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Low-temperature heat capacity and thermodynamic properties of 3,6-dichloro-2-methoxy-benzoic acid

You-Ying Di[a,b], Zheng-Ning Li[b], Shuang-He Meng[b], Zhi-Cheng Tan[b], Song-Sheng Qu[a,*]

[a]College of Chemistry and Environmental Science, Wuhan University, Wuhan 430072, PR China
[b]Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

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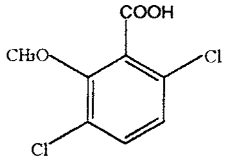
Abstract

The low-temperature heat capacity of 3,6-dichloro-2-methoxy-benzoic acid was precisely determined with an automated adiabatic calorimeter over the temperature range from 78 to 402 K. The sample was observed to melt at 388.15 ± 0.03 K. The molar enthalpy and entropy of melting as well as the chemical purity of the substance were determined to be 22244 ± 35 J mol^{-1}, 57.31 ± 0.09 J mol^{-1} K^{-1} and 99.31 ± 0.02 mol%, respectively. The extrapolated melting temperature for the absolutely pure compound obtained from fractional melting experiments was 388.52 ± 0.08 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 3,6-Dichloro-2-methoxy-benzoic acid; Low-temperature heat capacity; Adiabatic calorimetry; Purity determination

1. Introduction

3,6-Dichloro-2-methoxy-benzoic acid (abbreviated as: Dicamba; molecular formula: $C_8H_6O_3Cl_2$; CA Registry No.: 1918-00-9) is a wide-spectrum, high-efficiency and high-quality herbicide, which has been widely used to kill the broad-leaved weeds in wheat, corn and rice fields and lawn. The effect of the compound as a herbicide on the metabolic action of the farm crops and animals and the action mechanism? Of it on weeds has been much studied [1–3]. Recently, it has been considered as energy-storage material for aircrafts and factories due to its high enthalpy of fusion, noncorrosiveness, nontoxicity and good thermal stability. Its molecular structure is as follows:



In 1961, Richter [3] used 1,2,4-trichlorobenzene as raw material and successfully synthesized the compound through a three-step reaction. He reported that the m.p. of the compound was 114–116°C. Since then, no reports on the thermodynamic properties of the substance have been reported. For the application of the compound, thermodynamic data for this substance are required. In the present work, low-temperature heat capacity measurements were carried out with adiabatic calorimetry, and the basic thermodynamic parameters, such as molar enthalpy and entropy of melting have been determined. The chemical purity of the substance was determined by fractional melting method.

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[*] Corresponding author. Fax: +86-27-876-47617.
E-mail address: ipc@whu.edu.cn (S.-S. Qu).

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2. Experimental

2.1. Sample preparation and characterization

Dicamba ($C_8H_6O_3Cl_2$) is a white crystal with a lumpy crystalline shape. The sample used for the present calorimetric study was prepared according to the procedures given in literature [4,5], in which 2,5-dichlorophenol and 3-chloropropene were used as the reactants. The crude product was purified by column chromatography in which a mixed petroleum ether–dichloromethane solution was used as the eluant. The sample was recrystallized three times by the use of petroleum ether (A. R.) as solvent. The m.p. of the final product was determined to be 114.2–115.8°C with a microscopic melting point device (Yazawa Co., model: BY-1, Japan), in agreement with literature [3–6]. ^{1}H NMR (Varian Ltd., model: Unity Plus 500, USA, $CDCl_3$) absorption peaks were detected at $\delta = 7.33$ (s, 2H, ArH), 3.72 (s, 3H, $-CH_3$), and 10.11 (s, 1H, –COOH) ppm. IR (Hitachi, model: 260-10, Japan) showed characteristic absorption peaks at 3053, 2935, 1650, 1468, 1119, 1281, 873 and 803 cm^{-1}. These results were identical with those of the literature [6]. The actual purity of the sample was determined by HPLC (Shimadzu, model: LC-10AT, Japan) analysis to be higher than 99.30 mol%.

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 402 K. The construction of the calorimeter has been described previously in detail in [7,8]. It consists of a sample cell, a miniature platinum resistance thermometer (model: IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, PR China), a heater, two (inner and outer) adiabatic shields, differential thermocouples, a vacuum can and a Dewar vessel. Liquid nitrogen was used as the cooling medium.

The sample was heated using the standard discrete heating method and the temperature increments of the sample was measured. The heating period was 10 min, the equilibrium period of every experimental point is 5 min. During the heat-capacity measurements, the temperature difference between the inner adiabatic shield and the sample cell was automatically kept within 10^{-3}–10^{-4} K in order to obtain a satisfactory adiabatic condition. The data of heat capacities and corresponding equilibrium temperatures were corrected for heat loss [7,8].

The mass of the sample loaded in the sample cell amounted to 2.6615 g, which was equivalent to 0.0120 mol based on its molar mass of 221.0390 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 confirm 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, $M\ (Al_2O_3) = 101.9613$ 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 National Institute for Science and Technology [9] over the whole temperature range.

3. Results and discussion

3.1. Heat capacity

All heat-capacity determinations 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, nor did association or decomposition occur in the liquid phase ($T < 402$ K).

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

For the solid phase

$$C_{p,m}\ (J^{-1}\,K^{-1}\,mol^{-1}) = 182.4440 + 82.0183X + 1.2043X^2 - 23.2953X^3 - 33.1757X^4 + 55.1369X^5 + 49.7304X^6$$

where $X\ (K) = (T - 226.5)/148.5$. The above equation is valid from 78 to 375 K, with an uncertainty of ±0.30%.

For the liquid phase

$$C_{p,m}\ (J\,K^{-1}\,mol^{-1}) = 349.2432 + 4.9938X - 0.4312X^2$$

Table 1
The experimental molar heat capacities of Dicamba ($C_8H_6O_3Cl_2$) obtained from first series of repeated measurements ($M = 221.0390$ g mol^{-1})

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
78.427	86.539	211.996	175.358	338.704	247.949
81.526	89.144	215.387	177.401	341.946	250.673
85.594	92.324	218.683	179.324	345.171	253.657
89.556	95.810	222.051	179.777	348.359	256.888
93.370	99.418	225.347	181.757	351.530	262.128
97.058	102.171	228.639	183.284	354.665	266.472
100.641	105.352	231.822	184.899	357.782	272.838
104.139	108.593	235.005	186.807	361.741	279.951
107.554	110.734	238.133	188.275	365.019	286.636
110.883	113.547	241.271	190.624	367.849	294.318
114.150	116.055	244.331	192.459	370.966	302.148
117.353	118.624	247.391	194.073	373.492	311.786
120.494	120.703	250.451	195.615	376.322	326.697
123.592	123.028	253.488	196.862	379.009	345.779
126.647	125.291	256.502	198.550	381.234	369.266
129.661	127.248	259.516	200.459	383.309	433.180
132.907	129.388	262.483	201.779	384.506	611.284
136.426	131.835	265.821	204.055	385.416	1005.49
139.882	134.035	269.519	205.434	386.260	1638.55
143.297	136.361	273.205	207.399	386.819	2483.45
146.685	138.379	276.836	209.119	387.247	3400.64
150.378	140.214	280.466	210.587	387.541	4285.43
154.386	142.355	284.032	212.477	387.730	5347.17
158.381	143.945	287.614	213.948	387.882	6690.55
162.291	146.907	291.197	215.589	387.996	7884.39
166.232	148.774	294.708	218.021	388.114	9250.19
170.028	151.774	298.219	219.662	388.223	7328.59
173.796	153.976	301.659	221.869	388.356	5992.69
177.593	156.299	305.169	223.679	388.567	3595.05
181.351	157.656	308.609	225.885	389.542	865.917
185.005	159.579	312.048	227.865	391.495	344.577
188.707	162.416	315.416	229.393	393.304	345.871
192.393	164.251	318.784	231.995	395.469	348.098
196.177	166.391	322.152	233.919	397.577	350.528
199.806	167.859	325.519	236.578	399.625	352.047
203.116	169.468	328.887	239.350	401.599	353.358
206.467	171.101	332.183	241.896		
209.535	173.963	335.479	244.838		

where X (K) $= (T - 396.5)/5.5$. This equation applies to the range from 391 to 402 K, with an uncertainty of ±0.25%.

3.2. Melting point, enthalpy and entropy of fusion

Pre-melting occurred owing to the presence of impurities in the sample. The measurement of the m.p. and the molar enthalpy of fusion of the sample was done as follows: the temperatures for the start of the pre-melting and for complete melting were determined. Between these two temperatures the m.p. 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 enthalpy used to heat

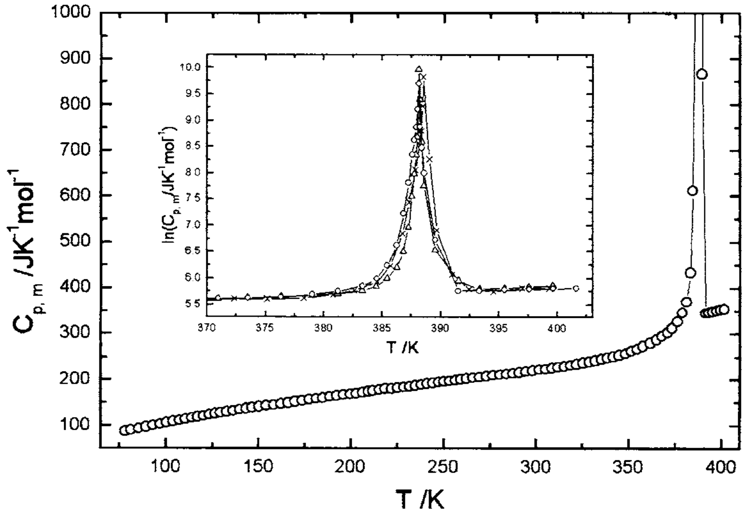

Fig. 1. Experimental molar heat capacities $C_{p,m}$ of Dicamba ($C_8H_6O_3Cl_2$) obtained by adiabatic calorimetry. (○) Represents the first series of heat capacity measurements; (△) the second series of heat capacity measurements; (×) the third series of heat capacity measurements.

the empty sample container and the sample itself (solid or liquid) was subtracted from the total amount of heat introduced to the sample and container during the whole fusion, the melting enthalpy of the sample can be obtained, as described in the literature [10,11].

Three series of heat-capacity experiments in the fusion region of the compound were carried out so that the reversibility and repeatability of the fusion region were verified. Before these series, the sample was cooled from 402 to lower than 293 K using different cooling rates. In the first series, the sample was quenched into liquid-nitrogen (about 20 K min^{-1}); in the second series, the sample was naturally cooled (about 0.5 K min^{-1}); and in the third series, the ice–water was used as coolant (about 5 K min^{-1}). The results of the three series of repeated experiments are plotted in the inset to Fig. 1 and also given in Table 2. It can be seen from Fig. 1 that the phase transition is reversible and repeatable, no supercooling and no other thermal anomaly was caused by the different cooling rates.

The melting temperature T_{fus} of the sample was calculated from an equation based on the heat capacity in the fusion region, as described in the literature [11]. The molar enthalpy of fusion $\Delta_{fus}H_m$ was determined following the method described in the literature [11,12]. The molar entropy of fusion $\Delta_{fus}S_m$ was derived from the molar enthalpy of fusion, using $\Delta_{fus}S_m = \Delta_{fus}H_m/T_{fus}$.

The results of T_{fus}, $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ obtained from the three series of repeated heat-capacity measurements are listed in Table 2.

Table 2
The results of the solid–liquid phase transition of Dicamba ($C_8H_6O_3Cl_2$) obtained from each series of heat capacity measurements

Thermodynamic properties	Series 1, x_i	Series 2, x_i	Series 3, x_i	Mean values, $\bar{x}$	S.D., σ_a[a]
T_m (K)	388.11	388.13	388.20	388.15	0.03
ΔH_m (J mol^{-1})	22255	22178	22299	22244	35
ΔS_m (J K^{-1} mol^{-1})	57.34	57.14	57.44	57.31	0.09
T_0 (K)	388.52	388.40	388.66	388.52	0.08
T_1 (K)	388.13	388.02	388.25	388.13	0.07
(1 − N) (%)	99.31	99.34	99.28	99.31	0.02

[a] Where $\sigma_a = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)}$, n is the experimental number ($n = 3$); x_i the results obtained from three series of repeated heat capacity measurements; $\bar{x}$ the mean values.

3.3. Purity determination of the sample

The purity of the sample is evaluated from a set of equilibrium melting temperatures (T) and melting fractions (F) corresponding to these temperatures [10,12]. The experimental results obtained from the heat-capacity measurements in the fusion region are listed in Table 3. The equilibrium melting temperature (T) versus the reciprocal of the melting fractions ($1/F$) is a straight line, as shown in Fig. 2. Extrapolation of the straight line to $1/F = 0$ and 1 gives T_0 and T_1 for each series of experiment, respectively, as indicated in Table 2. Here T_1 is the melting temperature of the impure compound obtained from fractional fusion experiments and T_0 is the m.p. of a theoretically or absolutely pure sample. The m.p. ($T_1 = 388.13 \pm 0.07$ K) obtained from the fractional melting agrees well with the value of $T_{\mathrm{fus}} = 388.15 \pm 0.03$ K obtained from the heat-capacity measurements as described above. The mole percentage (N) of impurities in the sample is obtained from the van't Hoff equation. The purity of the sample ($1 - N$) is 99.31 ± 0.02 mol%, in agreement with the result of chromatographic analysis (99.30 mol%).

Table 3
Experimental results of melting fractions (F) and equilibrium temperature (T) of Dicamba ($C_8H_6O_3Cl_2$)[a]

T (K)	F	$1/F$
Series 1		
383.309	0.0743	13.467
384.506	0.1001	10.002
386.260	0.1683	5.9410
387.247	0.3157	3.1675
387.541	0.3826	2.6139
387.730	0.5014	1.9943
Series 2		
380.355	0.0479	20.877
384.101	0.0884	11.309
385.409	0.1256	7.9618
386.817	0.2292	4.3635
387.262	0.3101	3.2253
387.587	0.4176	2.3947
387.843	0.5748	1.7396
387.953	0.6855	1.4589
Series 3		
380.765	0.0517	19.332
384.583	0.0992	10.077
385.741	0.1405	7.1157
386.781	0.2189	4.7416
387.235	0.3152	3.3834
387.821	0.5750	2.0251

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

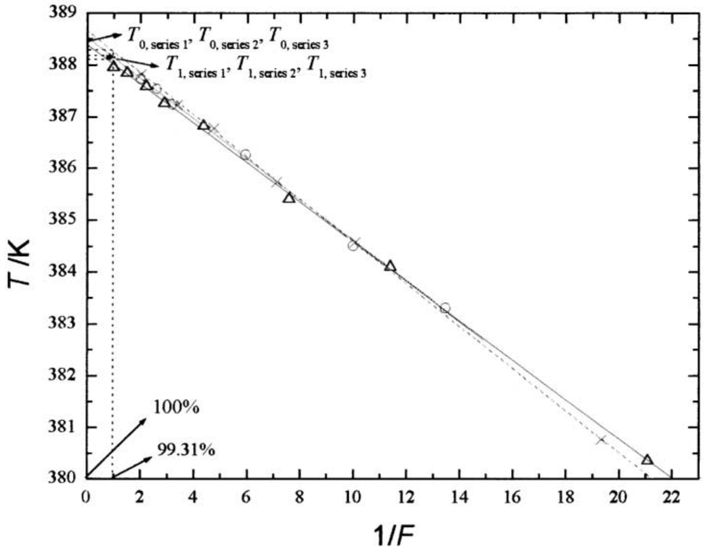

Fig. 2. The equilibrium temperature (T) vs. the reciprocal of the melting fractions ($1/F$) for Dicamba ($C_8H_6O_3Cl_2$) during fusion. (○) Represents the first series of fractional melting measurements; (△) the second series of fractional melting measurements; (×) the third series of fractional melting measurements.

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