

HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF CHRYSANTHEMIC ACID

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Abstract

The heat capacities of chrysanthemic acid in the temperature range from 80 to 400 K were measured with a precise automatic adiabatic calorimeter. The chrysanthemic acid sample was prepared with the purity of 0.9855 mole fraction. A solid–liquid fusion phase transition was observed in the experimental temperature range. The melting point, T_m , enthalpy and entropy of fusion, $\Delta_{fus}H_m$, $\Delta_{fus}S_m$, were determined to be 390.741 ± 0.002 K, 14.51 ± 0.13 kJ mol⁻¹, 37.13 ± 0.34 J mol⁻¹ K⁻¹, respectively. The thermodynamic functions of chrysanthemic acid, $H_{(T)}-H_{(298.15)}$, $S_{(T)}-S_{(298.15)}$ and $G_{(T)}-G_{(298.15)}$ were reported with a temperature interval of 5 K. The TG analysis under the heating rate of 10 K min⁻¹ confirmed that the thermal decomposition of the sample starts at ca. 410 K and terminates at ca. 471 K. The maximum decomposition rate was obtained at 466 K. The purity of the sample was determined by a fractional melting method.

Keywords: adiabatic calorimetry, chrysanthemic acid, heat capacity, TG, thermal decomposition, thermodynamic function

Introduction

The thermodynamic data is one of the important basis of improving synthesis process and studying on the reaction mechanism, and calorimetry is the effectual method for these researches [1–3].

The studies on the synthesis of widely used, highly efficient biopermethrin class insecticide and pesticide have a great progress recently. Separating the isomers of product and intermediates can reduce the using amount of insecticide, improve economic performance and decrease environmental pollution. Chrysanthemic acid, 2,2,3,3-tetramethylcyclopropane carboxylic acid, is one of the important intermediate of the preparation of fenprothrin pesticide. To purify 2,2,3,3-tetramethylcyclo-

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propane carboxylic acid and the determination of purity is important for improving the synthesis process of fenprothrin pesticide.

In this work, the heat capacity of chrysanthemic acid of high purity was measured in temperature range between 80 and 400 K with an automatic adiabatic calorimeter. At the same time, the melting point, enthalpy and entropy of fusion were calculated. The calorimetric determination of purity for the compound was carried out with the same calorimeter. The thermal decomposition behaviour of the sample was investigated by thermogravimetric (TG) analytic technique.

Experimental

Sample preparation and analysis

Chrysanthemic acid is the key intermediate of the preparation of biopermethrin class insecticide and pesticide, it was prepared by hydrolysis after the reaction of cyclopropane formation between 2,3-dimethyl-2-butylene and diazoacidic ester. 2,3-dimethyl-2-butylene was prepared by the isomerization of 2,3-dimethyl-1-butylene which was prepared by the polymerization of propylene. The crystal product of chrysanthemic acid was filtered and recrystallized three times. Finally, the sample of chrysanthemic acid was obtained. The molecular structure was verified with NMR (model: Bruker DRX-400). The purity of the sample was determined to be 98.61 mol% by HPLC (model: Shimadzu 10A).

Adiabatic calorimetry

The heat capacity measurements were carried out with an automatic calorimeter over the temperature range 80 to 400 K. The equipment was based on the Nernst step heating method [4]. The adiabatic calorimeter was described before in detail [5, 6] and only the major features of the equipment are described here.

The calorimeter consists of a calorimeter cell, an adiabatic shield, a guard shield, two sets of differential thermocouples, and a vacuum can. The calorimeter cell was made of silver of 99.95% purity, 0.2 mm thick, gold-plated and polished. The main body was 33 mm in diameter and 60 mm high. The mass of the empty cell was about 50 g and its effective capacity was 50 cm³. In its center a tapered entrant well was provided for insertion of the thermometer–heater assembly. Onto the well's outer wall, eight L-shape 0.15 mm thick radial silver vanes were brazed one by one by use of silver alloys. A space existed between the outer edges of the vanes and the cylindrical inner wall and four semi-circular vanes extended into the upper and lower hemispherical space in the cell. The thermometer (No.82021, 4-lead, capsule-type, 25 Ω , 50 mm long, 5 mm in diameter) was made by the Instrument Manufactory of Yunnan, China. It was calibrated in terms of ITS-90 at the Center of Low-Temperature Metrology and Measurements, Chinese Academy of Sciences, in the temperature range 50 to 400 K with an uncertainty about 1 mK. A gold plated copper lid with a length of copper capillary was sealed to the sample cell using a small amount of tin solder. After the sample was loaded in the cell, 0.1 MPa helium gas was introduced to the cell through the capillary to improve thermal equilibrium, and then the capillary was pinched off and bent as a hook.

In order to obtain good adiabatic conditions between the calorimeter and its surroundings, two adiabatic shields were used to resist the heat transfer between the cell and its environment. The cell and two shields were housed in a high vacuum can and immersed in a liquid nitrogen cryostat.

The two adiabatic shields were made of chromium plated copper (0.5 mm thick) and equipped with manganin heating wire (0.2 mm in diameter). The inner shield, which is a little smaller than the outer one, was hung from the top of the outer one by three pieces of fine nylon thread, while the outer shield was hung from the top of the vacuum can by the same means. Two sets of six-junction chromel-copel thermometers were used to indicate the temperature differences between the sample cell and the inner adiabatic shields, and between the inner and the outer shields. The temperatures of the two shields were controlled separately with two sets of automatic adiabatic controllers operating in PID mode. The principle of the automatic adiabatic control circuits was described in detail previously [6, 7].

The uncertainty temperature between the outer edges of the vanes and the sample cell was less than 1 mK in the determination of heat capacity, and the temperature change of the sample cell in the equilibrium period was in the range of 0.1–0.05 mK min⁻¹.

The energy introduced into the sample cell was supplied by a direct current supply with a stability of about 5 ppm. A computer-based on-line measuring system was designed which could automatically measure the current through the calorimeter heating wire, the voltage across it, the duration of energy input and then the introduced energy was obtained. The system was composed of a personal computer, I/O data channels, an A/D converter, a low contact potential switch, the input interface, and clock signals timer. A Model 5000 integrating digital multimeter (Sabtronics Instrument AG Switzerland) was used as the A/D converter. The duration of heating was measured by means of a digitally displayed electronic timer-controller with an accuracy of 10⁻³ s. The temperature of the platinum thermometer in the calorimeter cell was also automatically measured by the system.

In order to verify the reliability of the calorimeter, the molar heat capacities of α -Al₂O₃ were measured from 80 to 400 K. The deviations of the experimental results from the smoothed curve lie within $\pm 0.1\%$, while the inaccuracy was within $\pm 0.2\%$ compared with those [8] of the National Institute Science and Technology (formerly the National Bureau of Standards, NBS) in the whole temperature range.

The heating rate was controlled in the range of 0.2–0.4 K min⁻¹ while the sample in solid and liquid phase. The intervals of temperature rising was 2–4 K generally and the intervals was reduced a little while at the temperature of sample melting. The duration of heating was measured by means of a digitally displayed electronic timer-controller with an accuracy of 10⁻³ s. The data were read and calculated automatically by a computer on the real time.

TG analysis

Thermogravimetric analysis was performed with a TG 951 thermal balance in the temperature range 340–540 K. A nitrogen gas flow rate of 150 mL min⁻¹ and a heating rate of 10 K min⁻¹ were employed.

Results and discussion

Heat capacity

The experimental molar heat capacities of chrysanthemic acid of a typical run are shown in Fig. 1 and listed in Table 1. In solid region the heat capacities of chrysanthemic acid were measured with 95 points in temperature range from 80 to 365 K and 3 points in liquid region between 396–400 K. In fusion region the heat capacities of chrysanthemic acid were determined with 34 points in temperature range from 366 to 395 K. No thermal anomaly was observed in solid and liquid regions, it demonstrates that the structure of the compound is stable in the temperature range.

The values of heat capacities were fitted with the following polynomial expressions with least squares method. For solid region (80–365 K):

$$C_p = 177.756 + 90.8606X - 2.14490X^2 - 12.3754X^3 + 2.96330X^4 + 23.6069X^5 \quad (\text{J mol}^{-1} \text{K}^{-1}) \quad (1)$$

where $X = (T - 222.1)/143.5$ and T/K is temperature.

For liquid region (396–400 K):

$$C_p = 350.226 + 2.64436X \quad (\text{J mol}^{-1} \text{K}^{-1}) \quad (2)$$

where $X = (T - 398.0)/2.0$ and T/K is temperature. The deviation of the experimental data from the smoothed values in whole regions is within $\pm 0.2 \text{ J mol}^{-1} \text{K}^{-1}$.

Melting point, enthalpy and entropy of fusion, and purity determination

To determine the melting point (T_m) and enthalpy ($\Delta_{\text{fus}}H_m$), a step heating method was used. It is based on the following principle. The sample was heated with a small amount of heat once and to measure the equilibrium temperature. The increment of

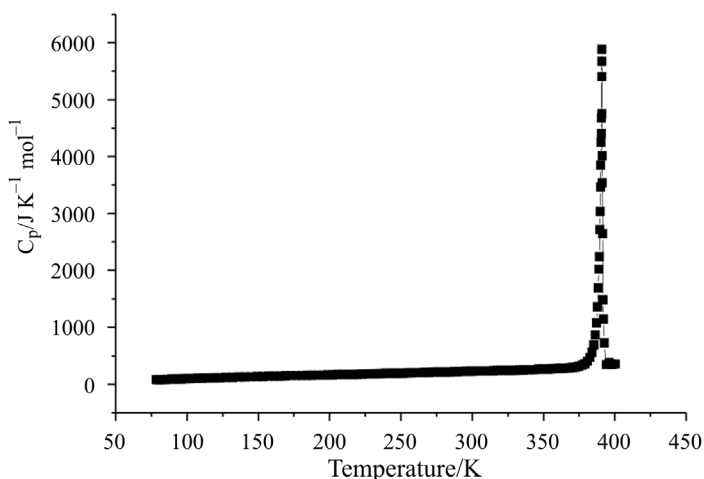


Fig. 1 Heat capacity curve of chrysanthemic acid

Table 1 Experimental molar heat capacities (in $\text{J mol}^{-1} \text{K}^{-1}$) of chrysanthemic acid ($M=142.198 \text{ g mol}^{-1}$)

T/K	C_p	T/K	C_p	T/K	C_p	T/K	C_p
78.659	78.28	187.808	155.9	292.813	221.8	376.837	331.7
79.542	80.19	191.451	158.0	295.616	225.8	378.865	359.9
80.432	80.10	195.058	160.1	298.415	227.0	380.749	404.6
81.693	79.98	198.629	162.2	301.197	228.1	382.451	467.0
83.301	81.56	202.166	164.3	303.958	229.6	383.937	559.2
85.812	84.09	205.670	166.9	306.709	231.0	385.199	688.1
89.245	86.45	209.141	169.0	309.447	232.1	386.238	868.2
92.517	90.14	212.580	170.7	312.170	233.0	387.078	1078
95.658	93.30	215.988	172.7	314.879	235.9	387.757	1360
98.804	95.86	219.366	174.5	317.572	238.1	388.300	1692
101.881	98.32	222.716	177.2	320.250	238.9	388.742	2019
104.894	101.1	226.031	180.7	322.912	240.7	389.119	2241
107.848	103.7	229.274	182.9	325.560	243.6	389.433	2714
110.750	106.0	232.492	184.6	328.192	244.6	389.691	3031
113.606	107.9	235.719	186.5	330.807	245.9	389.911	3468
116.420	109.8	238.894	188.1	333.405	248.8	390.095	3852
119.194	111.4	241.974	190.1	335.982	249.9	390.253	4251
122.888	114.6	245.060	192.0	338.547	251.4	390.395	4405
127.340	118.8	248.201	193.0	341.096	252.8	390.529	4680
131.824	121.0	251.328	194.9	343.629	253.8	390.645	5402
136.350	123.9	254.436	196.0	346.140	261.2	390.741	5887
140.665	126.9	257.518	199.0	348.629	262.4	390.831	5675
144.918	129.3	260.578	200.4	351.105	262.8	390.929	4754
149.104	132.4	263.612	204.0	353.570	265.1	391.048	4016
153.217	135.4	266.624	206.7	356.011	270.1	391.184	3540
157.256	138.9	269.620	208.1	358.430	273.3	391.338	2646
161.234	140.8	272.595	211.0	360.834	276.9	391.572	1485
165.168	142.7	275.546	211.8	363.218	277.6	391.890	1146
169.048	146.0	278.478	212.6	365.582	282.8	392.505	724.8
172.866	149.4	281.388	214.4	367.921	285.9	393.964	347.4
176.650	150.2	284.277	215.5	370.230	292.4	395.988	378.5
180.408	151.6	287.144	217.2	372.493	300.9	398.007	350.5
184.127	153.7	289.991	219.8	374.702	314.1	400.100	352.8

the energy required to heat the sample from the temperature T_1 , below the melting point, to the temperature T_2 , above it, was measured. With multiple times heating, the melting point was approached and the enthalpy of fusion of the sample was derived by the following Eq. (3).

$$\Delta_{\text{fus}}H_m = \frac{Q - n \int_{T_i}^{T_m} C_{P(S)} dT - n \int_{T_m}^{T_f} C_{P(L)} dT - \int_{T_i}^{T_f} H_0 dT}{n} \quad (3)$$

Summing up increments of the heat capacity in the melting region with corrections for lattice heat capacity from temperature T_1 to T_m , and for heat capacity of liquid from T_m to T_2 , where n is the molar number of the sample; Q , the total amount of heat introduced into the sample; $C_{P(S)}$, $C_{P(L)}$, H_0 , the heat capacity of sample in solid and liquid state and heat capacity of empty cell. The entropy of fusion $\Delta_{\text{fus}}S_m$ of chrysanthemmic acid was derived by combining the enthalpy and melting point.

During the heat capacity experiment, we found that the temperature of fusion from solid phase to liquid took place from about 375 to 395 K. The determination of temperature of fusion T_m and enthalpy of fusion $\Delta_{\text{fus}}H_m$ for the sample was carried out from three series of heat capacity measurements in this temperature range. The three runs of experimental and calculated results are listed in Table 2. The averaged melting point T_m was determined to be 390.741 ± 0.002 K, the averaged enthalpy $\Delta_{\text{fus}}H_m$ was 14.51 ± 0.13 kJ mol⁻¹, and the averaged entropy $\Delta_{\text{fus}}S_m$ was 37.13 ± 0.34 J mol⁻¹ K⁻¹.

The purity of the sample is determined based on a fractional melting method. The values of melting temperatures in the solid–liquid two-phase region are determined at a series of fractions melted. The basic principle is that at the temperature several degrees below the melting point, an enough amount of energy is supplied to the sample cell to melt a small fraction of the sample, say 10%, and the melting tem-

Table 2 Experimental and calculated results of temperature of fusion and enthalpy

T_i /K	T_f /K	T_m /K	Q /J	$\int_{T_i}^{T_f} H_0 dT / n$	$n \int_{T_i}^{T_m} C_{P(S)} dT$	$n \int_{T_m}^{T_f} C_{P(L)} dT$	$\Delta_{\text{fus}}H_m / \text{kJ mol}^{-1}$
367.921	393.964	390.741	4501.14	3209	1203	192.8	14.64
366.756	392.952	390.743	4502.22	3198	1261	182.3	14.39
369.086	394.975	390.740	4500.39	3215	1148	271.7	14.50

perature is observed until equilibrium is reached. Following the attainment of equilibrium, another amount of energy is supplied to the sample and another portion of sample is melted and a second equilibrium melting temperature observed. In this way, the values of melting temperatures in the solid–liquid two-phase region are determined at a series of fractions melted, for example 10, 25, 50, 75, 90%. Then, the sample is completely melted, and a final equilibrium temperature a few degrees above the melting point are determined. With the plot of equilibrium temperatures vs.

melting fractions, the melting points of sample and pure substance could be obtained. Then, the purity of the chrysanthemic acid sample can be obtained according to the following van't Hoff equation.

$$T_0 - T_m = \frac{RT_0^2 x}{\Delta_{\text{fus}} H_m}$$

where T_m is the melting point of sample and T_0 is the melting point of pure compound. $\Delta_{\text{fus}} H_m$ is the molar melting enthalpy of purity, x is the molar fraction of impurity.

In the present study, the experimental and calculated results are shown in Table 3 and Fig. 2. The purity of the sample was determined to be 98.55 mol%, it is very closed to 98.61 mol% obtained by HPLC. With Fig. 2, extrapolating the equilibrium temperatures vs. inverse of melting fraction ($1/F$, F is melting fraction) to zero, the melting point of pure chrysanthemic acid (100%) was obtained to be $T_0=392.43$ K.

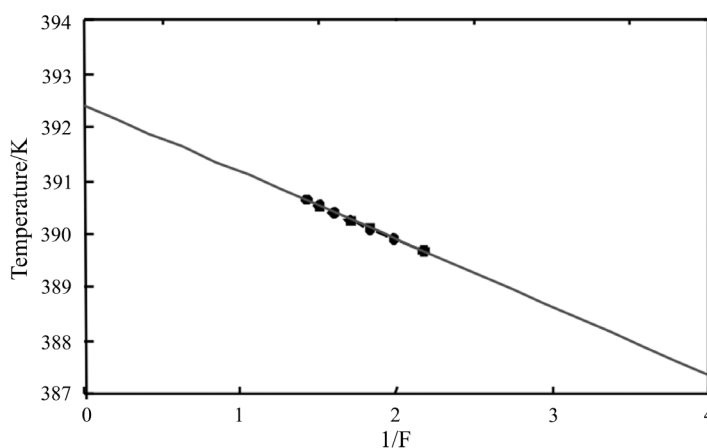


Fig. 2 Equilibrium temperature vs. inverse of melting fraction; ● – experimental data; — – linear fit of data

Table 3 Experimental results of purity measurement

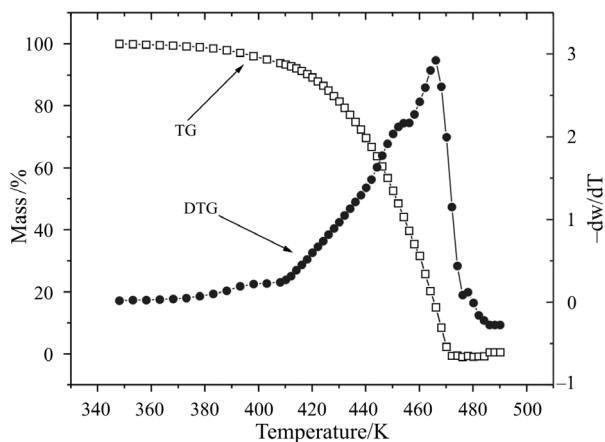
Q/J	6737.2	7383.9	8007.7	8603.5	9178.7	9745.0	10298.8
$F=Q/(\Delta H_m n)$	0.4591	0.5035	0.5455	0.5962	0.6254	0.6640	0.7020
$1/F$	2.178	1.986	1.833	1.706	1.599	1.506	1.425
T/K	389.691	389.911	390.095	390.253	390.401	390.534	390.645

Results of thermodynamic functions

In the present experiment the heat capacity near thermodynamic zero point was difficult to obtain. Therefore, only the thermodynamic function data in temperature range from 298.15 to 400 K were given based on standard state (298.15 K). The results of thermodynamic function $H_{(T)} - H_{(298.15 \text{ K})}$, $S_{(T)} - S_{(298.15 \text{ K})}$, and $G_{(T)} - G_{(298.15 \text{ K})}$ are listed in Table 4.

Table 4 Calculated thermodynamic function data of chrysanthemic acid

T/K	$C_p/$ $J mol^{-1} K^{-1}$	$[H_T^\ominus - H_{298.5K}^\ominus]/$ $kJ mol^{-1}$	$[S_T^\ominus - S_{298.5K}^\ominus]/$ $J mol^{-1} K^{-1}$	$-[G_T^\ominus - G_{298.5K}^\ominus]/$ $kJ mol^{-1}$
298.15	224.7			
300	228.7	0.420	1.411	0.486
305	232.0	1.572	5.218	1.809
310	235.3	2.740	9.016	3.150
315	238.6	3.924	12.81	4.511
320	241.8	5.125	16.59	5.890
325	245.1	6.343	20.37	7.289
330	248.4	7.583	24.13	8.706
335	251.7	8.827	27.89	10.14
340	255.0	10.09	31.65	12.14
345	258.3	11.38	35.39	13.07
350	261.6	12.68	39.13	14.56
355	264.9	13.99	42.87	16.07
360	268.2	15.33	46.60	17.60
365	271.5	16.68	50.32	19.15
370	297.1	18.10	54.19	20.72
375	326.1	19.66	58.37	22.31
380	384.1	21.43	63.07	23.91
385	695.7	24.13	70.11	25.55
390.741	maximum			
395	347.4	45.00	123.7	29.14
400	352.8	46.75	128.1	31.08

**Fig. 3** TG and DTG plots of chrysanthemic acid in N_2 atmosphere at a heating rate of $10 K min^{-1}$

To determine the decomposition temperature of chrysanthemic acid, a TG analysis experiment was performed with a thermobalance (Model TG 951) in nitrogen atmosphere. The heating rate was about 10 K min^{-1} . The results are shown in Fig. 3. It can be seen from the TG-DTG curves in Fig. 3 that there is only one mass loss activity in the whole temperature range. The decomposition started from ca. 410 and ended at ca. 471 K. The decomposition peak temperature obtained from DTG curve is ca. 466 K.

The decomposition reaction kinetic parameters can be obtained by processing TG data [9]. The order of reaction, pre-exponential factor, and activation energy are 0.16, $2.16 \cdot 10^8 \text{ min}^{-1}$ and 60.4 kJ mol^{-1} , respectively.

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