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HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF 2-BENZOYLPYRIDINE ($C_{12}H_9NO$)

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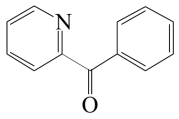
The heat capacities of 2-benzoylpyridine were measured with an automated adiabatic calorimeter over the temperature range from 80 to 340 K. The melting point, molar enthalpy, $\Delta_{fus}H_m$, and entropy, $\Delta_{fus}S_m$, of fusion of this compound were determined to be 316.49±0.04 K, 20.91±0.03 kJ mol^{-1} and 66.07±0.05 J mol^{-1} K^{-1}, respectively. The purity of the compound was calculated to be 99.60 mol% by using the fractional melting technique. The thermodynamic functions (H_T–$H_{298.15}$) and (S_T–$S_{298.15}$) were calculated based on the heat capacity measurements in the temperature range of 80–340 K with an interval of 5 K. The thermal properties of the compound were further investigated by differential scanning calorimetry (DSC). From the DSC curve, the temperature corresponding to the maximum evaporation rate, the molar enthalpy and entropy of evaporation were determined to be 556.3±0.1 K, 51.3±0.2 kJ mol^{-1} and 92.2±0.4 J K^{-1} mol^{-1}, respectively, under the experimental conditions.

Keywords: *adiabatic calorimetry, 2-benzoylpyridine, DSC, heat capacity, thermodynamic functions*

Introduction

2-benzoylpyridine ($C_{12}H_9NO$, CAS: 91-02-1) is an important intermediate of medicine which has been widely used in the synthesis of many new medicines [1]. Its molecular structure is as follows:



Most of the previous works carried out on this substance were concerned with how to effectively synthesize it and how to prepare some new compounds with it. However, the thermodynamic properties of this substance were scarcely reported in literature. Only the melting and boiling points have been reported to be 315–317 and 590 K in the Dictionary of Organic Compounds and the Handbook of Data on Organic Compounds [2, 3], respectively. In order to satisfy the requirements of application and theoretical research concerned with the substance, the thermodynamic property data of this substance are urgently needed.

Heat capacity is one of the fundamental thermodynamic properties of substances and closely related to the energetic structure, and is sensitive to the variations in other properties. Heat capacity determinations of various compounds had attracted many researchers' attention. Adiabatic calorimetry is the most accurate approach to obtain the heat capacity data, melting point and enthalpy of fusion of substances. In the present study, the low-temperature heat capacities have been measured in the temperature range from 79 to 340 K with an automated adiabatic calorimeter. The melting temperature, the molar enthalpy and entropy of fusion of the substance were determined. The thermal properties of the compound were further investigated by differential scanning calorimetry (DSC).

Experimental

Sample

The 2-benzoylpyridine is a white crystal. The sample used for the present calorimetric study was purchased from J&K Chemical Ltd. The labeled chemical purity is >0.990 mass fraction. The melting point of the sample was determined to be 316 to 317 K with a microscopic melting point device (model: BY-1, Yazawa Co., Japan), and in agreement with that of the literature [2]. The IR (model: 260-10, made by HITACHI, Japan) and ^{1}H NMR (model: Unity Plus 500, made by Varian Ltd., USA, $CDCl_3$) were employed to affirm the structure of the sample.

Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimetric system described in detail previously [4–6]. The sample amount used for the heat capacity measurement is

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3.7326 g, which is equivalent to 20.373 mmol based on its molar mass of 183.21 g mol^{-1}.

Prior to heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the standard reference material, synthetic sapphire (α-Al_2O_3, SRM 720). The deviation of our calibration results from the recommended values reported by Archer [7] is within of ±0.5% in the temperature range from 80 to 400 K.

Thermal analysis

DSC analysis was carried out in a DSC-141 calorimeter (Setaram Co., France). The sample of 4.6 mg was sealed in an aluminium pan and heated at the rate of 10 K min^{-1} under high purity nitrogen atmosphere with a flow rate of 50 mL min^{-1}.

Results and discussion

Heat capacity

The experimental molar heat capacities of the sample are shown in Fig. 1 and tabulated in Table 1. From Fig. 1 it can be seen that the heat capacities of the sample increase with temperature in a smooth and continuous manner from 79 to 304 K and no phase transition or thermal anomaly was observed in this temperature range. Therefore, the sample is stable in the above temperature range. However, a thermal anomaly was observed in the temperature range from 304 to 320 K with the peak temperature of 316.38 K. The thermal anomaly can be ascribed to a solid-liquid phase transition according to the previous measurements of melting point.

The experimental molar heat capacities have been fitted to the following polynomial in reduced temperature (X), by means of the least square fitting.

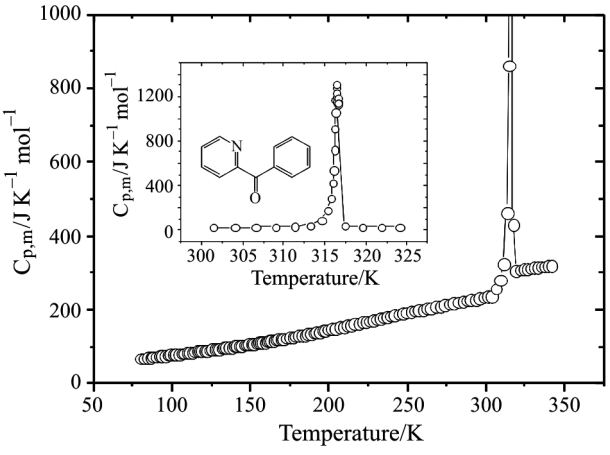

Fig. 1 Experimental molar heat capacity $C_{p,m}$ of 2-benzoylpyridine as a function of temperature

For the solid phase

$$C_{p,m}\ [\mathrm{J\ K^{-1}\ mol^{-1}}] = 138.9 + 94.371X + 23.88X^2 - 10.127X^3 - 10.929X^4$$

where $X=(T-192)/112$. The above equation is valid in the temperature range from 80 to 304 K. The deviations of experimental results from the smoothed curve lie within ±0.6%.

For the liquid phase

$$C_{p,m}\ [\mathrm{J\ K^{-1}\ mol^{-1}}] = 313.558 + 6.008X - 0.7418X^2 + 0.386X^3$$

where $X=(T-330)/10$. This equation applies to the temperature range from 320 to 340 K. The deviations of experimental results from the smoothed curve lie within ±0.2%.

Melting point, enthalpy and entropy of fusion

The melting point was determined to be 316.49±0.04 K from the heat capacity measurements by a progressive approach with step-by-step heating. The molar enthalpy, $\Delta_{fus}H_m$, and entropy, $\Delta_{fus}S_m$, of fusion were derived by the following equations [8, 9].

$$\Delta H_m = \frac{Q - n\int_{T_i}^{T_m} C_{p,s}\mathrm{d}T - n\int_{T_m}^{T_f} C_{p,l}\mathrm{d}T - n\int_{T_i}^{T_f} H_0\mathrm{d}T}{n} \quad (1)$$

$$\Delta S_m = \frac{\Delta H_m}{T} \quad (2)$$

where T_i is a temperature slightly lower than the initial melting temperature, T_f a temperature slightly higher than the final melting temperature, Q the total energy introduced into the sample cell from T_i to T_f, H_0 the heat capacity of the sample cell from T_i to T_f, $C_{p,s}$ the heat capacity of the sample in solid phase from T_i to T_m, $C_{p,l}$ the heat capacity of the sample in liquid phase from T_m to T_f and n the molar amount of the sample. The molar enthalpy and molar entropy of fusion of the sample were determined to be 20.91±0.03 kJ mol^{-1} and 66.07±0.05 J K^{-1} mol^{-1}, respectively.

Purity determination

Adiabatic calorimetry provides an accurate way for determining the purity of a substance. The purity of sample can be evaluated from a set of equilibrium melting temperature (T) and melting fraction (F) corresponding to these temperatures [10]. The equilibrium melting temperature (T) plotted *vs*. the reciprocal of the melting fractions ($1/F$) gives a straight line as illustrated in Fig. 2. The T_0 is the temperature when $1/F$ equals to 0 and T_1 is equivalent to the temperature when $1/F$ is 1. From Fig. 2, the T_0 and T_1 are determined to be 316.63 and 316.49 K, respectively. Thus

Table 1 The experimental molar heat capacity of 2-benzoylpyridine (molar mass M=183.21 g mol^{-1})

Temperature/K	$C_{p,m}$ /J K^{-1} mol^{-1}	Temperature/K	$C_{p,m}$ /J K^{-1} mol^{-1}	Temperature/K	$C_{p,m}$ /J K^{-1} mol^{-1}
80.40	67.51	160.62	114.2	265.09	205.5
82.20	68.48	161.99	115.5	268.07	207.5
84.21	69.59	163.34	116.5	270.99	209.8
86.18	70.61	164.68	117.7	273.88	212.6
88.10	71.84	166.00	118.3	276.76	215.9
90.01	72.99	167.32	119.8	279.61	217.5
91.89	73.98	168.97	121.0	282.44	219.8
93.74	75.04	171.01	121.4	285.24	222.4
95.57	76.05	173.03	123.4	287.99	224.8
97.37	76.88	175.00	124.8	290.71	226.3
99.15	77.86	176.97	125.7	293.40	228.6
100.92	78.89	178.93	127.5	296.07	230.5
102.66	79.68	180.87	128.9	298.73	233.8
104.39	80.66	182.80	130.7	301.38	235.2
106.11	81.61	184.72	131.9	303.97	238.0
107.81	82.30	186.62	133.4	306.50	257.2
109.49	83.43	188.50	135.8	308.96	280.3
111.15	84.34	190.38	137.5	311.25	323.5
112.81	85.15	192.24	139.2	313.19	463.9
114.44	85.83	194.08	140.8	314.58	861.9
116.06	87.22	195.91	142.7	315.34	1749
117.67	87.86	197.72	144.6	315.73	2897
119.27	88.60	199.53	145.9	315.94	4213
120.85	89.69	201.69	147.5	316.07	5399
122.43	90.29	204.24	149.1	316.15	7207
124.00	91.05	206.74	151.5	316.20	9138
125.56	92.17	209.22	153.7	316.25	10598
127.12	92.77	211.67	156.2	316.29	11735
128.66	93.40	214.09	158.1	316.32	11975
130.19	94.38	216.49	161.3	316.35	12761
131.72	95.96	218.85	163.4	316.38	13127
133.23	97.02	221.19	165.6	316.41	12320
134.76	98.02	223.51	167.2	316.45	11918
136.36	99.04	225.80	169.4	316.48	11553
138.01	99.57	228.08	171.4	316.51	11511
139.64	101.1	230.36	174.0	316.53	11406
141.27	102.1	232.64	176.2	316.53	11236
142.89	103.4	234.97	178.1	317.36	431.5
144.46	103.9	237.28	181.1	319.49	306.2
146.00	104.1	239.51	183.2	321.80	307.7
147.51	105.1	241.89	184.7	324.08	309.4
149.02	106.7	244.51	187.5	326.32	311.3
150.52	108.0	247.14	189.2	328.54	312.9
152.00	108.5	249.75	192.9	330.74	314.0
153.48	109.4	252.33	194.7	332.95	315.2
154.95	110.5	254.90	197.4	335.15	316.8
156.41	111.4	257.45	199.1	337.35	317.4
157.85	112.0	259.94	201.0	339.54	318.8
159.24	113.3	262.38	203.5	341.73	320.4

Table 2 The observed equilibrium temperature (T) and fraction melted (F) during the melting process

$F=q/Q$	$1/F$	Temperature/K
0.07108	14.07	314.58
0.1079	9.267	315.34
0.1508	6.630	315.73
0.1967	5.084	315.94
0.2439	4.099	316.07
0.2921	3.423	316.15
0.3410	2.933	316.20
0.3901	2.564	316.25
0.4394	2.276	316.29
0.4888	2.046	316.32
0.5384	1.857	316.35
0.5880	1.701	316.38

we calculate the mole percentage of impurities, N=0.40 mol% from the Van't Hoff equation, and the purity of 2-benzoylpyridine sample used in the calorimetric experiment accounts to 1–N=99.60 mol%.

Thermodynamic functions of 2-benzoylpyridine

Enthalpy and entropy of substances are the basic thermodynamic functions. Through the polynomial of heat capacity and the relationship between thermodynamic functions and heat capacity, the thermodynamic function data relative to the reference temperature (298.15 K) were calculated in the temperature range from 80 to 340 K with an interval of 5 K. The thermodynamic relationships used for the calculation are as follows:

- Before the melting of the sample,

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m}(s)\mathrm{d}T \quad (3)$$

$$S_T - S_{298.15} = \int_{298.15}^{T} [C_{p,m}(s)/T]\mathrm{d}T \quad (4)$$

- After the melting of the sample,

$$H_T - H_{298.15} = \int_{298.15}^{T_i} C_{p,m}(s)\mathrm{d}T + \Delta_{fus}H_m + \int_{T_f}^{T} C_{p,m}(l)\mathrm{d}T \quad (5)$$

$$S_T - S_{298.15} = \int_{298.15}^{T_i} [C_{p,m}(s)/T]\mathrm{d}T + \Delta_{fus}H_m/T_m + \int_{T_f}^{T} [C_{p,m}(l)/T]\mathrm{d}T \quad (6)$$

The values of thermodynamic function $H_T - H_{298.15}$, $S_T - S_{298.15}$ are listed in Table 3.

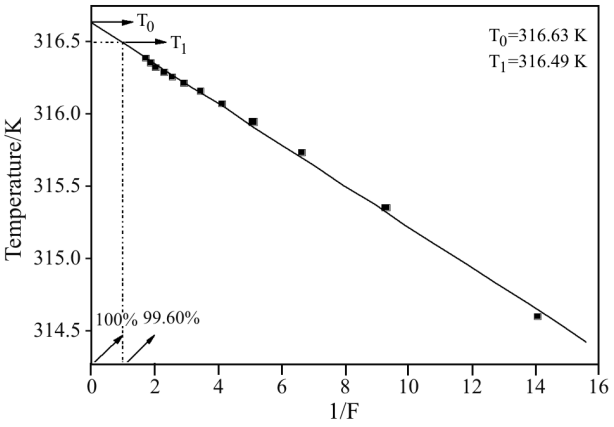

Fig. 2 The equilibrium temperature *vs*. the reciprocal of the melted fraction for 2-benzoylpyridine during melting process

The results of DSC analysis

It can be seen from the DSC curve (Fig. 3) that there are two endothermic processes in the temperature range from 304 to 590 K. The first sharply endothermic peak was assigned to melting with the peak temperature of 318.4 K. Based on the DSC curve, the melting point of the sample was determined to be 316 K, which is consistent with the value (316.49 K) obtained from the adiabatic calorimetric measurements. The second endothermic peak takes place in the range of 500–590 K. According to the boiling point of 2-benzoylpyridine, the endothermic process is really due to the evaporation of the sample. From the DSC curve, the temperature corresponding to the maximum evaporation rate, the molar enthalpy and entropy of evaporation were determined to be 556.3±0.1 K, 51.3±0.2 kJ mol^{-1} and 92.2±0.4 J K^{-1} mol^{-1}, respectively, under the experimental conditions.

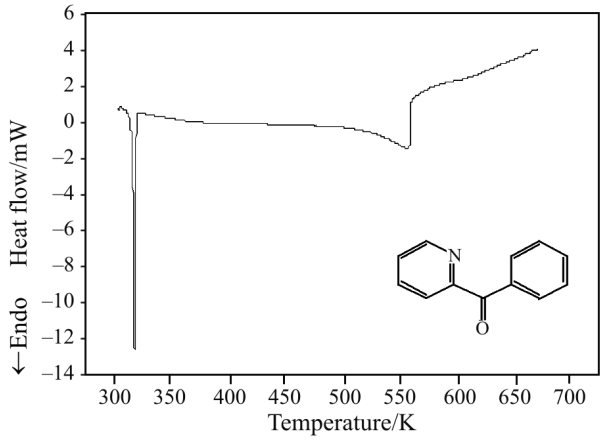

Fig. 3 DSC curve of 2-benzoylpyridine

Table 3 Calculated thermodynamic function data of 2-benzoylpyridine

Temperature/K	C_p/J K^{-1} mol^{-1}	H_T–$H_{298.15}$/kJ mol^{-1}	S_T–$S_{298.15}$/J K^{-1} mol^{-1}
		Crystal	
80	67.65	–31.05	–163.9
85	70.31	–30.70	–159.8
90	72.94	–30.34	–155.7
95	75.56	–29.97	–151.7
100	78.18	–29.59	–147.7
105	80.82	–29.19	–143.8
110	83.49	–28.78	–140.0
115	86.20	–28.36	–136.2
120	88.97	–27.92	–132.5
125	91.81	–27.47	–128.8
130	94.72	–27.00	–125.1
135	97.71	–26.52	–121.5
140	100.8	–26.02	–117.9
145	104.0	–25.51	–114.3
150	107.2	–24.98	–110.7
155	110.6	–24.44	–107.2
160	114.1	–23.88	–103.6
165	117.7	–23.30	–100.1
170	121.4	–22.70	–96.50
175	125.2	–22.08	–92.93
180	129.1	–21.45	–89.35
185	133.1	–20.79	–85.76
190	137.3	–20.12	–82.16
195	141.5	–19.42	–78.54
200	145.8	–18.70	–74.90
205	150.2	–17.96	–71.25
210	154.7	–17.20	–67.57
215	159.2	–16.41	–63.87
220	163.8	–15.61	–60.15
225	168.5	–14.78	–56.41
230	173.2	–13.92	–52.65
235	177.9	–13.04	–48.87
240	182.6	–12.14	–45.07
245	187.3	–11.22	–41.25
250	192.0	–10.27	–37.41
255	196.7	–9.297	–33.56
260	201.3	–8.302	–29.70
265	205.8	–7.284	–25.83
270	210.3	–6.244	–21.94
275	214.6	–5.182	–18.05
280	218.8	–4.098	–14.16
285	222.8	–2.994	–10.26
290	226.6	–1.871	–6.360
295	230.2	–0.7290	–2.460
298.15	233.4	0	0
300	233.6	0.431	1.440
		Liquid	
320	306.4	23.70	64.80
325	310.3	25.25	69.59
330	313.6	26.81	74.35
335	316.4	28.38	79.09
340	319.2	29.97	83.79

Acknowledgements

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