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Short communication

Synthesis and thermochemistry of $SrB_2O_4{\cdot}2.5H_2O$ and $SrB_6O_{10}{\cdot}5H_2O$

Hong-Sheng Huang, Zhi-Hong Liu *

School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, PR China

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Abstract

Two strontium hydrated borates, $SrB_2O_4{\cdot}2.5H_2O$ and $SrB_6O_{10}{\cdot}5H_2O$, have been synthesized and characterized by XRD, FT-IR, DTA-TG and chemical analysis. The molar enthalpies of solution of $SrB_2O_4{\cdot}2.5H_2O$ and $SrB_6O_{10}{\cdot}5H_2O$ in 1 mol dm^{-3} HCl(aq) were measured to be $-(7.02 \pm 0.21)$ and 51.92 ± 0.29 kJ mol^{-1}, respectively. With the incorporation of the enthalpy of solution of H_3BO_3 in 1 mol dm^{-3} HCl(aq), the enthalpy of solution of $Sr(OH)_2{\cdot}8H_2O$ in $(HCl + H_3BO_3)$(aq) and the standard molar enthalpies of formation of $Sr(OH)_2{\cdot}8H_2O$(s), H_3BO_3(s) and H_2O(l), the standard molar enthalpies of formation of $SrB_2O_4{\cdot}2.5H_2O$ and $SrB_6O_{10}{\cdot}5H_2O$ were calculated to be $-(2827.2 \pm 1.7)$ and $-(6177.6 \pm 4.9)$ kJ mol^{-1}, respectively.

Keywords: Strontium borates; Synthesis; Solution calorimetry

1. Introduction

We have already determined the standard molar enthalpies of formation of $SrB_2O_4{\cdot}4H_2O$, SrB_2O_4 and $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ by the method of solution calorimetry [1,2]. As part of the continuing study of the thermochemistry of the strontium borates, this paper reports the determination of standard molar enthalpies of formation of two strontium hydrated borates, $SrB_2O_4{\cdot}2.5H_2O$ and $SrB_6O_{10}{\cdot}5H_2O$.

2. Experimental

2.1. Preparation of $SrB_2O_4{\cdot}2.5H_2O$ and $SrB_6O_{10}{\cdot}5H_2O$ samples

All reagents used in the synthesis were analytic grade (made in Xi'an Chemical Factory, China). The new strontium borate, $SrB_2O_4{\cdot}2.5H_2O$, was prepared by the following procedure: a mixture of 1.30 g of $Sr(OH)_2{\cdot}8H_2O$, 2.45 g of H_3BO_3 and 30 cm^3 of H_2O was sealed in a Teflon-lined bomb and heated at 443 K for 5 days, and then cooled to room temperature. The resulting solid phase was separated, washed thoroughly with hot distilled water, alcohol and ether, respectively, and then dried at room temperature until the mass was constant. $SrB_6O_{10}{\cdot}5H_2O$ was prepared by the following procedure: 3.71 g of H_3BO_3 was added to a solution of 1.33 g of $Sr(OH)_2{\cdot}8H_2O$ in 40 ml of water; the mixture was put into the flask and was refluxed at the boiling point. After 10 h, the mixture was stirred at room temperature for 12 h. The resulting solid phase was separated and washed thoroughly with hot distilled water, and then with alcohol and ether, finally, dried at room temperature until the mass was constant. These two synthetic samples were characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target ($\lambda = 1.54178$ Å) at 8° min^{-1}), FT-IR spectroscopy (Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature) and TG–DTA (TA-SDT Q600 simultaneous thermal analyzer at a heating rate of 10 K min^{-1} in flowing N_2). The chemical compositions of the samples were determined by EDTA titration for Sr^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3 and by difference for H_2O.

2.2. Calorimetric experiment

The RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail

* Corresponding author.
E-mail address: liuzh@snnu.edu.cn (Z.-H. Liu).

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Table 1
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($SrB_2O_4 \cdot 2.5H_2O$, 298.15 K)

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$2H_3BO_3(s) + 94.252(HCl \cdot 54.506H_2O) = 2H_3BO_3(aq) + 94.252(HCl \cdot 54.506H_2O)$	43.66 ± 0.16
2	$Sr(OH)_2 \cdot 8H_2O(s) + 2H_3BO_3(aq) + 94.252(HCl \cdot 54.506H_2O) = SrCl_2(aq) + 2H_3BO_3(aq) + 92.252(HCl \cdot 55.796H_2O)$	−51.69 ± 0.15
3	$94.252(HCl \cdot 54.506H_2O) + 9.5H_2O(l) = 94.252(HCl \cdot 54.607H_2O)$	−0.19 ± 0.01
4	$SrB_2O_4 \cdot 2.5H_2O(s) + 94.252(HCl \cdot 54.607H_2O) = SrCl_2(aq) + 2H_3BO_3(aq) + 92.252(HCl \cdot 55.796H_2O)$	−7.02 ± 0.21
5	$Sr(OH)_2 \cdot 8H_2O(s) + 2H_3BO_3(s) = SrB_2O_4 \cdot 2.5H_2O(s) + 9.5H_2O(l)$	−0.82 ± 0.30

$\Delta_f H_m^\circ$ ($SrB_2O_4 \cdot 2.5H_2O$, s) = $\Delta_r H_m^\circ$ (5) + $\Delta_f H_m^\circ$ ($Sr(OH)_2 \cdot 8H_2O$, s) + 2$\Delta_f H_m^\circ$ (H_3BO_3, s) −9.5$\Delta_f H_m^\circ$ (H_2O, l). Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($SrB_6O_{10} \cdot 5H_2O$, 298.15 K)

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$6H_3BO_3(s) + 141.193(HCl \cdot 54.506H_2O) = 6H_3BO_3(aq) + 141.193(HCl \cdot 54.506H_2O)$	130.98 ± 0.48
2	$Sr(OH)_2 \cdot 8H_2O(s) + 6H_3BO_3(aq) + 141.193(HCl \cdot 54.506H_2O) = SrCl_2(aq) + 6H_3BO_3(aq) + 139.193(HCl \cdot 55.361H_2O)$	–51.69 ± 0.15
3	$141.193(HCl \cdot 54.506H_2O) + 13H_2O(l) = 141.193(HCl \cdot 54.598H_2O)$	–0.26 ± 0.01
4	$SrB_6O_{10} \cdot 5H_2O(s) + 141.193(HCl \cdot 54.598H_2O) = SrCl_2(aq) + 6H_3BO_3(aq) + 139.193(HCl \cdot 55.361H_2O)$	51.92 ± 0.29
5	$Sr(OH)_2 \cdot 8H_2O(s) + 6H_3BO_3(s) = SrB_6O_{10} \cdot 5H_2O(s) + 13H_2O(l)$	27.63 ± 0.58

$\Delta_f H_m^\circ$ ($SrB_6O_{10} \cdot 5H_2O$, s) = $\Delta_r H_m^\circ$ (5) + $\Delta_f H_m^\circ$ ($Sr(OH)_2 \cdot 8H_2O$, s) + 6$\Delta_f H_m^\circ$ (H_3BO_3, s) −13$\Delta_f H_m^\circ$ (H_2O, l). Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

previously [3]. Calorimetric experiments were performed five times at 298.15 K as previously described [1].

3. Results and discussion

3.1. Characterization of the synthetic samples

The chemical analytical data of $SrB_2O_4 \cdot 2.5H_2O$ are (calcd/found, %), SrO (45.52/45.24), B_2O_3 (33.87/33.93), H_2O (20.61/20.83). The chemical analytical data of $SrB_6O_{10} \cdot 5H_2O$ are (calcd /found, %), SrO (25.74/25.45), B_2O_3 (51.88/51.72), H_2O (22.38/22.83).

The XRD patterns of the synthetic samples of $SrB_2O_4 \cdot 2.5H_2O$ and $SrB_6O_{10} \cdot 5H_2O$ are given in Figs. S1 and S2 in Supplementary data files. All the diffraction peaks of the synthetic sample of $SrB_6O_{10} \cdot 5H_2O$ can be exactly indexed with those of JCPDS cards (File No.16-0495) and shows absence of other crystalline forms in the synthetic sample.

The FT-IR spectra of these two samples are given in Figs. S3 and S4 in supplementary data files.

The simultaneous TG–DTA curves of $SrB_2O_4 \cdot 2.5H_2O$ (Fig. S5 in Supplementary data files) indicate that the total weight loss is 20.13% from 303 to 1273 K, which corresponds to the loss of 2.5 water molecules and is near to the calculated value of 20.63%. The simultaneous TG–DTA curves of $SrB_6O_{10} \cdot 5H_2O$ (Fig. S6 in Supplementary data files) indicate that the total weight loss is 22.46% from 303 to 873 K, which corresponds to the loss of five water molecules and agrees with the calculated value of 22.38%.

All the above results indicate that the two synthetic samples are pure compounds and suitable for calorimetric measurements.

3.2. Results of calorimetric experiment

The molar enthalpies of solution of $SrB_2O_4 \cdot 2.5H_2O$ and $SrB_6O_{10} \cdot 5H_2O$ in HCl(aq) at 298.15 K are -7.02 ± 0.21 kJ mol^{-1} ($n = 5$) and 51.92 ± 0.29 kJ mol^{-1} ($n = 5$), respectively (Tables S1 and S2 in Supplementary data files). The uncertainty is estimated as twice the standard deviation of the mean.

Tables 1 and 2 give the thermochemical cycles for the derivation of the standard molar enthalpies of formation of $SrB_2O_4 \cdot 2.5H_2O$ and $SrB_6O_{10} \cdot 5H_2O$. The molar enthalpy of solution of H_3BO_3(s) of (21.83 ± 0.08) kJ mol^{-1} in 1 mol dm^{-3} HCl(aq) was taken from [4]. The enthalpy of dilution of HCl(aq) was calculated from NBS tables [5]. The molar enthalpy of solution of $Sr(OH)_2 \cdot 8H_2O$(s) of $-(51.69 \pm 0.15)$ kJ mol^{-1} in aqueous [1 mol dm^{-3} HCl(aq) + H_3BO_3(aq)] was taken from our previous work [1]. The standard molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values [6], namely $-(1094.8 \pm 0.8)$ and $-(285.830 \pm 0.040)$ kJ mol^{-1}, respectively. The standard molar enthalpy of formation of $Sr(OH)_2 \cdot 8H_2O$(s) of $-(3352.2 \pm 0.04)$ kJ mol^{-1} was taken from the NBS tables [5]. From these data, the standard molar enthalpies of formation of $SrB_2O_4 \cdot 2.5H_2O$ and $SrB_6O_{10} \cdot 5H_2O$ were calculated to be $-(2827.2 \pm 1.7)$ kJ mol^{-1} and $-(6177.6 \pm 4.9)$ kJ mol^{-1}, respectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.07.010.

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