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Low-temperature heat capacity and thermodynamic properties of crystalline carboxin ($C_{12}H_{13}NO_2S$)

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Abstract

Carboxin was synthesized and its heat capacities were measured with an automated adiabatic calorimeter over the temperature range from 79 to 380 K. The melting point, molar enthalpy ($\Delta_{\text{fus}}H_{\text{m}}$) and entropy ($\Delta_{\text{fus}}S_{\text{m}}$) of fusion of this compound were determined to be 365.29 ± 0.06 K, 28.193 ± 0.09 kJ mol^{-1} and 77.180 ± 0.02 J mol^{-1} K^{-1}, respectively. The purity of the compound was determined to be 99.55 mol% by using the fractional melting technique. The thermodynamic functions relative to the reference temperature (298.15 K) were calculated based on the heat capacity measurements in the temperature range between 80 and 360 K. The thermal stability of the compound was further investigated by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. The DSC curve indicates that the sample starts to decompose at ca. 290 °C with the peak temperature at 292.7 °C. The TG–DTG results demonstrate the maximum mass loss rate occurs at 293 °C corresponding to the maximum decomposition rate.

Keywords: Carboxin; Heat capacity; Thermodynamic functions; Adiabatic calorimetry; TG; DSC

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1. Introduction

Carboxin (molecular formula: $C_{12}H_{13}NO_2S$; CA registry no. 5234-68-4) belongs to the class of carboxanilide fungicide. Its chemical name is 5,6-dihydro-2-methy-*N*-phenyl-1,4-oxathin-3-carboxamlide. It is applied in the seed treatment of wheat, barley, peanut, sorghum, flax and cotton prior to planting and used in combination with other pesticides like imidacloprid to prevent the formation of plant diseases or to cure existing diseases [1,2].

In order to improve the process of chemical synthesis of this compound, develop its new application and carry out relevant theoretical research, the thermodynamic properties are needed. In 1972, Plato studied this compound by differential scanning calorimetry (DSC). He reported that the melting point and heat of fusion of the compound were 371.45 K and 22.26 kJ mol^{-1}, respectively [3]. Donnely et al. determined the melting point and heat of fusion to be 365 K and 28.88 kJ mol^{-1}, respectively, through DSC in 1990 [4]. The thermodynamic data measured by the two authors are not in agreement with each other and the heat capacity, the thermal stability of the compound have not been published till now, so we conduct the thermodynamic study of this compound.

Heat capacity is one of the fundamental thermodynamic properties of substances and closely related to the energetic structure, and is sensitive to the variations in other properties. Adiabatic calorimetry is the most accurate approach to obtain the heat capacity, melting point and enthalpy of fusion of substances. In the present study, the low-temperature heat capacities have been measured in the temperature range from 79 to 380 K with an automated adiabatic calorimeter. The melting temperature, the molar enthalpy and entropy of fusion of the substance were determined. In addition, the thermal stability of the compound was further investigated by DSC and thermogravimetric (TG) analysis.

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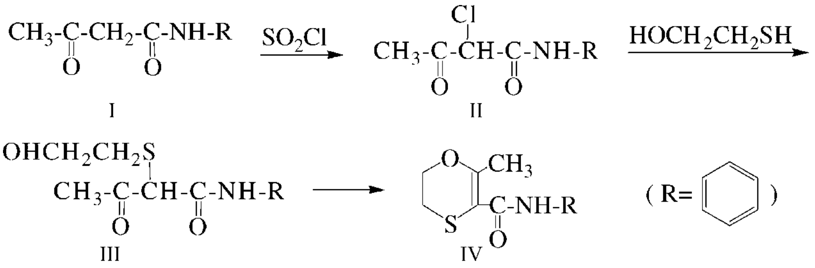
2. Experimental

2.1. Sample preparation

The sample used for the calorimetric measurement was synthesized by the method reported in the US Patent no. 3,393,202 [5]. Synthesis of the sample was carried out through the following three-step reaction: first, acetoacetamide (I) was chloridized with sulfuryl chloride in benzene to prepare α-chloroacetoacetamide (II), and then compound (II) reacted with 2-mercaptoethanol under basic conditions. The reaction proceeded through intermediates (III) which did not need to be isolated. The intermediate (III) was cyclized under slightly acidic conditions, and then dehydrated to yield the product (IV).



The crude product was condensed in vacuum and recrystallized from ethanol three times. The structure of the product was determined by IR, ^{1}H NMR and ^{13}C NMR. The purity of the compound is more than 99 mol% from GC result.

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimetric system described in detail previously [6]. The sample amount used for the heat capacity measurement is 1.9969 g, which is equivalent to 8.487 mmol based on its molar mass of 235.30 g mol^{-1}. The heating duration and temperature increment for each experimental heat capacity point were usually controlled to be about 10 min and 1–3 K, respectively, during the whole experimental process.

2.3. Thermal analysis

DSC analysis was carried out in a Setaram DSC-141 calorimeter. The sample about 2.6 mg was weighted into a closed aluminum pan, placed in the DSC cell and heated at the rate of 10 °C min^{-1} under high purity nitrogen atmosphere with a flow rate of 50 ml min^{-1}.

TG measurement was performed on Setaram setsys 16/18 apparatus. A mass of 7.4 mg was placed in a 100 μl α-alumina crucible and heated from room temperature to 500 °C with a rate of 10 °C min^{-1} under high purity nitrogen atmosphere with a flow rate of 25 ml min^{-1}.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacities of the sample are shown in Fig. 1 and tabulated in Table 1. From Fig. 1, it can be seen that the heat capacities of the sample increase with temperature in a smooth and continuous manner from 79 to 360 K and no phase transition or thermal anomaly was observed in this temperature range. Therefore, the sample is stable in the above temperature range. However, a thermal anomaly was observed in the temperature range from 360 to 367 K with the peak temperature of 365.28 K. The thermal anomaly can be ascribed to solid–liquid phase transition.

The experimental molar heat capacities have been fitted to the following polynomial in reduced temperature (X), by means of the least square fitting.

For the solid phase:

$$C_{p,\mathrm{m}}\ (\mathrm{J\,K^{-1}\,mol^{-1}}) = 185.09 + 118.11X - 2.0855X^2 - 31.388X^3 + 17.956X^4 + 34.227X^5$$

where $X = (T - 218.8)/139.4$, and T is the absolute temperature. The correlation coefficient of the fitted curve, $R^2 = 0.9999$. The above equation is valid from 79 to 360 K, with an uncertainty of ±0.2%.

For the liquid phase:

$$C_{p,\mathrm{m}}\ (\mathrm{J\,K^{-1}\,mol^{-1}}) = 441.88 + 7.413X - 3.619X^2 - 2.292X^3 - 3.458X^4 + 2.956X^5$$

where $X = (T - 373.9)/6.6$, and T is the absolute temperature. The correlation coefficient of the fitted curve, $R^2 = 0.9994$. This equation applies to the range from 367.3 to 380.5 K, with an uncertainty of ±0.25%.

3.2. Melting point, enthalpy and entropy of fusion

Three series of heat capacity measurements in the fusion region of the compound were carried out so that the repeatability of the fusion process was verified. The melting point was determined by a progressive approach with step-by-step heating. The molar enthalpy ($\Delta_{\mathrm{fus}}H_{\mathrm{m}}$) and entropy ($\Delta_{\mathrm{fus}}S_{\mathrm{m}}$) of fusion were derived by the following

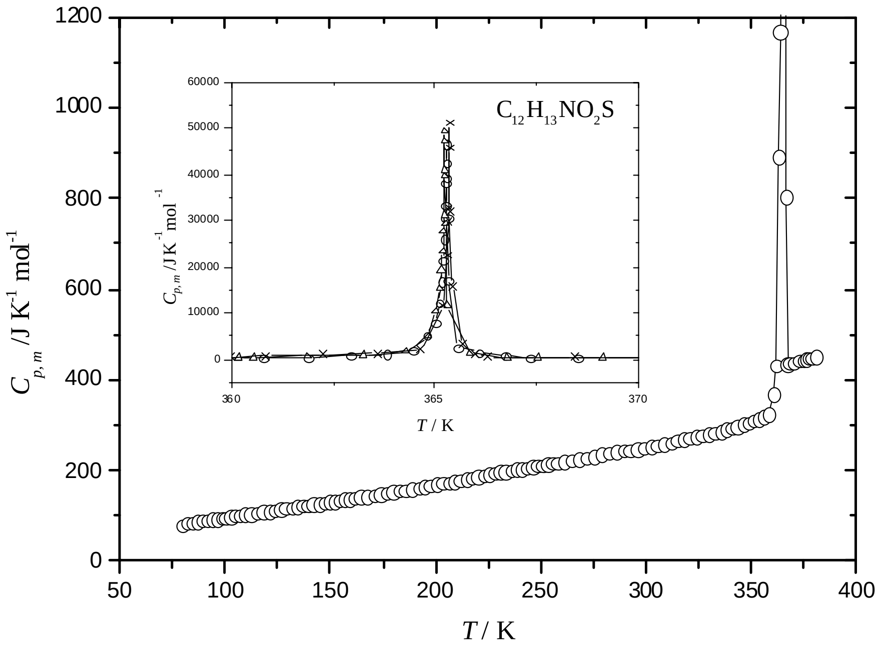


Fig. 1. Experimental molar heat capacity ($C_{p,\mathrm{m}}$) of carboxin as a function of temperature. (○), (△) and (×) represent the first, second and third series of heat capacity measurements, respectively.

Table 1
The experimental molar heat capacity of carboxin ($M = 235.30\,\mathrm{g\,mol^{-1}}$)

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})
Series 1					
79.36	80.311	197.76	166.64	329.97	280.39
81.94	82.751	200.64	168.97	332.86	284.19
84.43	84.813	203.50	171.48	335.70	287.03
86.85	86.911	206.34	173.75	338.47	290.12
89.22	88.504	209.16	176.18	341.19	293.45
91.53	90.351	211.95	178.72	343.69	296.98
93.79	91.662	214.71	180.86	346.27	300.85
96.01	93.149	217.45	183.44	348.80	305.82
98.18	94.877	220.16	186.21	351.25	309.20
100.32	96.207	222.86	188.98	353.60	313.89
102.42	97.898	225.53	191.08	355.84	317.45
104.50	99.474	228.17	193.45	358.24	323.30
106.54	100.53	230.79	196.01	360.78	368.39
109.06	102.39	233.40	198.23	361.89	432.17
112.05	104.29	235.98	200.03	362.91	892.13
114.99	106.14	238.53	201.67	363.80	1167.8
117.87	108.11	241.04	203.10	364.44	2097.2
120.70	109.97	243.53	205.86	364.80	5325.4
123.49	111.74	246.03	207.85	364.99	7978.6
126.24	113.71	248.53	210.41	365.09	12265
128.94	115.78	251.01	212.45	365.15	16764
131.61	118.01	253.47	214.32	365.19	21430
134.24	119.94	255.95	216.46	365.21	26025
136.85	121.72	258.26	217.77	365.23	30709
139.42	123.25	261.30	219.85	365.25	33194
141.96	125.04	264.89	222.68	365.26	38142
144.47	126.41	268.45	225.15	365.27	46370
146.95	128.05	271.98	228.55	365.28	46406
149.41	130.08	275.47	231.55	365.29	42476
151.84	131.63	278.92	235.34	365.29	39223
154.25	133.39	282.33	237.41	365.30	30515
156.65	135.51	285.98	240.89	365.32	16983

Table 1 (*Continued*)

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
159.02	137.12	289.35	243.66	365.55	2482.0
161.38	139.17	292.67	245.21	366.08	1530.1
164.17	141.02	295.91	247.06	366.72	803.34
167.38	143.48	299.15	249.94	367.32	433.98
170.56	146.03	302.37	252.59	368.50	436.80
173.70	148.27	305.56	255.24	370.32	438.83
176.81	150.38	308.73	258.30	373.08	441.13
179.89	152.64	311.86	261.41	374.78	442.66
182.94	154.95	314.96	264.99	376.21	444.78
185.95	156.98	318.03	268.51	377.65	446.80
188.94	159.45	321.07	271.70	379.13	448.25
191.91	162.08	324.07	274.22	380.54	450.16
194.84	164.13	327.04	277.31		
Series 2					
291.24	240.56	340.01	340.01	365.20	27737
293.76	243.06	342.37	342.37	365.22	31137
296.29	247.69	345.04	345.04	365.23	40834
298.83	250.45	348.97	348.97	365.23	49190
301.35	253.31	352.18	352.18	365.24	47083
303.86	255.07	353.95	353.95	365.24	39478
306.35	258.42	355.82	355.82	365.25	29332
308.83	260.43	357.60	357.60	365.30	11645
311.30	263.70	359.17	359.17	365.85	1256.6
313.76	265.68	360.17	360.17	366.75	536.57
316.20	268.98	360.19	360.19	367.52	437.23
318.63	270.94	360.54	360.54	369.12	440.19
321.05	273.86	361.87	361.87	370.55	443.22
323.45	275.66	363.25	363.25	372.78	445.88
325.85	278.27	364.28	364.28	374.81	447.99
328.24	281.70	364.83	364.83	377.33	450.23
330.61	284.93	365.02	365.02	379.43	453.42
332.97	288.02	365.11	365.11		
335.33	290.65	365.15	365.15		
337.65	293.33	365.18	365.18		
Series 3					
291.59	245.30	337.23	337.23	365.19	11697
294.21	247.06	339.32	339.32	365.30	22531
296.83	248.93	341.38	341.38	365.33	29942
299.44	250.03	343.40	343.40	365.35	32821
302.03	253.61	345.39	345.39	365.35	45695
304.60	255.23	347.33	347.33	365.35	51145
307.14	257.31	349.25	349.25	365.36	31868
309.66	259.91	350.85	350.85	365.43	15812
312.13	262.61	352.66	352.66	365.69	3216.4
314.57	265.54	354.41	354.41	365.99	997.24
316.98	267.41	356.10	356.10	366.31	440.54
319.35	270.97	357.71	357.71	368.42	443.85
321.69	272.25	359.22	359.22	370.31	446.95
324.01	275.52	359.87	359.87	372.95	448.96
326.30	278.63	359.98	359.98	375.33	450.84
328.56	281.32	360.85	360.85	377.43	452.66
330.77	283.69	362.27	362.27	379.12	455.12
332.96	285.70	363.58	363.58		
335.11	287.75	364.64	364.64		

equations [7]:

$$\Delta H_\mathrm{m} = \frac{Q - n\int_{T_\mathrm{i}}^{T_\mathrm{m}} C_{p,\mathrm{s}}\,\mathrm{d}T - n\int_{T_\mathrm{m}}^{T_\mathrm{f}} C_{p,\mathrm{l}}\,\mathrm{d}T - n\int_{T_\mathrm{i}}^{T_\mathrm{f}} H_0\,\mathrm{d}T}{n} \tag{1}$$

$$\Delta S_\mathrm{m} = \frac{\Delta H_\mathrm{m}}{T} \tag{2}$$

The results of the melting point, molar enthalpy and entropy of fusion obtained from the three series of heat capacity measurements are listed in Table 2.

Table 2
The melting point, enthalpy and entropy of fusion obtained from three series of heat capacity measurements

Thermodynamic properties	Series 1 (x_1)	Series 2 (x_2)	Series 3 (x_3)	Mean value ($\bar{x}$)	Standard deviation (σ_a)[a]
T_{fus} (K)	365.28	365.23	365.35	365.29	±0.06
$\Delta_{fus}H_m$ (kJ mol^{-1})	28.183	28.194	28.201	28.193	±0.09
$\Delta_{fus}S_m$ (J K^{-1} mol^{-1})	77.155	77.195	77.189	77.180	±0.02

x_i are the results obtained from three series of repeated heat capacity measurements; $\bar{x}$ the mean values.

[a] $\sigma_a = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)}$, where n is the experimental number ($n = 3$).

3.3. Purity determination

Adiabatic calorimetry provides an accurate way for determining the purity of a substance. The purity of sample can be evaluated from a set of equilibrium melting temperature (T) and melting fraction (F) corresponding to these temperatures [8]. The experimental results obtained from the heat capacity measurements in the fusion region are listed in Table 3. The equilibrium melting temperature (T) plotted versus the reciprocal of the melting fractions ($1/F$) gives a straight line as illustrated in Fig. 2. The T_0 is the temperature when $1/F$ equals to 0 and T_1 is equivalent to the temperature when $1/F$ is 1. From Fig. 2, the T_0 and T_1 are found to be 365.37 and 365.31 K, respectively. Thus, we calculate the mole percentage of impurities, $N = 0.45$ mol% from the Van't Hoff equation, and the purity of carboxin sample used in the calorimetric experiment accounts to $1 - N = 99.55$ mol%.

Table 3
The observed equilibrium temperature (T) and fraction melted (F) during the melting process

$F = q/Q$	$1/F$	T (K)
0.0361	27.6847	363.796
0.0661	15.1374	364.438
0.1447	6.9108	364.988
0.2510	3.9835	365.146
0.3632	2.7537	365.213
0.4775	2.0945	365.251
0.5932	1.6858	365.269
0.7079	1.4126	365.286
0.8231	1.2150	365.299

3.4. Thermodynamic functions of carboxin

Enthalpy and entropy of substances are the basic thermodynamic functions. Through the polynomial of heat capacity and the relationship between thermodynamic functions and heat capacity, the thermodynamic function data relative to the reference temperature (298.15 K) were calculated in the temperature range from 80 to 360 K with a interval of 5 K. The thermodynamic relationships are as follows:

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,\mathrm{m}}\, \mathrm{d}T \tag{3}$$

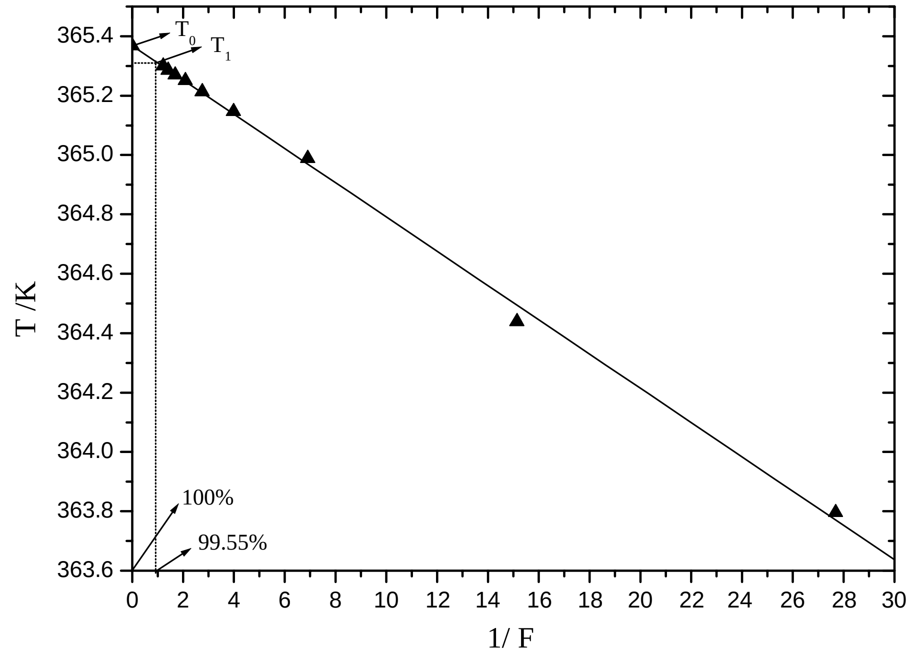


Fig. 2. The equilibrium temperature vs. the reciprocal of the melting fraction for carboxin during melting process.

Table 4
Calculated thermodynamic function data of carboxin

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	$H_T - H_{298.15}$ (kJ mol^{-1})	$S_T - S_{298.15}$ (J K^{-1} mol^{-1})
80	80.593	−35.503	−190.63
85	84.948	−35.089	−185.59
90	89.007	−34.654	−180.62
95	92.826	−34.200	−175.71
100	96.456	−33.726	−170.88
105	99.944	−33.235	−166.10
110	103.33	−32.727	−161.39
115	106.65	−32.202	−156.73
120	109.94	−31.661	−152.13
125	113.21	−31.103	−147.57
130	116.50	−30.529	−143.07
135	119.83	−29.938	−138.60
140	123.20	−29.330	−134.18
145	126.64	−28.706	−129.79
150	130.14	−28.064	−125.42
155	133.72	−27.404	−121.09
160	137.38	−26.726	−116.78
165	141.12	−26.030	−112.49
170	144.94	−25.315	−108.21
175	148.83	−24.581	−103.95
180	152.79	−23.827	−99.701
185	156.82	−23.053	−95.460
190	160.90	−22.258	−91.225
195	165.04	−21.444	−86.995
200	169.21	−20.608	−82.768
205	173.41	−19.751	−78.544
210	177.64	−18.874	−74.320
215	181.87	−17.975	−70.096
220	186.11	−17.055	−65.872
225	190.34	−16.114	−61.648
230	194.55	−15.152	−57.423
235	198.74	−14.169	−53.198
240	202.90	−13.164	−48.972
245	207.03	−12.140	−44.748
250	211.13	−11.094	−40.524
255	215.19	−10.028	−36.302
260	219.21	−8.942	−32.082
265	223.21	−7.836	−27.865
270	227.18	−6.710	−23.651
275	231.14	−5.565	−19.442
280	235.10	−4.399	−15.236
285	239.07	−3.214	−11.034
290	243.09	−2.008	−6.836
295	247.16	−0.783	−2.642
298.15	249.77	0.000	0.000
300	251.32	0.464	1.551
305	255.60	1.731	5.743
310	260.05	3.020	9.937
315	264.69	4.332	14.134
320	269.59	5.667	18.340
325	274.78	7.028	22.556
330	280.34	8.416	26.789
335	286.32	9.832	31.045
340	292.79	11.280	35.329
345	299.84	12.761	39.650
350	307.54	14.279	44.017
355	315.99	15.838	48.441
360	325.28	17.440	52.932

$$S_T - S_{298.15} = \int_{298.15}^{T} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T \qquad (4)$$

The values of thermodynamic functions $H_T - H_{298.15}$ and $S_T - S_{298.15}$ are listed in Table 4.

3.5. The results of DSC and TG analysis

From the DSC curve (Fig. 3), a sharply endothermic peak assigned to melting was observed, with the peak temperature

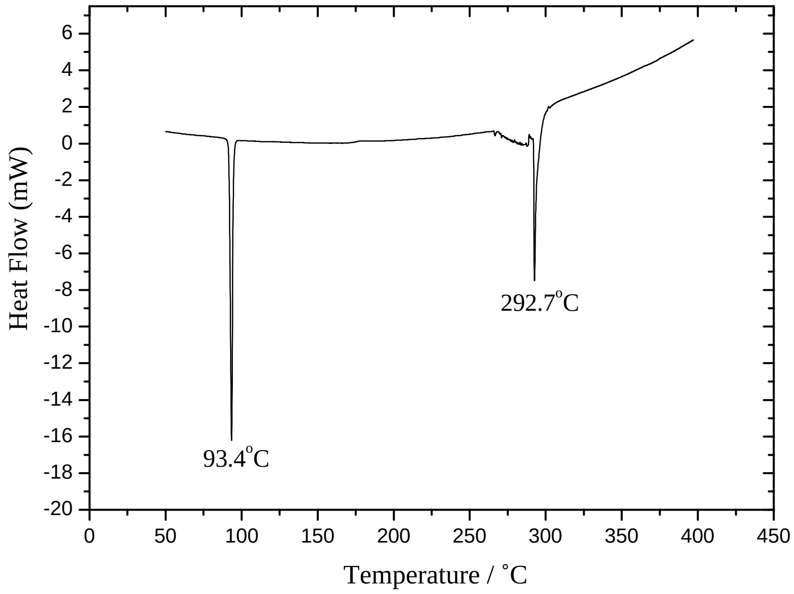


Fig. 3. DSC curve of carboxin under high purity nitrogen.

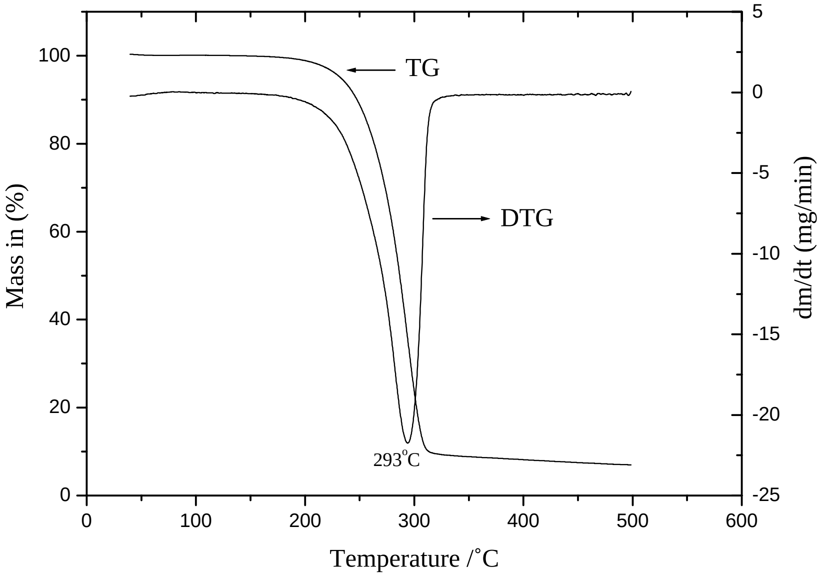


Fig. 4. TG–DTG curves of carboxin under high purity nitrogen.

of 93.4 °C. Based on the DSC curve, the melting point of the sample was determined to be 91.6 °C, which is consistent with the value (365.29 K) obtained from the adiabatic calorimetric measurements. In the range of 265–290 °C, a small endothermic effect occurs, it may be caused by evaporation of the compound. When the temperature is higher than 290 °C, another sharply endothermic peak associated with decomposition appears in the temperature range from 290 to 301 °C, with the peak temperature at 292.7 °C.

From the TG–DTG curves (see Fig. 4), it can be seen that the mass loss of the sample takes place in one step, with the maximum rate at 293 °C. The total mass lost in the heating process from ambient temperature to 500 °C corresponds to 93% of the initial sample weight, remaining 7% (mass) black residual in the crucible. Due to the high purity (99.55 mol%) of the sample, the residual may be the thermal decomposition product of the compound instead of the heavy impurity contained in the original sample. This case indicates the second sharply endothermic peak in the DSC curve is caused by the decomposition of the sample.

Acknowledgements

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