CALORIMETRIC STUDY AND THERMAL ANALYSIS OF CRYSTALLINE NICOTINIC ACID

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Abstract

As one primary component of Vitamin B_3, nicotinic acid [pyridine 3-carboxylic acid] was synthesized, and calorimetric study and thermal analysis for this compound were performed. The low-temperature heat capacity of nicotinic acid was measured with a precise automated adiabatic calorimeter over the temperature rang from 79 to 368 K. No thermal anomaly or phase transition was observed in this temperature range. A solid-to-solid transition at T_{trs}=451.4 K, a solid-to-liquid transition at T_{fus}=509.1 K and a thermal decomposition at T_d=538.8 K were found through the DSC and TG-DTG techniques. The molar enthalpies of these transitions were determined to be $_{trs}H_m$=0.81 kJ mol^{-1}, $_{fus}H_m$=27.57 kJ mol^{-1} and $_dH_m$=62.38 kJ mol^{-1}, respectively, by the integrals of the peak areas of the DSC curves.

Introduction

Nicotinic acid (pyridine 3-carboxylic acid; CA registry No. 59-67-6) is usually referred to as one primary component of Vitamin B_3, which plays an important role in the biological body due to its unique biological activity [1]. Whereas being an indispensable nutriment of human and animal, it has been widely used in food, forage, medicines and cosmetics as additive. Moreover, it is an important raw material and intermediate used widely in the syntheses of many medicines and dyes [2]. Molecular formula of nicotinic acid is $C_6H_5NO_2$. Its molecular structure is

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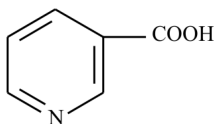
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In 1932, McElvain, using nicotine and concentrated nitric acid as reactants, successfully synthesized the compound through a simple method [3]. Since then, thermodynamic properties of nicotinic acid were scarcely reported in literature. Heat capacity was one of the fundamental thermodynamic properties of substances. Heat capacities determinations of various compounds had attracted many researchers' attention [4–8]. For the application of the compound, thermodynamic properties of this substance are urgently required.

In the present work, the low-temperature heat capacity of nicotinic acid has been measured over the temperature range from 79 to 368 K. The phase transitions and the thermal decomposition of this compound were investigated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC).

Experimental

Sample preparation

Nicotinic acid was prepared according to the procedure given in [3]. Nicotine (3-(2-(N-methylpyrrolidinyl)) pyridine) was slowly added to concentrated nitric acid. The mixture was stirred in steam-bath at 70°C for about 11 h. The crude product obtained was recrystallined three times in boiling water. The melting point of the final product was determined to be 236.5–237.5°C with a microscopic melting point device (model: BY-1, Yazawa Co., Japan). This value is in agreement with that reported in [9].

The structure of the synthesized sample was determined by infrared (IR), hydrogen-1 nuclear magnetic resonance (^{1}H NMR), carbon-13 nuclear magnetic resonance (^{13}C NMR). HPLC indicated that the purity of the sample was higher than 99.0%. Chemical and element analysis showed that the purity of the sample prepared was 99.6%.

Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter described in detail elsewhere [10, 11]. The principle of the calorimeter was based on the Nernst stepwise heating method. The calorimeter mainly consisted of a sample cell, an adiabatic (or inner) shield, a guard (outer) shield, a platinum resistance thermometer, an electric heater, two sets of chromel–copper (Ni: 55%, Cu: 45%) thermocouples and a high vacuum can. The sample cell was made of gold-plated copper and had an inner volume of 6 cm^3. Four gold-plated copper vans of 0.2 mm in thickness with an X shape were put into the cell to promote heat conduction from the cell to the sample. The platinum resistance thermometer was inserted into a copper sheath, which was soldered at the bottom of the sample cell. The heater wires were wound on the outside wall of the cell. The lid of the cell with a copper capillary was sealed to the sample cell with cycleweld after the sample was loaded in it. The air in the cell was pumped out and a small amount of helium gas (0.1 MPa) was introduced into it to enhance the heat transfer in the cell. The capillary was pinched off and the

resultant fracture was soldered with a little amount of solder to ensure the cell for sealing. The evacuated can was kept within ca.10^{-3} Pa during the heat capacity measurements so as to eliminate the heat loss due to gas convection between the sample cell and the inner shield. Liquid nitrogen was used as the cooling medium. Likewise, the other set of thermocouples was installed between the inner and outer shields. The temperature difference between them was automatically kept to be 0.5 mK during the whole experiment. The sample cell was heated by the standard discrete heating method. The temperature of the cell was alternatively measured. The temperature increment for a heating period was 2–4 K, and temperature drift was maintained at less than 10^{-3} K min^{-1} during each equilibrium period. All the data were automatically picked up through a data acquisition/switch unit (Model: 34970A, Agilent USA) and processed on line by a computer.

In the present study, the mass of nicotinic acid used for heat capacity measurement was 1.9406 g, which was equivalent to 0.01576 mol based on its molar mass of 123.11 g mol^{-1}.

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material -Al$_2$O$_3$ were measured. The deviation of our experimental results from the recommended values of the former National Bureau of Standard [12] was within 0.2% in the whole experimental temperature range.

Thermal analysis

A thermogravimetric analyzer (Model: setsys 16/18 from Setaram Company, France) was used for TG-DTG measurement of this sample under nitrogen atmosphere (99.999%). The heating rate was 10 K min^{-1} and the flow rate of nitrogen was 65 cm^3 min^{-1}. The mass of the sample was 7.9 mg. Two Al$_2$O$_3$ crucibles were used (capacity: 100 μL). The reference crucible was filled with -Al$_2$O$_3$. The TG-DTG equipment was calibrated by the SRM in thermal analysis, CaC$_2$O$_4$ H$_2$O (s).

A differential scanning calorimeter (Model: DSC 141, Setaram Company, France) was used to perform the thermal analysis of the sample with a heating rate of 10 K min^{-1}. Liquid nitrogen was used as the cooling medium. Dry nitrogen was used as a purge gas at a flow rate of 65 cm^3 min^{-1}. The mass of the sample was 2.9 mg. Two aluminum crucibles were used (capacity: 30 μL) and the reference crucible was empty. The calibrations for the temperature and heat flux of the calorimeter were performed prior to the experiment; the temperature scale was calibrated by measuring the melting points of Hg, In, Sn, Pb and Zn, at different heating rates, and the heat flux was calibrated by the Joule effect. Measurements of the melting temperature and the enthalpy of fusion of benzoic acid (NIST, Standard Reference Material 39i) were made in our laboratory to check the accuracy of the instrument.

Results and discussion

Heat capacity

The low-temperature experimental molar heat capacities of the solid compound are shown in Fig. 1 and listed in Table 1. The molar heat capacities of the sample are fit-
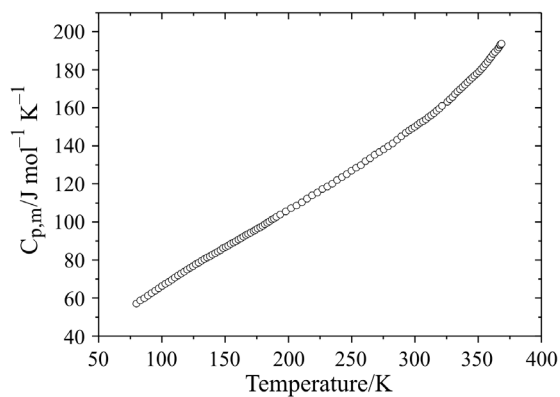
Fig. 1 Experimental molar heat capacities ($C_{p,m}$) of nicotinic acid as a function of the temperature (K)

Table 1 The experimental molar heat capacities of nicotinic acid (molecular formula: $C_6H_5NO_2$, molar mass: 123.11 g mol^{-1})

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}
79.77	57.168	170.15	94.452	295.45	148.18
82.88	58.679	172.50	95.281	297.65	149.07
85.98	59.892	173.94	95.852	299.85	149.94
88.93	61.254	175.83	96.619	302.07	151.16
91.82	62.576	177.73	97.209	304.21	152.18
94.62	63.880	179.55	97.951	306.36	152.93
97.42	65.088	181.41	98.799	308.56	153.98
100.09	66.361	183.24	99.589	310.68	155.15
102.72	67.489	185.07	100.33	312.88	156.14
105.31	68.467	186.89	101.29	315.00	157.23
107.85	69.647	188.04	101.84	317.12	158.45
110.34	70.776	190.45	102.66	319.24	159.66
112.80	71.847	193.48	103.95	321.36	161.07
115.22	72.899	197.88	105.55	325.53	163.17
117.61	73.814	202.18	107.25	327.57	164.56
119.96	74.913	206.26	108.72	329.62	165.75

Table 1 Continued

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}
122.29	75.945	210.57	110.41	331.64	167.27
124.58	76.756	214.72	112.25	333.64	168.59
126.58	77.780	218.79	114.01	335.57	169.80
129.09	78.607	222.86	115.43	337.58	170.95
131.31	79.631	226.79	117.33	339.57	172.31
133.48	80.501	230.79	118.66	341.44	173.48
135.68	81.306	234.64	120.14	343.43	174.74
137.84	52.016	238.50	122.01	345.29	175.89
139.98	82.833	242.29	12.62	347.14	177.01
142.10	83.563	246.00	125.07	348.93	178.06
144.21	84.345	249.79	126.98	350.71	179.14
146.29	85.169	253.50	128.51	352.43	180.47
148.36	86.254	257.29	129.89	354.14	181.65
150.41	86.835	260.90	131.95	355.79	183.05
152.45	87.545	264.57	133.50	357.36	184.37
154.47	88.516	268.00	135.39	357.93	185.71
156.44	89.188	274.59	136.70	360.29	186.86
158.48	89.854	275.26	138.20	361.79	188.26
160.45	90.787	278.86	139.74	363.36	189.43
162.41	91.468	282.50	141.32	365.29	190.79
164.36	92.302	285.86	143.26	366.36	191.80
166.31	93.159	289.23	145.14	367.21	192.83
168.23	93.725	292.05	146.88	367.43	193.24

ted to the following polynomial equation of heat capacities ($C_{p,m}$) with reduced temperature (X) by means of the least square fitting:

$$C_{p,m}\,(\text{J mol}^{-1}\,\text{K}^{-1})=115.77043+59.91381X+7.53269X^2+$$

$$+1.2433X^3-2.39857X^4+7.21254X^5+4.134X^6 \tag{1}$$

in which $X=(T-223.5)/144.5$, and T/K is the absolute temperature. The correlation coefficient of the fitting, $R^2=0.99998$. The above equation is valid in the temperature range from 79 to 368 K. Based on Eq. (1), the heat capacity of the sample at 298.15 K was calculated to be 149.08 J mol^{-1} K^{-1}.

From Fig. 1, it can be seen that the heat capacity of the sample increases with increasing temperature in a smooth and continuous manner in the temperature range
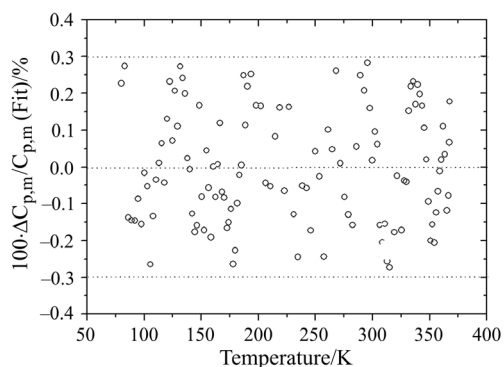
Fig. 2 The plot of relative deviations of the experimental heat capacity values
[$C_{p,m}$(Expt)] from the fitting heat-capacity values [$C_{p,m}$(Fit)] *vs*. the absolute
temperature (*T*). { $C_{p,m}$ =[$C_{p,m}$(Expt)–$C_{p,m}$(Fit)]}

from 79 to 368 K. In this temperature range, no phase transition and thermal anomaly
were observed, which indicates that this sample is stable in the above temperature range.

Figure 2 gives the plot of relative deviations of the experimental heat capacity
values of the sample, $C_{p,m}$(Expt), from the fitting heat-capacity values, $C_{p,m}$(Fit), *vs*.
the absolute temperature (*T*). It can be seen from Fig. 2 that relative deviations of all
the experimental points from the fitting heat-capacity values are within 0.30% in
the solid phase region.

DSC and TG-DTG results

From the DSC curve (Fig. 3), a weak endothermic peak assigned to a solid-solid
phase transition was observed [13] with the peak temperature of 452.4 K. Based on
the DSC curve, the temperature (T_{trs}) and the molar enthalpy ($\Delta_{trs}H_m$) of the
solid–solid phase transition of the sample were determined to be 451.4 K
and 0.81 kJ mol^{-1}, respectively, which was in agreement with that reported in [13].
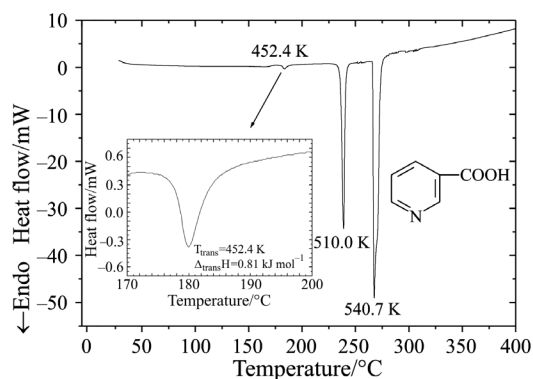
Fig. 3 DSC curve of nicotinic acid under high purity nitrogen (99.999%) atmosphere

Next to the solid–solid phase transition, a sharply endothermic peak corresponding to the melting of the sample [13] was observed with the peak temperature of 510.0 K. The melting point (T_{fus}) and the molar enthalpy ($_{fus}H_m$) were determined to be 509.1 K and 27.57 kJ mol^{-1}. When the temperature was higher than 538 K, another sharply endothermic peak associated with the thermal decomposition of the sample appeared in the temperature range from 538.8 to 552.7 K with the peak temperature at 540.7 K. The temperature and molar enthalpy of the thermal decomposition were determined to be 538.8 K and 62.38 kJ mol^{-1}, respectively.
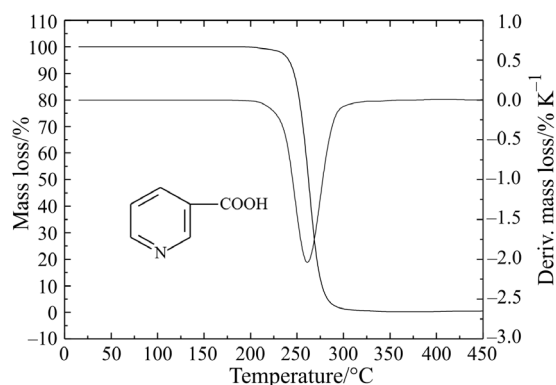
Fig. 4 TG-DTG curves of nicotinic acid under high purity nitrogen (99.999%) atmosphere

The TG-DTG measurement was carried out under N$_2$ atmosphere. The TG-DTG result was presented in Fig. 4. It can be seen from the curve of the Fig. 4 that the mass loss occurred in the temperature range from 504 to 573 K in one step. No residue was found in the crucible after the experiment was completed. The FT-IR spectrum of the condensation product of evaporation of the sample at about 540 K was not the same as that of original sample. So, we considered that the third endothermic peak in the DSC curve and the mass loss process in the TG-DTG curve corresponded to the decomposition of the sample, instead of evaporation.

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