Synthesis, Characterization, and Thermodynamic Study of Barium Benzoate $Ba(C_7H_5O_2)_2(s)$

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Benzoic acid and barium hydroxide octahydrate were used as reactants, and a compound $Ba(C_7H_5O_2)_2(s)$ was synthesized by the method of hydrothermal reaction. Chemical and elemental analyses, FTIR, and X-ray powder diffraction techniques were applied to characterize the composition and structure of the compound. Low-temperature heat capacities of the compound were measured by a precision automated adiabatic calorimeter over the temperature range from (77 to 402) K. A polynomial equation of the heat capacities as a function of temperature was fitted by the least-squares method. Smoothed heat capacities and thermodynamic functions of the compound were calculated on the basis of the fitted polynomial. The enthalpy change of the reaction of benzoic acid with barium hydroxide octahydrate was determined to be $(22.03 \pm 0.30)\ \mathrm{kJ \cdot mol^{-1}}$ by respective measuring enthalpies of dissolution of benzoic acid and $Ba(C_7H_5O_2)_2(s)$ in $0.1\ \mathrm{mol \cdot dm^{-3}}$ HCl and barium hydroxide octahydrate in $0.1\ \mathrm{mol \cdot dm^{-3}}$ HCl solution containing certain amounts of benzoic acid at 298.15 K by using an isoperibol solution−reaction calorimeter. The standard molar enthalpy of formation of the title compound $Ba(C_7H_5O_2)_2(s)$ was derived to be $-(1231.47 \pm 1.12)\ \mathrm{kJ \cdot mol^{-1}}$ in accordance with Hess' law.

Introduction

Benzoic acid has a prominent biological effect on the growth and development of humans and animals. It is a constituent of Whitfield's ointment, which is used for the treatment of fungal skin diseases such as tinea (athlete's foot) and ringworm. The compounds of benzoic acid with many metals can reduce or prevent the growth of the microorganism in biological bodies. The free state of barium is toxic, and the barium(II) ion is virulent. The barium element in the human body is mainly absorbed from air, soil, and water and accumulates gradually in the body. According to normal excretion speed, the absorption of the barium ion in the human body cannot achieve a toxic condition caused by excessive intake of the barium ion, but the long-term stay of the barium ion in the body is harmful to our health. Although barium is toxic, the compounds or complexes of barium with biologically or physiologically organic activating molecules could reduce the toxicity of the barium ion. Benzoic acid is a useful biological activating molecule in humans and animals, and the coordination compound of benzoic acid with the barium ion can accelerate the metabolism of the barium ion in the body and the removal of the barium ion from the body. Therefore, great attention is focused on the application of metallic compounds of benzoic acid in various fields such as food preservatives, feed additives, drugs, and so on.

Zhang et al. have synthesized anhydrous barium benzoate by using barium carbonate and benzoic acid as the reactants and characterized the composition and structure of the compound by FTIR, chemical and elemental analyses, TG, DTA, and XRD.[1] They investigated and proposed the possible mechanism of thermal decomposition of the compound on the basis of TG, DTA, FTIR, and gas chromatography−mass spectrometry. However, thermodynamic properties of the compound have not been found in the literature, which restricted the progress of relevant theoretical studies and the application development of the title compound. To calculate enthalpy changes, equilibrium constants, and theoretical yields of reactions in which the substance is involved, the thermodynamic properties for the substance are urgently needed and closely related to other physical, biological, physiological, and chemical properties. Therefore, the aim of the present work is to synthesize the compound $Ba(C_7H_5O_2)_2(s)$ by selecting barium hydroxide octahydrate and benzoic acid as the reactants using the method of liquid phase reaction and then measure low-temperature heat capacities of the compound by adiabatic calorimetry and determine the dissolution enthalpies of the reactants and products of the reaction of barium hydroxide octahydrate with benzoic acid by an isoperibol solution−reaction calorimetry. Finally, some thermodynamic parameters such as the enthalpy change of the reaction and the standard molar enthalpy of formation of the product $Ba(C_7H_5O_2)_2(s)$ were derived from these experimental results.

Experimental Section

Synthesis and Characterization of the Compound $Ba(C_7H_5O_2)_2(s)$. The synthetic route to the title compound is shown as follows. Benzoic acid reacts with barium hydroxide octahydrate at a molar ratio of n(benzoic acid)/n(barium hydroxide octahydrate) = 2:1. A certain amount of benzoic acid was first dissolved in 20 $\mathrm{dm^3}$ of twice-distilled water in a 250 $\mathrm{dm^3}$ beaker for the purpose of complete reaction. When the solution was heated to nearly boiling, the barium hydroxide octahydrate (about 7.6425 g or 0.024 mol) dissolved beforehand in water was slowly dripped in the

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Table 1. Data of IR Spectra of Main Groups of Benzoic Acid and Barium Benzoate (cm^{-1})

compd	$\nu_{C=O}$	$\nu_{-OH\ (-COOH)}$	δ_{-OH}	$\nu_{-OH\ (H_2O)}$	$\nu_{C=C}$	ν_{C-H}	δ_{C-H}
$C_7H_6O_2$	1416	2558, 2678, 2845, 2885	930		1594, 1575, 1452	3076, 2925	713, 684
$B_a(C_7H_5O_2)_2$	1510				1588, 1493, 1307	3095, 3062, 2918	719, 692

above solution with stirring to obtain a clear solution. The above solution was heated and condensed on the electric furnace until a crystal membrane appeared. The final solution was cooled naturally to room temperature and filtered; the crude product was washed with distilled water three times. The white solid product was recrystallized using a mixed solution of anhydrous ethanol and distilled water, and white crystals were obtained. Finally, the sample was placed in a vacuum desiccator at 90 °C to dry for 6 h. Theoretical contents of Ba, C, and H in the compound were calculated to be 36.18 %, 44.3 %, and 2.66 %, respectively. Chemical and element analyses (model: PE-2400, Perkin-Elmer) have shown that the practical contents of Ba, C, and H in the compound were measured to be 35.92 %, 44.0 %, and 2.64 %, respectively. This showed that the purity of the prepared sample was greater than 99.0 %. The elemental contents are slightly lower than the theoretical contents. This is possibly due to the selected barium hydroxide octahydrate, which contains trace heavy metal elements.

FTIR (Nicolet 5700 FT-IR, KBr) was used to determine the bond mode of the barium ion with benzoic acid; the range of the wavelength was (400 to 4000) cm^{-1}. Vibration characteristic absorptions of main groups obtained from the FTIR spectra of the compound and benzoic acid are listed in Table 1.

It can be seen from Table 1 that the organic component of the compound possesses distinctly different characteristic absorption peaks relative to that of benzoic acid. The strong absorption peaks of the O−H stretching vibration and bending vibration, which appeared at (2845 and 930) cm^{-1} in benzoic acid, have disappeared in barium benzoate. This shows that the oxygen atom of the organic component in the title compound was directly linked to the barium atom, and the replacement of the hydrogen atom in −COOH of benzoic acid with the barium ion resulted in the carboxyl (−COOH) possessing properties of the carboxylate ($-COO^-$). The shift of the absorption peak was caused completely by the change of the surroundings near the C−O bond after the formation of the compound. The absorption peak of the C=O stretching vibration, $\gamma_{C=O}$, shifted to the high wavenumber in the title compound, 1510 cm^{-1}, owing to the formation of the delocalization π bond including the benzene ring and carboxylate ($-COO^-$), which increased the density of the electron cloud around $-COO^-$ and enhanced the energy of the chemical bond −C=O. In addition, different shifts of other characteristic absorption peaks occurred and were also ascribed to the replacement of the hydrogen atom in the −COOH of benzoic acid with the barium ion. However, a wide and strong absorption peak of the complex at 3434 cm^{-1} was not found, which demonstrates that crystal water was not present in the title compound. In addition, by comparing the characteristic absorption peaks with those of the literature, it can be seen that these characteristic absorption peaks were almost the same as those briefly described in the literature.[1]

The X-ray powder diffraction (XRD) technique was used to determine whether the new synthesized compound is novel. XRD spectra of benzoic acid, barium hydroxide octahydrate, and barium benzoate have been plotted in Figure 1. The step length of the powder diffraction angle was 0.01 rad, the wavelength was 0.154056 nm (Cu Kα_1 radiation), the electric voltage was 36 kV, and the electric current was 20 mA. The scanning rate was 4 rad·min^{-1}, and a graphite monochromator was used for filtering. It was found from Figure 1 by comparison of the three charts that two obvious absorption peaks in the angle range of $2\theta = (16 \text{ to } 18)$ radians and seven other weak characteristic absorption peaks in the angle range of $2\theta = (24 \text{ to } 35)$ radians were seen in the diffractogram of benzoic acid, one strong absorption peak near $2\theta = 15$ radians and five other characteristic absorption peaks in the angle range of $2\theta = (19, 24, 46, 63, \text{ and } 74)$ radians were seen in the diffraction pattern of barium hydroxide octahydrate, and two distinct absorption peaks appeared near $2\theta = (12 \text{ and } 17)$ radians in the diffractogram of barium benzoate. Therefore, novel characteristic absorption peaks completely different from those of benzoic acid and barium hydroxide octahydrate appeared in the diffraction pattern of barium benzoate. It was shown that a new substance was produced by the liquid phase reaction of benzoic acid with barium hydroxide octahydrate. Because any kind of substance has its own unique X-ray diffraction pattern, the X-ray diffraction pattern of the mixture is just a simple superposition of characteristic absorption peaks of its components. Therefore, identification of different materials can be made from X-ray diffraction patterns. The X-ray diffraction pattern of the reactants and product have not been given in the literature.[1] They only gave the unit cell parameters of barium benzoate to prove the production of a new substance.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range of $78 \le (T/\mathrm{K}) \le 400$. The calorimeter was established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The cross-section diagram of the improved adiabatic calorimeter is shown in Figure 2. The principle and performance of the adiabatic calorimeter and the procedures of heat capacity measurements have been described in detail elsewhere.[2,3] Recently, the adiabatic calorimeter was improved. A new third adiabatic

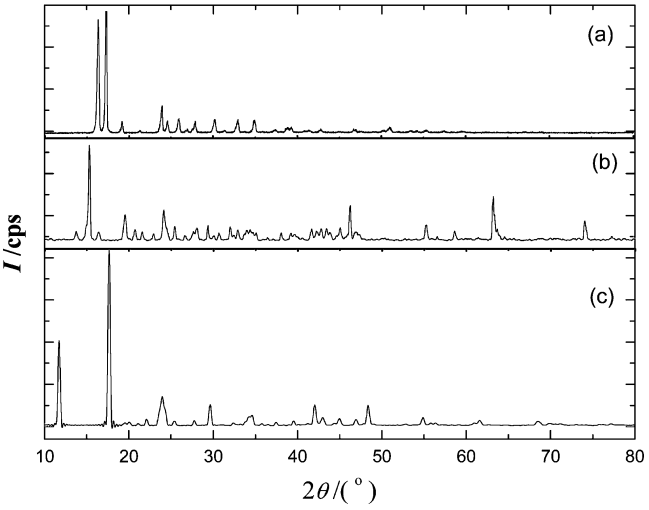

Figure 1. XRD spectra of (a) benzoic acid, (b) barium hydroxide octahydrate, and (c) barium benzoate.

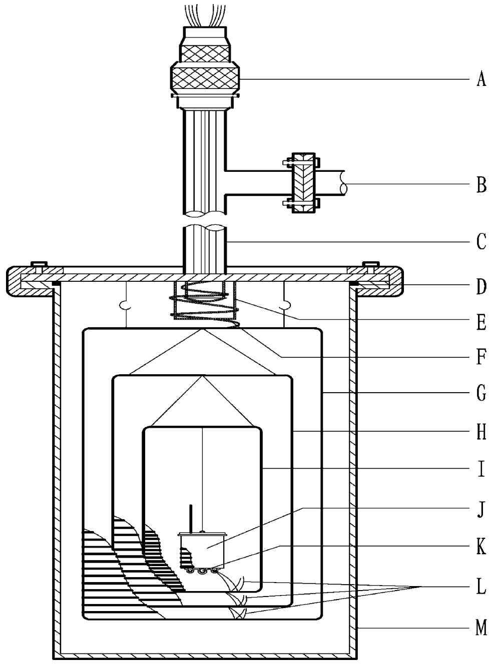

Figure 2. Cross-section diagram of the adiabatic calorimeter: (A) sealing junction unit; (B) high vacuum system; (C) vacuum tube; (D) fuse gasket; (E) temperature controlling ring; (F) lead bundles; (G) outer adiabatic shield; (H) middle adiabatic shield; (I) inner adiabatic shield; (J) sample cell; (K) platinum resistance thermometer, other sheaths for differential thermocouples; (L) differential thermocouples; (M) body of vacuum can.

shield was added, the sample cell was surrounded in turn by inner, middle, and outer adiabatic shields, and the electric heating wires were coiled on the outer wall of the sample cell for heating the sample. Three sets of six-junction chromel−constantan thermopiles were installed between the sample cell and the inner shield, between the inner and the middle shields, and between the middle and the outer shield to detect the temperature differences between them. The detection signals of thermal potentials caused by the temperature differences were inputted into a 340 temperature controller, which controls the currents of the heating wires on the inner, middle, and outer adiabatic shields, respectively, makes the temperatures of the inner, middle, and outer adiabatic shields closely follow that of the sample cell, minimizes the temperature difference between the sample cell and the shields, and obtains good adiabatic conditions.

The sample cell and the adiabatic shields were put into a high vacuum can to eliminate the heat loss of the sample cell caused by convection. During the heat capacity measurements, the vacuum can was evacuated to 10^{-5} bar by means of a combined high vacuum mechanical and molecular pump system.

The temperature of the sample cell was measured by a precision miniature platinum resistance thermometer (IPRT no. 2, produced by the Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω). The resistance of the thermometer was measured by a 7 $^1/_2$ digit nanovolt/micro-ohm meter (Agilent 34420A) with a four-terminal resistance measurement circuit and inputted into the computer for processing after A/D conversion. Then, the corresponding temperature was calculated according to the relationship between the resistance and temperature of the thermometer, which was calibrated in terms of ITS-90 by the Station of Low-Temperature Metrology and Measurements of the Chinese Academy of Sciences. The electrical energy introduced to the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a data acquisition/switch unit (model 34970A, Agilent) and processed online by a P_4 computer equipped with a matched module and interface card GPIB (IEEE 488).

Heat-capacity measurements were continuously and automatically carried out by means of a standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1 to 0.4) $K\cdot min^{-1}$ and (1 to 3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $K\cdot min^{-1}$ during the acquisition of all heat-capacity data. The data for heat capacities and corresponding equilibrium temperatures have been corrected for heat exchange of the sample cell with its surroundings.[2]

To verify the accuracy of the calorimeter, the heat capacities of a reference standard material (α-Al_2O_3) were measured over the temperature range of $78 \leq (T/K) \leq 400$. The sample mass was 1.71431 g, which was equivalent to 0.0168 mol on the basis of its molar mass, $M(Al_2O_3) = 101.9613\ g\cdot mol^{-1}$. The experimental molar heat capacities of α-Al_2O_3 were fitted by a least-squares method to a polynomial. Deviations of the experimental results from those of the smoothed curve lie within ± 0.29 %, whereas the uncertainty is 0.30 %, as compared with the values given by the former National Bureau of Standards[4] over the whole temperature range.

The sample mass of barium benzoate $Ba(C_7H_5O_2)_2(s)$ used for the calorimetric measurement was 1.54418 g, which is equivalent to 0.00407 mol in terms of its molar mass, $M = 379.55\ g\cdot mol^{-1}$.

Isoperibol Solution−Reaction Calorimetry. The isoperibol solution−reaction calorimeter primarily consisted of a precision temperature control system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter have been described in detail elsewhere.[5]

We previously verified the reliability of the calorimeter[5] by measuring the dissolution enthalpy of KCl (calorimetrical primary standard) in double-distilled water at $T = 298.15$ K. The mean dissolution enthalpy was (17 547 ± 13) $J\cdot mol^{-1}$ for KCl, which compares to the corresponding published data, (17 536 ± 3.4) $J\cdot mol^{-1}$.[6]

In all dissolution experiments of the sample, 100 mL of 0.1 $mol\cdot dm^{-3}$ HCl was chosen as the calorimetric solvent.

Finally, UV/vis spectra and data for refractive indices were used to confirm whether solution A was in the same thermodynamic state as that of solution B. These results have indicated that chemical components and physicochemical properties of solution A were consistent with those of solution B.

Results and Discussion

Low-Temperature Heat Capacities. All experimental results, listed in Table 2 and plotted in Figure 3, showed that the structure of the compound was stable over the temperature range between $T = (77$ and $402)$ K; namely, no phase change, association, or thermal decomposition occurred. The 117 experimental points in the temperature region between $T = (77$ and $402)$ K were fitted by means of least-squares, and a polynomial equation of the experimental molar heat capacities ($C_{p,m}$) versus reduced temperature (X), $X = f(T) = [T - ((T_1 +$

Table 2. Experimental Molar Heat Capacities of Barium Benzoate

T/K	$C_{p,m}$/J·mol^{-1}·K^{-1}	T/K	$C_{p,m}$/J·mol^{-1}·K^{-1}	T/K	$C_{p,m}$/J·mol^{-1}·K^{-1}
77.78	109.64	174.9	202.60	292.0	297.35
79.50	111.79	177.8	204.53	294.9	299.58
82.08	114.77	180.6	207.13	297.9	301.75
84.57	117.57	184.7	211.18	300.8	303.71
86.98	119.65	188.6	214.68	303.6	305.99
89.39	121.92	191.5	216.93	306.5	308.50
91.65	124.31	194.4	219.24	309.3	310.54
93.86	126.60	197.2	221.90	312.2	312.73
96.10	128.79	200.2	224.02	315.2	314.63
98.25	130.89	203.1	226.01	318.2	316.73
100.3	132.67	206.0	228.46	321.2	318.30
102.4	134.86	208.9	231.14	324.1	320.78
104.4	137.21	211.8	233.77	327.0	322.91
106.5	139.25	214.6	235.99	330.0	325.19
108.3	141.18	217.5	238.64	332.9	327.09
110.3	142.99	220.5	240.68	335.9	329.01
112.2	144.86	223.4	243.49	338.7	330.94
114.1	146.37	226.3	245.79	341.6	333.36
115.9	148.24	229.1	248.30	344.6	335.34
117.8	150.20	232.0	250.40	347.5	337.30
119.6	152.24	235.0	253.03	350.3	339.28
122.4	154.37	238.0	255.71	353.2	340.83
125.9	157.49	242.6	259.30	356.2	342.81
128.8	160.12	245.5	262.07	359.0	344.74
131.6	162.83	248.3	264.47	361.9	346.43
134.5	165.78	251.2	266.71	364.8	348.25
137.4	168.03	254.2	269.22	367.6	350.41
140.3	170.89	257.0	270.83	370.5	352.35
143.1	173.54	259.8	272.78	373.5	354.08
146.1	176.75	262.7	276.16	376.4	355.62
148.9	178.82	265.6	277.74	379.4	358.05
152.8	182.27	268.6	279.79	382.4	359.77
154.7	184.19	271.6	282.06	385.3	361.34
157.6	186.99	274.5	284.16	388.3	363.44
160.4	189.18	277.5	286.12	390.7	364.99
163.4	191.95	280.4	288.42	393.0	366.42
166.3	194.11	283.3	290.79	395.9	368.64
169.1	197.21	286.3	292.92	398.9	370.39
172.0	199.98	289.2	295.05	401.9	371.91

T_2)/2)]/[(($T_1 - T_2$)/2)] (where T_1 = 402 K and T_2 = 77 K), has been obtained

$$C_{p,m}/(\mathrm{J\cdot\ mol^{-1}\cdot K^{-1}}) = 256.847 + 131.084X - 15.859X^2 \tag{1}$$

in which $X = (T - 239.5)/162.5$. This equation is valid between T = 77 K and T = 402 K. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ± 0.4 %, except for several points around the lower temperature limit. This can be seen in Figure 4. The coefficient of determination for the fitting, R^2, was equal to 0.99998.

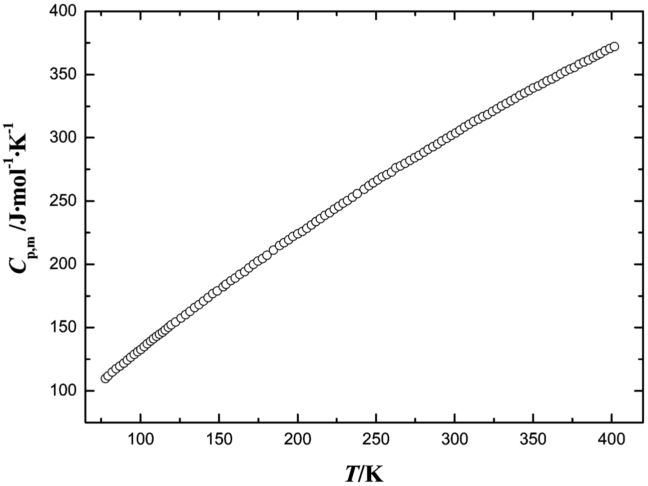

Figure 3. Curve of experimental molar heat capacities of barium benzoate Ba($C_7H_5O_2$)$_2$(s).

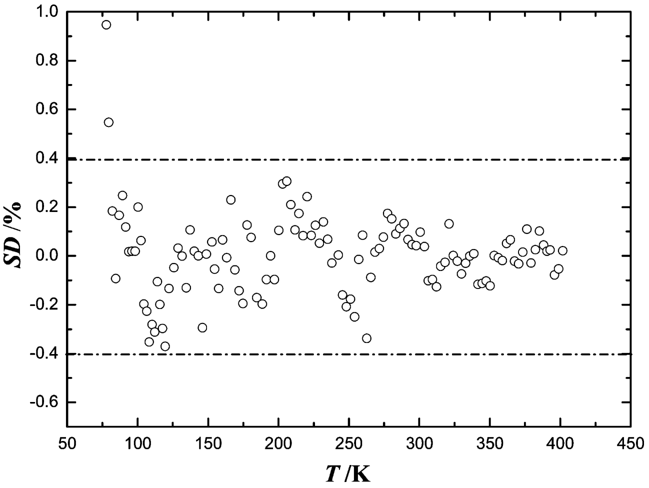

Figure 4. Plot of the standard deviation of heat capacity of barium benzoate Ba($C_7H_5O_2$)$_2$(s) against the absolute temperature, SD % = [($C_{\mathrm{smo}} - C_{\mathrm{exptl}}$)/$C_{\mathrm{smo}}$]·100 %, where C_{smo} represents the smoothed heat capacities of the compound and C_{exptl} represents the experimental heat capacities.

Thermodynamic Functions of the Compound. The smoothed molar heat capacities and thermodynamic functions were calculated on the basis of the fitted polynomial of the heat capacities as a function of the reduced temperature (X) according to the following thermodynamic equations

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p\, \mathrm{d}T \tag{2}$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p \cdot T^{-1}\, \mathrm{d}T \tag{3}$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p\, \mathrm{d}T - T\cdot \int_{298.15}^{T} C_p \cdot T^{-1}\, \mathrm{d}T \tag{4}$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature, 298.15 K, are tabulated in Table 3 at 5 K intervals.

Determination of Enthalpy Change of the Liquid Phase Reaction of Barium Hydroxide Octahydrate with Benzoic Acid. The reaction of barium hydroxide octahydrate with benzoic acid is shown as follows

$$2C_7H_6O_2(s) + Ba(OH)_2{\cdot}8H_2O(s) = Ba(C_7H_5O_2)_2(s) + 10H_2O(l) \tag{5}$$

The enthalpy change of reaction 5 can be determined by respectively measuring the enthalpies of dissolution of benzoic acid and Ba($C_7H_5O_2$)$_2$(s) in 0.1 mol·dm^{-3} HCl and barium hydroxide octahydrate in 0.1 mol·dm^{-3} HCl solution containing certain amounts of benzoic acid at 298.15 K.

The solid barium hydroxide octahydrate and benzoic acid were, respectively, ground within an agate mortar into a fine powder.

About 1.0·10^{-3} mol or 0.122 g of benzoic acid was dissolved in 100 mL of 0.1 mol·dm^{-3} HCl at 298.15 K. If "s" is calorimetric solvent, 0.1 mol·dm^{-3} HCl, then

$$\{C_7H_6O_2(s)\} + \text{“s”} = \text{solution A}'$$

The results obtained from five dissolution experiments are listed in Table 4.

Table 3. Smoothed Heat Capacities and Thermodynamic Functions of Barium Benzoate

T	$C_{p,m}$	$H_T - H_{298.15\text{K}}$	$S_T - S_{298.15\text{K}}$	$G_T - G_{298.15\text{K}}$
K	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
80	112.90	−35.73	−276.9	−13.57
85	117.88	−35.93	−268.2	−13.13
90	122.83	−36.08	−259.6	−12.71
95	127.74	−36.18	−251.2	−12.31
100	132.63	−36.22	−243.0	−11.92
105	137.49	−36.21	−234.9	−11.55
110	142.31	−36.15	−226.9	−11.19
115	147.11	−36.03	−219.0	−10.85
120	151.87	−35.87	−211.3	−10.51
125	156.61	−35.65	−203.7	−10.19
130	161.32	−35.38	−196.2	−9.873
135	165.99	−35.06	−188.9	−9.566
140	170.64	−34.70	−181.6	−9.267
145	175.25	−34.28	−174.5	−8.973
150	179.84	−33.81	−167.5	−8.684
155	184.39	−33.30	−160.6	−8.399
160	188.92	−32.74	−153.9	−8.117
165	193.42	−32.13	−147.2	−7.838
170	197.88	−31.47	−140.6	−7.561
175	202.32	−30.77	−134.2	−7.286
180	206.72	−30.02	−127.8	−7.010
185	211.10	−29.22	−121.6	−6.735
190	215.45	−28.38	−115.4	−6.459
195	219.76	−27.50	−109.3	−6.182
200	224.05	−26.57	−103.3	−5.904
205	228.30	−25.59	−97.41	−5.625
210	232.53	−24.58	−91.59	−5.343
215	236.72	−23.52	−85.86	−5.058
220	240.89	−22.42	−80.20	−4.772
225	245.02	−21.27	−74.61	−4.483
230	249.13	−20.08	−69.10	−4.191
235	253.20	−18.86	−63.67	−3.896
240	257.25	−17.59	−58.30	−3.598
245	261.27	−16.28	−52.99	−3.298
250	265.25	−14.93	−47.75	−2.995
255	269.21	−13.55	−42.57	−2.690
260	273.13	−12.12	−37.45	−2.382
265	277.03	−10.65	−32.38	−2.073
270	280.89	−9.151	−27.37	−1.762
275	284.73	−7.610	−22.40	−1.449
280	288.53	−6.032	−17.49	−1.136
285	292.31	−4.418	−12.61	−0.8226
290	296.05	−2.767	−7.786	−0.5091
295	299.77	−1.081	−2.997	−0.1964
298.15	302.09	0	0	0
300	303.45	0.6411	1.754	0.1150
305	307.11	2.398	6.470	0.4244
310	310.73	4.189	11.15	0.7310
315	314.33	6.014	15.81	1.034
320	317.89	7.873	20.44	1.333
325	321.43	9.764	25.04	1.626
330	324.93	11.69	29.62	1.913
335	328.41	13.65	34.18	2.193
340	331.85	15.63	38.73	2.465
345	335.27	17.65	43.26	2.728
350	338.65	19.70	47.78	2.980
355	342.01	21.78	52.29	3.220
360	345.33	23.89	56.80	3.448
365	348.63	26.03	61.30	3.661
370	351.89	28.20	65.80	3.859
375	355.12	30.40	70.30	4.039
380	358.33	32.63	74.81	4.202
385	361.50	34.88	79.32	4.344
390	364.65	37.16	83.84	4.465
395	367.76	39.47	88.37	4.563
400	370.85	41.80	92.92	4.636

The stoichiometric number of $Ba(OH)_2\cdot 8H_2O(s)$ in reaction 5, or $n(Ba(OH)_2\cdot 8H_2O)/n(\text{benzoic acid})] = 1:2$, was regarded as a norm for sample weighing; about $0.5\cdot 10^{-3}$ mol or 0.157 g of $\{Ba(OH)_2\cdot 8H_2O(s)\}$ was dissolved in solution A′, that is

$$\{Ba(OH)_2\cdot 8H_2O(s)\} + \text{solution A}' = \text{solution A}$$

The results obtained from five dissolution experiments are listed in Table 4.

About $0.5\cdot 10^{-3}$ mol or 0.189 g of $Ba(C_7H_5O_2)_2(s)$ was dissolved in 0.1 $\text{mol}\cdot\text{dm}^{-3}$ HCl at 298.15 K. Then

$$\{Ba(C_7H_5O_2)_2(s)\} + \text{“s”} = \text{solution B}'$$

The results obtained from five dissolution experiments are listed in Table 4.

The dilution enthalpy of $\{10\cdot H_2O(l)\}(\Delta H_4)$ as one of the products in reaction 5 in solution B was within the range of experimental error, cannot be detected, and may be omitted because the amount of $H_2O(l)$ was very small according to the stoichiometric number of $H_2O(l)$ in reaction 5, namely, $\Delta H_4 = 0$.

The enthalpy change of reaction 5 can be calculated in accordance with a thermochemical cycle, and the experimental results are as follows

$$\begin{aligned}\Delta_r H^o_m &= \sum \Delta_{sol} H^o_{m(\text{Reactants})} - \sum \Delta_{sol} H^o_{m(\text{Products})} = \\ &\quad 2\Delta H_1 + \Delta H_2 - \Delta H_3 - 10\Delta H_4 \\ &= (22.03 \pm 0.30)\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Standard Molar Enthalpy of Formation of the Compound $Ba(C_7H_5O_2)_2(s)$. A reaction scheme used to derive the standard molar enthalpy of formation of $Ba(C_7H_5O_2)_2(s)$ is given in Table 5. The experimental values of the dissolution enthalpies of the reactants and products in reaction 5 were combined with some auxiliary thermodynamic data of $\Delta_f H^o_m(C_7H_6O_2(s)) = -(384.8 \pm 0.50)\ \text{kJ}\cdot\text{mol}^{-1}$,[7] $\Delta_f H^o_m(Ba(OH)_2\cdot 8H_2O(s)) = -3342.2\ \text{kJ}\cdot\text{mol}^{-1}$,[8] and $\Delta_f H^o_m(H_2O(l)) = -(285.83 \pm 0.04)\ \text{kJ}\cdot\text{mol}^{-1}$[9] to derive the standard molar enthalpy of formation of $Ba(C_7H_5O_2)_2(s)$

$$\begin{aligned}&\Delta_f H^o_m(Ba(C_7H_5O_2)_2(s)) = \Delta H_8 \\ &= \Delta_r H^o_m + 2\Delta_f H^o_m(C_7H_6O_2(s)) + \Delta_f H^o_m(Ba(OH)_2\cdot \\ &\qquad 8H_2O(s)) - 10\Delta_f H^o_m(H_2O(1)) \\ &= (2\Delta H_1 + \Delta H_2 - \Delta H_3 - 10\Delta H_4) + 2\Delta H_5 + \Delta H_6 - 10\Delta H_7 \\ &= (2\cdot 29.57 + (-23.69) - 13.42 - 10\cdot 0) + (-384.8\cdot 2) + \\ &\qquad (-3342.2) - (-285.83\cdot 10) \\ &= -(1231.47 \pm 1.12)\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

in which ΔH_1 to ΔH_8 are the enthalpy changes of the reactions corresponding to the number of the reactions in Table 5.

The results of UV/vis spectroscopy and refrangibility (refractive indices) are two kinds of important information useful for detecting the differences in the structure and composition between two kinds of solutions. In this article, all of the reactants and products of reaction 5 can be easily dissolved in the selected solvent. The measured values of the refractive indexes of solution A and solution B were (1.3339 ± 0.0004) and (1.3338 ± 0.0003), respectively. The results of UV/vis spectrophotometry are shown in Figure 5. UV/vis spectra and the data of the refractive indices of solution A agree with those of solution B; no difference in the structure and chemical composition existed between the two solutions. These results have demonstrated that solutions A and B were the same; the designed Hess thermochemical cycle was reasonable and reliable and can be used to derive the standard molar enthalpy of formation of the compound $Ba(C_7H_5O_2)_2(s)$.

Conclusions

This article reports low-temperature heat capacities of the solid-state compound $Ba(C_7H_5O_2)_2(s)$ measured by adiabatic

Table 4. Dissolution Enthalpies of Reactants and Products of Reaction *5* in the Selected Solvent[a]

			$m_{C_7H_6O_2}$		t_e	Q_s	$\Delta_s H^o_m$
system	solvent	no.	g	$\Delta E_s/\Delta E_e$	s	J	$kJ \cdot mol^{-1}$
benzoic acid	$0.1\ mol \cdot dm^{-3}$ HCl	1	0.12246	−1.1357	53.715	29.646	29.564
		2	0.12217	−1.0788	56.486	29.613	29.601
		3	0.12214	−1.0563	57.642	29.589	29.584
		4	0.12201	−1.0421	58.873	29.815	29.841
		5	>0.12235	>−1.0470	>57.575	>29.294	>29.239
		avg $\Delta_s H^o_{m,1} = (29.57 \pm 0.10)\ kJ \cdot mol^{-1}$					
barium hydroxide octahydrate	solution A	1	0.15751	0.5759	42.572	−11.914	−23.863
		2	0.15742	0.5721	43.229	−12.019	−24.085
		3	0.15733	0.5547	42.683	−11.506	−23.071
		4	0.15737	0.5610	42.935	−11.705	−23.480
		5	0.15750	0.5714	43.071	−11.960	−23.956
		avg $\Delta_s H^o_{m,2} = -(23.69 \pm 0.18)\ kJ \cdot mol^{-1}$					
barium benzoate	solution B	1	0.18935	−0.4152	32.674	6.593	13.215
		2	0.18924	−0.5083	28.012	6.919	13.878
		3	0.18927	−0.4270	31.747	6.588	13.211
		4	0.18931	−0.4292	32.389	6.756	13.545
		5	0.18930	−0.4643	29.335	6.619	13.271
		avg $\Delta_s H^o_{m,3} = (13.42 \pm 0.13)\ kJ \cdot mol^{-1}$					

[a] *m*: mass of sample; t_e: heating period of electrical calibration; $Q_s = -(\Delta E_s/\Delta E_e)I^2Rt$: heat effect during the sample dissolution; ΔE_s: the voltage change during the sample dissolution; ΔE_e: the voltage change during the electrical calibration; $\Delta_s H^o_m = Q_s/n = -(\Delta E_s/\Delta E_e)I^2Rt(M/m)$, where *R* is the electroresistance ($R = 1213.09\ \Omega$ at $T = 298.15$ K), *I* is the current ($I = 20.015$ mA), and *M* is the molar mass of the sample.

Table 5. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of Barium Benzoate

no.	reactions	$\Delta_f H^o_m$ or $(\Delta_s H^o_m \pm \sigma_a)$ $kJ \cdot mol^{-1}$[a]
1	$\{C_7H_6O_2(s)\}$ + "s" = solution A′	(29.57 ± 0.10), ΔH_1
2	$\{Ba(OH)_2 \cdot 8H_2O(s)\}$ + solution A′ = solution A	$-(23.69 \pm 0.18)$, ΔH_2
3	$\{Ba(C_7H_5O_2)_2(s)\}$ + "s" = solution B′	(13.42 ± 0.13), ΔH_3
4	$\{10H_2O(l)\}$ + solution B′ = solution B	0, ΔH_4
5	$7C(s) + 3H_2(g) + O_2(g) = C_7H_6O_2(s)$	$-(384.8 \pm 0.50)$, ΔH_5
6	$Ba(s) + 9H_2(g) + 5O_2(g) = Ba(OH)_2 \cdot 8H_2O(s)$	-3342.2, ΔH_6
7	$H_2(g) + {}^1/{}_2O_2(g) = H_2O(l)$	$-(285.83 \pm 0.04)$, ΔH_7
8	$Ba(s) + 14C(s) + 5H_2(g) + 2O_2(g) = Ba(C_7H_5O_2)_2(s)$	$-(1231.47 \pm 1.12)$, ΔH_8

[a] $\sigma_a = [(\sum_{i=1}^{5}(x_i - \bar{x})^2))/(n(n-1))]^{1/2}$, in which *n* is the experimental number, x_i is a single value in a set of dissolution measurements, and $\bar{x}$ is the mean value of a set of measurement results.

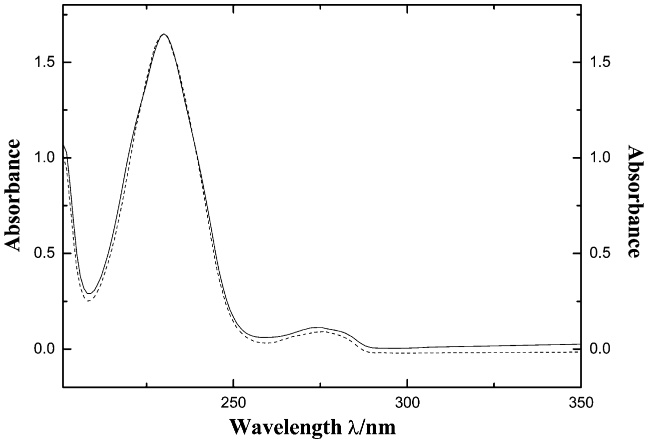

Figure 5. UV/vis spectra of solution A and solution B (diluted to 1:21): —, solution A; ---, solution B.

calorimetry and the dissolution enthalpies of the reactants and the products of the designed reaction of barium hydroxide octahydrate with benzoic acid by isoperibol solution calorimetry. Additionally, the thermodynamic functions and standard molar enthalpy of formation of the product $Ba(C_7H_5O_2)_2(s)$ were derived from these experimental results.

The enthalpy change of reaction 5 obtained by solution calorimetry was determined to be $\Delta_r H^o_m = (22.03 \pm 0.30)$ $kJ \cdot mol^{-1}$, which is an endothermic reaction. On the basis of thermodynamic theory, the reaction was not an enthalpy-driven process. However, all of the reactants were solid, and the products included a solid and a stable liquid. From an increase in the degree of disorder or chaos in the reaction, it is clear that the entropy change of the reaction is greater than zero. Therefore, this reaction was an entropy-driven process.

The standard molar enthalpy of formation of barium benzoate is negative with a large absolute value, which showed that it has lower energy and more stable structure than those of the stable elementary substances from which it was prepared. The uncertainty of the standard molar enthalpy of formation obtained by isoperibol solution calorimetry was estimated to be between 0.3 % and 0.5 %, chiefly considering the measurements of voltage changes, ΔE_s and ΔE_e, the duration time of electric calibration, t_e, final data processing, and so on.

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