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Heat capacity and thermal decomposition of 1,6-*bis*(diphenylphosphino)hexane

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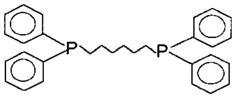
Abstract

A thermochemical study of 1,6-*bis*(diphenylphosphino)hexane(BDPH) has been performed using adiabatic calorimetry, differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The low-temperature heat capacity of BDPH was determined precisely with a small-sample automated adiabatic calorimeter in the temperature range from 80 to 350 K. No indication of any phase transition or thermal anomaly was observed in this temperature range. The high-temperature heat capacity of BDPH was measured with a differential scanning calorimeter in the temperature range from 310 to 730 K. From the DSC curve obtained for this compound, a solid–liquid transition was found at 399.4 K and the enthalpy and entropy of transition were evaluated at 66.8 kJ mol^{-1} and 167.2 J K^{-1} mol^{-1}, respectively. In addition, an endothermal change was observed between 690 and 710 K. The heat of reaction corresponding to the change was determined to be 81.6 kJ mol^{-1}. The TG analysis of BDPH was carried out in the temperature range from 300 to 800 K, from which it was found that this compound starts to decompose at 690 K and decomposes almost completely at 710 K in a single step.

Keywords: 1,6-*Bis*(diphenylphosphino)hexane (BDPH); DSC; Heat capacity; TG; Thermal decomposition

1. Introduction

1,6-*Bis*(diphenylphosphino)hexane (BDPH), $(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$, is a useful diphosphine ligand. It can undergo a dehydrogenation reaction with some metal complexes and the product is 1,6-*bis*(diphenylphosphino)-*trans*-hex-3-ene, $(C_6H_5)_2PCH_2CH_2CH{=}CHCH_2CH_2P(C_6H_5)_2$ [1], The dehydrogenation reaction represents the case in which an alkane, although anchored by two phosphorus atoms, reacts with a metal site in a homogeneous situation to give an olefin [2–4]. Its metal complexes can be used as the catalyst for the dimerization of olefins and unsaturated nitrites. The structure of BDPH is:



In order to further understand the nature of asymmetric catalytic reaction and synthesis of metal coordination complexes, a thermochemical study of BDPH was performed in our thermochemistry laboratory. Heat-capacity measurements of this compound were

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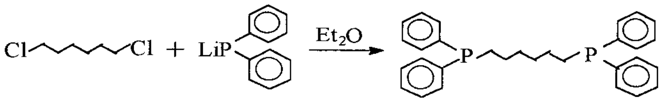
carried out in the low-temperature range, between 80 and 350 K, with an automated adiabatic calorimeter [5]. In the temperature range from 300 to 800 K, the thermal behavior of BDPH was investigated by both, a differential scanning calorimeter (DSC) and a thermobalance. The melting temperature, the molar enthalpy and molar entropy of melting and the decomposition temperature for BDPH were determined by DSC and TG, respectively.

2. Experimental

2.1. Sample preparation and characterization

1,6-*Bis*(diphenylphosphino)hexane in this work was synthesized by lithium diphenylphosphide reacting with 1,6-dichlorohexane [6]:



A solution of lithium diphenylphosphide was made from 4.0 g (572 mmol) of lithium and 40 g (152.6 mmol) of triphenylphosphine in 150 ml tetrahydrofuran. After filtration, 20 g (125 mmol) of 1,6-dichlorohexane was added at −5°C for one hour. The solution of the mixture was refluxed for one hour. The solution was concentrated and crystallized out by adding small amounts of ethanol. The crude product was washed and dried. The yield of BDPH after recrystallization from methylene chloride–methanol was 28 g (90%). The purity of the finally obtained BDPH product was >99.8%, as determined by HPLC (Column: Bondpak G18). Elementary analysis revealed: C, 79.10; H, 7.20; P, 13.4. Calculated values for $C_{30}H_{32}P_2$: C, 79.27: H, 7.10; P, 13.6.

2.2. Adiabatic calorimetry

The heat capacity measurements were carried out with a small-sample automatic adiabatic calorimeter over the temperature range from 80 to 350 K. The mass of the sample used for experiments was 2.6914 g, equivalent to 5.9213 mmol. The adiabatic calorimeter used was described earlier in detail [5]. Briefly, the calorimeter cell was made of gold-plated copper with an internal volume of 6 cm^3; four gold-plated copper vanes of 0.2 mm thickness were inserted into the cell to improve the heat distribution. The lid of the cell with capillary copper tubing was made of gold-plated silver (21.0 mm in diameter, 0.3 mm thick and 1.0 mm high). The calorimeter heater and the platinum resistance thermometer were mounted around the cell and at the bottom of the cell, respectively. A small amount of helium gas was introduced into the cell through the tubing to improve the heat transfer. The cryostat included an inner and an outer adiabatic shield, and a vacuum can. In order to obtain good adiabatic conditions between the calorimeter cell and its surroundings, two similar control circuits were used to control the temperatures of the two adiabatic shields. Each control circuit consisted of a modified DWT-702 precise temperature regulator (made by No. 6 Automatic Meter Plant of Shanghai, China) and a thermopile. When these control circuits were operating, the temperature difference between the calorimeter and its surroundings was held at 0.5 mK, or less, during the entire experimental process. A miniature platinum resistance thermometer (IPRT No.2 fabricated by Shanghai Institute of Industrial Automatic Meters, R_0=100 Ω, 1.6 mm in diameter and 16 mm long) was used in the adiabatic calorimeter for temperature measurements of the sample cell. The thermometer was calibrated on the basis of the ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. To verify the accuracy of the calorimeter, the molar heat capacity of α-Al_2O_3 was measured from 60 to 360 K. The deviations of experimental results from the smoothed curve lie within ±0.2%, while the error is within ±0.5%, compared with those of the National Bureau of Standards [7] over the entire temperature range.

2.3. Thermal analysis

A DuPont TA 2000 thermal analysis system coupled with a personal computer, loaded with a program for data acquisition and precision, was used. DSC measurements were carried out using a differential scanning calorimeter (Model 910) with aluminum sample pans and sapphire reference material. Both the sample and sapphire were scanned at a heating rate of 20 K min^{-1}, under nitrogen atmosphere at a flow rate of 100 ml min^{-1}. The mass of the sample used for experiments was 11.7500 mg. At the same time, the C_p measurements were performed under the same conditions as above over the 310–730 K range.

Thermogravimetric analysis was performed with the TG 951 thermobalance in the 300–800 K range. In the experiments, a DBPH sample of 4.9200 mg and a nitrogen flow rate of 100 ml min^{-1} were employed.

3. Result and discussion

The heat capacity measurement was carried out by the standard intermittent heating method. The temperature step for each measurement was 2 to 4 K in the whole region. The low-temperature experimental molar heat capacities of DBPH are shown in Fig. 1. The smoothed values can be obtained from a fourth-degree polynomial:

$$C_{p,\mathrm{m}} = 404.5077 + 254.2559X - 51.4645X^2 - 0.1609X^3 - 21.2574X^4 \ (\mathrm{J\,K^{-1}\,mol^{-1}})$$

where $X=(T-215)/135$. This equation is valid from 80 to 350 K. The deviation of the experimental points from the smoothed values in this temperature region is within ±0.2%. The C_p-T curve in Fig. 1 indicates there is no phase transition or thermal anomaly in the temperature region between 80 and 350 K, which means that the thermochemical property of BDPH is stable in this temperature region. The numerical values of the experimental molar heat capacities of this compound are listed in Table 1.

Although thermal analysis techniques, such as DSC and TGA, alone cannot correctly identify the reaction products that result from each thermal event, these techniques allow the determination of the enthalpy and weight change as a function of time and temperature. Owing to the need from both, theoretical research and practical application for the heat capacity of higher temperature, the DSC heat capacity measurements were carried out with the reference material of sapphire in the temperature range from 310 to 730 K. The accuracy of C_p determination is ca. ±2%. The DSC results are shown in Fig. 2 and listed in Table 2. For comparison, the heat capacity data obtained by adiabatic calorimetry are also plotted in Fig. 2. As can be seen from Fig. 2, the two sets of the heat capacity data accord well with each other between 330 and 350 K; a large peak reaching to ca. 7.54 kJ K^{-1} mol^{-1} was observed near 400 K. This anomaly corresponds

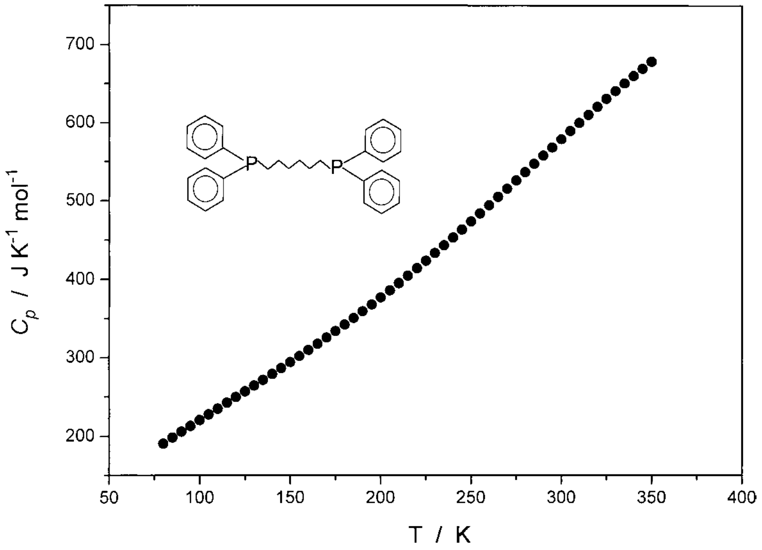


Fig. 1. Molar heat capacities of BDPH measured by adiabatic calorimetry.

Table 1
Experimental molar heat capacities of BDPH obtained by adiabatic calorimetry (M=454.5303 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})
78.75	188.7	164.11	316.1	255.48	484.9
82.68	194.7	166.97	320.7	258.93	492.1
84.51	197.5	169.81	325.3	262.35	499.3
86.28	200.1	172.61	329.9	265.74	506.4
88.27	203.1	175.40	334.5	272.47	520.6
90.49	206.4	178.16	339.1	275.79	527.6
92.66	209.6	180.90	343.7	279.08	534.6
95.17	213.3	183.61	348.3	282.33	541.6
97.99	217.4	186.30	352.8	285.56	548.4
101.01	221.8	188.97	357.4	288.76	555.3
104.22	226.5	191.63	362.1	291.96	562.1
107.36	231.1	194.25	366.7	295.13	568.8
110.44	235.5	196.85	371.3	298.27	575.5
113.46	239.9	199.45	375.9	301.37	582.0
116.42	244.2	202.02	380.5	304.44	588.5
119.34	248.4	204.56	385.2	307.59	595.2
122.20	252.6	207.80	391.1	310.54	601.3
125.03	256.7	211.69	398.3	313.55	607.6
127.82	260.8	215.55	405.6	316.55	613.8
130.58	264.9	219.37	412.8	319.54	619.9
136.89	274.2	223.14	420.0	322.96	626.9
140.07	279.0	226.85	427.2	326.78	634.6
143.21	283.7	230.52	434.4	330.57	642.1
146.40	288.5	234.19	441.7	334.34	649.5
149.35	293.0	237.82	448.9	338.08	656.7
152.37	297.6	241.39	456.1	341.79	663.8
155.35	302.3	244.93	463.3	345.51	670.7
158.30	306.9	248.47	470.5	349.20	677.4
161.22	311.5	251.99	477.7	352.72	683.6

Table 2
Experimental molar heat capacities of BDPH obtained by DSC (M=454.5303 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})
315	611	455	883	595	923
325	629	465	888	605	924
335	650	475	892	615	926
345	669	485	898	625	931
355	687	495	902	635	940
365	709	505	905	645	953
375	731	515	909	655	973
385	838	525	913	665	1001
395	1223	535	916	675	1168
405	7537	545	919	685	1382
415	1320	555	919	695	1608
425	870	565	920	705	2352
435	875	575	921	715	2420
445	879	585	922		

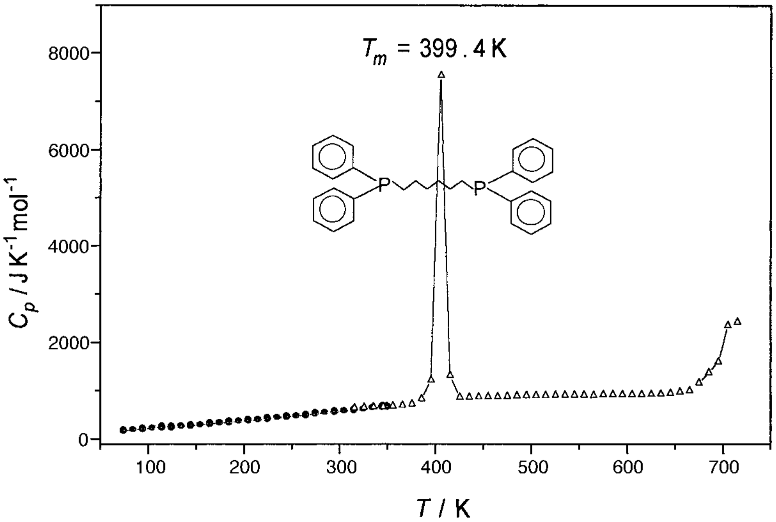


Fig. 2. Comparison of the heat capacities of BDPH obtained by (●) adiabatic calorimetry (ADC) and (Δ) DSC.

to the melting of BDPH, the temperature of this solid-to-liquid transition is ca. 400 K. A DSC curve is shown in Fig. 3, from which we can see that the structure of BDPH is stable below 390 K; BDPH melts at 399.4 K with a melting enthalpy of 66.8 kJ mol^{-1}. The molar entropy of melting was determined at 167.2 J K^{-1} mol^{-1}, based on $\Delta S_{\mathrm{m}} = \Delta H_{\mathrm{m}}/T_{\mathrm{m}}$. An obvious endothermic region was observed in the temperature range from 660 to 700 K. The peak temperature is 683 K and the respective energy change is 81.6 kJ mol^{-1}.

The TG measurements were carried out in N_2 atmosphere. The TG results are presented in Fig. 4. From Fig. 4, we can see that BDPH is stable below 600 K. The BDPH shows first a slow mass loss (approximately ±1%) from 400 to 550 K; this might be due to a slight evaporation of BDPH. The greatest

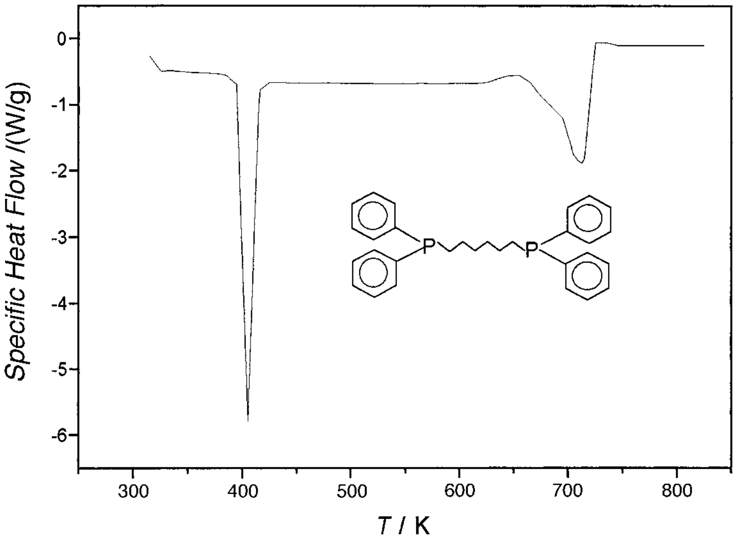


Fig. 3. DSC curve of BDPH under nitrogen atmosphere.

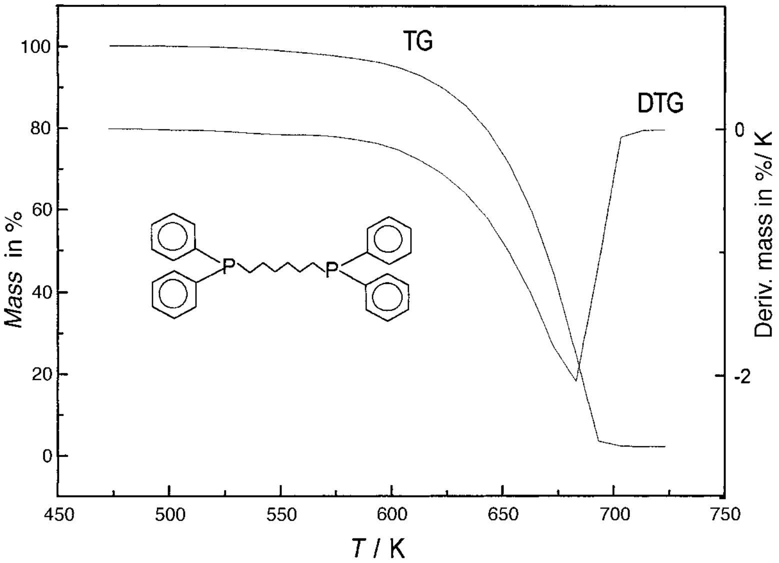


Fig. 4. TG and DTG curves of BDPH under nitrogen atmosphere.

mass loss occurs between 650 K (72%) and 700 K (2%) using a heating rate of 20 K min^{-1}. The decomposition of BDPH starts at 650 K and ends at 700 K in a single step. The peak temperature is 683.2 K. The big mass loss from 650 to 700 K, as shown in Fig. 4, corresponds to the second endothermic change in the same temperature range of the DSC curve, which proves the thermal anomaly obtained by DSC in the temperature region between 660 and 700 K is the decomposition reaction of BDPH. The major portion of BDPH decomposes completely in this region and the residual mass is only 2.21%.

Acknowledgements

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