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Short communication

Heat capacity and enthalpy of fusion of penconazole ($C_{13}H_{15}Cl_2N_3$)

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Abstract

Low-temperature heat capacities of penconazole ($C_{13}H_{15}Cl_2N_3$) were precisely measured with an automated adiabatic calorimeter over the temperature rang from 78 to 364 K. The sample was observed to melt at 332.38 ± 0.06 K. The molar enthalpy and entropy of fusion of the compound were determined to be 33580 ± 11 J mol^{-1}, 101.03 ± 0.02 J mol^{-1} K^{-1}, respectively. Further research of the melting process for this compound was carried out by means of differential scanning calorimetry (DSC) technique. The result was in agreement with that obtained from the measurements of heat capacities.

Keywords: Penconazole; Heat capacity; Thermodynamic functions; Adiabatic calorimetry; DSC

1. Introduction

Penconazole (molecular formula: $C_{13}H_{15}Cl_2N_3$; CA registry no.: 66246-88-6) is a high-efficiency fungicide. It is widely used to control powdery mildew and scab of squash, grape and some ornamental plants and vegetable. The application and synthetic methods of the compound have been reported [1–4], but no reports on the thermodynamic properties of the substance have been reported. For the application of the compound, the thermodynamic data for the penconazole is urgently required. In the present work, penconazole was synthesized by using a new method and low-temperature heat capacity measurements of the compound were carried out with an adiabatic calorimeter. The basic thermodynamic parameters, such as the melting point, molar enthalpy and entropy of melting have been determined. Furthermore, thermal stability and melting process of the compound were also studied by differential scanning calorimetry (DSC).

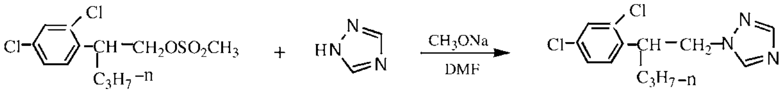
2. Experimental

2.1. Sample preparation and characterization

2.1.1. Equipments and reagents

2-(2,4-Dichlorophenyl)-pentyl methanesulfonate was made according to the method reported in literature [3], sodium methylate, *N,N*-dimethylformamide (DMF), methanol, 1H-1,2,4-triazole, isopropyl ether, *n*-hexane and dichlorometnane were of analytical grade. PE-2400 elemental analyzer, BRUKER EQUNINOX-55 IR spectral meter, Varian Inova-400 ^{1}H NMR spectrum, Agilent gas chromatograph/Hewlett-Packard mass spectrometry and SMP3 melting point apparatus were applied to characterize the structure of the compound.

2.1.2. The scheme of the formation reaction of penconazole



2.1.3. Experimental procedures

To mix 13.2 g of sodium methylate with methanol by a magnetic stirrer, and 100 ml of *N,N*-dimethylformamide was added with 21 g (0.3 mol) of 1H-1,2,4-triazole. After

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stirring for 0.5 h at room temperature, methanol was distillated out from the reaction mixture. Then, a solution of 31.5 g (0.1 mol) of 2-(2,4-dichlorophenyl)-pentyl methanesulfonate in 45 ml of *N,N*-dimethylformamide was added dropwise. The whole was stirred for 8 h at 80 °C. The reaction mixture was cooled and poured into water. The product was extracted three times with isopropyl ether. The combined extracts were washed with water, dried, filtered and evaporated. The residue was crystallized from *n*-hexane. The crude product was filtered off and purified three times with dichloromethane. The final product penconazole was a colorless crystal. Its purity was 99.36% (GC).

2.1.4. Analysis result of penconazole

The melting point of the final product was determined to be 59.6 °C in agreement with literature [2]. The results of elementary analysis were: N: 14.76 (14.78); C: 54.96 (54.89); H: 5.279 (5.278). ^{1}H MNR ($CDCl_3$) absorption peaks were detected at $\delta = 0.824$ (s, 3H, CH_3), 1.084–1.139 (m, 2H, CH_2), 1.573–1.626 (m, 2H, CH_2), 3.731–3.762 (m, 1H, CH), 4.415–4.483 (m, 2H, CH_2), 7.413–7.518 (m, 3H, H_3Ar), 7.895 (s, 1H, H-triazole), 8.259 (s, 1H, H triazole) ppm. IR (KBr disks) showed characteristic absorption peaks at 3396, 3965, 1590 and 1349 cm^{-1}. MS (EI) *m*/*z*: 282 $[M - 2H]^+$.

2.2. Adiabatic calorimetry

The heat capacity measurements were made by an adiabatic calorimetric system for small samples over the temperature range from 78 to 364 K. The construction of the calorimeter has been described previously [5,6] in detail. It consists of a sample cell, a platinum resistance thermometer, a heater, two (inner and outer) adiabatic shields, two sets of differential thermocouples, a vacuum can and a Dewar vessel. Liquid nitrogen was used as the cooling medium. The evacuated can or chamber was kept within 10^{-3} Pa vacuum in the temperature range of 78–364 K to eliminate the heat loss owing to the gas convection, and a small amount of helium gas was introduced through a length of copper capillary at the center of the upper cover into the cell to improve the heat transfer of the whole sample cell. The sample cell was sealed with the tin solder after the copper capillary was pinched off from the tube end. Two adiabatic shields surrounded the sample cell in turn and a vacuum can was immersed in liquid nitrogen. The two adiabatic shields were made of chromium-plated copper and equipped with manganin heating wires. Two sets of six-junction chromel-contantan (Ni 55%, Cu 45%) thermocouples were used to measure the temperature differences between the sample cell and the inner adiabatic shied and between the inner and the outer adiabatic shields. The temperatures of the two shields were controlled separately and automatically with two units of auto-adiabatic controller. When the temperature in the sample cell increases due to heating, the thermocouples measure the temperature differences. This signal is used to control the heaters distributed on the walls of the inner and outer shields, respectively. Both shields were heated under the control of the signal and kept at the same temperature as that of the sample cell. In this way, the heat loss caused by the radiation is greatly reduced. The miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter and a nominal resistance of 100 Ω) was applied 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 sample was heated using the standard discrete heating method and the temperature of the sample was alternatively measured. The heating duration was 10 min, the equilibrium time of each temperature point is 5 min, and the temperature drift rates of the sample cell measured in an equilibrium period were usually within 10^{-3} to 10^{-4} K min^{-1}. During the heat-capacity measurements, the temperature difference between the inner adiabatic shield and the sample cell was automatically kept within 10^{-3} K min^{-1} in order to obtain a satisfactory adiabatic effect and corresponding equilibrium temperature were corrected for heat loss [5,6].

The mass of the sample loaded in the sample cell amounted to 2.4846 g, which was equivalent to 0.008743 mol based on its molar mass of 284.19 g mol^{-1}.

The molar heat capacities of α-Al_2O_3 used as the standard substance were measured in the same temperature range as that of the sample measurement in order to verify the reliability of the calorimeter. The sample mass used for the measurements was 1.8219 g, which was equivalent to 0.0179 mol based on its molar mass, $M(Al_2O_3) = 101.96$ g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the inaccuracy is within ±0.5%, as compared with those of the former National Bureau of Standard [7] over the whole experimental temperature range.

2.3. Differential scanning calorimetry (DSC)

A TA 2100 Thermal Analysis System coupled with a personal computer loaded with the program for data processing was used for the DSC measurements, the DSC with aluminum sample tray and sapphire reference was operated at a heating rate of 10 K min^{-1} under nitrogen atmosphere with a flow rate of 60 ml min^{-1}. The mass of the sample used for experiment was 1.4 mg.

3. Results and discussion

3.1. Heat capacity

All heat capacity measurements are listed in Table 1 and plotted in Fig. 1. The structure of the compound is stable; no phase change occurred in the solid phase from $T = 78$ to 321 K, nor did association or decomposition occur in the liquid phase from $T = 333$ to 364 K.

Table 1
Experimental molar heat capacities of penconazole ($M = 284.19\,\mathrm{g\,mol^{-1}}$)

T (K)	$C_{\mathrm{p.m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{\mathrm{p.m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{\mathrm{p.m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
78.537	131.79	174.796	217.34	308.021	367.61
80.361	133.28	177.851	219.77	311.178	372.44
82.147	135.13	181.712	222.98	314.312	375.71
83.897	137.61	186.306	228.58	317.413	378.44
85.62	139.31	190.865	236.32	319.968	381.33
87.309	141.08	195.355	240.14	321.406	384.25
88.976	143.11	199.778	246.02	324.447	398.36
90.999	144.91	204.137	252.17	327.364	450.62
93.373	147.15	208.438	257.16	329.762	823.84
95.706	149.39	212.687	262.61	331.108	2851.5
98.014	152.06	216.877	269.49	331.614	6874.1
100.976	155.81	221.015	273.57	331.838	10330
103.871	158.07	225.095	280.08	331.976	10743
103.904	162.59	229.141	288.19	332.075	11537
104.001	164.59	233.145	291.95	332.156	12688
106.249	166.31	237.061	293.95	332.224	13378
110.262	168.81	240.924	295.97	332.293	13507
114.088	170.27	244.808	297.16	332.358	13699
117.686	173.66	248.673	299.67	332.428	13131
121.209	175.03	252.499	303.24	332.569	7262.2
124.868	177.88	256.291	306.16	332.588	553.21
128.539	179.16	260.045	311.17	333.595	482.11
132.154	181.83	263.757	314.99	335.642	483.42
135.716	184.12	267.391	319.02	337.655	486.86
139.213	187.04	270.991	321.91	339.608	492.63
142.643	194.24	274.552	326.59	342.717	496.66
145.998	198.55	278.074	331.12	345.109	498.38
149.342	200.41	281.556	335.75	348.662	501.56
152.648	202.94	284.996	337.28	351.216	504.76
155.911	205.94	288.381	339.49	353.758	507.58
159.152	207.91	291.727	341.75	356.285	510.43
162.303	209.59	295.052	347.59	358.807	513.76
165.436	210.87	298.345	355.47	361.332	516.03
168.587	211.35	301.602	358.78	363.814	519.41
171.709	213.84	304.826	363.63		

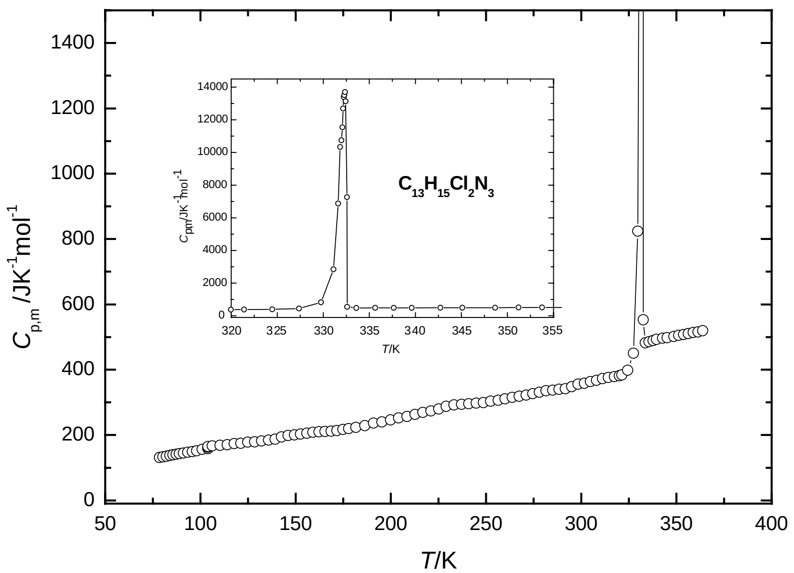

Fig. 1. The experimental molar heat-capacity curve of penconazole ($C_{13}H_{15}Cl_2N_3$).

The experiment values of the heat capacities have been fitted to polynomial equations by the least square fitting.

For the solid phase:

$$C_{\mathrm{p.m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 88.23 + 51.19 \times 10^{-2} X + 17.00 \times 10^{-4} X^2 - 1.512 \times 10^{-6} X^3$$

In which $X = [(T(\mathrm{K})) - 199.5]/121.5$. The above equation is valid from $T = 78$ to 321 K, with an uncertainty of ±0.3%.

For the liquid phase:

$$C_{\mathrm{p.m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 477.9 + 4.114X - 0.3404X^2 + 4.800 \times 10^{-3} X^3$$

In which $X = [(T(\mathrm{K})) - 348.5]/15.5$. This equation applies to the range from $T = 333$ to 364 K, with an uncertainty of ±0.25%.

3.2. Melting point, molar enthalpy and entropy and fusion

Pre-melting occurred owing to the presence of impurities in the sample. The measurement of the melting point and molar enthalpy of fusion of the sample was done as follows: first, the temperatures for the start of the pre-melting and for compete melting were determined. Between these two temperatures, the melting point was determined by successive approximation through stepwise heating. Then, by heating the sample from a temperature slightly lower than the initial melting temperature to a temperature slightly higher than the final melting temperature, the enthalpy of fusion of the sample was evaluated. The heat used for heating the empty container and the sample was subtracted from the total amount of heat introduced to the sample and container during the whole melting process [6].

The melting temperature, T_{fus} of the sample was calculated from an equation based on the heat capacity measurements in the fusion region, as described in literature [6,8]. The molar enthalpy of fusion, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, was determined in accordance with the method reported in the literature [8–10]. The molar entropy of fusion, $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$, was derived from the molar enthalpy of fusion, using $\Delta_{\mathrm{fus}}S_{\mathrm{m}} = \Delta_{\mathrm{fus}}H_{\mathrm{m}}/T_{\mathrm{fus}}$ [8,9].

The results of T_{fus}, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ obtained from the heat capacity measurements are listed in Table 2.

The purity of the sample was determined from the fractional melting in accordance with the method given in the literature [6,8,9] to be higher than 99.50 mol%.

3.3. DSC analysis

It can be seen from the DSC curve (Fig. 2) that there is a melting endothermic peak in the temperature range from

Table 2
Thermodynamic properties for phase transition of penconazole obtained from three series of repeated measurements

Thermodynamic properties	Series 1, x_i	Series 2, x_i	Series 3, x_i	Mean value, $\bar{x}$	Standard deviation, σ_{a}
T_{fus} (K)	332.36	332.50	332.29	332.38	0.06
$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ ($\mathrm{J\,mol^{-1}}$)	33573	33601	33565	33580	11
$\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	101.02	101.06	101.01	101.03	0.02

$\sigma_a = \sqrt{\sum_{i=1}^{n}(xi - \bar{x})^2/n(n-1)}$, in which n is experimental number ($n = 3$); x_i, experimental value of each series of repeated measurement; $\bar{x}$, mean value.

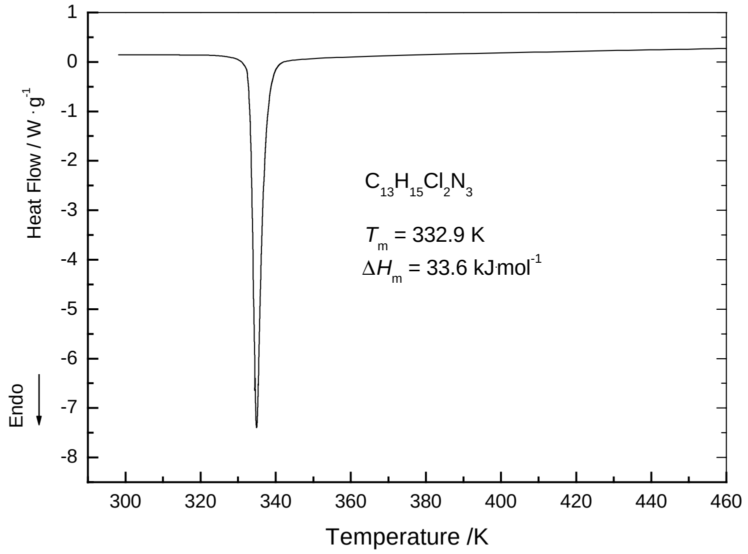

Fig. 2. The DSC curve of penconazole ($C_{13}H_{15}Cl_2N_3$).

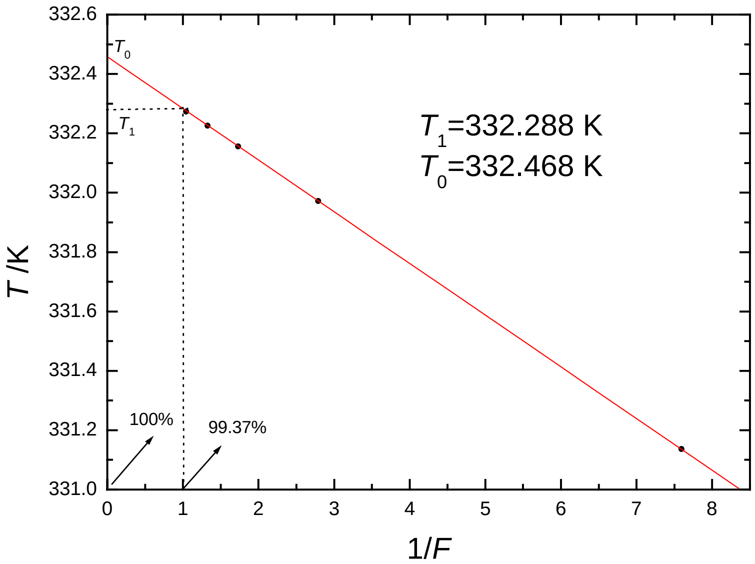

Fig. 3. The equilibrium temperature (T) vs. the reciprocal of the melting fractions ($1/F$) for the penconazole ($C_{13}H_{15}Cl_2N_3$) during fusion.

25 to 220 °C. It begins from 332.2 K and ends at 334.6 K. This peak is in agreement with that of the experimental molar heat-capacity curve. The melting point and the molar enthalpy of fusion were determined from DSC to be 332.9 K and 33.6 kJ mol^{-1}, respectively. These values are in agreement with the results obtained from heat-capacity measurements. This further verifies the reliability of the thermodynamic data of the melting process of the substance over the temperature range from $T = 321$ to 333 K.

3.4. Purity determination of the sample

The purity of the sample is evaluated from a set of equilibrium melting temperature (T) and melting fractions (F) corresponding to these temperatures [8,9]. The experimental results obtained from the heat capacity measurements in the fusion region are listed in the Table 3. The equilibrium melting temperature (T) versus the reciprocal of the melting fractions ($/F$) is a straight line, as shown in Fig. 3. Extrapolation of the straight line to $1/F = 0$ and 1 gives T_0 and T_1 for the experiment, as indicated in Table 3. Here, T_1 is the melting temperature of the impure compound obtained form fraction fusion experiment and T_0 is the melting temperature of a theoretically or absolutely pure sample. The melting point ($T_1 = 332.288$ K) obtained from the fractional melting agrees well with that ($T_{\rm fus} = 332.38 \pm 0.06$ K) obtained from the heat capacity measurements as described from the Van't Hoff equation [10]. The purity of the sample $(1-N)$ is 99.37%, in agreement with the result of gas chromatograph analysis (99.36%).

Table 3
Experimental results of melting fractions (F) and equilibrium temperature (T) of penconazole ($C_{13}H_{15}Cl_2N_3$)

T (K)	F	$1/F$
331.137	0.1317	7.5928
331.972	0.3586	2.7888
332.156	0.5773	1.7321
332.226	0.7546	1.3252
332.274	0.9570	1.0449

$F = q/(\Delta_{\rm fus}H_{\rm m}n)$, in which q is the amount of the heat introduced to melt the sample for the melting fraction F; n the mole number of the sample.

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