



Synthesis, characterization, and thermodynamic study of ammonium benzoate $C_7H_5O_2NH_4(s)$

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ABSTRACT

Benzoic acid and concentrated ammonia were chosen as reactants and a novel compound (ammonium benzoate) was synthesized using the method of liquid phase reaction. FTIR, elemental analysis and X-ray powder diffraction technique were applied to characterize the structure and composition of the compound. Low-temperature heat capacities of the solid compound were measured by a precision automated adiabatic calorimeter over the temperature range from 80 to 399 K. A polynomial equation of the heat capacities was fitted by the least-squares method. In accordance with Hess' law, a thermochemical cycle was designed, the enthalpy change of the reaction of benzoic acid with ammonium acetate was determined as $\Delta_r H_m^\circ = (15.59 \pm 0.50) \text{ kJ mol}^{-1}$, and the standard molar enthalpy of formation of the compound was calculated as $\Delta_f H_m^\circ [C_7H_5O_2NH_4, s] = -(472.65 \pm 0.62) \text{ kJ mol}^{-1}$ by an isoperibol solution–reaction calorimeter.

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1. Introduction

Benzoic acid has a prominently biological effect in the growth and development of humans and animals. It is an important precursor for the synthesis of many other organic substances [1]. It has an antiseptic action, inhibits the growth of mold, yeast and some bacteria [2], and is often applied for ulcers, wounds, blisters, and chapped hands in the form of the tincture. In addition, it can be used for the treatment of chronic bronchitis and phthisis. Ammonium benzoate has a similar action to benzoic acid as shown above. It can be used as a significant raw material to produce the electrolytic capacitors in electronic industry. It is an excellent anti-corrosion treatment agent for metal and rubber. In medicine, it can be served as stimulants, diuretics, antirheumatic drugs, etc.

Miller et al. [3] have synthesized ammonium benzoate by the reaction of solid benzoic acid, either as powders or as single crystals, with ammonia gas at constant pressure to give 1:1 microcrystalline ammonium salt, and characterized the composition and structure of the title compound by microanalysis, infrared spectra, nuclear magnetic resonance spectra, X-ray powder camera, and elemental analysis. They investigated the reaction rate and possible reaction mechanism of solid benzoic acid with ammonia gas. However, up to now, thermodynamic properties of ammonium benzoate have not been found in the literature, which restricted the progress of

relevant theoretical studies and application development of the title compound. In order 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. The aim of the present work is to synthesize the compound $C_7H_5O_2NH_4(s)$ by the method of liquid phase reaction, to measure low-temperature heat capacities of the compound by adiabatic calorimetry, and to determine the dissolution enthalpies of the reactants and products of the reaction of ammonium acetate with benzoic acid by 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 $C_7H_5O_2NH_4(s)$ were derived from these experimental results.

2. Experimental

2.1. Synthesis and characterization of the compound $C_7H_5O_2NH_4(s)$

Benzoic acid reacts with concentrated ammonia at a molar ratio of n (benzoic acid): n (concentrated ammonia) = 1:1. Concentrated ammonia is slightly excessive for the purpose of complete reaction of benzoic acid. A certain amount of benzoic acid was firstly put into a 250 mL beaker. Then excess concentrated ammonia and appropriate amount of distilled water were successively added into the beaker with stirring to obtain a clear solution. The above solution was heated and condensed on the electric furnace until

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Table 1

Characteristic vibration absorptions of main groups obtained from FTIR spectra of benzoic acid and ammonium benzoate (cm^{-1}).^a

Compound	$\nu_{\text{C=O}}$	$\nu_{\text{O-H}}$	$\nu_{\text{C=C}}$	$\delta_{\text{C-H}}$	$\nu_{\text{N-H}}$
$\text{C}_6\text{H}_5\text{COOH}$	1689	3070	1603, 1585, 1464	812, 805, 708, 685	–
$\text{C}_6\text{H}_5\text{COONH}_4$	1595	–	1554, 1449, 1398	717, 707, 692	3128

^a ν , stretching vibration; δ , out-of-plane bending vibration.

a crystal membrane appeared. The final solution was cooled naturally to room temperature and filtered; the crude product was washed with anhydrous ethanol (A.R.) three times. The white solid product was recrystallized using anhydrous ethanol, and white crystals were obtained. Finally, the sample was placed in a vacuum desiccator at 60°C to vacuum dry for 6 h. Theoretical contents of C, H, and N in the compound were calculated to be 60.42%, 6.52%, and 10.07%, respectively. Element analysis (Model: PE-2400, PerkinElmer, USA) has shown that the practical contents of C, H, and N in the compound were measured to be 60.35%, 6.50%, and 10.03%, respectively. This showed that the purity of the sample prepared was higher than 99.5%.

FTIR (Nicolet 5700 FT-IR, USA, KBr) was used to determine the bond mode of ammonium cation with benzoic acid, the range of the wavelength was $400\text{--}4000\text{ cm}^{-1}$. 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 peak of the O–H stretching vibration ($\nu_{\text{O-H}}$) which appeared at 3070 cm^{-1} in benzoic acid has disappeared in ammonium benzoate. It showed that the oxygen atom of the organic component in the title compound was directly linked with nitrogen atom of NH_4^+ . The absorption peak of the C=O stretching vibration, $\nu_{\text{C=O}}$, shifted to the low wave number in the title compound, 1595 cm^{-1} , as a result of the formation of the delocalization π bond including the benzene ring and carboxylate ($-\text{COO}^-$), which lowered the density of the electron cloud around $-\text{COO}^-$. The absorption peak of the N–H stretching vibration in the compound appeared at $\nu_{\text{N-H}} = 3128\text{ cm}^{-1}$. In addition, different shifts of other characteristic absorption peaks occurred, which were also ascribed to the change of the surrounding near the C–O bond after the formation of the compound.

The X-ray powder diffraction (XRD) technique was used to determine whether the new synthesized compound is novel. XRD spectra of benzoic acid and ammonium benzoate have been plotted in Fig. 1. Step length of powder diffraction angle was 0.01 rad , wavelength was 0.154056 nm (Cu $\text{K}\alpha$ 1 radiation), electric voltage was 36 kV , and electric current was 20 mA . The scanning rate was 4 rad min^{-1} and a graphite monochromator was used for the filtering. It was found from Fig. 1 by comparison of the two charts that two obvious diffraction peaks in the angle range of $2\theta = 16\text{--}18\text{ rad}$ and seven other weak characteristic diffraction peaks in the angle range of $2\theta = 24\text{--}35\text{ rad}$ were seen in the diffractogram of benzoic acid. One distinct new diffraction peak appeared near $2\theta = 12\text{ rad}$, three other weak characteristic diffraction peaks in the angle range of $2\theta = 18, 29,$ and 36 rad were seen in the diffraction pattern of ammonium benzoate. 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 diffraction peaks of its components. In other words, identification of different materials can be made from X-ray diffraction patterns. Therefore, novel characteristic diffraction peaks completely different from those of benzoic acid appeared in the diffraction pattern of ammonium benzoate, which showed that a new substance was produced by the liquid phase reaction of benzoic acid with concentrated ammonia.

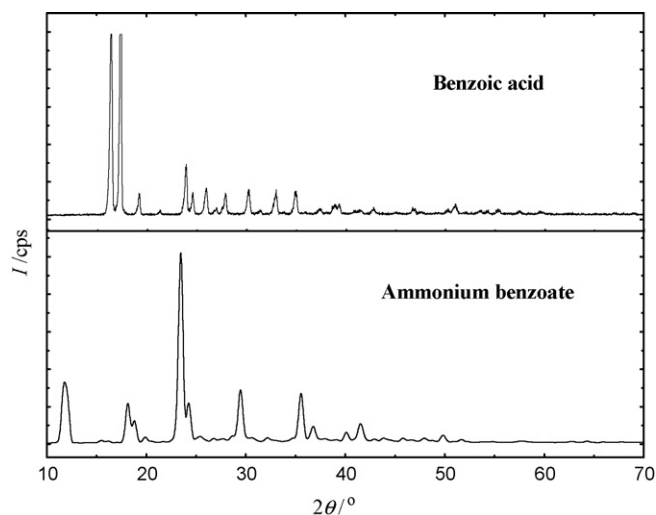


Fig. 1. XRD spectra of benzoic acid and ammonium benzoate.

2.2. Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $78 \leq (T/\text{K}) \leq 400$. The calorimeter was established in the Thermochemistry Laboratory of the College of Chemistry and Chemical Engineering, Liaocheng University, China. The principle and structure of the adiabatic calorimeter have been described in detail elsewhere [4,5]. Briefly, the calorimeter comprised mainly a sample cell; a platinum resistance thermometer; an electric heater; inner, middle and outer adiabatic shields; three sets of six-junction chromel-constantan thermopiles were installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields; and a high vacuum can. The 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 $100\ \Omega$) was used to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into 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, USA), and processed on line by a computer.

To verify the accuracy of the calorimeter, the heat capacities of a reference standard material ($\alpha\text{-Al}_2\text{O}_3$) were measured over the temperature range $78 \leq (T, \text{K}) \leq 400$. The sample mass was 1.71431 g , which was equivalent to 0.0168 mol based on its molar mass, $M(\text{Al}_2\text{O}_3) = 101.9613\text{ g mol}^{-1}$. Deviations of the experimental results from those of the smoothed curve lie within $\pm 0.2\%$, while the uncertainty is 0.3% , as compared with the values given by the former National Bureau of Standards [6] over the whole temperature range.

Heat-capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at $0.1\text{--}0.4\text{ K min}^{-1}$ and $1\text{--}3\text{ K}$. 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 $10^{-4}\text{ K min}^{-1}$ 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 surround-

Table 2
Experimental heat capacities of ammonium 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)
80.24	65.17	170.7	124.1	287.9	194.1
81.77	66.20	173.7	125.5	291.0	195.7
84.03	67.46	176.7	127.1	294.0	197.3
86.20	68.89	179.7	129.4	297.0	199.6
88.38	69.94	183.8	131.9	300.0	200.9
90.56	71.51	187.8	134.2	302.9	203.1
92.57	72.72	190.8	136.4	305.8	204.6
94.64	74.19	193.8	138.6	308.8	205.9
96.64	75.80	196.7	140.4	311.7	207.7
98.62	77.01	199.7	142.2	314.7	209.4
100.6	78.04	202.7	144.2	317.7	210.9
102.4	79.33	205.7	146.1	320.8	212.6
104.3	80.86	208.7	148.1	323.7	214.0
106.2	81.80	211.6	149.9	326.7	215.5
108.0	83.16	214.6	152.0	329.8	217.0
109.8	84.27	217.6	154.0	332.8	218.8
111.6	85.30	220.6	155.6	335.8	220.3
113.4	86.37	223.6	157.5	338.7	222.1
115.2	87.62	226.6	159.3	341.7	223.7
116.8	88.74	229.6	161.3	344.6	225.4
118.6	90.01	232.5	163.1	347.6	226.8
120.3	91.47	235.5	164.9	350.5	228.4
123.0	92.90	238.7	166.7	353.5	229.7
126.3	94.89	242.5	169.3	356.6	231.2
129.2	96.99	246.2	170.9	359.5	232.7
132.2	98.85	249.2	172.6	362.6	234.1
135.1	101.0	252.1	174.3	365.6	235.6
138.0	102.8	255.0	176.3	368.6	237.6
141.0	104.6	258.0	177.8	371.5	239.1
144.0	106.2	261.1	179.4	374.5	240.9
147.0	108.2	264.1	180.9	377.5	242.4
149.9	110.5	267.1	182.9	380.5	244.0
152.9	112.3	270.1	184.6	383.4	245.7
155.9	113.9	273.1	186.5	386.3	247.6
158.9	116.1	276.1	188.1	389.3	249.4
161.8	118.2	279.0	189.4	392.4	251.2
164.8	120.0	282.0	191.0	395.3	252.7
167.7	122.0	285.0	192.6	398.3	254.1

ings [4]. The sample mass used for calorimetric measurements was 1.79816 g, which was equivalent to 0.01292 mol in terms of its molar mass, $M(\text{C}_7\text{H}_5\text{O}_2\text{NH}_4) = 139.1519 \text{ g mol}^{-1}$.

2.3. Isoperibol solution–reaction calorimetry

The isoperibol solution–reaction calorimeter consisted primarily of a precision temperature controlling 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 [7].

The reliability of the calorimeter was verified previously [7] by measuring dissolution enthalpy of KCl (calorimetric primary standard) in double distilled water at $T = 298.15 \text{ K}$. The mean dissolution enthalpy was $17,547 \pm 13 \text{ J mol}^{-1}$ for KCl, which compares with corresponding published data, $17,536 \pm 3.4 \text{ J mol}^{-1}$ [8].

3. Results and discussion

3.1. Low-temperature heat capacities

All experimental results, listed in Table 2 and plotted in Fig. 2, showed that the structure of the compound was stable over the temperature range between $T = 80 \text{ K}$ and 399 K , namely, no phase change, association nor thermal decomposition occurred. The 114 experimental points in the temperature region were fitted by means of least-squares, and a polynomial equation of

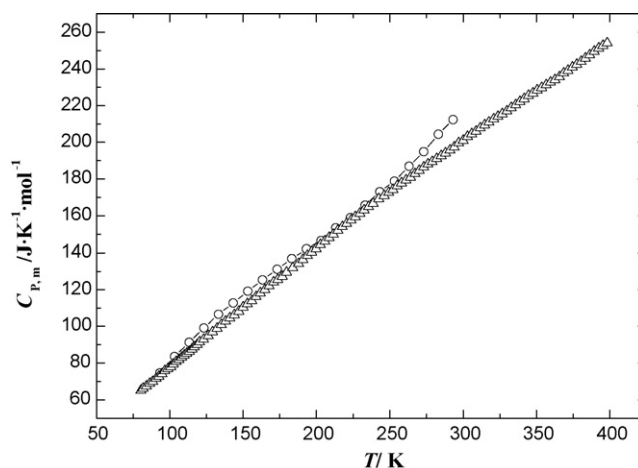


Fig. 2. The curve of experimental molar heat capacities of ammonium benzoate $\text{C}_7\text{H}_5\text{O}_2\text{NH}_4(\text{s})$. “o” represents the values of the literature and “Δ” represents the values of our experiment.

experimental molar heat capacities ($C_{p,m}$) vs. reduced temperature (X), $X = f(T) = [T - (T_1 - T_2)/2] / [(T_1 - T_2)/2]$ (where $T_1 = 399 \text{ K}$ and $T_2 = 80 \text{ K}$), has been obtained:

$$C_{p,m}(\text{J mol}^{-1} \text{K}^{-1}) = 166.852 + 94.760X - 11.979X^2 - 0.067X^3 + 4.942X^4 \quad (1)$$

in which $X = (T - 239.5)/159.5$. This equation is valid between $T = 80 \text{ K}$ and $T = 399 \text{ K}$.

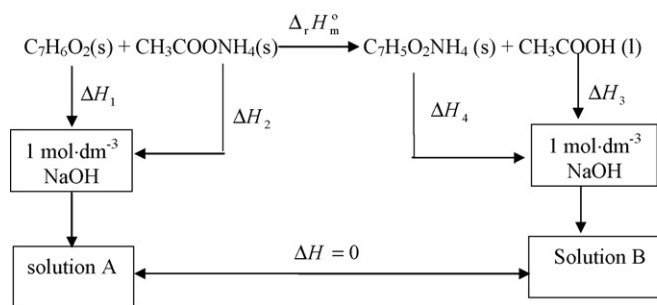
The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within $\pm 0.3\%$ except for several points around the lower temperature limit. The coefficient of determination for the fitting, R^2 , was equal to 0.99998.

In addition, the heat capacity of ammonium benzoate was measured between 93 K and 293 K in 1932 by Crenshaw and Ritter [9]. The comparison of the two results has been given in Fig. 2, it can be seen from Fig. 2 that the heat-capacity values of the literature is slightly higher than ours. This is caused probably due to the different structure and adiabatic performance of our adiabatic calorimeter from theirs. In the reference, the calorimetric cell is surrounded with only one adiabatic shield. However, in our device, the calorimetric cell is surrounded by inner, middle and outer adiabatic shields and the electric heating wires were coiled on the outer wall of cell. Three sets of six-junction chromel–copel thermocouple piles were installed between the calorimetric cell and the inner shield, between the inner and middle shields, and between the middle and outer shields to detect the temperature differences between them. The same electrical energy is introduced into the sample cells of the two devices, one which has poor adiabatic effect will lose more heat to its surroundings by means of the heat radiation, the corrected temperature difference will be smaller, and will lead to the larger heat-capacity value. By comparison with the results in the reference, our adiabatic calorimeter is more stable than theirs in the measurements of the heat capacities, as shown from two curves of Fig. 2.

3.2. The determination of enthalpy change for the solid-state reaction of ammonium acetate with benzoic acid

The reaction of ammonium acetate with benzoic acid is shown as follows:



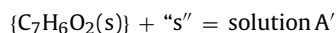


Scheme 1.

The enthalpy change of reaction (2) can be determined by respective measuring enthalpies of dissolution of benzoic acid and acetic acid in 1 mol dm^{-3} NaOH, ammonium acetate in 1 mol dm^{-3} NaOH solution containing certain amounts of benzoic acid, and $\text{C}_7\text{H}_5\text{O}_2\text{NH}_4(\text{s})$ in 1 mol dm^{-3} NaOH solution containing certain amounts of acetic acid at 298.15 K.

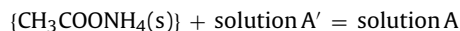
The solid ammonium acetate and benzoic acid were respectively ground within an agate mortar into a fine powder.

About 1×10^{-3} mol of benzoic acid was dissolved in 100 mL of 1 mol dm^{-3} NaOH at 298.15 K. If “s” = calorimetric solvent, 1 mol dm^{-3} NaOH, then,



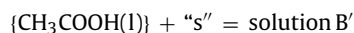
The results obtained from five dissolution experiments are listed in Table 3.

The stoichiometric number of $\text{CH}_3\text{COONH}_4(\text{s})$ in reaction (2) or $[n(\text{CH}_3\text{COONH}_4)/n(\text{benzoic acid})] = 1:1$ was regarded as a norm for sample weighing, about 1×10^{-3} mol of $\{\text{CH}_3\text{COONH}_4(\text{s})\}$ was dissolved in solution A', i.e.,



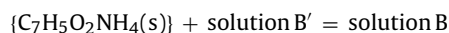
The results obtained from five dissolution experiments are listed in Table 3.

About 1×10^{-3} mol of $\text{CH}_3\text{COOH}(\text{l})$ was dissolved in 1 mol dm^{-3} NaOH at 298.15 K. Because of the volatilization of acetic acid, when the liquid was weighed, the temperature in room must be controlled at $17\text{--}18^\circ\text{C}$ to reduce the rate of volatilization, and the sample cell in which acetic acid was put should be covered with plug made of polytetrafluoroethylene, then,



The results obtained from five dissolution experiments are listed in Table 3.

The dissolution enthalpy of $\text{C}_7\text{H}_5\text{O}_2\text{NH}_4(\text{s})$ in solution B' was measured under the same condition as the above,



The results obtained from five dissolution experiments are listed in Table 3.

The enthalpy change of reaction (2) can be calculated in accordance with a thermochemical cycle and the experimental results.

The designed thermochemical cycle was shown in Scheme 1.

The results of UV/vis spectroscopy and refrangibility (refractive index) are both of important information used to detect whether the differences of the structure and composition between two kinds of solutions existed. In this paper, all of the reactants and products of reaction (2) can be easily dissolved in the selected solvent. The measured values of the refractive indices of solution A and solution B were (1.3441 ± 0.0004) and (1.3439 ± 0.0003) , respectively. The results of UV/vis spectroscopy are shown in Fig. 3. UV/vis spectra and the data of the refractive indices of solution A obtained

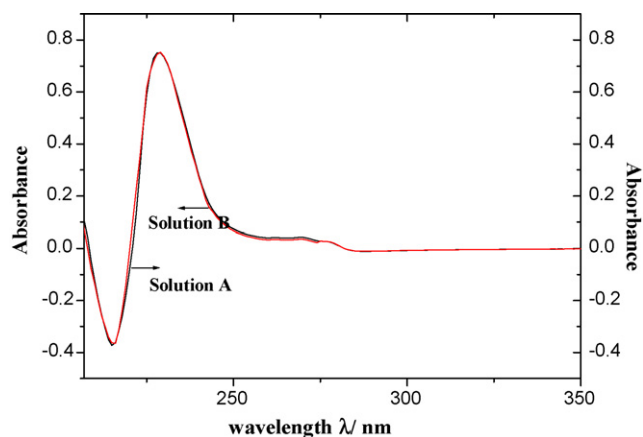
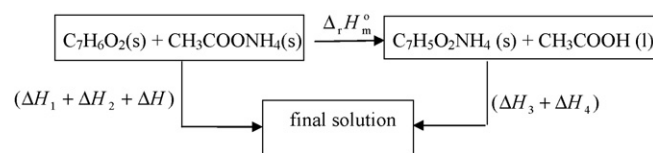


Fig. 3. UV/vis spectra of solutions A and B obtained from the dissolution of the $[\text{C}_7\text{H}_6\text{O}_2(\text{s})$ and $\text{CH}_3\text{COONH}_4(\text{s})]$ mixture and the $[\text{C}_7\text{H}_5\text{O}_2\text{NH}_4(\text{s})$ and $\text{CH}_3\text{COOH}(\text{l})]$ mixture in the supposed reaction (2) in 100 mL of 1 mol dm^{-3} NaOH (diluted to 1:20).



Scheme 2.

agree with those of solution B, no difference in the structure and chemical composition existed between the two solutions. These results have demonstrated that the solutions A and B were same, namely, $\Delta H = 0$, the designed Hess thermochemical cycle was reasonable and reliable, and can be used to derive the standard molar enthalpy of formation of the compound $\text{C}_7\text{H}_5\text{O}_2\text{NH}_4(\text{s})$. Then, solution A or solution B was defined as final solution. Therefore, the above thermochemical cycle also can be expressed as (Scheme 2):

According to Hess's law, the enthalpy change of the reaction can be calculated as,

$$\Delta H_1 + \Delta H_2 + \Delta H = \Delta_r H_m^\circ + (\Delta H_3 + \Delta H_4)$$

$$\Delta_r H_m^\circ = (\Delta H_1 + \Delta H_2 + \Delta H) - (\Delta H_3 + \Delta H_4)$$

Then,

$$\Delta_r H_m^\circ = \sum \Delta_{\text{sol}} H_m^\circ(\text{Reactants}) - \sum \Delta_{\text{sol}} H_m^\circ(\text{Products})$$

Therefore, the enthalpy change of the reaction (2) can be derived as,

$$\begin{aligned} \Delta_r H_m^\circ &= \sum \Delta_{\text{sol}} H_m^\circ(\text{Reactants}) - \sum \Delta_{\text{sol}} H_m^\circ(\text{Products}) = \Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 \\ &= [-26.496 + (-7.362)] - 4.536 - (-53.979) = (15.59 \pm 0.50) \text{ kJ mol}^{-1}. \end{aligned}$$

3.3. The standard molar enthalpy of formation of the compound $\text{C}_7\text{H}_5\text{O}_2\text{NH}_4(\text{s})$

A reaction scheme used to derive the standard molar enthalpy of formation of $\text{C}_7\text{H}_5\text{O}_2\text{NH}_4(\text{s})$ is given in Table 4. The experimental values of the dissolution enthalpies of the reactants and products in reactions (2) were combined with some auxiliary thermodynamic data of, $\Delta_f H_m^\circ[\text{C}_6\text{H}_5\text{COOH}, \text{s}] = -(384.8 \pm 0.50) \text{ kJ mol}^{-1}$ [10], $\Delta_f H_m^\circ[\text{CH}_3\text{COONH}_4, \text{s}] = -586.95 \text{ kJ mol}^{-1}$ [11], and $\Delta_f H_m^\circ[\text{CH}_3\text{COOH}, \text{l}] = -(483.52 \pm 0.36) \text{ kJ mol}^{-1}$ [12], to derive

Table 3
Dissolution enthalpies of reactants and products of the reaction (2) in the selected solvents at 298.15 K.^a

System	Solvent	No.	<i>m</i> (g)	$\Delta E_s/\Delta E_e$	<i>t_e</i> (s)	<i>Q_s</i> (J)	$\Delta_{sol}H_m^\circ$ (kJ mol ⁻¹)
Benzoic acid	1 mol dm ⁻³ NaOH	1	0.12233	1.4429	37.781	-26.485	-26.439
		2	0.12200	0.9774	55.373	-26.293	-26.319
		3	0.12243	0.9977	55.313	-26.811	-26.743
		4	0.12213	1.1905	45.281	-26.190	-26.188
		5	0.12270	1.8250	30.360	-26.918	-26.791
Avg. $\Delta_{sol}H_{m,1}^\circ = -(26.50 \pm 0.12)$ kJ mol ⁻¹							
Ammonium acetate	Solution A	1	0.07151	0.5707	25.999	-7.208	-7.769
		2	0.07446	0.7040	19.969	-6.823	-7.071
		3	0.07788	0.8853	17.015	-7.318	-7.243
		4	0.07589	0.8955	15.999	-6.961	-7.070
		5	0.07326	0.9745	15.375	-7.279	-7.659
Avg. $\Delta_{sol}H_{m,2}^\circ = -(7.36 \pm 0.15)$ kJ mol ⁻¹							
Ammonium benzoate	Solution B	1	0.13936	-1.2424	7.421	4.479	4.473
		2	0.13974	-1.2375	7.109	4.274	4.256
		3	0.13956	-1.2820	7.206	4.488	4.475
		4	0.13977	-1.4402	6.653	4.655	4.634
		5	0.13974	-1.4300	6.997	4.861	4.841
Avg. $\Delta_{sol}H_{m,3}^\circ = (4.54 \pm 0.10)$ kJ mol ⁻¹							
Acetic acid	1 mol dm ⁻³ NaOH	1	0.06066	0.8939	123.985	-53.895	-53.317
		2	0.06045	0.9320	123.672	-56.013	-55.642
		3	0.06073	0.9069	123.718	-54.525	-53.914
		4	0.06088	0.9109	123.749	-54.779	-54.032
		5	0.06058	0.8902	123.578	-53.460	-52.992
Avg. $\Delta_{sol}H_{m,4}^\circ = -(53.98 \pm 0.46)$ kJ mol ⁻¹							

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

Table 4
Reaction scheme used to determine the standard molar formation enthalpy of ammonium benzoate.

No.	Reactions	$\Delta_f H_m^\circ$ or $(\Delta_{sol} H_m^\circ \pm \sigma_a)$ ^a (kJ mol ⁻¹)
1	{C ₇ H ₆ O ₂ (s)} + "s" = solution A'	$-(26.50 \pm 0.12)$, ΔH_1
2	{CH ₃ COONH ₄ (s)} + solution A' = solution A	$-(7.36 \pm 0.15)$, ΔH_2
3	{C ₇ H ₅ O ₂ NH ₄ (s)} + solution B' = solution B	(4.54 ± 0.10) , ΔH_3
4	{CH ₃ COOH(l)} + "s" = solution B'	$-(53.98 \pm 0.46)$, ΔH_4
5	7C(s) + 3H ₂ (g) + O ₂ (g) = C ₇ H ₆ O ₂ (s)	$-(384.8 \pm 0.50)$, ΔH_5
6	2C(s) + (7/2)H ₂ (g) + O ₂ (g) + (1/2)N ₂ (g) = CH ₃ COONH ₄ (s)	-586.95, ΔH_6
7	2C(s) + 2H ₂ (g) + O ₂ (g) = CH ₃ COOH(l)	$-(483.52 \pm 0.36)$, ΔH_7
8	7C(s) + (9/2)H ₂ (g) + O ₂ (g) + (1/2)N ₂ (g) = C ₇ H ₅ O ₂ NH ₄ (s)	$-(472.65 \pm 0.62)$, ΔH_8

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

the standard molar enthalpy of formation of C₇H₅O₂NH₄(s),

$$\begin{aligned} \Delta_f H_m^\circ(\text{C}_7\text{H}_5\text{O}_2\text{NH}_4, \text{s}) &= \Delta H_8 = \Delta_f H_m^\circ + \Delta_f H_m^\circ(\text{C}_7\text{H}_6\text{O}_2, \text{s}) \\ &+ \Delta_f H_m^\circ(\text{CH}_3\text{COONH}_4, \text{s}) \\ &- \Delta_f H_m^\circ(\text{CH}_3\text{COOH}, \text{l}) = \Delta H_1 + \Delta H_2 \\ &- \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6 - \Delta H_7 \\ &= [-26.496 + (-4.362)] - 4.536 \\ &- (-53.979) + (-384.8) + (-586.95) \\ &- (-483.52) = -(472.65 \pm 0.62) \text{ kJ mol}^{-1} \end{aligned}$$

in which $\Delta H_1 - \Delta H_8$ are the enthalpy changes of the reactions corresponding to number of the reactions in Table 4.

4. Conclusions

This paper reports low-temperature heat capacities of the solid-state compound C₇H₅O₂NH₄(s) measured by adiabatic calorimetry

and the dissolution enthalpies of the reactants and products of the designed solid-state reaction of ammonium acetate with benzoic acid by isoperibol solution–reaction calorimetry. Additionally, the thermodynamic functions and standard molar enthalpy of formation of the product C₇H₅O₂NH₄(s) were derived from these experimental results.

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