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Short communication

Thermochemistry of triimidazolium nonaborate

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Abstract

The crystalline triimidazolium nonaborate $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ has been prepared and identified by XRD, TG, elemental analysis and chemical analysis. The molar enthalpy of solution of $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ in 0.9996 mol dm^{-3} HCl(aq) and of imidazole 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 $C_3H_4N_2$(s), H_3BO_3(s), and H_2O(l), the standard molar enthalpy of formation of -7116 ± 7 kJ mol^{-1} of $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ was obtained.

Keywords: $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$; Standard molar enthalpy of formation; Solution calorimetry

1. Introduction

Borate compounds have considerable mineralogical and industrial importance. Boron exists as polyborate anions composed of BO_3 and BO_4 groups. The crystallized solid phase is effected by many factors. Some organic borates can be synthesized by the reaction between boric acid and an organic base. For example, Schubert et al. synthesized a nonaborate $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ by the reaction between boric acid and imidazole [1]. They reported the synthesis and structural characterization of this borate. This paper reports the determination of standard molar enthalpy of formation of $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$.

2. Experimental

2.1. Preparation of $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ sample

$[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ was prepared by the literature [1] method. To a solution of 1.3490 g imidazole in 10 cm^3 of water at 313 K was added 3.7162 g of boric acid. The mixture was heated to 363 K and maintained with stirring for 1 h, and cooled to room temperature. The crystalline solid was separated, washed thoroughly with ethanol and diethyl ether, and finally, dried at 333 K to constant mass. The crystal structure was identified by X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at 8° min^{-1}) and TG (Perkin-Elmer TGA7 at a heating rate of 10 K min^{-1} in flowing N_2). The chemical composition was determined by C, H, N elemental analysis and B by titration with NaOH standard solution in the presence of mannitol [2]. One molar HCl(aq) 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

$[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ can be regarded as the product of reaction (1):

$$3C_3H_4N_2(s) + 9H_3BO_3(s) \rightarrow [C_3H_5N_2]_3[B_9O_{12}(OH)_6](s) + 9H_2O(l) \quad (1)$$

One molar HCl(aq) rapidly dissolves all components of reaction (1). The thermochemical cycle is given in Table 1.

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Table 1
Thermochemical cycle for the derivation of $\Delta_f H_m^\circ$ ($[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$, 298.15 K)

	Reaction	$\Delta_r H_m^\circ$(kJ mol^{-1})
$\Delta_r H_m^\circ(1)$	$9H_3BO_3(s) + 159.132(HCl{\cdot}54.506H_2O) = 9H_3BO_3(aq) + 159.132(HCl{\cdot}54.506H_2O)$	196.5 ± 0.7
$\Delta_r H_m^\circ(2)$	$3C_3H_4N_2(s) + 9H_3BO_3(aq) + 159.132(HCl{\cdot}54.506H_2O) = 3C_3H_5N_2Cl(aq) + 9H_3BO_3(aq) + 156.132\ (HCl{\cdot}55.553H_2O)$	−80.1 ± 0.7
$\Delta_r H_m^\circ(3)$	$159.132(HCl{\cdot}54.506H_2O) + 9H_2O(l) = 159.132\ (HCl{\cdot}54.562H_2O)$	−0.18 ± 0.01
$\Delta_r H_m^\circ(4)$	$[C_3H_5N_2]_3[B_9O_{12}(OH)_6](s) + 159.132(HCl{\cdot}54.562H_2O) = 3C_3H_5N_2Cl(aq) + 9H_3BO_3(aq) + 156.132\ (HCl{\cdot}55.553H_2O)$	101.5 ± 0.2
$\Delta_r H_m^\circ(5)$	$9H_3BO_3(s) + 3C_3H_4N_2(s) = [C_3H_5N_2]_3[B_9O_{12}(OH)_6](s) + 9H_2O(l)$	15 ± 1

Strict control of the stoichiometries in each step of the cycle must be obeyed, with the objective that dissolution of the reactants give the same composition as those of the products. Applying Hess's law, $\Delta_r H_m^\circ(5)$ is calculated according to the following expression:

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

The molar enthalpy of formation of $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ is obtained from the value of $\Delta_r H_m^\circ(5)$ in combination with the molar enthalpies of formation of $H_3BO_3(s)$, $C_3H_4N_2(s)$, 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.

To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ≥0.9999) in deionized water and of THAM (trishydroxymethylaminomethane) in 0.1 mol dm^{-3} HCl(aq) were made. The average values 17.31 ± 0.20 kJ mol^{-1} of $\Delta_r H_m^\circ$ of KCl(s) and -29.75 ± 0.04 kJ mol^{-1} of THAM agree with the 17.241 ± 0.018 kJ mol^{-1} [6] and -29.73 ± 0.04 kJ mol^{-1}[7] reported in the literature.

3. Results and discussion

3.1. Identification of synthetic sample

Calc. for $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ as mass fraction: C, 0.1806; H, 0.0353; N, 0.1404; B, 0.1625. Found: C, 0.1794; H, 0.0334; N, 0.1366; B, 0.1650.

Fig. 1 shows the powder XRD pattern of synthetic sample and the simulated pattern on the basis of single-crystal structure of $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ [1]. The diffraction peaks in both patterns correspond well, indicating the phase purity of synthetic sample. The characteristic d values of the XRD pattern of synthetic sample are 0.6095, 0.5786, 0.3186, 0.2914, 0.2244, 0.2089, 0.2077, 0.1593 nm. No peaks from H_3BO_3 or $C_3H_4N_2$ were observed.

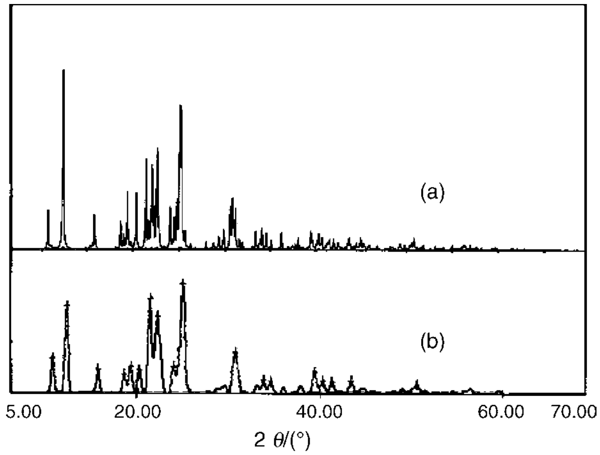

Fig. 1. XRD patterns of the synthetic samples (a) simulated and (b) experimental.

The TG–DTG curve (Fig. 2) of the synthetic sample shows two weight loss stages between 323 and 970 K. The first weight loss, from 323 to 515 K, is 17.76%. The second weight loss, from 515 to 970 K, is 27.71%. The total residue of 54.58% corresponds to the mass of $4.5B_2O_3$ with a calculated value of 52.34%.

3.2. Results of calorimetric experiment

The measured molar enthalpy of solution of 2.55 mg $C_3H_4N_2$ in 2.00 cm^3 of [0.9996 mol dm^{-3} HCl(aq) and 6.95 mg H_3BO_3] at 298.15 K was -26.70 ± 0.24 kJ mol^{-1} ($n = 5$, uncertainty is twice the standard deviation of the mean). The molar enthalpy of solution of 7.52 mg

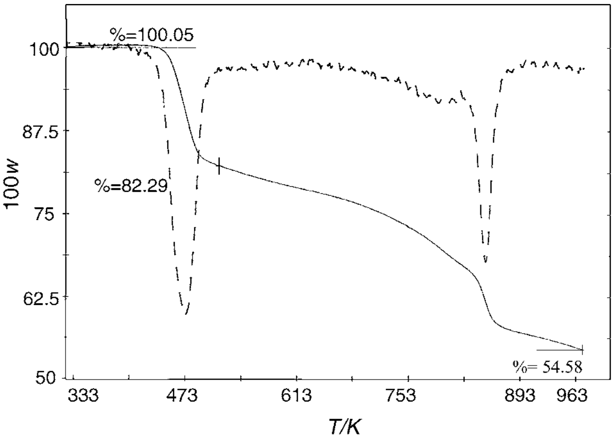

Fig. 2. TG and DTG curves of the synthetic sample.

$[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ in 2.00 cm^3 of 0.9996 mol dm^{-3} HCl(aq) at 298.15 K was 101.52 ± 0.15 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 $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$. The molar enthalpy of solution of H_3BO_3(s) of 21.83 ± 0.08 kJ mol^{-1} in 0.9996 mol dm^{-3} HCl(aq) was taken from [7]. The enthalpy of dilution of HCl(aq) was calculated from the NBS tables [8]. The molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA key values [9], namely −1094.8 ± 0.8 and −285.830 ± 0.040 kJ mol^{-1}. The molar enthalpy of formation of $C_3H_4N_2$(s) was taken from [10], namely 49.8 ± 0.6 kJ mol^{-1}. From these data, the standard molar enthalpy of formation of $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$ was calculated to be −7116 ± 7 kJ mol^{-1}.

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