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Thermochemistry of Cs(hydrogen phthalate) and Cs_2(terephthalate)

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Abstract

New compounds of phthalic acid, Cs(HPHT), and terephthalic acid, Cs_2(TPA), have been synthesized. The enthalpy of solution of Cs(HPHT) in water was determined and combined with the standard molar enthalpies of formation of CsOH(aq), H_2O(l) and phthalic acid(s) to calculate the standard molar enthalpy of formation of Cs(HPHT) of $-(1035.6 \pm 0.5)\,\mathrm{kJ\,mol^{-1}}$. The enthalpies of solution of Cs_2(TPA) and TPA in approximately $0.11\,\mathrm{mol\,dm^{-3}}$ CsOH were determined and combined with the standard molar enthalpies of formation of TPA(s), H_2O(l) and CsOH(aq, 1:500) to calculate the standard molar enthalpy of formation of Cs_2(TPA) of $-(1266.2 \pm 0.3)\,\mathrm{kJ\,mol^{-1}}$.

Keywords: Synthesis; Characterization; Standard enthalpy of formation

1. Introduction

We synthesized two compounds Cs(HPHT) and Cs_2(TPA) which have been studied with XRD, FT-IR and Raman spectra as well as TG. This paper reports the synthesis and standard molar enthalpy of formation of these compounds.

2. Experimental

2.1. General information

Analytical grade cesium sulfate (purity >99.5%), analytical grade barium hydroxide, analytical grade phthalic anhydride, phthalic acid, terephthalic acid, and double distilled water were used in all experiments.

2.2. Synthesis

2.2.1. Synthesis of Cs(HPHT)

About 18.7 mmol phthalic anhydride was added to CsOH (18.7 mmol) solution in 5 mL of water. The suspension was stirred for 2 h at 333 K, filtered under reduced pressure and white crystals of Cs(HPHT) obtained from the filtered solution 7 days later. Then the compound was dried in the desiccator at room temperature.

2.2.2. Synthesis of Cs_2(TPA)

19.1 mmol telephthalic acid was added to 10 mL of CsOH (38.2 mmol) solution. The suspension was stirred for 2 h at 333 K, filtered and the solution concentrated to a volume of 3 mL under reduced pressure. Then alcohol was added and a white solid appears. The mixture was then filtered under reduced pressure, leaving behind a white solid which was

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Table 1
The molar enthalpies of the samples solved in solutions at 298.15 K[a]

Sample	$\Delta_{sol}H_m$ (kJ mol^{-1})
PHT in CsOH(aq)	
Mean	−24.50 ± 0.16 (n = 5)
Cs(HPHT) in water	
Mean	26.45 ± 0.06 (n = 5)
TPA in CsOH(aq, 1:500)	
Mean	−27.59 ± 0.16 (n = 5)
Cs_2(TPA) in CsOH(aq, 1:500)	
Mean	18.73 ± 0.22 (n = 5)

[a] Uncertainty is estimated as twice the standard deviation of the mean.

washed with 10 mL of alcohol and dried under vacuum at room temperature to obtain Cs_2(TPA).

The chemical composition was determined by C, H, N element analysis and Cs^+ by Tas-986 atomic absorption spectrophotometry at 852.1 nm.

2.3. Calorimetric experiments

Cs(HPHT) (7 mg) was dissolved in 8 mL H_2O, then PHT (5 mg) in 8 mL of aqueous 0.014 mol dm^{-3} CsOH(aq), Cs_2(TPA)(s) (5 mg) and TPA (2 mg) in 6 mL 0.11 mol dm^{-3} CsOH solution. The CsOH solvent was prepared from Cs_2SO_4 and $Ba(OH)_2$ [1], and the concentration determined by titration with standard potassium acid phthalate.

A RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) was used at 298.15 K and has been described in detail previously [2]. The sample was pressed into the solvent by a rod after thermal equilibration for at least 1 h [3]. Total time required for the complete reaction was about 40 min. There were no solid residues observed after the reactions.

The enthalpy of solution of KCl (spectral purity) in deionized water was measured to verify calorimeter calibration. The mean value (17.23 ± 0.04) kJ mol^{-1} of $\Delta_{sol}H_m$ agrees with the literature value of (17.241 ± 0.018) kJ mol^{-1} reported in [4].

3. Results

3.1. Characterization of the synthetic samples

Anal. Calc. for Cs(HPHT): C, 32.21; H, 1.68; Cs, 44.59. Found: C, 31.43; H, 1.62; Cs, 44.30.

Anal. Calc. for Cs_2(TPA): C, 22.34; H, 0.93; Cs: 61.84. Found: C, 22.35; H, 0.87; Cs, 61.07.

There is no impurity line observed in XRD, FT-IR or Raman spectra which shows the synthetic sample is suitable for the calorimetric experiments.

3.2. Result of calorimetric experiment

The results of the calorimetric measurements are given in Table 1. Tables 2 and 3 give the thermochemical cycles for the derivation of the standard molar enthalpies of formation of Cs(HPHT) and Cs_2(TPA). In Table 3, the concentrations of the CsOH solutions in reactions 1 and 2 are almost the same, approximately, 0.11 mol dm^{-3}. The standard molar enthalpies of formation of H_2O(l), Cs^+(aq) and OH^-(aq) were taken from the CODATA Key Values [5], namely, −(285.83 ± 0.04) kJ mol^{-1}, −(258.28 ± 0.50) kJ mol^{-1} and −(230.15 ± 0.04) kJ mol^{-1}, respectively. The enthalpy of formation of CsOH(aq) in H_2O, −(488.43 ± 0.50) kJ mol^{-1}, which was calculated from standard molar enthalpies of formation of Cs^+(aq) and OH^-(aq). The standard molar enthalpies of formation of PHT, TPA and CsOH solution ($n_{CsOH}:n_{H_2O}$ = 1:500, 0.11 mol dm^{-3}) were taken from Lange's handbook of chemistry [6] and the NBS tables [7], namely, −782.0, −816.1 and −487.73 kJ mol^{-1}. From these data, the standard molar enthalpy of formation of Cs(HPHT) was calculated to be −(1035.6 ± 0.5) kJ mol^{-1} and the standard molar enthalpy of formation of Cs_2(TPA) was −(1266.2 ± 0.3) kJ mol^{-1}.

Table 2
Thermochemical cycle and results for the derivation of Δ_rH_m(Cs(HPHT), 298.15 K)

	Reaction	Δ_rH_m (kJ mol^{-1})
1	$Cs^+(aq) + OH^-(aq) + PHT(s) = Cs^+(aq) + HPHT^-(aq) + H_2O(l)$	−24.50 ± 0.16
2	$Cs^+(aq) + HPHT^-(aq) + H_2O(l) = Cs(HPHT)(s) + H_2O(l)$	−26.45 ± 0.06
3	$CsOH(aq) + PHT(s) = Cs(HPHT)(s) + H_2O(l)$	−50.95 ± 0.17

Table 3
Thermochemical cycle and results for the derivation of Δ_rH_m(Cs_2(TPA), 298.15 K)

	Reaction	Δ_rH_m (kJ mol^{-1})
1	$TPA(s) + 66(CsOH\cdot 500H_2O) = 2Cs^+(aq) + TPA^-(aq) + 64(CsOH\cdot 515.63H_2O) + 2H_2O(l)$	−27.59 ± 0.16
2	$2Cs^+(aq) + TPA^-(aq) + 64(CsOH\cdot 515.63H_2O) + 2H_2O(l) = Cs_2(TPA)(s) + 64(CsOH\cdot 515.66H_2O)$	−18.73 ± 0.22
3	$66(CsOH\cdot 500H_2O) + TPA(s) = Cs_2(TPA)(s) + 64(CsOH\cdot 515.63H_2O) + 2H_2O(l)$	−46.32 ± 0.27

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