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Heat capacity and thermodynamic properties of (1*R*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl diazoacetate

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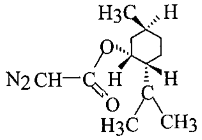
Abstract

Heat capacities of (1*R*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl diazoacetate have been measured with a small sample adiabatic calorimeter over the temperature range from 78 to 344 K. The melting point, molar enthalpy and entropy of fusion as well as the chemical purity of this compound were determined to be 320.419 ± 0.017 K, 17.203 ± 0.005 kJ mol^{-1}, 53.689 ± 0.013 J K^{-1} mol^{-1} and 99.61 mol%, respectively, on the basis of the heat-capacity measurements. The extrapolated melting temperature for the absolutely pure compound obtained from fractional melting experiments was 320.602 K. © 2000 Elsevier Science B.V. All rights reserved.

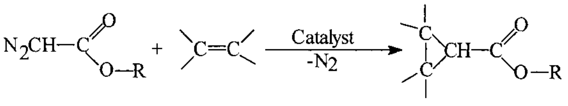
Keywords: (1*R*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl diazoacetate; Heat capacity; Adiabatic calorimeter; Chemical purity

1. Introduction

(1*R*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl diazoacetate (abbreviated as PMCD, CA Registry No. 63254-50-2) is an important intermediate in organic synthesis, which has been widely used for stereoselective asymmetrical cyclopropanation reactions [1–4]. Its molecular formula is $C_{12}H_{20}N_2O_2$, and its molecular structure is



It is because of the steric effect and the active diazonium present in the compound that the yield in the following reaction has greatly improved [1]:



In addition, the characteristics of the catalyst (bisoxalone–copper complex) used in the above reaction can be tested through the reaction. Thus, thermodynamic data for this compound are needed in order to develop its new application fields, to improve the technique of chemical synthesis in which it participates, and to carry out relevant theoretical research. The thermodynamic properties of this compound have not been reported in the literature. In the present work,

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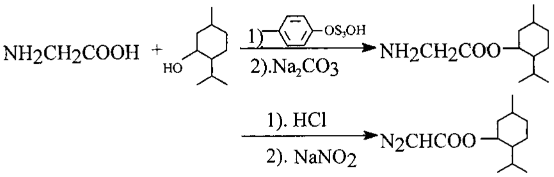
low-temperature heat capacities have been measured over the temperature range from 78 to 344 K. At the same time, the molar enthalpy and entropy of fusion and the melting point of the compound have been determined. The chemical purity has been deduced from fractional melting experiments.

2. Experimental

2.1. Synthesis, purification and characterization of the sample

Synthesis of the sample was carried out through the following two-stage reaction [3]:



The crude product was lumpy light yellow crystals. After it was condensed in vacuum and recrystallized three times in petroleum ether, its purity exceeded 99.00 mol%. After recrystallizing three times again in absolute ethyl alcohol, followed by vacuum drying for 4 h, it turned into yellow needle-like crystals. The purity of the final product was proved to be more than 99.50 mol% by a high performance liquid chromatography (HPLC, model: Simazu 10 A) analysis. ^{13}C NMR (model: Brucker DRX-400, 100 MHz, $CDCl_3$) [1,3] absorption peaks were detected at 166.90, 75.16, 47.61, 46.48, 41.68, 34.60, 31.81, 26.84, 24.11, 22.37, 21.05, and 16.86 cm^{-1}. The specific rotation $[\alpha]_D^{25}$ measured by a high-sensitivity polarimeter (model: SEPA-2007, Horiba, Japan) was 89.13 (the concentration was 1.00 g dl^{-1}, $CHCl_3$ as solvent). This value is higher than that given in [4] (−86.8; the concentration was 1.00 g dl^{-1}, $CHCl_3$ as solvent). This indicates that our prepared sample had higher purity than that discussed in [4]. The TG (model: TGS-2, Perkin Elmer, USA) analysis showed that the starting decomposition temperature was about 348.68 K. The first mass-loss observed in the TG curve was 12.76%. This corresponds to the nitrogen content, 12.48%, of the molecule. This result agrees with literature [3].

2.2. Adiabatic calorimetry

Heat-capacity measurements were carried out in a precision automatic adiabatic calorimetric system described in detail elsewhere [5]. The equipment is based on the Nernst stepwise heating method. The calorimeter consists mainly of a sample cell, an adiabatic (or inner) shield, a guard (or outer) shield, two sets of differential thermocouples and a high vacuum can. Liquid nitrogen was used as the cooling medium. The evacuated chamber was kept within ca. 1×10^{-3} Pa during the heat-capacity measurements so as to eliminate the heat loss owing to gas transport. Six pairs of differential thermocouples (connected in series) were used to detect the temperature difference between the sample cell and the inner shield. Likewise, six pairs of differential thermocouples (connected in series) were installed between the inner and outer shields. When the temperature in the sample cell increases due to heating, the thermocouples measure the temperature differences. This signal is used to control the heater distributed to the walls of the inner and outer shields, respectively. Both shields were heated under the control of the signal and kept at the same temperatures as the sample cell. In this way, the heat loss caused by radiation is greatly reduced. Since the starting decomposition temperature of the compound measured by TG is about 348.68 K, the experiments were limited to 344 K in order to avoid possible explosion due to the decomposition of the sample at higher temperature.

To confirm the reliability of our automatic adiabatic calorimeter, the molar heat capacity of the standard reference material α-Al_2O_3 was measured over the temperature range from 60 to 370 K. The sample mass used for the measurements was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, $M(Al_2O_3) = 101.9613\ g\,mol^{-1}$. The results indicated that the relative deviations of the experimental data from the smoothed values were within ±0.2%, while the inaccuracy was within ±0.5% compared with the data of the National Bureau of Standards [6] in the same temperature range.

These automatic experimental measurements were continuously carried out by means of the method of intermittently heating the sample and alternately measuring the temperature. For the solid and liquid phase regions, the heating rate and temperature increments were generally controlled at 0.1–0.4 K min^{-1} and 1–3 K, respectively, whereas for the melting region the temperature increment is reduced to within 0.1 K. In the fusion region, the heating step length near the fusion peak was within 0.04 K. Thus, the deviation of the experimental melting point from the actual melting point is not more than 0.04 K. The heating time was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were usually within 10^{-4}–10^{-5} K min^{-1}. During the heat-capacity measurements, the temperature difference between the inner adiabatic shield and the sample cell was automatically kept within 10^{-3}–10^{-4} K in order to obtain a satisfactory adiabatic condition. The data of heat capacities and corresponding equilibrium temperatures were corrected for heat loss [5,7]. The sample mass used for calorimetric measurements was 1.5839 g, which was equivalent to 0.00706 mol in terms of its molar mass of 224.3022 g mol^{-1}.

3. Results and discussion

3.1. Heat capacity

Ninety-six experimental points in heat-capacity measurements were made in the solid region from 78 to 316 K, whereas 12 points were obtained in the liquid region from 322 to 344 K. All the results, listed in Table 1 and plotted in Fig. 1, showed that the

Table 1
Experimental molar heat capacities of PMCD ($M = 224.3022$ 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})
Series 1 (*liquid nitrogen as the coolant*, ~15 K min^{-1})		*Series 2* (*natural cooling*, ~0.5 K min^{-1})	
78.815	115.86	293.793	382.72
80.633	117.57	295.973	387.24
82.361	119.41	297.192	393.74
84.522	121.61	299.387	396.38
86.446	123.44	301.601	399.77
88.336	125.15	303.998	405.09
90.449	126.99	306.207	410.23
92.737	128.82	308.412	417.81
95.121	131.64	311.602	423.99
97.408	133.59	313.598	428.78
99.602	135.92	315.505	434.13
101.891	137.75	317.488	448.89
104.649	139.46	318.595	710.79
107.408	141.31	319.301	1090.6
110.167	144.36	319.682	1710.9
112.424	146.68	319.802	2409.1
115.182	148.39	320.099	3102.4
118.380	151.45	320.156	3802.2
120.669	153.17	320.207	4710.7
122.926	155.01	320.269	5707.9
125.214	156.83	320.301	7013.8
127.503	158.55	320.349	8990.2
129.791	160.38	320.399	10698.5
131.609	162.09	320.410	12303.2
133.428	163.93	320.430	14050.3
135.716	165.64	320.440	16980.2
137.535	167.48	320.504	15662.5
139.353	169.19	320.575	10460.1
141.171	171.02	320.638	5401.7
142.989	172.86	320.866	2070.5
145.278	174.57	321.529	653.69
147.096	176.41	323.072	460.91
148.914	178.12	324.999	460.30
150.764	179.95	326.872	460.70
152.582	181.67	328.801	460.98
154.839	183.51	330.709	461.58
157.127	185.21	332.755	461.98
159.507	187.05	334.811	462.09
161.704	190.59	336.939	462.25
163.962	192.43	338.993	462.42
166.251	195.98	341.107	463.08
168.538	197.69	343.213	463.29
170.896	199.53		
173.554	203.07		
175.902	206.62		
178.571	210.41		
180.827	212.61		
183.207	213.72		
185.494	217.26		
188.131	219.09		
191.329	222.65		
194.088	226.19		
196.436	228.03		
200.605	233.04		
204.618	238.91		
206.941	243.32		
210.138	247.59		
214.245	251.15		
217.881	256.41		
220.891	260.08		
223.649	265.34		
226.879	268.88		
231.703	274.02		
234.183	279.65		
237.945	284.91		

Table 1 (*Continued*)

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})
240.578	289.19		
243.114	293.59		
246.124	297.51		
249.133	301.42		
252.083	306.31		
254.811	311.08		
257.932	315.24		
260.928	320.99		
263.914	326.49		
267.131	332.37		
269.548	335.18		
271.922	341.31		
274.281	344.85		
277.190	348.39		
279.451	352.55		
281.331	357.32		
283.619	362.71		
285.852	366.25		
288.113	370.87		
290.352	375.18		
292.574	380.57		
294.781	385.83		
296.979	391.21		
299.859	396.47		
302.554	402.46		
304.373	407.72		
306.787	413.12		
308.793	418.49		
311.266	424.72		
313.273	429.13		
315.781	434.51		
317.732	449.01		
318.783	727.65		
319.287	1005.4		
319.577	1641.3		
319.788	2388.3		
319.933	3017.3		
320.051	3750.2		
320.114	4682.7		
320.147	5677.9		
320.181	6753.6		
320.213	7837.8		
320.248	8953.2		
320.273	10610.5		
320.308	12223.2		
320.345	14009.3		
320.379	16900.1		
320.414	15632.5		
320.455	10448.1		
320.508	5396.7		
320.726	2067.5		
321.379	646.61		
322.946	460.79		
324.500	460.17		
325.706	460.50		
327.091	460.80		
328.296	461.05		
329.965	461.38		
331.727	461.71		
333.947	462.08		
336.543	462.48		
339.227	462.85		
341.916	463.14		
343.936	463.36		

structure of the compound was stable: no phase change occurred in the solid phase, neither association nor decomposition occurred in the liquid phase.

The experimental values of the heat capacities have been fitted to polynomial equations by the least-squares method.

For the solid phase,

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 230.0502 + 144.7187X + 39.1472X^2 + 1.4702X^3 + 12.1658X^4 + 14.5193X^5 - 5.8595X^6$$

in which $X = [T\,(\mathrm{K}) - 197]/119$. The above equation is valid from 78 to 316 K, with an accuracy of ±0.2%.

For the liquid phase,

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 461.9356 + 1.8902X - 0.4734X^2$$

in which $X = [T\,(\mathrm{K}) - 333]/11$. This equation applies to the range from 322 to 344 K, with an accuracy of ±0.18%.

3.2. Melting point, enthalpy and entropy of fusion

Pre-melting occurred owing to the presence of impurities in the sample. The measurement of the melting point and the molar enthalpy of fusion of the sample was done as follows. First, the temperatures for initial pre-melting and for complete melting were determined. Between these two temperatures, the melting point was determined by successive approximation through stepwise heating. Then, by

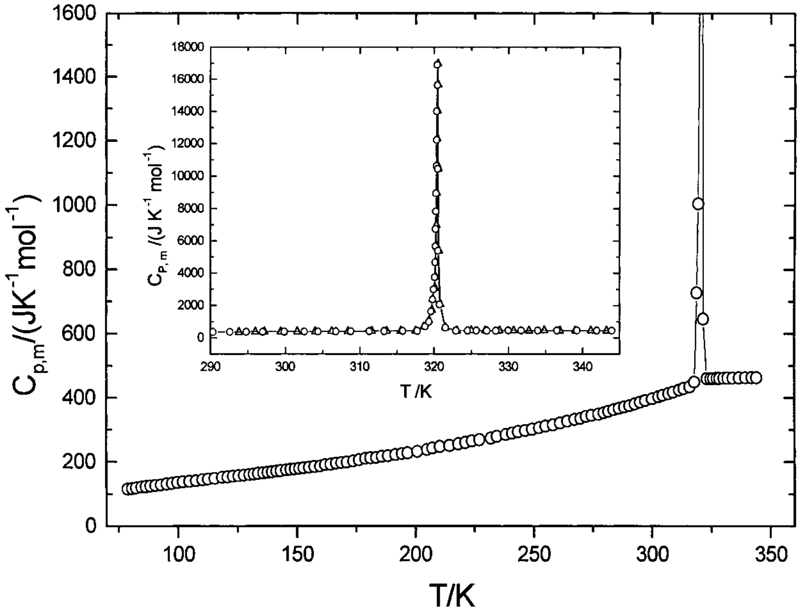


Fig. 1. Experimental molar heat capacities $C_{p,\mathrm{m}}$ of PMCD ((1*R*,2*S*,5*R*)-$C_{12}H_{20}N_2O_2$) obtained by adiabatic calorimetry. (○) represents the first series of heat-capacity measurements; (△), the second series of heat-capacity measurements.

heating the sample from a temperature slightly lower than the initial melting temperature to a temperature slightly higher than the final melting temperature, the enthalpy of fusion of the sample was evaluated. The enthalpy used to heat the empty sample container was subtracted from the total amount of heat introduced to the sample and container during the whole fusion [7].

Two series of experiments in the fusion region of the compound, using different cooling rates, were carried out so that the reversibility and repeatability of the fusion region were verified. The cooling rate of series 1 was about 15 K min^{-1} (liquid nitrogen as the coolant) and that of the series 2 was about 0.5 K min^{-1} (natural cooling). Both series are given in Table 1 and plotted in Fig. 1. It can be seen from Fig. 1 that the phase transition is reversible and repeatable, and that different cooling rates did not affect the experimental results.

The melting temperature T_{fus} of the sample was calculated from an equation based on the heat capacity in the fusion region, as described in the literature [7]. The molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ was determined in accordance with a method introduced in the literature [7]. The molar entropy of fusion $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ was derived from the molar enthalpy of fusion, using $\Delta_{\mathrm{fus}}S_{\mathrm{m}} = \Delta_{\mathrm{fus}}H_{\mathrm{m}}/T_{\mathrm{fus}}$ [7,8]. The results of T_{fus}, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ obtained from the two series of heat-capacity measurements are listed in Table 2.

3.3. Purity determination of the sample

The purity of the sample is evaluated from a set of equilibrium melting temperatures (*T*) and melting

Table 2
The temperature, enthalpy and entropy of fusion obtained from two series of experiments

Thermodynamic properties	Series 1 (x_1)	Series 2 (x_2)	Mean value ($\bar{x}$)
Melting point, T_{fus} (K)	320.401	320.436	320.419
$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (kJ mol^{-1})	17.198	17.208	17.203
$\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ (J K^{-1} mol^{-1})	53.676	53.702	53.689

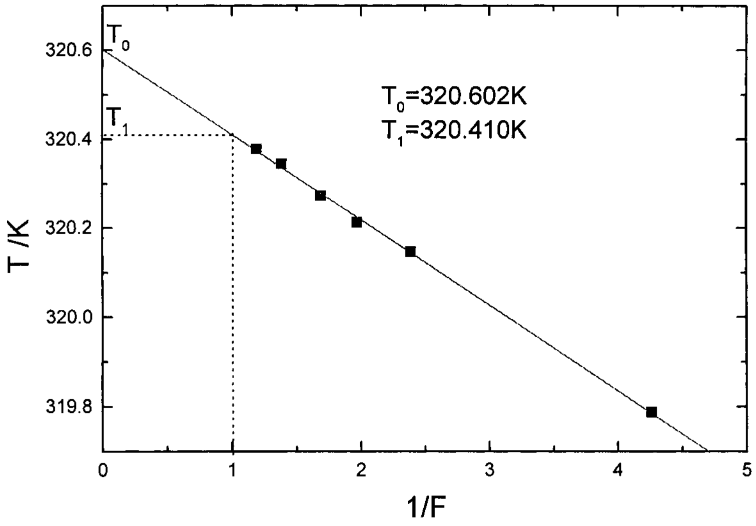


Fig. 2. The equilibrium temperature (T) versus the reciprocal of the melting fractions ($1/F$) for PMCD during fusion.

fractions (F) corresponding to these temperatures [7–9]. 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 shown in Fig. 2. Extrapolation of the straight line to $1/F = 0$ and 1 gives $T_0 = 320.602\,\mathrm{K}$ and $T_1 = 320.410\,\mathrm{K}$, respectively. Here T_1 is the melting point of the sample obtained from fractional fusion experiments and T_0 is the melting point of a theoretically or absolutely pure sample. The difference between T_{fus} and T_1 is the deviation between two different evaluation methods. The melting point ($T_1 = 320.410\,\mathrm{K}$) obtained from the fractional melting agrees well with that ($T_{\mathrm{fus}} = 320.419 \pm 0.017\,\mathrm{K}$) obtained from the heat-capacity measurements as described above. The mole percentage (N) of impurities in the sample is obtained from the Van't Hoff equation [9]. $N = 0.39\,\mathrm{mol\%}$, and the purity of the sample is $(1 - N) = 99.61\,\mathrm{mol\%}$, in agreement with the result of chromatographic analysis (99.53 mol%).

Table 3
Experimental melting fractions (F) and corresponding equilibrium temperatures (T) of PMCD[a]

F	$1/F$	T (K)
0.2347	4.2604	319.788
0.4192	2.3854	320.147
0.5077	1.9698	320.213
0.5932	1.6857	320.273
0.7230	1.3831	320.345
0.8406	1.1896	320.379

[a] $F = q/\Delta_{\mathrm{fus}}H_{\mathrm{m}}\,n$, in which q is the amount of heat introduced to melt the sample for the melting fraction F, n is the mole number of the sample.

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