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Thermochimica Acta 297 (1997) 1–5

thermochimica acta

A thermochemical study of 2,2′-bis(di-*p*-toluenephosphino)-1,1′-binaphthyl

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Received 4 February 1997; received in revised form 24 April 1997; accepted 26 April 1997

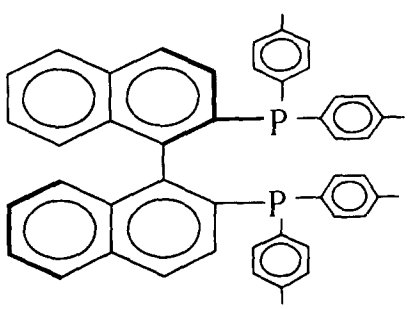
Abstract

A thermochemical study of 2,2′-bis(di-*p*-toluenephosphino)-1,1′-binaphthyl(Tol-*p*-BINAP) has been performed using adiabatic calorimetry, differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The low-temperature heat capacity of Tol-*p*-BINAP 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 region. The high-temperature heat capacity of Tol-*p*-BINAP was measured with a differential scanning calorimeter in the temperature range from 310 to 660 K. From the DSC curve obtained for this compound, a solid–liquid transition was found at 528.29 K and the enthalpy and entropy of transition were evaluated as 41.98 kJ mol^{-1} and 79.47 JK^{-1} mol^{-1}, respectively. The TG analysis of Tol-*p*-BINAP was carried out in the temperature range from 300 to 850 K, from which it was found that this compound starts to decompose at 662.13 K and transforms completely to naphthalene at 716.22 K in a single step. © 1997 Elsevier Science B.V.

Keywords: Adiabatic calorimetry; DSC; Heat capacity; TG; Tol-*p*-BINAP

1. Introduction

Since Noyori and Takaya first reported chiral diphosphine ligands (R)- or (S)-2,2-bis(diphenylphosphine)-1,1-binaphthyl(BINAP) and their Rh- and Ru-complexes [1,2], which have extremely high enantioselective recognition of hydrogen, various modified chiral BINAPs have been synthesized to improve the enantioselectivity of a variety of complexes. (R)- or (S)-2,2-bis(di-*p*-tolylphosphino)-1,1-binaphthyl(Tol-*p*-BINAP) is a useful ligand for transition-metal catalyzed asymmetric hydrogenation of unsaturated olefins and ketones [3]. The structure of (R)-Tol-*p*-BINAP is:



In order to improve the synthetic process and to perform the relevant theoretical research, the industries concerned are in urgent need of thermodynamic data for this compound.

Since heat capacity is a basic quantity for evaluation of thermodynamic properties, heat capacity measure-

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PII S0040-6031(97)00185-8

ments of this compound were carried out in the temperature range between 80 and 350 K with a small sample automated adiabatic calorimeter [4] and in the temperature range from 310 to 660 K with a differential scanning calorimeter. The melting temperature, the molar enthalpy and molar entropy of transition and the decomposition temperature for Tol-*p*-BINAP were determined by DSC and TG, respectively.

2. Experimental

2.1. Sample preparation and characterization

Tol-*p*-BINAPO (8) was prepared from 2,2′-dibromo-1,1′-binaphthyl and ditolylphosphinyl chloride, and then their optical antipodes were obtained by optical resolution using chiral dibenzoyl tartaric acid (5). After the reduction of 8 with $HSiCl_3$ Tol-*p*-BINAP was produced (Scheme 1).

^1H NMR and ^{13}C NMR spectra of Tol-*p*-BINAP were determined with BRUKER DRX 400 MHz, HPLC: BIORONIK, UV detector.

Di-*p*-tolylphosphinyl chloride, 2,2′-dibromo-1,1′-binaphthyl were prepared according to the literature method [5,6].

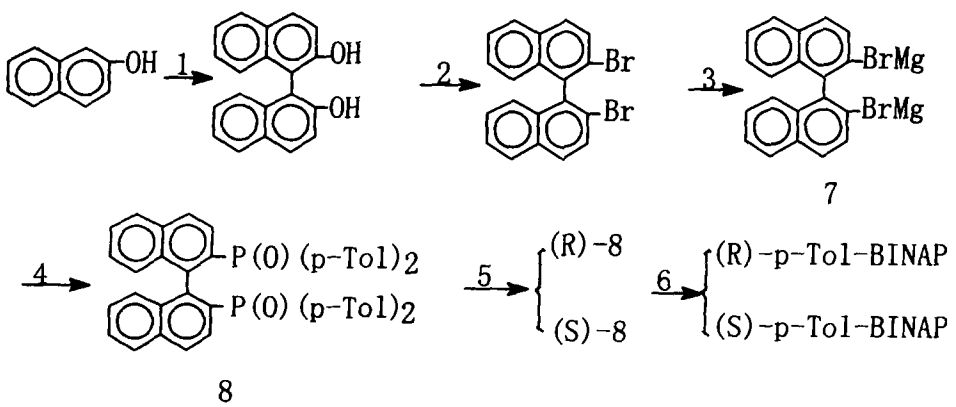
Tol-*p*-BINAPO (8) was synthesized by using Magnesium (7 g, 0.285 mol) and 2,2′dibromo-1,1′binaphthyl (48 g, 0.117 mol), and 15 g of (8) was obtained. The optical resolution of racemic 8 (12.55 g, 16.14 mmol) with L-(+)-5 (6.33 g, 17.67 mmol) and then the white precipitate was treated with NaOH aq. to yield 5.82 g of (+)-(8) as white crystal. The reduction of (+)-8 (3.1 g, 4.57 mmol) was effected with $HSiCl_3$ (11.4 g, 85.2 mmol).

Crude Tol-*p*-BINAP was recrystallized to give white crystals (1.3 g). The purity of Tol-*p*-BINAP was > 99.8% as determined by HPLC (column: Bondpak G18).

^1H NMR ($CDCl_3$) δ_H (ppm) 1.989–2.023 (m, 6H), 6.725 (2H), 6.768 (^3J=7.77, 4H), 6.898 (^3J=7.72, 4H), 7.046 (^3J=8.46, 2H), 7.092 (^3J=7.22, 2H), 7.200 (^3J=7.54, 4H), 7.387 (^3J=7.56, 4H), 7.561 (^3J=8.12, 2H), 7.710 (^3J=8.52, 2H), 7.787 (^3J=1.76 2H), ^{13}C: δ_c (ppm) 21.070, 125.911(s), 126.415(s), 127.966(s), 128.395(s), 129.258, 131.013(s), 134.339, 133.445 (^2J=10.07), 133.866(s), 134.073–134.130 (^3J=5.19), 134.719–134.831 (^2J=11.03), 134.101, 135.656–135.701 (^1J=-7.6), 136.817–136.854 (^1J=-7.0), 145.514–145.730 (^2J=20.75). elementary analysis: $C_{48}H_{40}P_2$: C, 84.9; H, 5.94; P, 9.13. found: C, 84.86; H, 5.71; P, 8.89.

2.2. Adiabatic calorimetry

The heat capacity measurements were carried out by means of a small sample automatic adiabatic calorimeter over the range 80 to 350 K. The mass of the sample for experiments was 2.3544 g, which was equivalent to 3.4685 mmol based on its molar mass of 678.7915 g mol^{-1}. The adiabatic calorimeter used was described before in detail [4]. Briefly, a calorimeter cell was made of gold-plated copper



Scheme 1. 1 – $FeCl_3$, 2 – Br_2PPh_3, 3 – Mg/THF, 4 – *p*-$Tol_2P(O)Cl$, 5 – L-(+)-dibenzoyltartrric acid (optical resolution), 6 – $HSiCl_3$.

and had an internal volume of 6 cm^3; four gold-plated copper vanes of 0.2 mm thickness were inserted into the cell to aid in the heat distribution. The lid of the cell 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 to promote 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) and a thermopile. When these control circuits were operating, the temperature difference between the calorimeter and its surroundings was kept to be 0.5 mK or smaller during the entitle 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) used in the adiabatic calorimeter 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 350 K. The deviations of experimental results from the smoothed curve lie within ±0.2%, while the inaccuracy within ±0.5% compared with those of the National Bureau of Standards [7] in the whole temperature range.

2.3. Thermal analysis

A Du Pont TA 2000 Thermal Analysis system coupled with a personal computer loaded with a program for processing the obtained results 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 10 K min^{-1}, under nitrogen atmosphere with a flow rate of 150 ml min^{-1}. The mass of the sample used for experiments was 2.3200 mg. At the same time, the C_p measurements were performed under the same conditions as above in the temperature range 310–660 K.

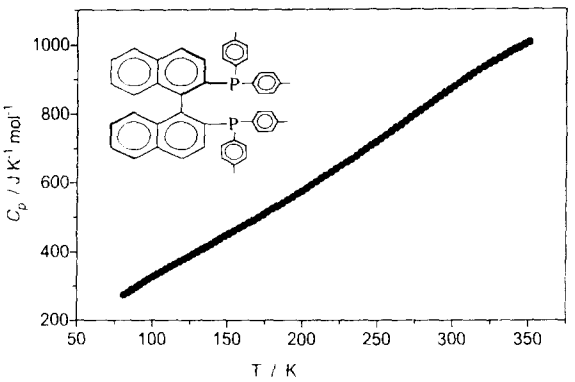


Fig. 1. Molar heat capacities of Tol-*p*-BINAP measured by adiabatic calorimetry.

Thermogravimetric analysis was performed with a TG951 Thermobalance in the temperature range 300–850 K. In the experiments, a Tol-*p*-BINAP sample of 2.5700 mg, and a nitrogen flow rate of 150 ml min^{-1} were employed.

3. Result and discussion

The low-temperature experimental molar heat capacity for Tol-*p*-BINAP data are shown in Fig. 1. 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 that there is no phase transition or thermal anomaly in the temperature region between 80 and 350 K, which means that the thermochemical property of Tol-*p*-BINAP is stable in this temperature region. From the structure of Tol-*p*-BINAP, we can see that the C–P bond and the C–C bond are rather difficult to rotate because the space resistance and the chemical property of Tol-*p*-BINAP should be stable; this accords well with the experimental result of the C_p–T curve in Fig. 1. The experimental molar heat capacity of this compound is also listed in Table 1 in temperature increment sequence so that the temperature increments can be deduced approximately from the adjacent mean temperatures.

Owing to the need from both theoretical research and practical application for the heat capacity of

Table 1
Experimental molar heat capacities of Tol-*p*-BINAP obtained by adiabatic calorimetry (M=6789.7915 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})	T (K)	C_p (J K^{-1} mol^{-1})
81.077	273.07	145.061	437.08	215.482	620.86	288.405	839.88
83.913	281.21	148.143	444.57	218.927	630.27	291.635	849.86
86.637	289.21	151.188	452.12	222.334	639.76	294.830	859.78
89.287	297.09	154.196	459.74	225.707	649.33	298.015	869.61
91.877	304.84	157.361	467.42	229.048	658.98	301.192	879.35
94.631	312.50	160.684	475.19	232.367	668.71	304.346	888.99
97.550	320.07	163.973	483.03	235.669	678.50	307.480	898.51
100.403	327.55	167.225	490.95	238.943	688.36	310.592	907.91
103.193	334.97	170.440	498.96	242.169	698.29	313.686	917.16
105.929	342.33	173.619	507.05	245.375	708.26	316.977	926.26
108.866	349.65	176.766	515.24	248.692	718.29	320.459	935.18
111.997	356.92	180.018	523.52	252.091	728.36	323.912	943.93
115.056	364.17	183.375	531.89	255.463	738.46	327.337	952.48
118.083	371.41	186.702	540.35	258.810	748.60	330.743	960.81
121.060	378.63	189.998	548.92	262.138	758.76	334.118	968.92
123.998	385.86	193.262	557.58	265.441	768.93	337.451	976.78
126.894	393.09	196.492	566.33	268.716	779.12	340.756	984.39
129.870	400.34	199.692	575.18	271.970	789.30	344.042	991.72
132.925	407.61	202.863	584.13	275.200	799.47	347.311	998.76
135.934	414.92	206.005	593.18	278.483	809.62	350.570	1005.48
138.901	422.26	209.120	602.31	281.824	819.75		
141.943	429.64	212.212	611.54	285.824	829.80		

higher temperature, the DSC heat capacity measurements were carried out with the reference material of sapphire in the temperature range 310–660 K. The accuracy of C_p determination is about ±2%. The DSC results are shown in Fig. 2 and listed in Table 2. From Fig. 2, a solid-to-liquid transition is found at 528.29 K. For the comparison, the heat capacity data obtained by adiabatic calorimetry are also plotted in Fig. 2, from which we can see that the two sets of the heat capacity data accord with each other well. A DSC curve is shown in Fig. 3, from which we can see that Tol-*p*-BINAP is stable in structure below 650 K, starts melting at about 528 K and decomposes at about 650 K with an exothermic reaction. From Fig. 3,

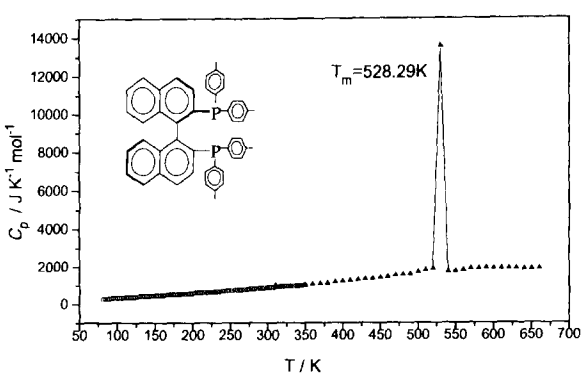


Fig. 2. Comparison of the heat capacities of Tol-*p*-BINAP obtained by adiabatic calorimetry (ADC) and DSC (○: ADC ; ▲: DSC).

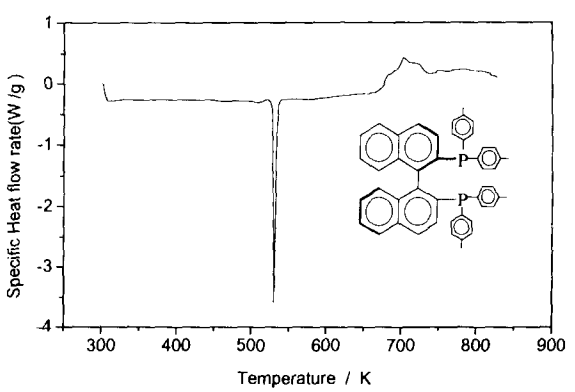


Fig. 3. DSC curve of Tol-*p*-BINAP under nitrogen atmosphere.

Table 2
Experimental molar heat capacities of Tol-*p*-BINAP obtained by DSC (M=678.7915 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})	T (K)	C_p (J K^{-1} mol^{-1})
310	1002.48	400	1202.29	490	1614.52	580	1872.40
320	909.58	410	1259.57	500	1688.64	590	1933.43
330	937.08	420	1289.23	510	1792.43	600	1910.13
340	967.59	430	1322.83	520	1871.23	610	1890.07
350	1001.08	440	1360.75	530	13542.59	620	1895.23
360	1040.59	450	1406.69	540	1734.14	630	1890.45
370	1080.12	460	1446.54	550	1743.14	640	1867.04
380	1119.48	470	1516.95	560	1804.41	650	1866.33
390	1163.83	480	1564.88	570	1863.87	660	1881.70

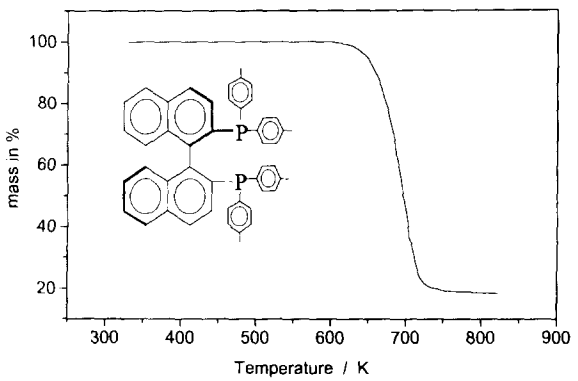


Fig. 4. TG curve of Tol-*p*-BINAP under nitrogen atmosphere.

the melting temperature, the molar enthalpy and molar entropy of transition for Tol-*p*-BINAP, as determined by DSC, are 528.29 K, 41.98 KJ mol^{-1} and 79.47 J K^{-1} mol^{-1}, respectively.

The TG measurements were carried out in N_2 atmosphere. The TG results are presented in Fig. 4. As can be seen from the mass-loss curve, most of the activities occur in the temperature range 670–720 K; Tol-*p*-BINAP is very stable below 600 K, it starts decomposing at 662.13 K and ends at 716.22 K in a single step. These accord well with the results obtained by DSC; the residue mass (%) is 20.64%. We consider that the residue is naphthalene. Theoretically, if the residue is naphthalene, the residue mass (%) should be 37.71%. But naphthalene melts at lower temperature (353.45 K) and sublimates easily even at room temperature, a part of naphthalene escapes with the nitrogen flow, thus the experimental residue mass (%) of naphthalene is lower than the theoretical value. Moreover, if the residue is another substance, the residue mass (%) should be larger. That is why we think the residue is naphthalene. The maximum mass loss took place at 696.14 K and the total mass loss was 79.36% at 716.22 K. The course and dynamics of the decomposition reaction for Tol-*p*-BINAP will be reported in detail in the next study.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China for financial support of this work under Grant No. 29573133.

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