Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 470 (2008) 113–114
thermochimica acta
www.elsevier.com/locate/tca

Short communication

Synthesis and enthalpy of formation of $SrB_4O_7{\cdot}3H_2O$

Yi-Hong Gao, Hong-Sheng Huang, Zhi-Hong Liu *

Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, PR China

Received 20 January 2008; received in revised form 17 February 2008; accepted 19 February 2008
Available online 23 February 2008

Abstract

Hydrated strontium borate, $SrB_4O_7{\cdot}3H_2O$, has been synthesized and characterized by XRD, FT-IR, DTA-TG and chemical analysis. The molar enthalpy of solution of $SrB_4O_7{\cdot}3H_2O$ in 1 mol dm^{-3} HCl(aq) was measured to be (21.15 ± 0.29) kJ mol^{-1}. With incorporation of the previously determined enthalpies of solution of $Sr(OH)_2{\cdot}8H_2O$(s) in [HCl(aq) + H_3BO_3(aq)] and H_3BO_3 in HCl(aq), and the enthalpies of formation of H_2O(l), $Sr(OH)_2{\cdot}8H_2O$(s) and H_3BO_3(s), the enthalpy of formation of $SrB_4O_7{\cdot}3H_2O$ was found to be $-(4286.7 \pm 3.3)$ kJ mol^{-1}.

Keywords: Strontium borates; Standard molar enthalpy of formation; Solution calorimetry

1. Introduction

We have determined the enthalpies of formation of strontium borates $SrB_2O_4{\cdot}4H_2O$, SrB_2O_4, and $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ by solution calorimetry [1,2]. As part of the continuing study of the thermochemistry of the strontium borates, this paper reports the synthesis and determination of the enthalpy of formation of a new hydrated strontium borate $SrB_4O_7{\cdot}3H_2O$, which is the precursor of the luminescent material SrB_4O_7 [3].

2. Experimental

2.1. Synthesis and characterization of $SrB_4O_7{\cdot}3H_2O$

All reagents used in the synthesis were of analytic grade (made in Xi'an Chemical Factory, China). 0.54 g of $Sr(OH)_2{\cdot}8H_2O$ (98.0%), 0.62 g of H_3BO_3 (99.5%) and 30 ml of H_2O were put into a small autoclave (40 ml), and placed in an oven at 373 K. The autoclave was cooled naturally and opened after 7 days. The solid phase was separated, washed thoroughly with hot distilled water, and then with alcohol and ether. Finally, the solid phase was dried at room temperature to constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target 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 composition of the sample was 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

Thermochemical reaction designed for the derivation of $\Delta_r H_m^\circ$ of $SrB_4O_7{\cdot}3H_2O$ is

$$Sr(OH)_2{\cdot}8H_2O(s) + 4H_3BO_3(s) = SrB_4O_7{\cdot}3H_2O(s) + 12H_2O(l) \quad (I)$$

The 1 mol dm^{-3} HCl(aq) solvent rapidly dissolves all components of reaction (I).

The designed thermochemical cycle is given in Table 1. The molar enthalpies of solution of H_3BO_3(s) in 1 mol dm^{-3} HCl(aq), $Sr(OH)_2{\cdot}8H_2O$(s) in (hydrochloric acid + boric acid) aqueous solution which consisted of 1 mol dm^{-3} HCl(aq) and the calculated amount of H_3BO_3(s), and the $SrB_4O_7{\cdot}3H_2O$(s) in 1 mol dm^{-3} HCl(aq) were measured, namely $\Delta_r H_m^\circ$ (1), $\Delta_r H_m^\circ$ (2), $\Delta_r H_m^\circ$ (4), respectively. In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be maintained, with the objective that the

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

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.02.014

Table 1
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($SrB_4O_7{\cdot}3H_2O$, 298.15 K)[a]

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})	References
1	$4H_3BO_3(s) + 107.924(HCl{\cdot}54.506H_2O) = 4H_3BO_3(aq) + 107.924(HCl{\cdot}54.506H_2O)$	87.32 ± 0.32	[5]
2	$Sr(OH)_2{\cdot}8H_2O(s) + 4H_3BO_3(aq) + 107.924(HCl{\cdot}54.506H_2O) = SrCl_2(aq) + 4H_3BO_3(aq) + 105.924(HCl{\cdot}55.629H_2O)$	−51.69 ± 0.15	[1]
3	$107.924(HCl{\cdot}54.506H_2O) + 12H_2O(l) = 107.924(HCl{\cdot}54.617H_2O)$	−0.24 ± 0.01	[6]
4	$SrB_4O_7{\cdot}3H_2O(s) + 107.924(HCl{\cdot}54.617H_2O) = SrCl_2(aq) + 4H_3BO_3(aq) + 105.924(HCl{\cdot}55.629H_2O)$	21.15 ± 0.29	This work
5	$Sr(OH)_2{\cdot}8H_2O(s) + 4H_3BO_3(s) = SrB_4O_7{\cdot}3H_2O(s) + 12H_2O(l)$	14.72 ± 0.46[b]	

[a] $\Delta_f H_m^\circ(SrB_4O_7 \cdot 3H_2O, s) = \Delta_r H_m^\circ(5) + \Delta_f H_m^\circ(Sr(OH)_2 \cdot 8H_2O, s) + 4\Delta_f H_m^\circ(H_3BO_3, s) - 12\Delta_f H_m^\circ(H_2O, l)$.
[b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

dissolution of the reactants gives the same composition as those of the products. Applying Hess's law, the enthalpy of reaction (5) ($\Delta_r H_m^\circ(5)$) can be calculated according to the following expression:

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

where $\Delta_r H_m^\circ(3)$ is the enthalpy of dilution of HCl(aq).

The enthalpy of formation of $SrB_4O_7{\cdot}3H_2O$ can be obtained from the value of $\Delta_r H_m^\circ(5)$ in combination with the molar enthalpies of formation of H_3BO_3(s), $Sr(OH)_2{\cdot}8H_2O$(s), and H_2O(l).

The RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously [4]. Calorimetric experiment was performed five times at 298.15 K as previously described [1].

3. Results and discussion

3.1. Characterization of the synthetic sample

The chemical analytical data of $SrB_4O_7{\cdot}3H_2O$ are (calcd/found, %), SrO (34.90/34.98), B_2O_3 (46.90/46.67), H_2O (18.20/18.35).

The XRD pattern of synthetic sample is given in Fig. S1 in Supplementary data files. The characteristic *d* values are 0.7029, 0.6622, 0.6243, 0.5152, 0.4771, 0.4548, 0.3940, 0.3877, 0.3604, 0.3550, 0.3485, 0.3173, 0.3112, 0.3050, 0.2897, 0.2962, 0.2897, 0.2845, 0.2702, 0.2624, 0.2569, 0.2508, 0.2481, 0.2390, 0.2324, 0.2265, 0.2212, 0.2148, 0.2125, 0.2105, 0.2077, 0.2055, 0.2032, 0.1989, 0.1949, 0.1933 and 0.1899 nm. No peaks from H_3BO_3 or $Sr(OH)_2{\cdot}8H_2O$ were observed.

FT-IR spectrum is given in Fig. S2 in Supplementary data files.

The simultaneous TG-DTA curves of synthetic sample (Fig. S3 in Supplementary data files) indicate that the total mass loss is 18.48% from 303 to 1273 K, which corresponds to the loss of 3 water molecules with the calculated value of 18.20%.

3.2. Results of calorimetric experiment

The enthalpy of solution of $SrB_4O_7{\cdot}3H_2O$ in HCl(aq) at 298.15 K is (21.15 ± 0.29) kJ mol^{-1} where the uncertainty is estimated as twice the standard deviation of the mean with $n = 5$.

Table 1 gives the thermochemical cycles used for the derivation of the standard molar enthalpy of formation of $SrB_4O_7{\cdot}3H_2O$. The enthalpy of formation of $Sr(OH)_2{\cdot}8H_2O$(s) of −3352.2 kJ mol^{-1} was taken from the NBS tables [6]. The enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values [7], namely −(1094.8 ± 0.8) and −(285.830 ± 0.040) kJ mol^{-1}, respectively. From these data, the standard molar enthalpy of formation of $SrB_4O_7{\cdot}3H_2O$ was calculated to be −(4286.7 ± 3.3) 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.2008.02.014.

References

[1] Z.H. Liu, H.S. Huang, Thermochim. Acta 448 (2006) 59.
[2] Z.H. Liu, H.S. Huang, Thermochim. Acta 459 (2007) 130.
[3] F. Pan, G.Q. Shen, R. Wang, X.Q. Wang, D.Z. Shen, J. Cryst. Growth 241 (2002) 108.
[4] M. Ji, M.Y. Liu, Sh.L. Gao, Q.Zh. Shi, Instrum. Sci. Technol. 29 (1) (2001) 53.
[5] J. Li, Sh.Y. Gao, Sh.P. Xia, B. Li, R.Z. Hu, J. Chem. Thermodyn. 29 (1997) 491.
[6] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Chumey, R.L. Nuttall, The NBS tables of chemical thermodynamic properties, J. Phys. Chem. Ref. Data 11 (Suppl. 2) (1982).
[7] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.