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Molar heat capacity and thermodynamic properties of 1-cyclohexene-1,2-dicarboxylic anhydride [$C_8H_8O_3$]

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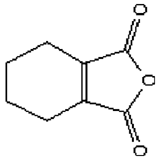
Abstract

The molar heat capacity $C_{p,m}$ of 1-cyclohexene-1,2-dicarboxylic anhydride was measured in the temperature range from $T = (80$ to $360)$ K with a small sample automated adiabatic calorimeter. The melting point T_m, the molar enthalpy $\Delta_{fus}H_m$ and the entropy $\Delta_{fus}S_m$ of fusion for the compound were determined to be (343.46 ± 0.24) K, (11.88 ± 0.02) $kJ \cdot mol^{-1}$ and (34.60 ± 0.06) $J \cdot K^{-1} \cdot mol^{-1}$, respectively. The thermodynamic functions $[H_{(T)} - H_{(298.15)}]$ and $[S_{(T)} - S_{(298.15)}]$ were derived in the temperature range from $T = (80$ to $360)$ K with temperature interval of 5 K. The mass fraction purity of the sample used in the adiabatic calorimetric study was determined to be 0.9928 by using the fractional melting technique. The thermal stability of the compound was investigated by differential scanning calorimeter (DSC) and thermogravimetric (TG) technique, and the process of the mass-loss of the sample was due to the evaporation, instead of its thermal decomposition.

Keywords: 1-Cyclohexene-1,2-dicarboxylic anhydride; Adiabatic calorimeter; Low-temperature heat capacity; Purity determination; Thermal analysis

1. Introduction

The 1-cyclohexene-1,2-dicarboxylic anhydride (CAS No.: 2426-02-0), is also named 3,4,5,6-tetrahydrophthalic anhydride (3,4,5,6-THPA). Its molecular formula is $C_8H_8O_3$, the molar mass is 152.15 $g \cdot mol^{-1}$ and the structural formula is



The 3,4,5,6-THPA is curing agent for epoxy resin. Curing agents for epoxy resins promote attractive characteristics of high tensile strength and modulus, low shrinkage on curing, high resistance to chemicals and corrosion, excellent dimensional stability, and superior electrical properties [1,2]. Although epoxy resin can be cured with different hardeners, most studies performed to date have been devoted to different aspects related to epoxy resins cured with amine curing agents, and few of papers have been devoted to epoxy/anhydride mixtures. In fact, anhydride-like curing agents are preferred for electrical and electronic applications or when chemical safety has to be taken into account [3]. Besides being used as a curing agent for epoxy resin, 3,4,5,6-THPA is also used as an intermediate in the preparation of many pesticides and herbicides. However, the thermodynamic data of 3,4,5,6-THPA have not been reported up to now, except for the boiling temperature measured to be from $T = (441$ to $443)$ K by Frinton Laboratories Inc. in 1986.

Because the compound is very useful in many fields, for the purpose of its application, in the present paper, a thermodynamic study was performed including

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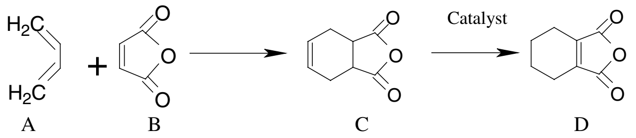
low-temperature heat capacity and thermal stability of 3,4,5,6-THPA.

2. Experimental

2.1. Sample

The sample used in these experiments was provided by Huicheng Chemicals Co. of China and synthesized by the following procedures. Briefly, C (THPA) is synthesized with A (butadiene) and B (maleic acid anhydride) in terms of Diels–Alder reaction, and D (3,4,5,6-THPA) is obtained by the isomerization of C (THPA).



2.2. Adiabatic calorimetry

A precision automatic adiabatic calorimeter was used to measure the heat capacity of the compound. The instrument was established by Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The structure and principle of the

TABLE 1
Experimental molar heat capacities of 3,4,5,6-THPA ($M = 152.16\ \mathrm{g \cdot mol^{-1}}$) ($R = 8.314427\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)[a]

T/K	$C_{p,m}$/R	T/K	$C_{p,m}$/R	T/K	$C_{p,m}$/R	T/K	$C_{p,m}$/R
80.338	6.763	176.722	9.683	246.397	15.989	323.122	27.891
83.466	6.757	178.632	9.806	247.803	16.110	325.109	28.506
86.528	6.773	180.459	9.948	249.309	16.252	327.121	29.009
89.585	6.783	182.282	10.055	250.752	16.405	329.091	29.668
92.476	6.840	184.113	10.176	252.205	16.553	330.993	31.499
95.299	6.877	185.950	10.277	253.658	16.675	332.598	34.953
98.081	6.911	187.767	10.418	255.101	16.839	333.834	39.212
100.822	6.957	189.635	10.561	256.477	17.010	335.197	42.699
103.562	6.971	191.379	10.683	257.937	17.220	336.725	48.736
106.095	7.013	193.210	10.807	259.384	17.384	338.112	55.643
108.628	7.039	194.950	10.966	260.760	17.591	339.271	71.683
111.119	7.065	196.735	11.128	262.216	17.784	340.213	92.890
113.610	7.111	198.559	11.286	263.558	17.993	340.923	120.524
116.018	7.133	200.317	11.440	264.978	18.196	341.475	155.287
118.427	7.176	202.045	11.546	266.442	18.481	341.902	196.802
120.752	7.222	203.794	11.721	267.797	18.645	342.234	240.791
123.077	7.267	205.496	11.917	269.170	18.827	342.497	285.337
125.349	7.336	207.281	12.068	270.616	19.040	342.709	325.120
127.644	7.353	208.942	12.219	271.993	19.279	342.883	355.415
129.845	7.441	210.645	12.373	273.829	19.557	343.030	377.816
132.121	7.489	212.306	12.493	276.058	19.877	343.153	396.178
134.329	7.561	214.008	12.667	278.265	20.230	343.258	419.638
136.529	7.646	215.669	12.780	280.472	20.550	343.342	474.093
138.647	7.715	217.288	12.937	282.767	20.949	343.397	674.305
140.806	7.786	218.949	13.083	284.996	21.312	343.452	700.778
142.924	7.911	220.527	13.225	287.129	21.649	343.504	855.315
145.083	7.997	222.270	13.373	289.235	22.028	343.560	801.251
147.118	8.085	223.724	13.481	291.399	22.313	343.626	738.725
149.152	8.182	225.459	13.646	293.540	22.620	343.696	672.998
151.270	8.299	227.045	13.820	295.616	22.880	343.775	630.334
153.304	8.404	228.582	13.960	297.758	23.271	343.864	560.087
155.297	8.510	230.243	14.145	299.899	23.588	344.005	319.347
157.373	8.578	231.742	14.319	302.041	23.923	344.681	41.361
159.366	8.663	233.191	14.504	304.161	24.247	346.464	33.086
161.359	8.769	234.697	14.690	306.281	24.575	348.182	33.188
163.269	8.894	236.222	14.801	308.444	25.027	350.000	33.324
165.221	9.017	237.675	15.000	310.586	25.369	351.670	33.458
167.131	9.142	239.170	15.171	312.727	25.839	353.409	33.627
169.124	9.228	240.664	15.308	314.773	26.220	355.079	33.755
171.048	9.371	242.118	15.493	316.970	26.507	356.667	33.895
172.944	9.441	243.561	15.789	318.996	26.984	360.303	34.233
174.853	9.595	244.917	15.870	321.059	27.343		

[a] Obtained from [12].

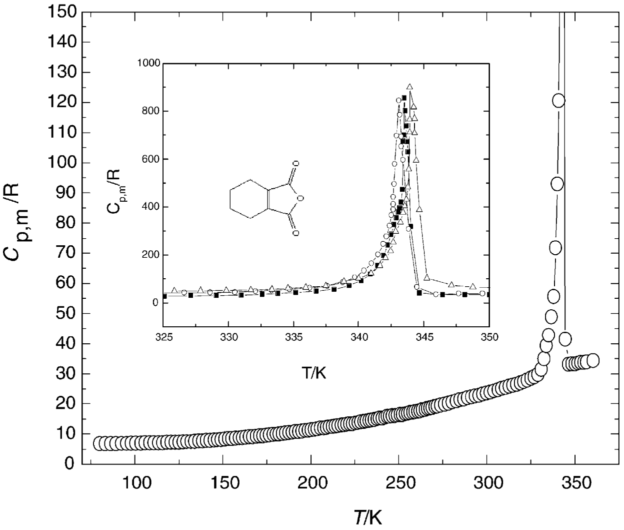


FIGURE 1. Experimental molar heat-capacity plotted against temperature for the sample 3,4,5,6-THPA. The "■" represents the first series of heat capacity measurement; "○", the second series of heat-capacity measurement and "△", the third series of heat-capacity measurement.

calorimeter have been described in detail elsewhere [4–6]. Its working temperature range is from the low temperature of 78 K, cooled by liquid nitrogen, to the high temperature of 400 K. The automatic adiabatic calorimeter mainly consists of a sample cell, a miniature platinum resistance thermometer, an electric heater, the inner and the outer adiabatic shields, two sets of six-junctions chromel-constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and the outer shields, respectively, and a high vacuum can [7]. Prior to the heat capacity measurement of the sample, the molar heat capacities of α-Al_2O_3, the standard reference material, were measured from $T = (78 \text{ to } 400)$ K to verify the reliability of the adiabatic calorimeter. The results showed that the deviation of our calibration data from those of NIST [8] was within ±0.3%.

The heat capacity measurements were conducted by the standard procedure of intermittently heating the sample and alternately measuring the temperature. The heating rate was (0.1 to 0.4) $\text{K} \cdot \text{min}^{-1}$; the temperature increments of the experimental points were between (1 and 4) K; the heating duration was 10 min and the temperature drift rates of the sample cell measured in an equilibrium period were kept within (10^{-3} to 10^{-4}) $\text{K} \cdot \text{min}^{-1}$.

The mass of 3,4,5,6-THPA used for the measurement was 4.3256 g, which was equivalent to 0.0284 mol based on $M = 152.16 \text{ g} \cdot \text{mol}^{-1}$.

2.3. DSC and TG technique

A differential scanning calorimeter (DSC-141, SETARAM, France) was used to perform the thermal analysis of 3,4,5,6-THPA at the heating rate of 10 $\text{K} \cdot \text{min}^{-1}$ under a purity nitrogen with flowing rate of 50 $\text{ml} \cdot \text{min}^{-1}$. The mass of the sample used in the experiment was 2.6 mg.

The TG measurement of the sample was carried out by a thermogravimetric analyzer (Model: DT-20B, Shimadzu, Japan) at the heating rate of 10 $\text{K} \cdot \text{min}^{-1}$ under a purity nitrogen with flow rate of 30 $\text{ml} \cdot \text{min}^{-1}$. The mass of the sample used in the experiment was 8.9 mg.

3. Results and discussion

3.1. Molar heat capacity and thermodynamic functions

The experimental molar heat capacities, $C_{p,m}$/R, of 3,4,5,6-THPA were presented in table 1 in the order of increasing temperature over the temperature range from $T = (80 \text{ to } 360)$ K.

Two polynomial equations were obtained by the least square fitting by using the experimental molar heat capacities ($C_{p,m}$) and the experimental temperatures (T).

From $T = (80 \text{ to } 330)$ K (solid phase)

$$C_{p,m}/(\text{J} \cdot \text{K} \cdot \text{mol}^{-1}) = 98.122 + 88.571x + 47.221x^2 + 0.3347x^3 + 5.1149x^4 + 5.6167x^5 + 0.4864x^6, \qquad (1)$$

where x is the reduced temperature, $x = [(T/\text{K}) - 205]/125$, T is the experimental temperature, 205 is obtained from polynomial $(T_{max} + T_{min})/2$, 125 is obtained from polynomial $(T_{max} - T_{min})/2$, T_{max} is the upper limit (330 K) of the above temperature region, T_{min} is the lower limit (80 K) of the above temperature region.

TABLE 2
The results of melting obtained from three series of heat capacity measurements of the sample

Thermodynamic properties	Series 1, x_1	Series 2, x_2	Series 3, x_3	$(\bar{x} \pm \sigma_a)^a$
T_{fus}/K	343.50	343.02	343.85	343.46 ± 0.24
$\Delta_{fus}H_m$/(kJ · mol^{-1})	11.84	11.89	11.91	11.88 ± 0.02
$\Delta_{fus}S_m$/(J · K^{-1} · mol^{-1})	34.47	34.68	34.64	34.60 ± 0.06

[a] $\sigma = \sqrt{\sum_{i=1}^{3}(x_1 - \bar{x})/n(n-1)}$, in which n is the experimental number; x is a single value in a set of heat capacity measurements; $\bar{x}$ is the mean value of a set of measurements.

TABLE 3
The thermodynamic functions of 3,4,5,6-THPA ($R = 8.314427\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)[a]

T/K	$C_{p,m}$/R	$[H_{(T)} - H_{(298.15)}]$/R·K	$[S_{(T)} - S_{(298.15)}]$/R
80	6.792	−2620.223	−13.743
85	6.797	−2586.290	−13.333
90	6.814	−2552.302	−12.944
95	6.843	−2518.196	−12.574
100	6.886	−2483.905	−12.222
105	6.945	−2449.359	−11.884
110	7.018	−2414.480	−11.558
115	7.108	−2379.191	−11.244
120	7.215	−2343.410	−10.939
125	7.338	−2307.051	−10.642
130	7.479	−2270.029	−10.352
135	7.639	−2232.254	−10.067
140	7.816	−2193.637	−9.787
145	8.011	−2154.087	−9.509
150	8.225	−2113.512	−9.235
155	8.458	−2071.819	−8.962
160	8.709	−2028.915	−8.690
165	8.979	−1984.708	−8.418
170	9.267	−1939.105	−8.146
175	9.574	−1892.013	−7.873
180	9.900	−1843.340	−7.598
185	10.244	−1792.993	−7.322
190	10.606	−1740.882	−7.044
195	10.986	−1686.913	−6.764
200	11.385	−1630.998	−6.481
205	11.801	−1573.043	−6.194
210	12.236	−1512.960	−5.904
215	12.689	−1450.656	−5.611
220	13.161	−1386.041	−5.314
225	13.651	−1319.024	−5.012
230	14.159	−1249.510	−4.707
235	14.687	−1177.408	−4.397
240	15.233	−1102.620	−4.082
245	15.800	−1025.051	−3.762
250	16.386	−944.601	−3.437
255	16.994	−861.166	−3.107
260	17.623	−774.640	−2.771
265	18.275	−684.912	−2.429
270	18.951	−591.868	−2.082
275	19.651	−495.387	−1.728
280	20.377	−395.340	−1.367
285	21.131	−291.593	−1.000
290	21.915	−184.004	−0.626
295	22.730	−72.420	−0.244
298.15	23.260	0.000	0.000
300	23.578	43.319	0.145
305	24.462	163.387	0.542
310	25.385	287.968	0.947
315	26.348	417.262	1.361
320	27.356	551.480	1.784
325	28.410	690.852	2.216
330	29.516	835.623	2.658
335	Melting region		
340	Melting region		
345	Melting region		
350	33.324	2381.340	7.143
355	33.753	2548.603	7.618
360	34.201	2720.278	8.093

[a] Obtained from [12].

TABLE 4
The experimental results of melting fractions and equilibrium temperatures of 3,4,5,6-THPA [$F = q/(\Delta H_m \cdot n)$]

q/J	F	$1/F$	T/K
75.81	0.2252	4.4404	341.4752
139.80	0.4153	2.4079	342.4974
207.31	0.6158	1.6239	343.0297
270.17	0.8026	1.2460	343.3417
324.76	0.9647	1.0366	343.5045

Correlation coefficient R^2 of least square fitting is 0.9998. The relative deviations of the smoothed heat capacities from those obtained from the experiment were within ±0.3%.

From $T = (345 \text{ to } 360)$ K (liquid phase)

$$C_{p,m}/(\mathrm{J \cdot K \cdot mol^{-1}}) = 279.57 + 5.3883x - 0.2019x^2 - 0.2304x^3 + 0.7481x^4, \quad (2)$$

where, $x = [(T/\mathrm{K}) - 353.5]/7.5$, its correlation coefficient R^2 is 0.9998. The relative deviations of the smoothed heat capacities from those obtained from the experiment were within ±0.2%.

A plot of experimental heat capacities $C_{p,m}$/R against T from $T = (80 \text{ to } 360)$ K is shown in figure 1. The curve indicated that 3,4,5,6-THPA melted from $T = (329 \text{ to } 346)$ K with the peak temperature of 343.50 K. The molar enthalpy $\Delta_{fus}H_m$ and entropy $\Delta_{fus}S_m$ of fusion of the compound were derived according to the following equations:

$$\Delta H_m = \left[Q - n\int_{T_i}^{T_m} C_p(\mathrm{s})\,\mathrm{d}T - n\int_{T_m}^{T_f} C_p(\mathrm{l})\,\mathrm{d}T - \int_{T_i}^{T_f} H_0\,\mathrm{d}T \right] \Big/ n, \quad (3)$$

$$\Delta S_m = \Delta H_m / T_m, \quad (4)$$

where T_i is the temperature a few degrees lower than the initial melting temperature, Q the total energy introduced into the sample cell from T_i to T_f, T_f a temperature slightly higher than the final melting temperature, $C_p(\mathrm{s})$ the heat capacity of the sample in the solid phase from T_i to T_m, $C_p(\mathrm{l})$ the heat capacity of the sample in liquid phase from T_m to T_f.

From these equations and the three series of repeated heat-capacity measurements, the values of melting temperature T_m, molar enthalpy $\Delta_{fus}H_m$ and entropy $\Delta_{fus}S_m$ of fusion of the sample were determined to be (343.46 ± 0.24) K, (11.88 ± 0.02) $\mathrm{kJ \cdot mol^{-1}}$ and (34.60 ± 0.06) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and are presented in table 2.

In terms of the polynomials of heat capacity and the thermodynamic relationship, the thermodynamic functions $[H_{(T)} - H_{(298.15)}]$ and $[S_{(T)} - S_{(298.15)}]$ of the compound were calculated in the temperature range from $T = (80 \text{ to } 360)$ K with a temperature interval of 5 K and listed in table 3.

3.2. The purity determination of 3,4,5,6-THPA

The purity of 3,4,5,6-THPA was determined using the fraction melting technique, which was described in detail in the literature [9–11]. The experimental equilibrium melting temperature (T) and melting fraction (F) corresponding to the temperature are listed in table 4. The equilibrium melting temperature (T) is plotted against the reciprocal of the melting fractions ($1/F$) were plotted in figure 2. The melting points of the absolute pure sample $T = 344.04$ K and that of the sample $T = 343.45$ K can be obtained at $1/F = 0$ and $1/F = 1$, respectively. The mass fraction purity of the sample was determined to be 0.9928.

3.3. The results of DSC and TG analysis

The DSC and TG curves of the sample were shown in figures 3 and 4, respectively.

Based on the DSC curve, the melting temperature of 3,4,5,6-THPA was determined to be $T_m = 343.27$ K, which is in agreement with the value of the heat capacity measurement, (343.46 ± 0.24) K, and the enthalpy of fusion of the compound was determined to be 11.79 $\mathrm{kJ \cdot mol^{-1}}$, which is consistent with that obtained by adiabatic calorimetry, (11.88 ± 0.02) $\mathrm{kJ \cdot mol^{-1}}$.

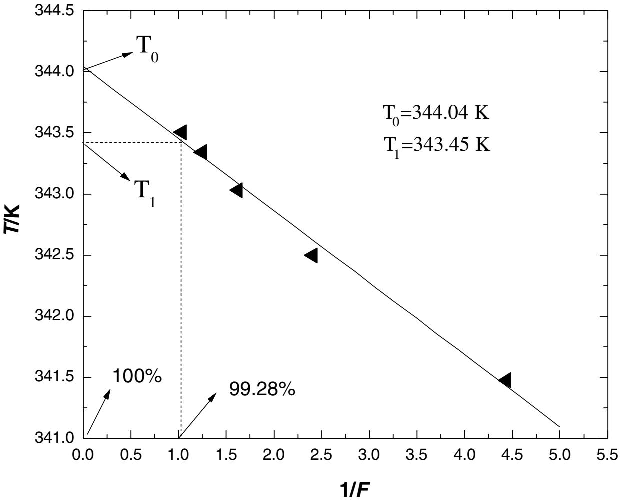


FIGURE 2. Plot of melting temperature against reciprocal mass fraction melted for 3,4,5,6-THPA.

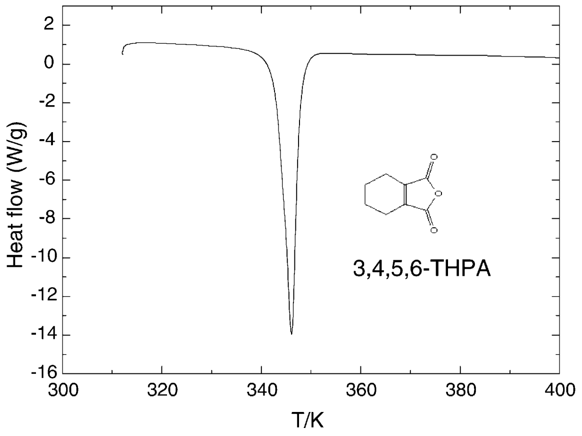


FIGURE 3. DSC curve of 3,4,5,6-THPA.

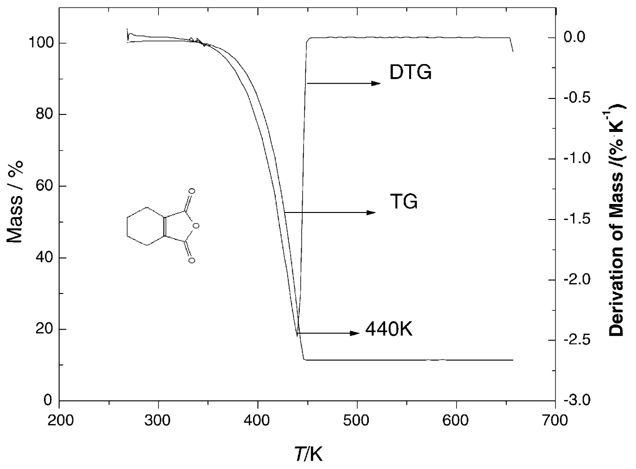


FIGURE 4. TG-DTG curve of 3,4,5,6-THPA.

The TG-DTG curves indicated that mass loss of 3,4,5,6-THPA began at about $T = 390$ K and ended at about $T = 492$ K. It can be seen from figure 4 that the maximum mass-loss rate of the compound occurred at $T = 440$ K, which is consistent with the boiling temperature, (441 to 443) K, of the sample reported by NIST. Thus, the process of the mass-loss of the sample was due to the evaporation, instead of its thermal decomposition.

Acknowledgements

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