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Heat capacities and thermodynamic properties of (-)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis (diphenylphosphino) butane [(-)-DIOP]

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Abstract

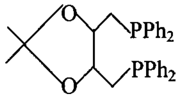
Heat capacities of (-)-DIOP have been measured with a precision automatic adiabatic calorimeter in the temperature range from 78 to 380 K. A solid–solid phase transition for the compound was observed at 348.65 K and the molar enthalpy and entropy of the transition were determined to be 3.415 kJ mol^{-1} and 9.795 J mol^{-1}, respectively. A solid–liquid phase transition was found at 364.23 K and the molar enthalpy and entropy of fusion were determined to be 38.606 kJ mol^{-1} and 106.0 J K^{-1} mol^{-1}, respectively. The purity of the sample under investigation was determined to be 0.9837 molar fraction by the fractional melting method. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: DIOP; Heat capacity; Phase transition; Enthalpy of fusion; Purity determination

1. Introduction

Asymmetric synthesis is a promising method in organic synthesis. It is widely used to produce valuable optical medicines, perfume, food, additives and so on. In recent decades, asymmetric synthesis has been focussing on the catalytic asymmetric synthesis, among which one of the frontier projects is to prepare asymmetric catalyst. DIOP is an important chiral diphosphine ligand in the synthesis of optically active compound [1].

DIOP is an unstable compound with a formula of $C_{31}H_{32}P_2$, and the structure is as follows:



In 1971, Kagan first synthesized this compound from tartaric acid. After that many researchers have studied this new catalytic system with optical activation to improve its stability and selectivity [2]. Up to now, DIOP is one of the most effective ligand for preparation of chiral catalysts. In order to improve the technique of chemical synthesis in which it participates, and develop its new application fields, the industries concerned are in urgent need of the thermo-

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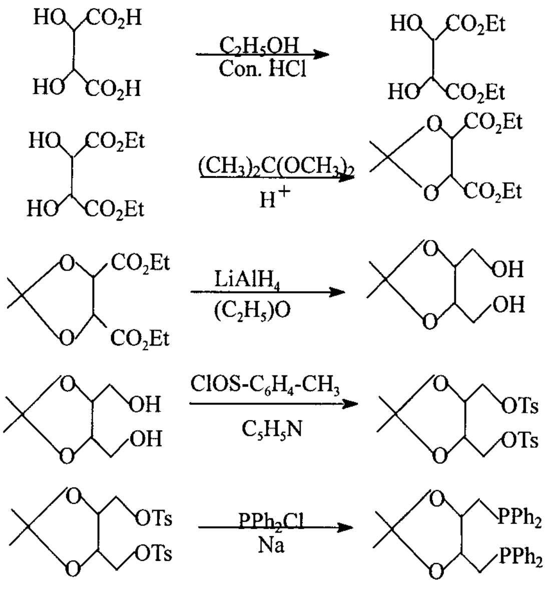
dynamic data of this compound to serve a basis. Till now, however, the thermodynamic properties of this compound have been scarcely studied, and virtually no calorimetric work had been reported before we undertook to investigate it. Since the heat capacity is a basic quantity for evaluation of the thermodynamic properties, in the present work, the heat capacity measurements of (-)-DIOP were carried out with an adiabatic calorimeter in the temperature range from 78 to 380 K. Furthermore, the melting temperature, the molar enthalpy and entropy of fusion of the compound were determined based on the heat capacity measurements.

2. Experimental

2.1. Sample preparation and characterization

DIOP was synthesized from tartaric acid under protection of argon. The synthesis process of the sample proceeded through the following five stages:



The prepared DIOP sample is a white crystal with the melting point of 89.1°C and $[\alpha]_D^{22}$ of-12.7 (C 4.57, C_6H_6), which are close to those reported in literature [3] (T_{fus} 88–89°C, $[\alpha]_D^{22}=-12.3$ (C 4.57, C_6H_6)).

^{1}H NMR ($CDCl_3$): δ 1.35 (s, 6H, CH_3) CH_2 (4 H, 2.39 ppm, m). CH (2H, 3.92 ppm, m). C_6H_5 (20H, 7.27 ppm, m). ^{31}P NMR ($CHCl_3$): 50.2 ppm.

2.2. Adiabatic calorimetry

The heat capacity measurements of the sample were performed with a precise automatic adiabatic calorimeter for small sample in the temperature region of 78–380 K. The calorimeter mainly consists of a gold-plated copper sample cell equipped with a Karma wire heater and a miniature platinum resistance thermometer, two adiabatic shields, two sets of differential thermocouples, a vacuum can and a Dewar vessel. The structure and procedures of the adiabatic calorimeter were described in detail previously [4].

The DIOP sample was put into the sample cell under the protection of argon in high purity. The lip of the sample cell was sealed with cycleweld. The loaded sample cell was put into a vacuum desiccator which was then evacuated to 1.33 Pa. Afterwards, argon gas was introduced into the vacuum desiccator in which the cell was kept for 24 h to solidify the cycleweld. After that, the argon gas was pumped out and helium gas was filled into the cell. Finally, the copper capillary on the lip of the sample cell was pinched off and the resultant fracture was soldered to ensure the cell for sealing.

The sample was heated using the standard discrete heating method and the temperature of the sample was alternatively measured. The temperature increment for a heating cycle was 2–4 K in both solid and liquid phases; the temperature drift rate of the sample cell was usually kept at 10^{-4} K min^{-1} in equilibrium period. The mass of the sample used for the calorimetric measurements was 1.4996 g, which is equivalent to 3.0079 m mol based on its molecular mass of 498.55 g mol^{-1}.

3. Results and discussion

3.1. Heat capacity and phase transitions

One hundred and forty-two experimental heat capacity points were obtained during the whole measurement, which are listed in Table 1, and the relation curve of C_p versus T is shown in Fig. 1.

It can be seen from Fig. 1 that DIOP exists in solid state in the temperature range between 78 and 335 K

Table 1
Experimental molar heat capacities of DIOP (M=498.55 g mol^{-1})

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
78.824	211.23	154.983	339.35	273.532	602.32
80.197	213.12	156.766	342.47	276.384	610.98
81.385	214.87	158.537	343.17	279.210	625.21
82.572	216.01	160.306	350.55	282.016	629.48
83.749	218.12	162.063	353.79	284.805	641.34
84.915	220.65	163.807	356.62	287.671	667.08
86.135	222.15	165.542	358.35	291.005	674.42
87.404	224.14	167.271	360.48	294.670	685.66
88.657	228.23	168.991	364.09	298.378	694.29
89.893	230.28	170.701	367.42	302.055	708.20
91.115	232.62	172.404	368.69	305.716	713.28
92.326	236.12	174.095	370.36	309.344	737.73
93.525	237.69	175.778	374.25	312.950	740.63
94.778	238.57	177.755	382.20	316.547	751.71
96.002	239.92	180.014	391.46	320.129	757.75
97.300	241.69	181.254	397.47	323.706	763.20
98.626	243.45	184.480	398.51	327.256	776.64
99.903	244.75	186.706	399.45	330.775	781.49
101.179	246.15	188.929	400.78	334.277	789.81
102.421	248.40	191.127	406.94	337.738	824.46
103.667	250.96	193.307	409.20	341.382	859.20
104.895	252.17	195.482	413.57	344.953	1259.93
106.185	256.13	197.647	416.49	347.869	2075.74
107.543	258.32	200.006	424.39	350.528	854.39
108.883	260.92	202.549	433.71	353.283	902.70
110.203	262.57	205.071	438.18	355.566	1137.23
111.519	264.78	207.573	446.52	357.344	1276.12
112.832	268.63	210.058	447.45	358.988	1309.62
114.308	270.47	212.528	450.66	360.261	1687.53
115.947	272.70	214.987	456.77	361.153	2485.50
117.679	277.24	217.438	466.38	361.857	3735.13
119.500	281.18	219.871	474.77	362.393	4789.71
121.301	284.82	222.287	480.74	362.711	5804.48
123.090	288.14	224.690	488.67	363.013	6028.67
124.863	290.58	227.076	497.02	363.348	7368.77
126.625	292.17	229.442	507.55	363.562	8475.79
128.374	295.16	231.840	516.89	363.747	9585.71
130.108	296.89	234.225	525.39	363.922	9738.40
131.828	300.25	236.536	530.26	364.072	10273.7
133.534	300.33	238.831	533.20	364.196	11451.3
135.227	306.81	241.136	538.59	364.216	14118.4
136.901	310.38	243.427	547.01	364.225	14263.6
138.564	311.70	245.711	549.02	364.529	11581.8
140.219	314.95	247.995	551.95	364.668	9892.02
141.866	316.03	250.496	557.87	365.263	1342.94
143.501	318.01	253.216	561.39	366.391	943.18
145.120	321.44	256.037	566.26	367.618	946.00
146.732	323.65	258.981	570.24	368.842	952.88
148.338	326.64	261.929	572.10	370.712	959.61
149.932	328.87	264.858	582.73	373.225	966.66
151.512	330.54	267.767	587.87	375.727	975.43
153.193	335.65	270.660	594.29	378.216	980.86

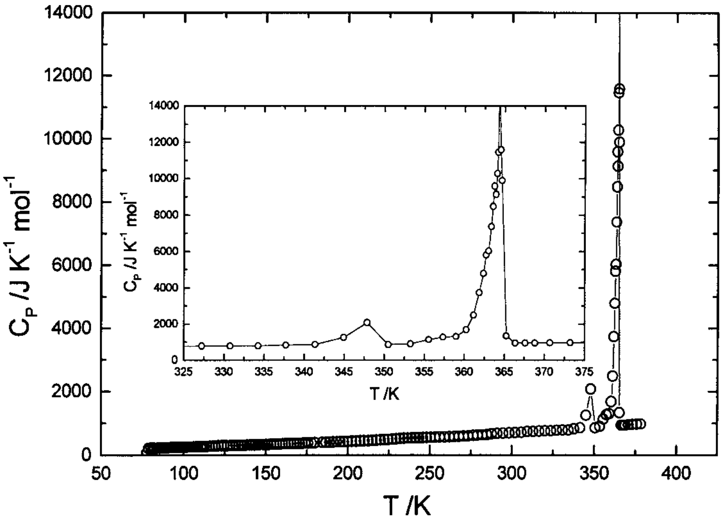


Fig. 1. Experimental molar heat capacity and the melting peak curve of DIOP.

and in liquid state at temperature above 366 K. The heat capacity curve is smooth in the temperature region of 78–335 K, which means that the compound is stable under the protection of the inert gas and there is no phase transition in solid state below 335 K. The experimental heat capacity data were fitted by using the least squares method, and two polynomial equations were obtained.

In solid phase between 78 and 335 K:

$$C_p = 443.519 + 292.45X + 84.017X^2 - 0.3538X^3 - 23.334X^4 + 3.458X^5$$

where $X=(T-206.5)/128.5$, and relative coefficient $R^2=0.9988$.

In liquid phase between 366 and 373 K:

$$C_p = 965.137 + 21.031X - 3.287X^2$$

where $X=(T-3\ 72.5)/6.5$, and relative coefficient $R^2=0.9964$.

Two phase transitions were observed in the temperature region of 335–366 K from the heat capacity curve. One is the solid–solid phase transition with a peak temperature of 348.65 K, and the other is solid–liquid phase transition with a peak temperature of 362.23 K. In this range, the sample was heated and melted by stepwise heating and fractional melting [5].

3.2. The molar enthalpy and entropy of phase transition

The molar enthalpy of fusion of the compound was calculated from the following equation:

$$\Delta H_m = \left[\frac{Q - n\int_{T_i}^{T_m} C_p(s)\,dT - n\int_{T_m}^{T_f} C_p(l)\,dT - \int_{T_i}^{T_f} H_0\,dT}{n}\right]$$

where T_i (350.17 K) is the temperature at which the sample fusion begins, while T_f (265.92 K) is the temperature at which the sample fusion finishes. T_m is the melting point of the sample (364.23 K), Q is the total energy introduced to the sample cell during the melting process, its value being 225.1 J, C_p (s),C_p (l) are the heat capacities of the sample the in the solid and liquid phases, and H_0, the heat capacity of the empty cell. The three terms of integrals in the above equation were calculated as follows:

$$\int_{T_i}^{T_f} H_0\,dT = 67.7\,\mathrm{J},$$

$$\int_{T_i}^{T_m} C_p(s)\,dT + \int_{T_m}^{T_f} C_p(l)\,dT = 41.34\,\mathrm{J},$$

$$n = \frac{m}{M} = 0.0030079\,\mathrm{mol}.$$

Consequently, we obtained from the above values:

$$\Delta H_{\mathrm{m}} = 38.606\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta S_{\mathrm{m}} = \frac{\Delta H_{\mathrm{m}}}{T_{\mathrm{m}}} = 106.0\,\mathrm{J}\,K^{-1}\,\mathrm{mol^{-1}}.$$

The same method is used to calculate the molar enthalpy and entropy of the solid–solid phase transition for the compound. The results are:

$$\Delta H_{\mathrm{m}} = 3.415\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta S_{\mathrm{m}} = 9.795\,\mathrm{J\,K^{-1}\,mol^{-1}}.$$

3.3. The purity of the sample

The chemical purity of the sample was determined from a set of equilibrium melting temperatures and the fractions melted corresponding to these temperatures [5,6]. According to the ideal solution low, the relation between the mole fraction N of a small amount of impurities in the sample and its melting-point depression is as follows:

$$N = \frac{\Delta H_{\mathrm{m}}(T_0 - T_1)}{R T_0^2} \tag{1}$$

where T_0 is the melting point of an absolutely pure substance; T_1, the melting point of the tested sample; ΔH_{m}, the molar enthalpy of fusion of the sample; R, the molar gas constant.

Table 2
Observed equilibrium temperatures and fractions melted for DIOP [$F=q/(\Delta H_{\mathrm{m}} n)$]

q (J)	26.25	35.93	46.06	56.69	67.63
F	0.2285	0.3094	0.3966	0.4882	0.5824
$1/F$	4.3769	3.2322	2.5212	2.0484	1.7172
T (K)	362.681	363.123	363.461	363.726	363.949

As for the liquid solution formed by a part of the sample melted, given that N' is the mole fraction of the impurities and T is the melting point of the solution, then

$$N' = \frac{\Delta H_{\mathrm{m}}(T_0 - T_1)}{R T_0^2} \tag{2}$$

Suppose that the impurities are solid-insoluble and all of the impurities are transferred completely into the liquid phase when the melting started, the relative amount of the sample in the liquid phase will be increasingly more remains constant, the mole fraction in the melting process; on the other hand, since the total amount of the impurities in the liquid phase will gradually decrease. Given that F is the ratio of the amount of the sample in the liquid phase to the total amount of the sample, then

$$F = \frac{q}{Q} \tag{3}$$

where F is also designated as the fraction melted, its value being the ratio of the heat (q) required to melt a part of the sample to the total heat (Q) required to melt the whole sample. Obviously, F is inversely propor-

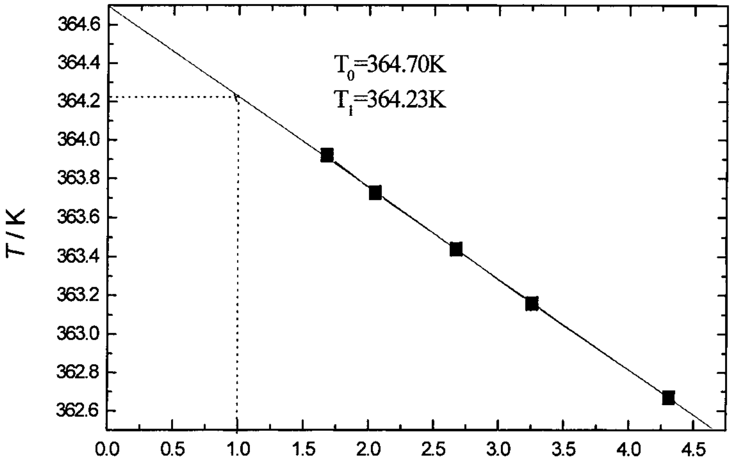


Fig. 2. The melting curve of DIOP.

tional to the whole mole fraction of the impurities in the liquid phase, i.e.,

$$N' = \frac{N}{F} \tag{4}$$

Substituting Eqs. (1) and (2) into Eq. (4), we obtain:

$$T_0 - T = \frac{1}{F}(T_0 - T_1) \tag{5}$$

From Eq. (5) it is clear that the relation between the melting point, or the equilibrium melting temperature T and $1/F$ is linear. By plotting T versus $1/F$, and extrapolating the straight line to $1/F=1$ and $1/F=0$, T_1 and T_0 can be derived.

We have chosen five fusion equilibrium temperatures to calculate the F values. The result was tabulated in Table 2 and plotted in Fig. 2. From the figure, $T_0=364.70$ and $T_1=364.23$ K were obtained. From Eq. (1) N is evaluated to be 1.63 mol%. Hence, the purity of the studied sample is $(1-N)=98.37$ mol%.

Acknowledgements

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