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HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF FENPROPATHRIN ($C_{22}H_{23}O_3N$)

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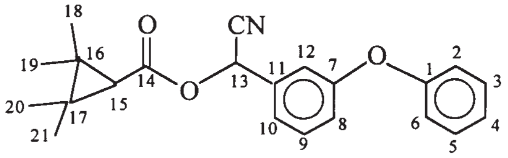
Abstract

The heat capacities of fenpropathrin in the temperature range from 80 to 400 K were measured with a precise automatic adiabatic calorimeter. The fenpropathrin sample was prepared with the purity of 0.9916 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 322.48±0.01 K, 18.57±0.29 kJ mol^{-1} and 57.59±1.01 J mol^{-1} K^{-1}, respectively. The thermodynamic functions of fenpropathrin, $H_{(T)}–H_{(298.15)}$, $S_{(T)}–S_{(298.15)}$ 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. 450 K and terminates at ca. 575 K. The maximum decomposition rate was obtained at 558 K. The purity of the sample was determined by a fractional melting method.

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

Introduction

Fenpropathrin, (*R,S*)α-cyano-3-phenoxy benzyl-2,2,3,3-tetramethyl-cyclopropane carboxylic ester, is a highly efficient insecticide and pesticide and widely used in agricultural production. Its formula is $C_{22}H_{23}O_3N$ and its structure is



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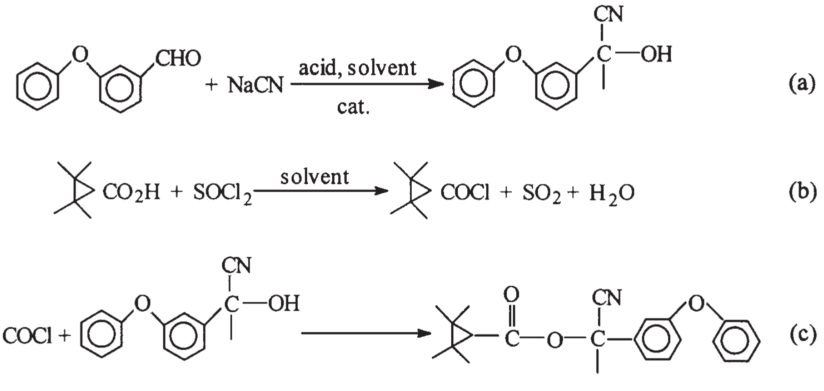
In 1989, Kasamatsu *et al.* [1] reported the melting point and thermal decomposition of fenpropathrin. However, low purity of the sample used made their results dissatisfactory. Up to now, the heat capacity, enthalpy and entropy of fusion and thermodynamic properties of fenpropathrin have not been reported.

To obtain the thermodynamic data and improve the synthesis of fenpropathrin, heat capacity measurements of this compound were carried out in temperature range between 80 and 400 K with an automated adiabatic calorimeter. At the same time, the melting point, enthalpy and entropy of fusion were calculated. A TG analysis was conducted above 380 K in order to investigate the thermal decomposition behaviour of the sample.

Experimental

Sample preparation and analysis

Fenpropathrin was prepared by catalytic reactions, called modified cyanohydrin method [2], with 2,2,3,3-tetramethylcyclopropane carboxylic acid [3] and α-cyano-3-metolphenoxy-benzoic alcohol. The synthesis route is as follows:



The fenpropathrin crystal product was filtered and recrystallized three times. Finally, the sample of fenpropathrin, a white crystal, was obtained [4]. The purity of the sample was determined to be 99.16 mol% by HPLC (model: Shimazu 10A) and 99.10 mol% by fractional melting method in the heat capacity experiment later. The molecular structure was verified with NMR (model: Bruker DRX-400).

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 [5]. Generally the calorimeter consists of a calorimeter cell, an adiabatic shield, a guard shield, two sets of differential thermocouples, and a vacuum can. The adiabatic calorimeter was described before in detail elsewhere [6] and only the major features of the equipment are described here.

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 around 50 cm^3. 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 shield, 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 were described in detail previously [6, 7].

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, and the duration of energy input. Finally 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 above mentioned system.

In order to verify the reliability of the calorimeter, the molar heat capacities of α-Al_2O_3 were measured from 80 to 400 K. The deviations of the experimental results from the smoothed curve lie within ±0.1%, while the inaccuracy was within ±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.

TG analysis

Thermogravimetric analysis was performed with a TG 951 thermal balance in the temperature range 380–680 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 fenpropathrin of a typical run are shown in Fig. 1 and listed in Table 1. In solid region the heat capacities of fenpropathrin were measured with 65 points in temperature range from 80 to 308 K and 23 points in liquid region between 326 and 400 K. In fusion region the heat capacities of fenpropathrin were determined with 20 points. No thermal anomaly was observed in solid and liquid regions.

The values of heat capacities were fitted with the following polynomial expressions with least squares method. For solid region (80–308 K),

$$C_{pm}=324.092+164.146X+3.084X^2-37.201X^3+3.608X^4+43.284X^5 \text{ (J mol}^{-1}\text{ K}^{-1}) \quad (1)$$

where, $X=(T-194.80)/114.10$ and T/K is temperature.

For liquid region (326–400 K),

$$C_{pm}=657.698+45.186X-20.143X^2-23.766X^3+17.932X^4+9.981X^5 \text{ (J mol}^{-1}\text{ K}^{-1}) \quad (2)$$

where, $X=(T-363.50)/36.50$ and T/K is temperature. The deviation of the experimental data from the smoothed values in whole regions is within ±0.3%.

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

To determine the melting point (T_m) and enthalpy ($\Delta_{fus}H_m$), a step heating method was used. It is based on the following principle. To heat the sample with a small amount of heat once and to measure the equilibrium temperature. The increment of 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 Eq. (3),

$$\Delta_{fus}H_m=\frac{Q-n\int_{T_1}^{T_m}C_{p(S)}dT-n\int_{T_m}^{T_2}C_{p(L)}dT-\int_{T_1}^{T_2}H_0dT}{n} \quad (3)$$

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 mount 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 $\Delta_{fus}S_m$ of fenpropathrin was derived by combining the enthalpy and melting point.

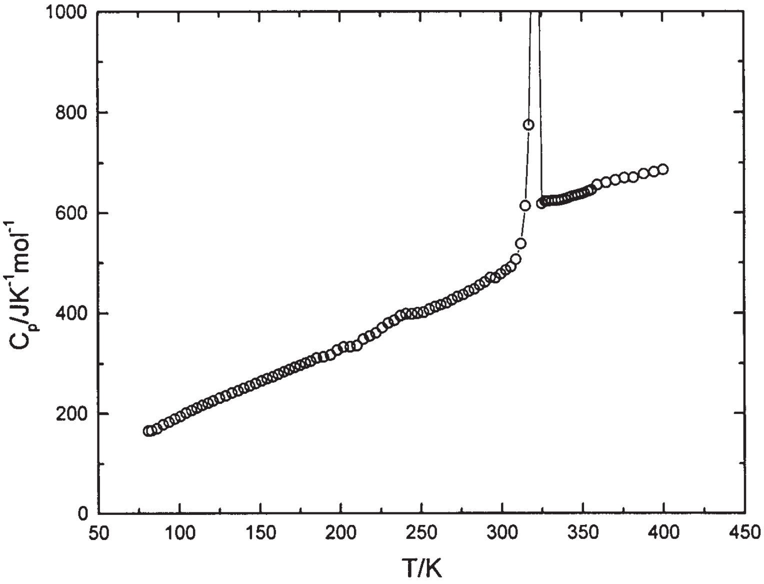


Fig. 1 Heat capacity curve of fenpropathrin

During the heat capacity experiment, we found that the temperature of fusion from solid phase to liquid took place from about 307 to 327 K. The determination of temperature of fusion T_m and enthalpy of fusion ($\Delta_{fus}H_m$) 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 T_m=322.48±0.01 K. The averaged enthalpy and entropy of fenpropathrin were determined to be 18.57±0.29 kJ mol^{-1} and 57.59±1.01 J mol^{-1} K^{-1}.

In reference [1], Kasamatsu *et al.* reported the melting point of fenpropathrin as 320.25 K (47.1°C), lower about 2.2°C than the present result 322.48 K (49.33°C). Perhaps this difference is caused mainly by sample purity although they did not define the purity of sample in their paper.

The purity of the sample is determined based on a fractional melting method. 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 temperature is observed until equilibrium is

Table 1 Experimental molar heat capacities of fenpropathrin (M=331.43 g mol^{-1})

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
80.745	165.833	210.088	335.837	321.545	6031.56
82.930	166.281	214.099	348.395	321.783	8242.98
86.147	170.185	218.064	354.716	321.957	11206.2
89.960	177.903	221.993	360.883	322.095	12365.2
93.666	183.328	225.867	371.582	322.208	13715.5
97.279	189.122	229.630	380.545	322.296	14123.6
100.805	194.347	233.367	385.897	322.368	14606.8
104.258	201.150	237.110	395.176	322.431	15515.7
107.646	206.395	240.713	398.069	322.485	20312.8
110.976	210.983	244.291	398.150	322.534	15127.0
114.246	216.099	247.938	399.777	322.636	5127.30
117.963	220.553	251.576	401.953	323.284	1192.06
121.039	225.372	255.180	407.182	324.900	618.708
124.954	230.547	258.754	412.329	326.984	623.298
128.833	235.572	262.302	415.914	329.064	623.420
132.643	240.734	265.82	419.824	331.140	624.734
136.393	245.524	269.305	425.700	333.211	624.864
140.089	250.317	272.764	431.978	335.280	625.373
143.743	255.065	276.203	436.046	337.347	626.389
147.354	260.082	279.616	442.778	339.413	627.926
150.920	264.880	282.999	447.311	341.475	630.062
154.443	269.313	286.353	454.897	343.528	632.867
157.923	273.565	289.674	461.231	345.505.	634.469
161.374	278.606	292.955	470.031	347.476	636.223
164.788	283.671	296.207	469.629	349.511	638.102
168.170	288.098	299.445	477.244	351.540	640.335
171.518	292.255	302.654	485.135	353.563	643.028
174.834	296.388	305.829	491.475	355.582	645.952
178.118	300.758	308.953	506.527	359.180	655.991
181.37	304.896	311.984	538.030	364.830	660.431
185.141	310.768	314.833	614.073	370.451	665.753
189.417	313.084	317.08	774.658	376.039	669.836
193.639	316.869	318.667	1039.84	381.592	670.724
197.808	326.356	319.863	1584.64	388.025	677.962
201.931	332.601	320.675	2606.64	394.456	681.912
206.025	333.246	321.199	4078.28	400.010	686.100

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

T_1/	T_2/	T_m/	Q/J	$\int_{T_1}^{T_2} H_0 \mathrm{d}T/n$	$n\int_{T_1}^{T_m} C_{p(S)} \mathrm{d}T$	$n\int_{T_{m1}}^{T_2} C_{p(L)} \mathrm{d}T$	ΔH_m/kJ mol^{-1}
	K						
307.413	325.941	322.485	2162.38	389.621	474.965	132.523	18.943
307.464	327.013	322.462	1713.53	411.338	365.523	125.850	18.350
307.187	327.312	322.480	1738.45	410.083	380.523	133.142	18.423

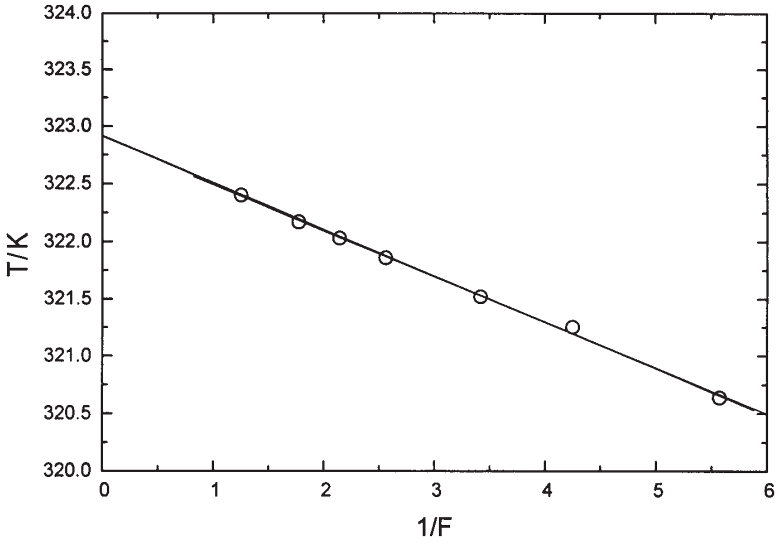


Fig. 2 Equilibrium temperature *vs.* inverse of melting fraction; o – experimental data; —— – linear fit of data

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, 70 and 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 sample can be obtained according to van't Hoff equation.

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 99.10 mol%. It is very closed to 99.16 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 fenpropathrin (100%) was obtained to be 322.89 K (49.74°C).

Table 3 Experimental results of purity measurement

Q/J	928.4	655.4	543.0	454.5	340.5	273.6	208.7
$F=Q/(\Delta H_m n)$	0.7981	0.5634	0.4668	0.3907	0.2927	0.2352	0.1795
$1/F$	1.253	1.775	2.142	2.560	3.417	4.251	5.573
T/K	322.40	322.17	322.03	321.86	321.52	321.25	320.64

Table 4 Calculated thermodynamic function data of fenpropathrin

T/K	C_p/J mol^{-1} K^{-1}	$H_{(T)}$–$H_{(298.15)}$/ kJ mol^{-1}	$S_{(T)}$–$S_{(298.15)}$/ J mol^{-1} K^{-1}	–[$G_{(T)}$–$G_{(298.15)}$]/ kJ mol^{-1}
80	159.020	–69.219	–374.9	39.227
85	169.514	–68.398	–365.0	37.373
90	179.026	–67.527	–355.0	35.577
95	187.724	–66.609	–345.1	33.825
100	195.759	–65.65	–335.2	32.130
105	203.264	–64.652	–325.5	30.475
110	210.359	–63.618	–315.9	28.869
115	217.146	–62.549	–306.4	27.313
120	223.715	–61.447	–297.0	25.807
125	230.144	–60.312	–287.7	24.350
130	236.497	–59.146	–278.6	22.928
135	242.826	–57.947	–269.5	21.565
140	249.174	–56.717	–260.6	20.233
145	255.575	–55.456	–251.7	18.960
150	262.051	–54.161	–243.0	17.711
155	268.619	–52.835	–234.3	16.519
160	275.288	–51.475	–225.6	15.379
165	282.059	–50.082	–217.1	14.261
170	288.929	–48.654	–208.5	13.209
175	295.891	–47.192	–200.1	12.175
180	302.933	–45.695	–191.6	11.207
185	310.040	–44.163	–183.2	10.271
190	317.195	–42.595	–174.9	9.3640
195	324.380	–40.991	–166.5	8.5235
200	331.576	–39.351	–158.2	7.7110
205	338.764	–37.675	–150.0	6.9250
210	345.929	–35.963	–141.7	6.2060
215	353.053	–34.216	–133.5	5.5135
220	360.126	–32.433	–125.3	4.8670
225	367.138	–30.615	–117.1	4.2675
230	374.086	–28.762	–109.0	3.6920
235	380.971	–26.874	–100.9	3.1625
240	387.800	–24.952	–92.76	2.6896
245	394.588	–22.996	–84.69	2.2470
250	401.358	–21.006	–76.65	1.8435

Table 4 Continued

T/K	C_p/J mol^{-1} K^{-1}	$H_{(T)}–H_{(298.15)}$/ kJ mol^{-1}	$S_{(T)}–S_{(298.15)}$/ J mol^{-1} K^{-1}	$–[G_{(T)}–G_{(298.15)}]$/ kJ mol^{-1}
255	408.141	–18.982	–68.64	1.4788
260	414.977	–16.925	–60.65	1.1560
265	421.919	–14.832	–52.68	0.8718
270	429.029	–12.705	–44.72	0.6306
275	436.381	–10.542	–36.78	0.4275
280	444.063	–8.341	–28.85	0.2630
285	452.176	–6.100	–20.92	0.1378
290	460.838	–3.818	–12.98	0.0538
295	470.178	–1.491	–5.027	0.0080
298.15	475.218	0	0	0
300	478.782	0.882	2.951	0.0033
305	488.949	3.302	10.947	0.0368
310	500.009	5.774	18.986	0.1117
315	512.118	8.304	27.081	0.2265
320	525.446	10.898	35.249	0.3817
322.48	maximum			
325	622.310	32.710	103.660	0.9795
330	622.286	35.820	113.157	1.522
335	624.720	38.397	122.531	2.111
340	628.925	42.070	131.815	2.747
345	634.302	45.230	141.035	3.427
350	640.340	48.417	150.204	4.154
355	646.609	51.635	159.331	4.928
360	652.770	54.883	168.418	5.747
365	658.568	58.162	177.462	6.612
370	663.832	61.468	186.459	7.522
375	668.480	64.800	195.401	8.475
380	672.514	68.151	204.283	9.476
385	676.023	71.523	213.097	10.52
390	679.182	74.911	221.841	11.61
395	682.252	79.214	230.512	11.84
400	685.578	81.734	239.114	13.91

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 80 to 400 K were given based on standard state (298.15 K). The results of thermodynamic function $H_{(T)}–H_{(298.15)}$, $S_{(T)}–S_{(298.15)}$, and $G_{(T)}–G_{(298.15)}$, are listed in Table 4.

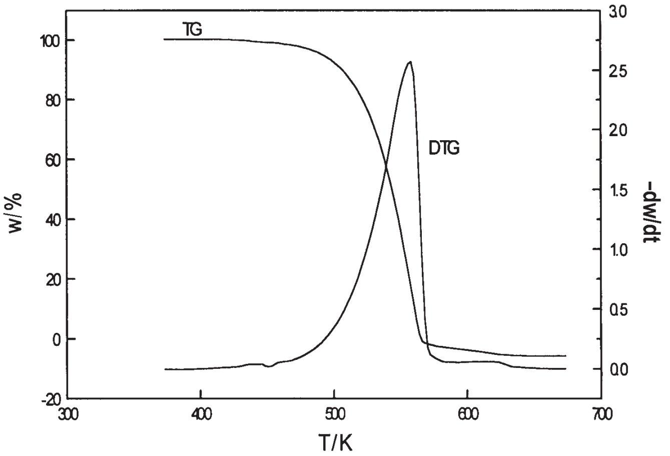


Fig. 3 TG and DTG plots of fenopropathrin in N_2 atmosphere at a heating rate of 10 K min^{-1}

To determine the decomposition temperature of fenpropathrin, a thermogravimetric (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. 470 K and ended at ca. 575 K. The decomposition peak temperature obtained from DTG curve is ca. 558 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 0.18, $1.3\cdot10^{10}$ min^{-1}, and 94.50 kJ mol^{-1}, respectively.

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References

1 K. Kasamatsu, N. Matsuo and S. Tsuda, Insecticide-acaricide Rody (fenpropathrin), Sumitomo Kagaku, 2 (1989) 19.
2 J. Q. Cai, Z. R. Li, J. X. Yu, S. W. Lu, Z. W. Si, X. H. Yuan and H. F. Guo, Synthesis of fenpropathrin from 2,2,3,3-tetramethylcyclopropane carboxylic acid by cyanohydrin method, CN 1062348A, 1992.

3 J. Q. Cai, J. X. Yu, X. H. Yuan, Z. W. Si, Z. R. Li, S. W. Lu and H. F. Guo, Synthesis of 2,2,3,3,-tetramethylcyclopropane carboxylic acid, CN 1062345A, 1992.

4 X. H. Yuan, S. W. Lu and Z. R. Li, A method to prepare fenpropathrin with a concentration of more than 90%, CN 1194265, 1998.

5 E. F. Jr. Westrum, G. T. Furukawa and J. P. McCullough, Experimental Thermodynamics, Vol. 1, J. P. McCullough and D. W. Scott (Eds.), Butterworths, London 1968, p. 133.

6 Z. C. Tan, L. X. Zhou, S. X. Chen and A. X. Yin, Scientia Sinica (Series B), 26 (1983) 1014.

7 Z. C. Tan, A. X. Yin, S. X. Chen and L. X. Zhou, Science in China (Series B), 34 (1991) 560.

8 D. A. Ditmars, S. Ishihara, S. S. Chang, G. Bernstein and E. D. West, J. Res. Natl. Bur. Stands., 87 (1982) 159.

9 J. H. Chen and C. R. Li, Reaction kinetics of thermal analysis, Huaxue Tongbo, 1 (1980) 7.