the oxygenolysis of $(CH_2)_6N_4$.

3.2. Results of calorimetric experiment

The measured molar enthalpy of solution of 3.00 mg $(CH_2)_6N_4$ in 2.00 cm^3 of [$HCl\cdot54.506H_2O$ and 6.62 mg H_3BO_3] at 298.15 K was −(22.86 ± 0.16) kJ mol^{-1} ($n = 5$, uncertainty is twice the standard deviation of the mean). The molar enthalpy of solution of 7.88 mg [$(CH_2)_6N_4H$][$B_5O_6(OH)_4$]·$0.5H_2O$ in

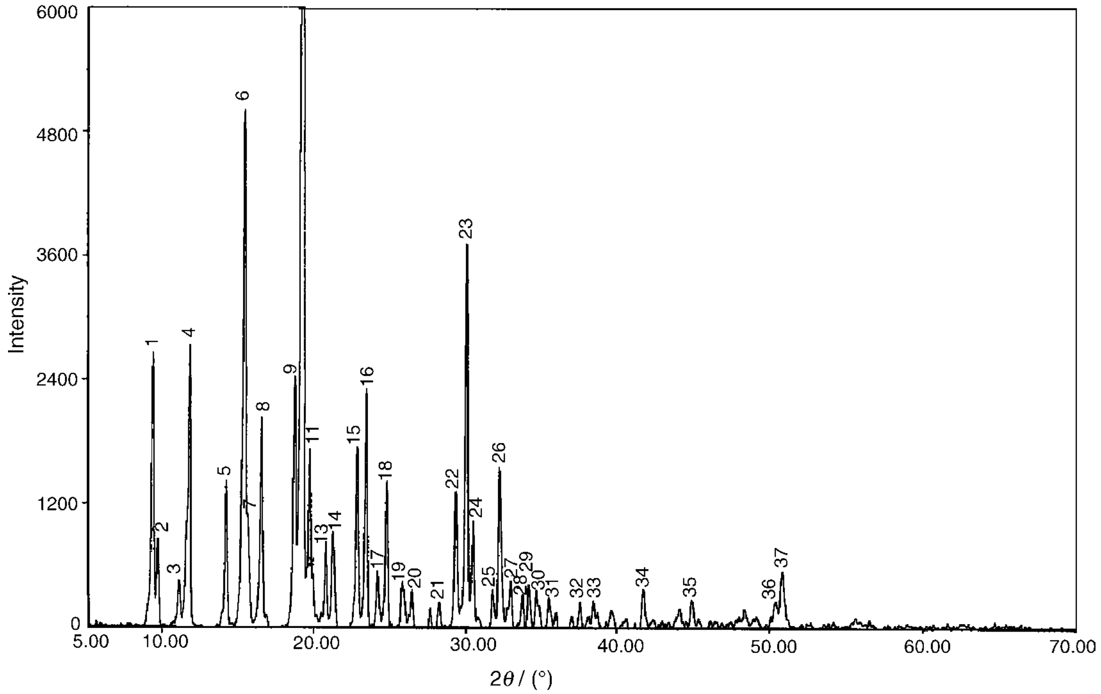

Fig. 1. XRD patterns of the synthetic sample.

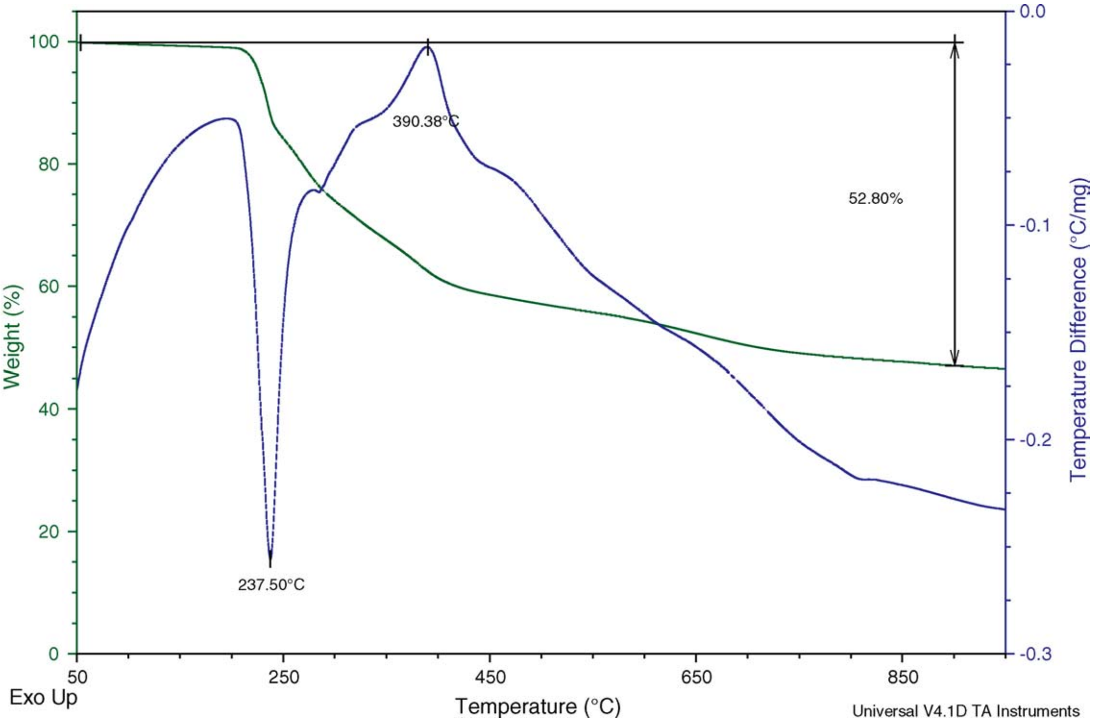

Fig. 2. Simultaneous DTA-TG curves of synthetic sample.

2.00 cm^3 of ($HCl\cdot 54.554H_2O$) at 298.15 K was (65.40 ± 0.35) kJ mol^{-1} ($n = 5$, uncertainty is twice the standard deviation of the mean).

Table 1 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$. The molar enthalpy of solution of H_3BO_3(s) of (21.83 ± 0.08) kJ mol^{-1} in $HCl\cdot 54.506H_2O$ was taken from [6]. The enthalpy of dilution of HCl(aq) was calculated from the NBS tables [7]. The molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values [8], namely $-(1094.8 \pm 0.8)$ and $-(285.830 \pm 0.040)$ kJ mol^{-1}. The molar enthalpy of formation of $(CH_2)_6N_4$(s) was taken from [9], namely (124.06 ± 0.75) kJ mol^{-1}. From these data, the standard molar enthalpy of formation of $[(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O$ was calculated to be $-(4042.7 \pm 4.1)$ kJ mol^{-1}.

The $\Delta_f H_m^o$ of $(CH_2)_6N_4H^+$(aq) can be estimated by a group contribution method [10], which can be expressed in following equation:

$$\begin{aligned}&\Delta_f H_m^o([(CH_2)_6N_4H][B_5O_6(OH)_4]\cdot 0.5H_2O, s)\\&\quad = \Delta_f H_m^o((CH_2)_6N_4H^+, aq)\\&\qquad + \Delta_f H_m{}^o([B_5O_6(OH)_4]^-, aq) + 0.5\Delta_f H_m^o(H_2O, l)\end{aligned}$$

in which the $\Delta_f H_m^o$ of -3989.97 kJ mol^{-1} of $[B_5O_6(OH)_4]^-$(aq) and the $\Delta_f H_m^o$ of -285.83 kJ mol^{-1} of H_2O(l) were taken from the literature [10]. Using this scheme, the standard molar enthalpy of formation of ($(CH_2)_6N_4H^+$, aq) is 90.2 kJ mol^{-1}.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2005.08.021.

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