Low-Temperature Heat Capacity and Thermodynamic Properties of Crystalline 2-Chloro-5-trichloromethylpyridine

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The low-temperature heat capacities of 2-chloro-5-trichloromethylpyridine were measured with a high-precision automated adiabatic calorimeter in the temperature range from 80 K to 345 K. A solid-liquid phase transition was observed from 318.57 K to 327.44 K with peak temperature 324.67 K; the molar enthalpy and entropy of phase transition, ΔH_{m} and ΔS_{m}, were determined to be 14.50 ± 0.02 kJ mol^{-1} and 44.66 ± 0.07 kJ K^{-1} mol^{-1}, respectively. The thermal stability was investigated through thermogravimetric analysis (TG). The TG and DTG results reveal that 2-chloro-5-trichloromethylpyridine starts to lose mass at 332 K due to evaporation and completely changes into vapour at 483 K under the present experimental conditions.

2-Chloro-5-trichloromethylpyridine ($C_6H_3NCl_4$) is an important intermediate compound for synthesizing 2-chloro-5-trifluoromethylpyridine, an organic compound widely used in fine chemical engineering field, such as pesticide, dye, and medicine industries [1]. The thermodynamic properties of 2-chloro-5-trichloromethylpyridine have not been reported till now. In order to improve the processes of chemical synthesis and contribute to a better understanding of the properties of the compound, the thermodynamic properties of this compound were investigated through adiabatic calorimetry and thermal analysis techniques in the present study. The low-temperature heat capacities were measured in the temperature range from 80 K to 345 K. A solid-liquid phase transition was observed and the entropy and enthalpy increments of the phase transition, ΔH_{m} and ΔS_{m}, were determined. In addition, the thermal behaviour of evaporation was further investigated by thermogravimetric analysis.

Traditional methods of synthesis of 2-chloro-5-trichloromethylpyridine [2, 3] have the disadvantages of low productivity, low selectivity, and yielding many by-products. New synthesizing method [4] employed in the present experiment overcame these drawbacks.

EXPERIMENTAL

The 2-chloro-5-trichloromethylpyridine sample used in the present experiment was synthesized by the method reported in the patent [4]. 2-Chloro-5-methylpyridine reacted with chlorine at the temperature 120—140 ℃ with the initiator 2,2′-azobisisobutyronitrile. Then the mixture was distilled at 150 ℃ under reduced pressure.

The structure of the product was determined by IR, ^{1}H NMR, and ^{13}C NMR spectra and its purity was determined to be higher than 99.9 % through gas chromatographic analysis.

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter in the temperature range from 80 K to 400 K. The structure, procedures, and performance of the apparatus had been described in detail elsewhere [5]. The sample amount used for the measurement was 2.0405 g, equivalent to 8.8368 mmol, based on a molar mass of 230.91 g mol^{-1}. The heating duration and temperature increment for each experimental point were controlled to be about 10 min and 3—4 K, respectively, in the whole experimental temperature range.

Thermogravimetric measurement was performed on a Setaram setsys 16/18 apparatus, France. A mass

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of 5.7 mg of sample was placed in a 100 mm^3 α-Al_2O_3 crucible and heated from 18 K to 700 K with a rate of 10 K min^{-1} under high purity (99.999 %) nitrogen atmosphere with a flow rate of 25 cm^3 min^{-1}.

RESULTS AND DISCUSSION

The temperature dependence of experimental molar heat capacities of 2-chloro-5-trichloromethylpyridine is shown in Fig. 1. The dependence was fitted to the following polynomial in reduced temperature (X) by means of the least-square fitting.

Over the temperature range of 80—318 K

$$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = 149.96+58.850X-16.136X^2- \\ -22.911X^3 - 1.0326X^4 + 26.923X^5 + 13.825X^6$$

where $X = (T - 199)/119$ and T is the absolute temperature. The correlation coefficient of the fitted curve $R^2 = 0.99927$ and the average deviation of the fitted

Table 1. Calculated Thermodynamic Function Data of 2-Chloro-5-trichloromethylpyridine

T/K	$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	$H_T - H_{298.15\,K}/(\mathrm{kJ\ mol^{-1}})$	$S_T - S_{298.15\,K}/(\mathrm{J\ K^{-1}\ mol^{-1}})$
80	83.754	−30.897	−171.27
85	87.010	−30.470	−166.11
90	90.203	−30.027	−161.04
95	93.328	−29.568	−156.08
100	96.384	−29.093	−151.22
105	99.374	−28.604	−146.44
110	102.30	−28.100	−141.75
115	105.17	−27.581	−137.15
120	107.99	−27.048	−132.62
125	110.78	−26.501	−128.16
130	113.52	−25.940	−123.77
135	116.24	−25.366	−119.44
140	118.94	−24.778	−115.17
145	121.63	−24.177	−110.96
150	124.31	−23.562	−106.79
155	126.98	−22.934	−102.68
160	129.65	−22.292	−98.61
165	132.31	−21.637	−94.58
170	134.97	−20.969	−90.59
175	137.61	−20.287	−86.63
180	140.24	−19.593	−82.72
185	142.85	−18.885	−78.84
190	145.43	−18.164	−74.99
195	147.97	−17.431	−71.17
200	150.45	−16.685	−67.39
205	152.88	−15.926	−63.64
210	155.24	−15.156	−59.92
215	157.53	−14.374	−56.24
220	159.72	−13.581	−52.59
225	161.82	−12.777	−48.98
230	163.82	−11.963	−45.40
235	165.72	−11.139	−41.86
240	167.52	−10.306	−38.35
245	169.23	−9.464	−34.88
250	170.85	−8.614	−31.45
255	172.41	−7.755	−28.06
260	173.93	−6.890	−24.70
265	175.44	−6.016	−21.37
270	176.99	−5.135	−18.08
275	178.62	−4.246	−14.82
280	180.40	−3.349	−11.59
285	182.41	−2.442	−8.380
290	184.73	−1.524	−5.187
295	187.48	−0.594	−2.004
298.15	189.48	0.000	0.000
300	190.77	0.352	1.177
305	194.74	1.315	4.367
310	199.56	2.301	7.575
315	205.40	3.312	10.816

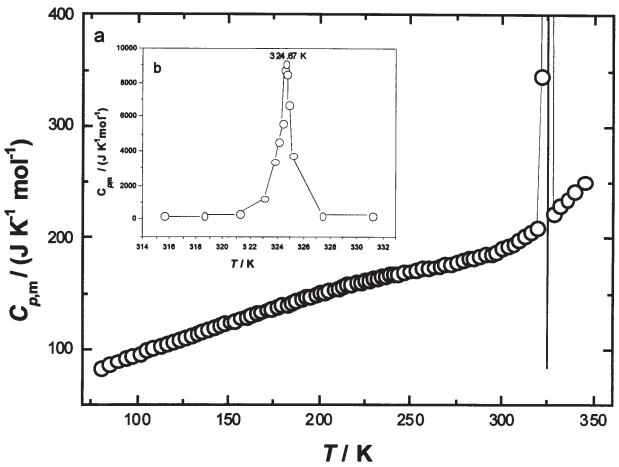

Fig. 1. Experimental molar heat capacity $C_{\mathrm{p,m}}$ of 2-chloro-5-trichloromethylpyridine as a function of temperature (T) (a), with the insertion indicating the solid-liquid phase transition (b).

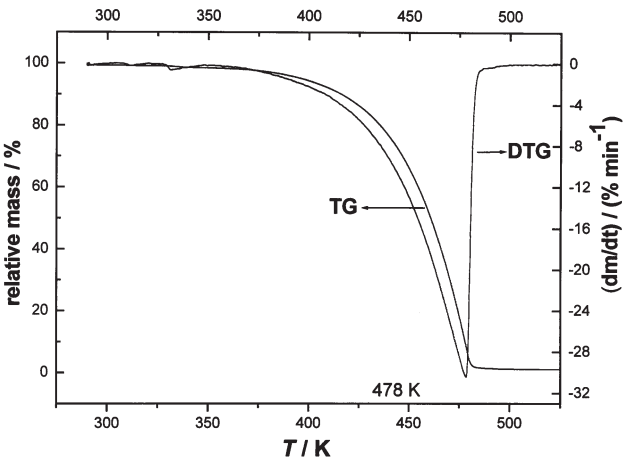

Fig. 2. TG-DTG curves of 2-chloro-5-trichloromethylpyridine.

values from the experimental ones is within ± 0.2 %.

From Fig. 1 it can be seen that the heat capacities of the sample vary with increasing temperature in a smooth and continuous manner from 80 K to 319 K. No phase transition was observed in this temperature range. Therefore, the sample is stable in the above temperature range. However, thermal anomaly was observed from 319 K to 327 K. The temperature at the highest point of the peak, 324.67 K, was determined to be the melting point. The thermal anomaly was ascribed to a solid-liquid phase transition. The heat capacity measurement of the phase transition region was repeated three times.

The molar enthalpy ΔH_{m} and entropy ΔS_{m} of the phase transition derived by the literature method [6] are 14.50 ± 0.02 kJ mol^{-1} and 44.67 ± 0.07 J K^{-1} mol^{-1}, respectively. These values and the melting point are lower than those of 2-chloro-6-trichloromethylpyridine [7], a structurally similar compound. The result of the comparison is reasonably acceptable considering that the polarity of the molecule of 2-chloro-6-trichloromethylpyridine is larger than that of 2-chloro-5-trichloromethylpyridine, which may indicate the stronger intermolecular interaction of 2-chloro-6-trichloromethylpyridine. Comparing pyridine with its derivatives, pyridine with T_{fus} = 231.49 K, ΔH_{m} = 8.28 kJ mol^{-1}, and ΔS_{m} = 35.76 J mol^{-1} K^{-1} [8], 2-methylpyridine with T_{fus} = 206.45 K, ΔH_{m} = 9.72 kJ mol^{-1}, and ΔS_{m} = 47.10 J mol^{-1} K^{-1} [9], 3-methylpyridine with T_{fus} = 255.01 K, ΔH_{m} = 14.18 kJ mol^{-1}, and ΔS_{m} = 55.61 J mol^{-1} K^{-1} [10], and 4-methylpyridine with T_{fus} = 276.82 K, ΔH_{m} = 12.58 kJ mol^{-1}, and ΔS_{m} = 45.45 J mol^{-1} K^{-1} [11], it can be seen that the enthalpies and entropies of fusion of these compounds differ largely and it seems not easy to correlate these parameters with their structures.

Through the polynomial of heat capacity temperature dependence and the relationships of thermodynamic functions, the thermodynamic function data were calculated in the temperature range from 80 K to 315 K based on the reference temperature 298.15 K. The values of thermodynamic function $H_T - H_{298.15\,\mathrm{K}}$, $S_T - S_{298.15\,\mathrm{K}}$ are listed in Table 1.

The TG and DTG curves of 2-chloro-5-trichloromethylpyridine are shown in Fig. 2. It can be seen that 2-chloro-5-trichloromethylpyridine starts to lose mass at 332 K and reaches the maximal rate of mass loss at 478 K under the present experimental conditions. The sample completely loses its mass when the temperature reaches 483 K. The product collected during the heating up to 490 K proved to be the same substance as the initial sample judging from its colour and melting point. So we can deduce that 2-chloro-5-trichloromethylpyridine begins to vaporize at 332 K and completely changes into vapour when the temperature reaches 483 K under the present experimental conditions.

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