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Low-temperature heat capacity and thermodynamic properties of endo-Tricyclo[5.2.1.$0^{2,6}$]decane

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Abstract

Endo-Tricyclo[5.2.1.$0^{2,6}$]decane (CAS 6004-38-2) is an important intermediate compound for synthesizing diamantane. The lack of data on the thermodynamic properties of the compound limits its development and application. In this study, endo-Tricyclo[5.2.1.$0^{2,6}$]decane was synthesized and the low temperature heat capacities were measured with a high-precision adiabatic calorimeter in the temperature range from (80 to 360) K. Two phase transitions were observed: the solid–solid phase transition in the temperature range from (198.79 to 210.27) K, with peak temperature 204.33 K; the solid–liquid phase transition in the temperature range from 333.76 K to 350.97 K, with peak temperature 345.28 K. The molar enthalpy increments, ΔH_m, and entropy increments, ΔS_m, of these phase transitions are $\Delta H_m = 2.57\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S_m = 12.57\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for the solid–solid phase transition at 204.33 K, and, $\Delta_{\mathrm{fus}} H_m = 3.07\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_{\mathrm{fus}} S_m = 8.89\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for the solid–liquid phase transition at 345.28 K. The thermal stability of the compound was investigated by thermogravimetric analysis. TG result shows that endo-Tricyclo[5.2.1.$0^{2,6}$]decane starts to sublime at 300 K and completely changes into vapor when the temperature reaches 423 K, reaching the maximal rate of weight loss at 408 K.

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1. Introduction

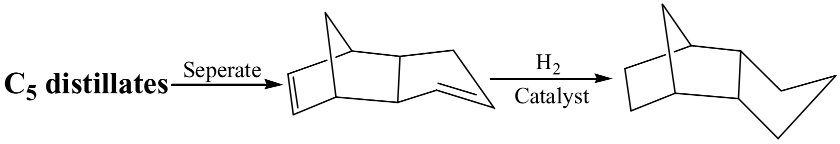
Diamantane has been widely used in medicine, dye and pesticide industries. An important route to synthesize the compound is the isomerization of endo-Tricyclo[5.2.1.$0^{2,6}$]decane (molecular formula: $C_{10}H_{16}$, CAS 6004-38-2), which is produced through hydrogenation of dicyclopentadiene, the main component of C_5 distillates of oil plants [1]. Endo-Tricyclo[5.2.1.$0^{2,6}$]decane, as one important intermediate compound of synthesizing diamantine, has been studied recently. But the thermodynamic properties of the compound has not been reported sufficiently. In order to increase understanding of the properties of the compound, we measured some thermodynamic properties of this compound.

In the present study, the low-temperature heat capacities of the compound have been measured in the temperature range from (80 to 360) K. Two phase transitions were observed. The enthalpy and entropy increments of the two phase transitions have been determined. In addition, the thermal behavior of sublimation and evaporation was further investigated through thermogravimetric analysis.

2. Experimental

2.1. Sample preparation and purity analysis

C_5 distillates of oil plants were separated to obtain dicyclopentadiene. Then dicyclopentadiene reacted with hydrogen in an autoclave for 10 h at the temperature 393 K with the pressure 1.0 MPa using Raney Ni as the catalyst. Then the mixture was filtered to get liquid mixture. Then the liquid mixture was fractionated to produce endo-Tricyclo[5.2.1.$0^{2,6}$]decane with high purity. The process is



(1)

The sample was dissolved in ethanol and analyzed to test the purity and the analysis was conducted on an Agilent 4890D gas chromatograph with FID. No impurity was found in the sample in the present experiment.

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail previously [2]. The sample amount used for the heat capacity measurement is 2.5168 g, equivalent to 15.840 mmol, based on a molar mass of 136.236 $g \cdot mol^{-1}$.

Prior to the heat capacity measurements on the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material α-Al_2O_3. The deviations of our calibration results from the recommended values reported by Ditmars *et al.* [3] of the former National Bureau of Standards are within of ±0.2% in the temperature range from (80 to 400) K.

2.3. TG analysis

Thermogravimetric analysis of the sample was carried out by a TG analyzer (Model: TA2950, Du Pont, USA) under high purity nitrogen (99.999%) with the flow rate of 60 $ml \cdot min^{-1}$. The mass of the sample used for TG analysis was 7.8 mg. The heating rate was 0.17 $K \cdot s^{-1}$.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacities of endo-Tricyclo[5.2.1.$0^{2,6}$]decane are shown in figure 1. and tabulated in table 1. The molar heat capacities were fitted to the following polynomials in reduced temperature (X), by means of least square fitting.

In the temperature range of (78 to 198) K

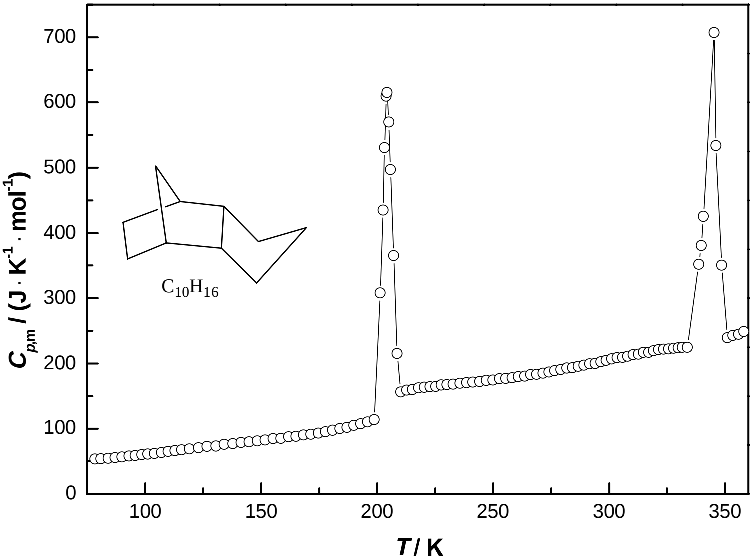


FIGURE 1. Experimental molar heat capacities $C_{p,m}$ of endo-Tricyclo[5.2.1.$0^{2,6}$]decane as a function of temperature T.

TABLE 1
The experimental molar heat capacity of endo-Tricyclo[5.2.1.$0^{2,6}$]decane molar mass $M = 136.236\ \mathrm{g \cdot mol^{-1}}$

T/K	$C_{p,m}$	T/K	$C_{p,m}$	T/K	$C_{p,m}$
	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$		$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$		$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
78.33	53.694	210.27	156.35	329.83	223.86
80.96	53.857	212.79	159.13	331.62	224.31
84.11	54.589	215.31	160.09	333.76	224.60
87.15	55.981	217.82	162.43	338.65	352.06
90.11	56.482	220.32	163.46	339.71	380.36
92.98	57.809	222.79	164.28	340.69	425.28
95.78	58.990	225.24	164.98	345.28	706.96
98.52	60.069	227.67	166.98	346.09	534.02
101.19	61.205	230.11	167.48	348.52	350.75
104.03	62.140	232.79	168.28	350.97	239.32
107.03	63.074	235.71	169.68	353.38	242.85
109.97	64.894	238.56	170.58	355.79	244.57
112.86	66.520	241.37	171.38	358.21	248.54
115.69	67.849	244.22	172.38		
119.09	68.794	247.08	173.78		
122.96	70.560	249.93	174.49		
126.75	72.724	252.74	176.60		
130.49	73.586	255.51	177.12		
134.15	75.835	258.22	178.04		
137.79	76.980	260.92	179.66		
141.38	78.634	263.59	180.79		
144.88	79.978	266.25	182.63		
148.35	81.225	268.88	183.08		
151.78	82.561	271.50	185.13		
155.16	84.803	274.08	186.78		
158.52	85.456	276.65	188.94		
161.81	87.306	279.20	190.61		
165.01	88.357	281.74	192.78		
168.27	90.513	284.25	193.46		
171.47	91.386	286.73	195.34		
174.66	93.266	289.19	197.42		
177.8	95.158	291.61	199.60		
180.91	97.358	294.03	200.09		
183.98	99.964	296.44	202.57		
187.01	102.01	298.82	204.85		
190.01	104.84	301.17	206.93		
192.98	107.51	303.51	208.81		
195.91	110.10	305.81	209.29		
198.79	113.74	308.09	211.06		
201.29	308.06	310.35	213.42		
202.59	434.85	312.59	214.08		
203.21	530.79	314.82	216.92		
203.89	609.54	317.03	217.07		
204.33	614.96	319.22	219.17		
205.01	569.67	321.38	220.91		
205.80	497.11	323.53	221.72		
207.16	365.20	325.68	222.32		
208.66	215.39	327.77	223.30		

$$C_{p,m}(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 77.179 + 24.686X - 2.9365X^2 + 4.9479X^3 + 8.8659X^4, \tag{2}$$

where $X = (T - 138)/60$, and T is the absolute temperature. The correlation coefficient of the fitted curve and $R^2 = 0.9998$.

In the temperature range of (211 to 333) K

$$C_{p,m}(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 185.61 + 36.593X + 19.319X^2 - 3.0765X^3 - 13.956X^4, \tag{3}$$

where $X = (T - 272)/62$ and $R^2 = 0.9996$.

From figure 1, it can be seen that the heat capacities of the sample vary with increasing temperature in a smooth and continuous manner from 78 K to 198 K and from 211 K to 333 K. No thermal anomaly was observed in these temperature ranges. Therefore, the sample is stable in the above temperature ranges. However, thermal anomalies were observed in the temperature range from 199 K to 210 K and from 334 K to 351 K. The peak temperatures at the highest point of the peaks were found to be 204.33 K and 345.28 K, respectively. The two thermal anomalies are ascribed to a solid–solid phase transition and solid–liquid phase transition, respectively.

The molar enthalpy increments, ΔH_m, and the entropy increments, ΔS_m, of the two phase transitions derived by the literature method [4] are for the solid–solid phase transition, $\Delta H_m = 2.57\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta S_m = 12.57\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 204.33 K, and, for the solid–liquid phase transition, $\Delta_{\mathrm{fus}}H_m = 3.07\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_{\mathrm{fus}}S_m = 8.89\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 345.28 K. The melting point and the molar enthalpy of fusion of exo-Tricyclo[5.2.1.0^{2,6}]decane, stereoisomer of the compound under study, are 182 K and 4.6 $\mathrm{kJ \cdot mol^{-1}}$ [5], respectively. Although the two compounds are structurally similar, the melting point of exo-Tricyclo[5.2.1.0^{2,6}]decane is far below that of endo-Tricyclo[5.2.1.0^{2,6}]decane and the molar enthalpy of fusion of exo-Tricyclo[5.2.1.0^{2,6}]decane is higher than that of endo-Tricyclo[5.2.1.0^{2,6}]decane.

3.2. Thermodynamic functions

Through the polynomials of heat capacity and the relationship of thermodynamic functions, the thermodynamic function data were calculated in the temperature range from (80 to 330) K with a temperature interval of 5 K, based on the reference temperature 298.15 K. The values of thermodynamic function $H_T - H_{298.15}$, $S_T - S_{298.15}$ are listed in table 2.

3.3. The results of TG and DTG analysis

The TG and DTG curves of endo-Tricyclo[5.2.1.0^{2,6}]decane are shown in figure 2. It can be seen that endo-Tricyclo[5.2.1.0^{2,6}]decane begins to lose weight at 300 K and reaches the maximal rate of weight loss at 408 K. The sample completely loses its weight when the temperature reaches 413 K. The product collected during the

Table 2
Calculated thermodynamic function data of endo-Tricyclo[5.2.1.$0^{2,6}$]decane

T/K	C_p / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$H_T - H_{298.15}$ / $\mathrm{kJ \cdot mol^{-1}}$	$S_T - S_{298.15}$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Solid–solid phase transition at 204.33 K			
80	53.844	−29.150	−149.95
85	55.069	−28.877	−146.65
90	56.649	−28.598	−143.45
95	58.497	−28.310	−140.32
100	60.536	−28.013	−137.27
105	62.701	−27.705	−134.26
110	64.937	−27.386	−131.3
115	67.197	−27.056	−128.37
120	69.447	−26.714	−125.47
125	71.662	−26.361	−122.60
130	73.826	−25.997	−119.75
135	75.937	−25.623	−116.92
140	77.999	−25.238	−114.12
145	80.029	−24.843	−111.35
150	82.053	−24.438	−108.59
155	84.107	−24.022	−105.86
160	86.240	−23.597	−103.15
165	88.507	−23.160	−100.46
170	90.978	−22.711	−97.78
175	93.728	−22.250	−95.11
180	96.846	−21.773	−92.43
185	100.43	−21.280	−89.73
190	104.59	−20.768	−87.01
195	109.44	−20.233	−84.23
Solid–liquid phase transition at $T = 345.28$ K			
210	156.71	−15.718	−62.06
215	160.16	−14.926	−58.34
220	162.99	−14.118	−54.62
225	165.37	−13.297	−50.93
230	167.44	−12.465	−47.27
235	169.32	−11.623	−43.64
240	171.12	−10.772	−40.06
245	172.93	−9.911	−36.52
250	174.83	−9.042	−33.01
255	176.89	−8.163	−29.53
260	179.16	−7.273	−26.07
265	181.67	−6.371	−22.64
270	184.43	−5.456	−19.21
275	187.46	−4.526	−15.80
280	190.73	−3.581	−12.39
285	194.23	−2.618	−8.980
290	197.91	−1.638	−5.570
295	201.71	−0.639	−2.155
298.15	204.13	0.000	0.000
300	205.56	0.379	1.267
305	209.38	1.416	4.694

TABLE 2 (*continued*)

T/K	$\frac{C_p}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$	$\frac{H_T - H_{298.15}}{\mathrm{kJ \cdot mol^{-1}}}$	$\frac{S_T - S_{298.15}}{\mathrm{J \cdot K^{-1} \cdot mol^{-1}}}$
	Solid–solid phase transition at 204.33 K		
310	213.06	2.473	8.127
315	216.48	3.546	11.56
320	219.52	4.637	15.00
325	222.02	5.741	18.42
330	223.82	6.856	21.83

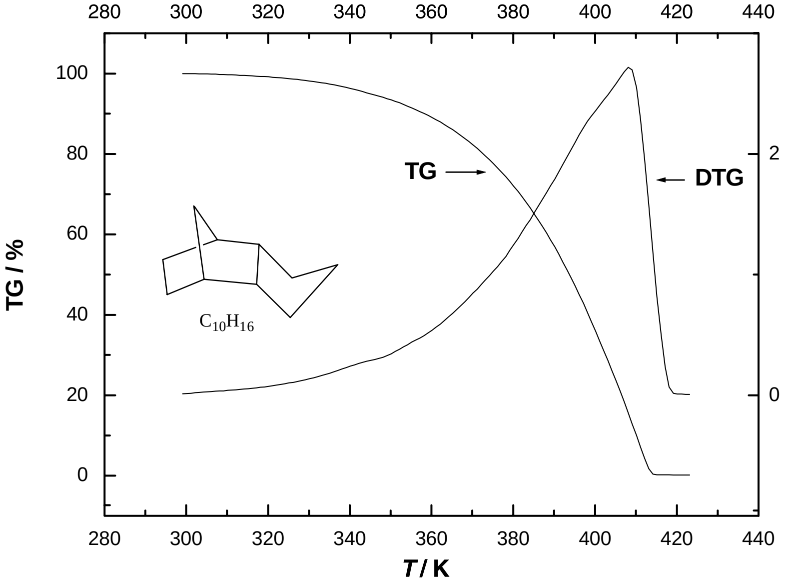


FIGURE 2. Thermogravimetric analysis (TG) and differential thermal analysis (DTG) curve of endo-Tricyclo[5.2.1.0^{2,6}]decane.

heating until 425 K proves to be the same substance as the initial sample judging from its color, melting point and morphology. Considering that endo-Tricyclo[5.2.1.0^{2,6}]decane is in solid state at room temperature and melts at 345.236 K, we can deduce that endo-Tricyclo[5.2.1.0^{2,6}]decane sublimes before melting at first and then melts with subliming as the temperature increases. When the temperature reaches 423.15 K, endo-Tricyclo[5.2.1.0^{2,6}]decane completely changes into vapor under the present experimental conditions.

Acknowledgements

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