J. Chem. Thermodynamics 97 (2016) 179–182

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermochemical properties for a series of transition metal borates of $M[B_{12}O_{14}(OH)_{10}]$ (M^{II} = Mn, Zn, Fe, Co, Ni)

Pan Liang, Jie Wang, Zhi-Hong Liu *

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

ARTICLE INFO

Article history:
Received 26 December 2015
Received in revised form 23 January 2016
Accepted 30 January 2016

Keywords:
Transition metal borates
Standard molar enthalpy of formation
Solution calorimetry
A group contribution method

ABSTRACT

A pure zinc borate, $Zn[B_{12}O_{14}(OH)_{10}]$, has been synthesized and characterized by XRD, FT-IR, simultaneous TG-DTA techniques, and chemical analysis. The molar enthalpy of solution of $Zn[B_{12}O_{14}(OH)_{10}]$ (s) in 1 mol·dm^{-3} HCl(aq) was measured by microcalorimeter at T = 298.15 K. The molar enthalpy of solution of ZnO(s) in the mixture solvent of 2.00 cm^3 of 1 mol·dm^{-3} HCl(aq) and calculated amount of H_3BO_3 was also measured. With the incorporation of the previously determined enthalpy of solution of H_3BO_3(s) in 1 mol·dm^{-3} HCl(aq), together with the use of the standard molar enthalpies of formation for ZnO(s), H_3BO_3(s), and H_2O(l), the standard molar enthalpy of formation of $-(9646.6 \pm 9.6)$ kJ·mol^{-1} at T = 298.15 K was obtained on the basis of an appropriate thermochemical cycle. In addition, the molar enthalpy of formation of -9492.7 kJ·mol^{-1} for $[B_{12}O_{14}(OH)_{10}]^{2-}$ has also been estimated by a group contribution method, which has been used to predict the $\Delta_f H^0_m$ of a series of transition metal borates of M$[B_{12}O_{14}(OH)_{10}]$ (M^{II} = Mn, Zn, Fe, Co, Ni). These estimated data have been used to further compare the stability of this series of transition metal borates.

1. Introduction

Borate materials have attracted a great deal of attention in the past decades owing to their structural chemistry and potential applications in mineralogy, luminescence, nonlinear optics and industrial importance [1–5]. Transition metal borates are potentially important, which may display catalytic activities, and various magnetic behaviors, such as $M[B_{12}O_{14}(OH)_{10}]$ (M^{II} = Mn, Zn, Fe, Co, Ni) [6].

Thermodynamic properties play very important roles in scientific research and industrial applications. Thermochemical data can provide information on stabilities and reactivities of molecules that are used, and also are a key factor in the safe and successful scale-up of chemical processes in the chemical industry. Our group has reported the determination of standard molar enthalpies of formation of a few transition metal zinc borates by using a heat conduction microcalorimeter, such as $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$, $3ZnO{\cdot}5B_2O_3{\cdot}14H_2O$, $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ [7–9].

As part of the continuing study of this work, this paper reports the determination of standard molar enthalpy of formation of $ZnB_{12}O_{14}(OH)_{10}$ by solution calorimetry, and the estimation of the standard molar enthalpies of formation for this series of transition metal borates for $M[B_{12}O_{14}(OH)_{10}]$ (M^{II} = Mn, Zn, Fe, Co, Ni) by a group contribution method on the basis of this measured result.

2. Experimental

2.1. Synthesis and characterization of $Zn[B_{12}O_{14}(OH)_{10}]$ sample

All reagents used in the synthesis were commercially available with analytic grade and used without further purification. Table 1 summarizes relevant information on sample material purities.

In a typical synthesis, 0.22 g of $Zn(NO_3)_2{\cdot}6H_2O$ and 0.618 g of H_3BO_3 were added in 25 cm^3 of Teflon-lined stainless steel vessels, stirred and heated at T = 493 K for about 5 days, then cooled to room temperature. The resulting white solid powder was washed with hot distilled water (T = 343 K) in order to remove the redundant boric acid, and dried in air at ambient temperature.

The sample obtained was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu target at 8°·min^{-1}), FT-IR spectroscopy recorded over the (400 to 4000) cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellet at room temperature, and TG-DTA (TA-SDT Q600 simultaneous thermal analyser under a N_2 atmosphere with a heating rate of T = 10 K·min^{-1}). The chemical compositions of the sample

* Corresponding author. Tel.: +86 29 81530805; fax: +86 29 81530727.
E-mail address: liuzh@snnu.edu.cn (Z.-H. Liu).

http://dx.doi.org/10.1016/j.jct.2016.01.024
0021-9614/

TABLE 1
Provenance and mass fraction purity of the chemical reagents used in this study.

Chemical name	Source	State	Mass fraction purity[a]
ZnO	Xian Chemical Reagent Factory	Solid	⩾0.995
H_3BO_3	Xian Chemical Reagent Factory	Solid	⩾0.990
$Zn(NO_3)_2{\cdot}6H_2O$	Sinopharm Chemical Reagent Co., Ltd	Solid	⩾0.990
KCl	Aladdin	Solid	⩾0.9999
HCl	Sinopharm Chemical Reagent Co., Ltd	Aqueous	0.38[b]
$ZnB_{12}O_{14}(OH)_{10}$	Synthesized	Solid	0.993[c]

[a] Stated purity from the commercial supplier.
[b] Concentration of HCl aqueous solution.
[c] Evaluated by averaging based on the measured contents of B_2O_3 and ZnO.

were determined by EDTA titration for Zn^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the mass loss in the TG curve for H_2O.

2.2. Calorimetric experiment

The thermochemical cycle designed for the derivation of the molar enthalpy formation of $ZnB_{12}O_{14}(OH)_{10}$ is shown in figure 1. The 1 mol·dm^{-3} HCl(aq) solvent can dissolve all components of the virtual reaction (5), and its concentration, (1.0004 ± 0.0001) mol·dm^{-3}, was determined by titration with standard sodium carbonate. With the use of its density of 1.019 g·cm^{-3} (taken from chemical handbook [10]), its concentration can also be expressed as the form of $HCl{\cdot}54.561H_2O$.

The molar enthalpy of solution of $ZnB_{12}O_{14}(OH)_{10}$ in 1 mol·dm^{-3} HCl(aq) was measured. The molar enthalpy of solution of ZnO(s) in the mixture of 1 mol·dm^{-3} HCl(aq) and calculated amount of H_3BO_3(s) was also measured. In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be observed, *viz.*, 0.58 mg of ZnO(s) and 4.20 mg of $ZnB_{12}O_{14}(OH)_{10}$ (s) samples were calculated respectively when the mass of sample H_3BO_3 was used as 5.30 mg in literature [11] according to the stoichiometry of reaction (5) in figure 1, with the objective that the dissolution of the reactants give the same composition as those of the products.

Applying Hess's law, $\Delta_r H^\theta_m$ (5) can be calculated according to the following expression:

$$\Delta_r H^\theta_m(5) = \Delta_r H^\theta_m(1) + \Delta_r H^\theta_m(2) - \Delta_r H^\theta_m(3) - \Delta_r H^\theta_m(4).$$

The standard molar enthalpy of formation of $ZnB_{12}O_{14}(OH)_{10}$ can be obtained by the values of $\Delta_r H^\theta_m$ (5) in combination with the standard molar enthalpies of formation of ZnO(s), H_3BO_3(s) and H_2O(l).

All the enthalpies of solution were measured with a RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China), which has been described in detail previously [12]. Calorimetric experiments were performed five times at T = 298.15 K. The total time required for the complete dissolution reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ⩾0.9999) in deionized water was determined to be (17.54 ± 0.10) kJ·mol^{-1}, which is in agreement with that of (17.524 ± 0.028) kJ·mol^{-1} reported in the literature [13]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

3. Results and discussion

3.1. Characterization of the synthetic sample

Figure 2 shows the powder XRD pattern of as-synthesized sample and the simulated patterns (obtained by a software of Diamond Crystal and Molecular Structure Visualization) on the basis of single-crystal structure of $Zn[B_{12}O_{14}(OH)_{10}]$. The diffraction peaks on patterns corresponded well in position, indicating the phase purity of the as-synthesized sample.

The FT-IR spectrum of synthetic sample (figure 3) exhibited the following absorption bands and they were assigned referring to the literature [14]. The band at 3342 cm^{-1} is the stretching of O–H. The band at 2506 cm^{-1} is the O–H stretching because of hydrogen bond. The band at 1241 cm^{-1} might be the in-plane bending of B–O–H. The bands at (1380 and 972) cm^{-1} are the asymmetric and symmetric stretching of B(3)–O, respectively. The bands at (1096, 1041, and 854) cm^{-1} are the asymmetric and symmetric stretching of B(4)–O, respectively. The bands at (750 and 620) cm^{-1} are the out-of-plane bending mode of B(3)–O. The band at 461 cm^{-1} is the bending of B(4)–O.

The simultaneous TG-DTA curves of the synthesized sample are shown in figure 4. It can be seen that the total weight loss is 15.22% from T = (473 to 873) K, which corresponds to the continuous loss of 5 water molecules and can be compared with calculated value of 15.29%. In the DTA curve, the endothermic peaks appearing at T = (637 and 707) K are related to the dehydration and formation of the amorphous phase $ZnO{\cdot}6B_2O_3$, which might re-crystallize at T = 912 K.

The chemical analytical data of synthetic sample are (calcd/found,%), ZnO (13.81/13.67), B_2O_3 (70.90/70.64), and H_2O (15.29/15.22), which are consistent with the theoretical values. The mass fraction purity of sample $Zn[B_{12}O_{14}(OH)_{10}]$ is evaluated as 0.993 by averaging based on the measured contents of B_2O_3 and ZnO.

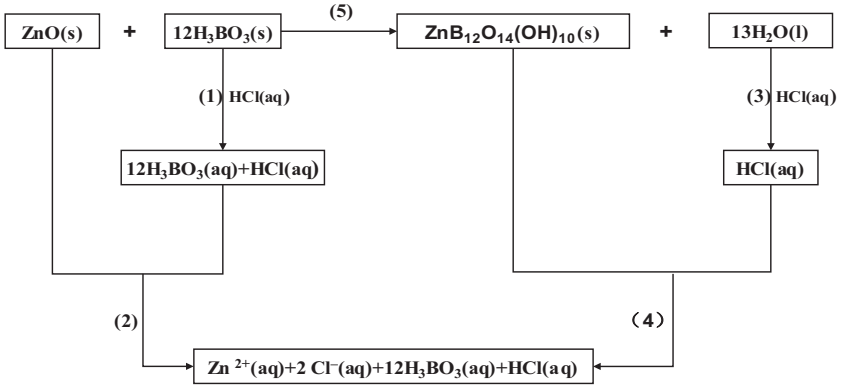

FIGURE 1. The designed thermochemical cycle of $ZnB_{12}O_{14}(OH)_{10}$.