Standard Molar Enthalpies of Formation for the Two Alkali Metal Borates $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2[B_7O_9(OH)_5]$

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Two new hydrated alkali borates, $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$, have been synthesized under mild hydrothermal conditions and characterized by X-ray diffraction, infrared spectra, thermogravimetric analysis, differential thermal analysis, and chemical analysis. The enthalpies of solution of $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ in 1 $mol\cdot dm^{-3}$ HCl(aq) were measured to be $-(7.53 \pm 0.25)$ $kJ\cdot mol^{-1}$ and (64.38 ± 0.15) $kJ\cdot mol^{-1}$. With the incorporation of the previously determined enthalpies of solution of H_3BO_3(s) in 1 $mol\cdot dm^{-3}$ HCl(aq) and of $LiCl\cdot H_2O$(s) and CsCl(s) in (HCl + H_3BO_3) aqueous solution, together with the standard molar enthalpies of formation of $LiCl\cdot H_2O$(s), CsCl(s), H_3BO_3(s), HCl(aq), and H_2O(l), the standard molar enthalpies of formation were found to be $-(15943 \pm 13)$ $kJ\cdot mol^{-1}$ for $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $-(6099 \pm 6)$ $kJ\cdot mol^{-1}$ for $Cs_2B_7O_9(OH)_5$ by solution calorimetry.

Introduction

Boron exists as polyborate anions composed of BO_3 and BO_4 groups. Borate compounds have considerable mineralogical and industrial importance. In recent years, studies of alkali borates have attracted much interest because some of these compounds show interesting physical properties, such as nonlinear optical behavior for $CsLiB_6O_{10}$, CsB_3O_5, and $KB_5O_8\cdot 4H_2O$. Thermodynamic properties play very important roles in scientific research and industrial applications. The standard molar enthalpies of formation of some hydrated lithium borates and hydrated cesium borates have been reported, such as $Li_2B_4O_7\cdot 4H_2O$,[1] $LiB_5O_8\cdot 5H_2O$,[1] $LiBO_2\cdot 2H_2O$,[2] $LiBO_2\cdot 8H_2O$,[2] $CsB_5O_8\cdot 4H_2O$,[3] and $Cs_2[B_4O_5(OH)_4]\cdot 3H_2O$.[4] Recently, we obtained two new alkali borates, $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$, and reported their single crystal structures.[5,6] As part of the continuing study of the thermochemistry of hydrated alkali borates, this paper reports the determination of the standard molar enthalpies of formation of these two alkali borates using a heat conduction microcalorimeter.

Experimental Section

Reagents. Cs_2CO_3 (mass fraction $\geq$ 0.9990), $LiOH\cdot H_2O$ (mass fraction $\geq$ 0.9950), H_3BO_3 (mass fraction $\geq$ 0.9980), hydrochloric acid (mass fraction $\geq$ 0.3800), and KCl (mass fraction $\geq$ 0.9999) were produced by Xi'an Chemical Factory, China.

Synthesis and Characterization of Samples. $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ single crystal samples were taken from our previous work.[5,6] The samples were further characterized by chemical analysis, thermogravimetric analysis (TGA), and differential thermal analysis (DTA) (performed on an SDT Q600 simultaneous thermal analyzer under an N_2 atmosphere with a heating rate of 10 $K\cdot min^{-1}$). The B_2O_3 content was determined by NaOH titration in the presence of mannitol. The H_2O content was determined by the mass loss in the TG curve.

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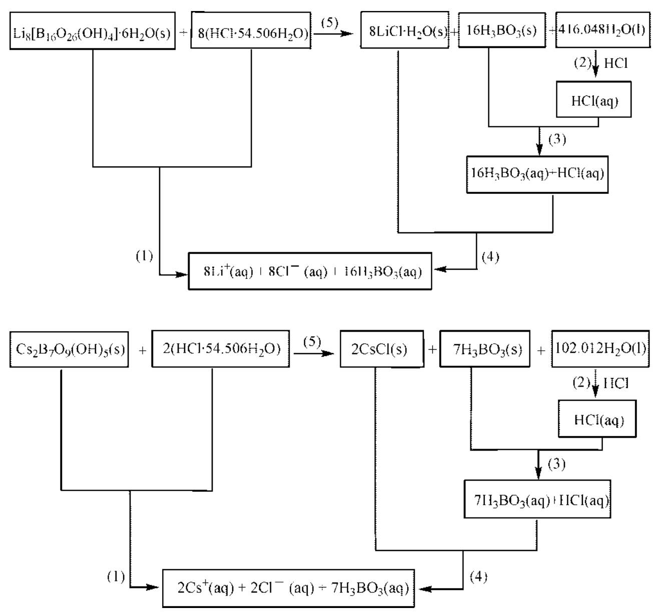

Figure 1. Designed thermochemical cycles.

Calorimetric Experiment. The thermochemical cycles designed for the derivation of the $\Delta_f H_m^o$ of $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ are shown in Figure 1.

The 1 $mol\cdot dm^{-3}$ HCl(aq) solvent can dissolve all components of the designed reaction (5), and its concentration of 0.9996 $mol\cdot dm^{-3}$ was determined by titration with standard sodium carbonate. The standard molar enthalpies of formation of $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ were obtained by solution calorimetry in combination with the standard molar enthalpies of formation of $LiCl\cdot H_2O$(s), CsCl(s), H_3BO_3(s), HCl(aq), and H_2O(l).

The RD496−III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously.[7,8] To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction $\geq$

10.1021/je800612j CCC: $40.75
Published on Web 02/02/2009

Table 1. Molar Enthalpies of Solution of $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ in 1 mol·dm^{-3} HCl(aq) at 298.15 K[a]

no.	m/mg	$\Delta_r H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
	$Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$		
1	4.96	−183.183	−7.742
2	5.14	−215.987	−7.827
3	5.09	−177.970	−7.173
4	5.08	−184.720	−7.564
5	5.00	−178.594	−7.328
Mean			−7.53 ± 0.25[b]
	$Cs_2B_7O_9(OH)_5$		
1	6.58	745.077	64.604
2	6.57	739.345	64.204
3	6.51	732.680	64.212
4	6.58	743.460	64.463
5	6.54	738.209	64.400
Mean			64.38 ± 0.15[b]

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used. [b] Uncertainty is estimated as twice the standard deviation of the mean, namely, $\delta = 2\sqrt{\sum(x_i-\bar{x})^2/n(n-1)}$, in which n is the number of experimentals ($n = 5$); x_i is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value.

0.9999) in deionized water was determined to be (17.31 ± 0.20) kJ·mol^{-1}, which is in agreement with that of 17.234 kJ·mol^{-1} reported in the literature.[9] This shows that the device used for measuring the enthalpy of solution in this work is reliable.

Calorimetric experiments were performed five times at 298.15 K as previously described.[8] No solid residues were observed after the reactions.

Results and Discussion

Characterization of the Synthetic Samples. The chemical analytical data of the synthetic samples are (found/calcd, %) B_2O_3 (67.40/67.87), H_2O (17.76/17.55) for $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and B_2O_3 (42.56/42.71), H_2O (8.24/7.89) for $Cs_2B_7O_9(OH)_5$. The chemical analytical results are consistent with the theoretical values.

The thermal behaviors of the $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ samples are given in the previous paper.[5,6] The TG curve for $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ showed that it had a three-step mass loss between (35 and 785) °C, and the total mass loss was 17.76 %, which corresponded to the loss of eight water molecules and could be compared with the calculated value of 17.55 %. The TG curve for $Cs_2B_7O_9(OH)_5$ showed that it had a one-step mass loss between (160 and 650) °C, and the total mass loss was 8.24 %, which corresponded to the loss of 2.5 water molecules due to the condensation of five hydroxyl groups and could be compared with the calculated value of 7.89 %.

As stated above, the synthetic single crystal samples are pure and suitable for the calorimetric experiments.

Results of Calorimetric Experiment. The molar enthalpies of solution of $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ in 1 mol·dm^{-3} HCl(aq) at 298.15 K are listed in Table 1, in which m is the mass of the sample; $\Delta_{sol}H_m$ is the molar enthalpy of solution of the solute; and the uncertainty is estimated as twice the standard deviation of the mean.

Tables 2 and 3 give the thermochemical cycles for the derivation of the standard molar enthalpies of formation of $Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$, respectively. 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 the literature.[10] The molar enthalpy of solution of $LiCl\cdot H_2O$(s) of −(14.36 ± 0.11) kJ·mol^{-1} in (1 mol·dm^{-3} HCl + H_3BO_3)(aq) was taken from the literature.[1] The molar enthalpy of solution of CsCl(s) of (16.14 ± 0.14) kJ·mol^{-1} in (1 mol·dm^{-3} HCl + H_3BO_3)(aq) was also taken from the literature.[3] The standard molar enthalpies of formation of $LiCl\cdot H_2O$(s) and CsCl(s) were taken from the NBS tables,[11] namely, −(712.58 ± 0.36) kJ·mol^{-1} and −(443.04 ± 0.08) kJ·mol^{-1}. The standard molar enthalpy of formation of HCl(aq) and the enthalpy of dilution

Table 2. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^o$ ($Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O$, 298.15 K)

no.	reaction	$\Delta_r H_m^o$/(kJ·mol^{-1})
(1)	$Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O(s) + 81.15(HCl\cdot 54.506H_2O) = 8Li^+(aq) + 8Cl^-(aq) + 16H_3BO_3(aq) + 73.15(HCl\cdot 60.303H_2O)$	−7.53 ± 0.25
(2)	$73.15(HCl\cdot 60.194H_2O) = 73.15(HCl\cdot 54.506H_2O) + 416.048H_2O(l)$	7.61 ± 0.35
(3)	$16H_3BO_3(aq) + 73.15(HCl\cdot 60.194H_2O) = 16H_3BO_3(s) + 73.15(HCl\cdot 60.194H_2O)$	−349.28 ± 1.28
(4)	$8Li^+(aq) + 8Cl^-(aq) + 16H_3BO_3(aq) + 73.15(HCl\cdot 60.303H_2O) = 8LiCl\cdot H_2O\ (s) + 16H_3BO_3(aq) + 73.15(HCl\cdot 60.194H_2O)$	114.88 ± 0.88
(5)	$4H_2(g) + 4Cl_2(g) + 436.048H_2O(l) = 8(HCl\cdot 54.506H_2O)$	−1323.64 ± 0.64
(6)	$8LiCl\cdot H_2O(s) = 8Li(s) + 4Cl_2(g) + 8H_2(g) + 4O_2(g)$	5700.64 ± 2.88
(7)	$16H_3BO_3(s) = 16B(s) + 24H_2(g) + 24O_2(g)$	17516.8 ± 12.8
(8)	$20H_2(g) + 10O_2(g) = 20H_2O(l)$	−5716.60 ± 0.80
(9)	$Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O\ (s) = 8Li(s) + 16B(s) + 8H_2(g) + 18O_2(g)$	15943 ± 13[a]

[a] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

Table 3. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^o$ ($Cs_2B_7O_9(OH)_5$, 298.15 K)

no.	reaction	$\Delta_r H_m^o$/(kJ·mol^{-1})
(1)	$Cs_2B_7O_9(OH)_5(s) + 173.98(HCl\cdot 54.506H_2O) = 2Cs^+(aq) + 2Cl^-(aq) + 7H_3BO_3(aq) + 171.98\ (HCl\cdot 55.099H_2O)$	64.38 ± 0.15
(2)	$171.98\ (HCl\cdot 55.099H_2O) = 171.98\ (HCl\cdot 54.506H_2O) + 102.012H_2O(l)$	2.06 ± 0.08
(3)	$7H_3BO_3(aq) + 171.98\ (HCl\cdot 55.099H_2O) = 7H_3BO_3(s) + 171.98(HCl\cdot 55.099H_2O)$	−152.81 ± 0.56
(4)	$2Cs^+(aq) + 2Cl^-(aq) + 7H_3BO_3(aq) + 171.98(HCl\cdot 55.099H_2O) = 2CsCl(s) + 7H_3BO_3(aq) + 171.98(HCl\cdot 55.099H_2O)$	−32.52 ± 0.28
(5)	$H_2(g) + Cl_2(g) + 109.012\ H_2O(l) = 2(HCl\cdot 54.506H_2O)$	−330.91 ± 0.20
(6)	$2CsCl(s) = 2Cs(s) + Cl_2(g)$	886.08 ± 0.16
(7)	$7H_3BO_3(s) = 7B(s) + (21/2)H_2(g) + (21/2)O_2(g)$	7663.6 ± 5.6
(8)	$7H_2(g) + (7/2)O_2(g) = 7H_2O(l)$	−2000.81 ± 0.28
(9)	$Cs_2B_7O_9(OH)_5(s) = 2Cs(s) + 7B(s) + (5/2)H_2(g) + 7O_2(g)$	6099 ± 6[a]

[a] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

of HCl(aq) were calculated from the NBS tables.[11] The standard molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values,[12] namely, $-(1094.8 \pm 0.8)$ and $-(285.830 \pm 0.040)$ $kJ \cdot mol^{-1}$, respectively. From these data, the standard molar enthalpies of formation of $Li_8[B_{16}O_{26}(OH)_4] \cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ were calculated to be $-(15943 \pm 13)$ $kJ \cdot mol^{-1}$ and $-(6099 \pm 6)$ $kJ \cdot mol^{-1}$, respectively.

Estimation of the Thermodynamic Properties by a Group Contribution Method. The standard molar enthalpies of formation of $[B_{16}O_{26}(OH)_4]^{8-}$ and $[B_7O_9(OH)_5]^{2-}$ can be estimated by a group contribution method,[13] which is expressed in the following equation

$$\Delta_f H_m^o(Li_8[B_{16}O_{26}(OH)_4] \cdot 6H_2O, s) = 8\Delta_f H_m^o(Li^+, aq) + \Delta_f H_m^o([B_{16}O_{26}(OH)_4]^{8-}, aq) + 6\Delta_f H_m^o(H_2O, l)$$

$$\Delta_f H_m^o(Cs_2B_7O_9(OH)_5, s) = 2\Delta_f H_m^o(Cs^+, aq) + \Delta_f H_m^o([B_7O_9(OH)_5]^{2-}, aq)$$

The $\Delta_f H_m^o$ of structural H_2O is -290.42 $kJ \cdot mol^{-1}$, which was taken from the literature.[13] The $\Delta_f H_m^o$ of Li^+ and Cs^+ are -278.48 $kJ \cdot mol^{-1}$ and -258.28 $kJ \cdot mol^{-1}$, respectively, which were taken from the NBS tables.[11] Using this scheme, the standard molar enthalpies of formation of $[B_{16}O_{26}(OH)_4]^{8-}$ and $[B_7O_9(OH)_5]^{2-}$ are $-11\,973$ $kJ \cdot mol^{-1}$ and -5582 $kJ \cdot mol^{-1}$, respectively. Using these data, we can predict the standard molar enthalpies of formation of other hydrated borates containing $[B_{16}O_{26}(OH)_4]^{8-}$ and $[B_7O_9(OH)_5]^{2-}$ polyborate anions by a group contribution method.[13]

Conclusions

Through an appropriate thermochemical cycle, the standard molar enthalpies of formation of $Li_8[B_{16}O_{26}(OH)_4] \cdot 6H_2O$ and $Cs_2B_7O_9(OH)_5$ have been obtained from measured enthalpies of solution, together with the standard molar enthalpies of formation of $LiCl \cdot H_2O$(s), CsCl(s), H_3BO_3(s), HCl(aq), and H_2O(l).

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Received for review August 4, 2008. Accepted January 8, 2009. Project supported by the National Natural Science Foundation of China (No. 20871078) and the Natural Science Foundation of Shaanxi Province of China (No. SJ08B01).

JE800612J