J. Chem. Eng. Data **2010,** *55,* 4267–4272

Low-Temperature Heat Capacities and Thermodynamic Properties of *N*-Benzyloxycarbonyl-L-3-phenylalanine ($C_{17}H_{17}NO_4$)[†]

Jun-Ning Zhao,[‡] Li-Xian Sun,[‡] and Zhi-Cheng Tan*[,‡,§]

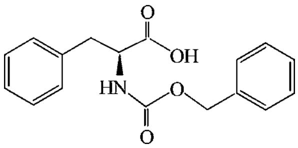
Materials & Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China, and China Ionic Liquid Laboratory Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

---

The heat capacities of *N*-benzyloxycarbonyl-L-3-phenylalanine were measured by means of a fully automated adiabatic calorimeter over the temperature range from (79 to 395) K. A solid−liquid phase transition corresponding to the melting process was observed. The temperature, the molar enthalpy, and entropy of the phase transition were determined to be 358.799 K, 31.787 $\mathrm{kJ \cdot mol^{-1}}$, and 88.594 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. The mole fraction purity of the sample used in the adiabatic calorimetric study was determined to be 0.9830 according to the Van't Hoff equation. Two equations of temperature dependence for heat capacities in the solid and liquid state are presented. The thermodynamic functions, ($H_T - H_{298.15K}$) and ($S_T - S_{298.15K}$), were calculated based on the heat capacity data in the temperature range from (80 to 400) K with an interval of 5 K. The standard molar enthalpies of combustion have been determined to be $\Delta_c H_m^0(C_{17}H_{17}NO_4, s) = -(8308.52 \pm 3.22)\ \mathrm{kJ \cdot mol^{-1}}$, with a precision oxygen-bomb combustion calorimeter at $T = 298.15$ K. The standard molar enthalpy of formation of the compound has been derived from the enthalpy of combustion, $\Delta_f H_m^0(C_{17}H_{17}NO_4, s) = -(815.05 \pm 0.67)\ \mathrm{kJ \cdot mol^{-1}}$. The thermal stability of the compound was further studied using TG and DSC, and a possible mechanism for thermal decomposition was suggested.

Introduction

N-Benzyloxycarbonyl-L-3-phenylalanine (CAS: 1161-13-3, abbreviated as NBLP in this paper) is an important chemical intermediate that can be used to synthesize proteins and polypeptides in medical, biochemical, food additive, and cosmetic industries.[1,2] It can also be used as a precursor in the synthesis of novel N-protected α-amino glyoxals via oxidation with distilled dimethyldioxirane, then to produce polyfunctional amino acid and peptide derivatives via Wittig reactions.[3] The molecular formula of NBLP is $C_{17}H_{17}NO_4$; the molar mass is 299.32 $\mathrm{g \cdot mol^{-1}}$; and the molecular structure is:



Heat capacity is a fundamental thermodynamic property and characteristic quantity closely related to the energetics and structure of materials. From heat capacity data, many other thermodynamic properties such as enthalpy and Gibbs energy, which are of importance for both theoretical and practical purposes, can be calculated.[4] However, until now, the fundamental thermodynamic data of NBLP have not been reported in the literature. To improve the process of chemical and medicinal synthesis, the thermodynamic property study of this substance is necessary. In the present study, the low-temperature heat capacity of this compound over the temperature range from (78 to 395) K was measured by an automated adiabatic calorimeter. The thermodynamic functions, ($H_T - H_{298.15K}$) and ($S_T - S_{298.15K}$), were derived from the heat capacity data. The standard molar enthalpy of formation at $T = 298.15$ K was determined by oxygen-bomb combustion calorimetry.

Experimental Section

The sample used for the present calorimetric study was purchased from ACROS ORGANICS Company. The labeled chemical mass factor purity was higher than 0.99.

DSC analysis was carried out in a TA MDSC-Q1000 differential scanning calorimeter. Prior to measurements of the sample, the calorimeter was calibrated with indium standards for the temperature and heat flow calibration. The sample mass about 0.00350 g was weighted and put into a closed aluminum pan, placed in the DSC cell, and heated at the rate of (5, 10, 15, 20, and 25) $\mathrm{K \cdot min^{-1}}$, respectively, under high purity nitrogen atmosphere (99.99 %) with a flow rate of 50 $\mathrm{cm^{-3} \cdot min^{-1}}$. TG analysis was performed on Thermo Cahn TG500 and calibrated by $CaC_2O_4 \cdot H_2O$ (99.9 %) before the experiment. A mass of 0.02693 g of sample was placed in a 100 μL α-alumina crucible and heated from room temperature to 875 K with a rate of 20 $\mathrm{K \cdot min^{-1}}$ under high purity argon atmosphere (99.99 %) with a flow rate of 60 $\mathrm{cm^{-3} \cdot min^{-1}}$.

A precision automatic adiabatic calorimeter was used to measure the heat capacity over the temperature range from (78 to 395) K. The calorimeter was developed in our Materials & Thermochemistry Laboratory. The principle and structure of the calorimeter were described in detail elsewhere.[5−7] The temper-

---

[†] Part of the "Sir John S. Rowlinson Festschrift".

* Corresponding author. E-mail: tzc@dicp.ac.cn. Fax: +86-411-84691570. Tel.: +86-411-84379199.

[‡] Materials & Thermochemistry Laboratory.

[§] China Ionic Liquid Laboratory Laboratory.

10.1021/je1004092

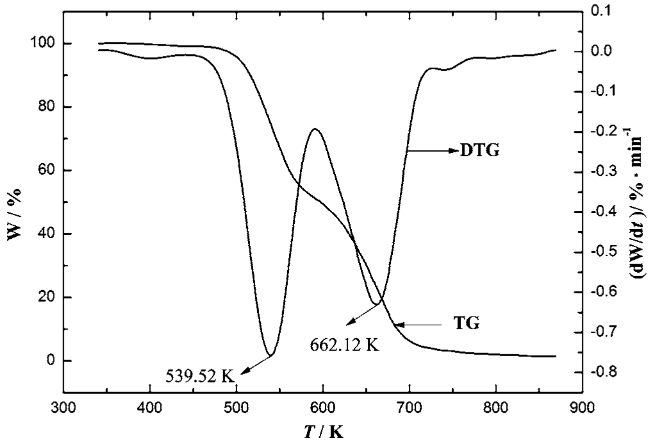


Figure 1. TG-DTG curves of *N*-benzyloxycarbonyl-L-3-phenylalanine.

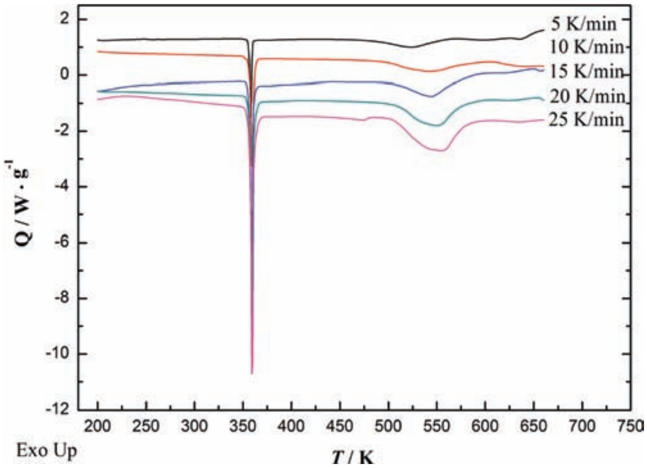


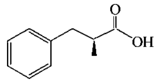
Figure 2. DSC curve of *N*-benzyloxycarbonyl-L-3-phenylalanine.

ature increment for each experimental heat capacity point was usually controlled to about 3 K for the whole experiment. The sample mass used for calorimetric measurements was 1.45521 g, which is equivalent to 0.0048616 mol based on the molar mass $M = 299.32\ \text{g}\cdot\text{mol}^{-1}$. Prior to the heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the synthetic sapphire (α-Al_2O_3), Standard Reference Material 720. The relative deviations of our calibration results from those of the smoothed curve lie within ± 0.2 %, while the relative uncertainty is within ± 0.3 %, as compared with the recommended values reported by Archer[8] of NIST in the temperature range from (80 to 405) K.

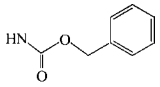
The standard molar energy of combustion of NBLP was measured by means of a homemade precision oxygen-bomb combustion calorimeter. It was an isoperibolic macrocalorimeter with a static oxygen bomb. The structure and principle of the calorimeter have been described previously.[9] A sample (about 0.60 g) was pressed into a pellet and put in a small sample crucible of about 4 cm^3, which was suspended in the bomb with internal volume of about 300 cm^3, and burned under an oxygen pressure of about 3 MPa. It was ignited by a nickel fuse of about 16 cm in the presence of 1 cm^3 of distilled water in the bomb to ensure equilibrium in the final state after the combustion. The real energy of combustion of the nickel fuse (Q_{Ni}) was calculated from the formula $Q_{Ni}/J = 2.929\cdot\Delta L$, in which ΔL/cm was the length of the combusted nickel wire. The energy of formation of the aqueous nitric acid produced by oxidation of a trace of nitrogen, which was contained in the oxygen bomb and was produced from the combustion reaction, was determined by the neutral titration with 0.05922 mmol·cm^{-3} of sodium hydroxide solution by using phenolphthalein as the indicator. The enthalpy of formation of the aqueous nitric acid in the oxygen bomb can be derived from the equation, $Q_{HNO_3}/J = 59.831NV$, in which N/mol·cm^{-3} is the concentration of the sodium hydroxide solution and V/cm^3 is the volume of the consumed sodium hydroxide solution.[10]

Results and Discussion

DSC and TG Analysis. The TG-DTG technique was applied to determine the thermostability of NBLP. It can be seen from the TG-DTG curves shown in Figure 1 that two mass-loss processes take place with an increase of temperature. The first mass-loss took place over the temperature range from (450 to 590.79) K (the maximum differential mass-loss temperature in the DTG was 539.52 K), and the real mass-loss percentage was 47.97 %, which is in agreement with the theoretical percent content (49.8 %) of the part

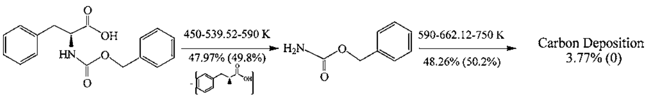


in NBLP. The second mass-loss process happened over the temperature region from (590.79 to 750) K (the maximum differential mass-loss temperature in the DTG was 662.12 K), and the actual mass-loss percentage was 48.26 %, which is in agreement with the theoretical percent (50.2 %) content of this part



in NBLP.

A possible mechanism for the thermal decomposition of NBLP was deduced from the results of the TG-DTG analysis as follows



in which the temperatures above the arrows correspond to the starting, the maximum differential mass-loss, and the ending decomposition temperatures in every mass-loss step, and the values below the arrows are the real mass-loss percentages for each decomposition step (the values in the brackets were obtained from theoretical calculation based on the chemical formula of NBLP).

The result of the DSC analysis is plotted in Figure 2 and listed in Table 6. From Figure 2, it can be seen that there are two endothermic peaks appearing in the curves. For instance, in the curve of 10 K·min^{-1}, the onset points, peak temperatures (T_{peak}), and molar enthalpies of the two endothermic processes were determined to be 357.75 K, 358.80 K, and 26.51 kJ·mol^{-1} for the first peak, then 496.15 K, 536.25 K, and 34.86 kJ·mol^{-1} for the second peak, which corresponds to the decomposition process in the temperature range from (450 to 590.79) K in TG-DTG curves of NBLP.

Table 1. Experimental Molar Heat Capacities of *N*-Benzyloxycarbonyl-L-3-phenylalanine

T / K	$C_{p,\mathrm{m}}$ / J·K^{-1}·mol^{-1}	T / K	$C_{p,\mathrm{m}}$ / J·K^{-1}·mol^{-1}	T / K	$C_{p,\mathrm{m}}$ / J·K^{-1}·mol^{-1}
79.129	109.2	191.952	219.3	304.152	339.5
81.175	111.4	194.984	223.0	307.188	340.6
84.318	114.7	198.004	226.3	310.219	343.9
87.260	119.7	201.005	229.2	313.241	348.3
90.203	124.4	204.654	233.5	316.259	351.4
93.146	128.0	208.275	236.2	319.267	353.7
96.096	130.2	211.230	238.9	322.269	358.3
99.051	132.6	214.166	242.0	325.266	362.5
103.158	135.7	217.086	248.7	328.252	367.6
107.224	140.4	220.000	250.5	331.235	371.4
110.145	143.8	222.892	252.5	334.210	375.1
113.081	146.3	225.770	254.9	337.173	380.6
116.026	149.3	228.720	256.4	340.126	389.8
118.995	150.1	231.727	258.0	343.067	396.6
121.918	156.4	234.734	260.1	345.967	418.3
124.865	158.7	237.770	264.5	348.883	508.8
127.826	160.7	240.784	266.6	351.809	582.8
130.809	161.9	244.332	268.1	354.373	1079.8
133.809	165.1	247.888	270.2	356.227	2370.4
136.776	168.9	250.894	273.1	357.328	4796.4
139.764	171.3	253.882	277.4	358.031	5811.0
142.777	172.5	256.866	280.9	358.520	12856.8
145.753	176.2	259.834	282.4	358.799	17704.9
148.702	181.2	262.791	286.2	359.363	4488.5
152.530	181.4	265.735	290.4	361.429	549.6
156.300	185.2	268.669	292.7	364.562	551.9
159.199	189.8	271.584	297.9	367.701	552.7
162.163	191.9	274.489	302.3	370.829	553.6
165.093	194.2	277.382	301.8	373.947	554.9
168.086	197.5	280.255	307.3	377.053	555.6
171.135	198.8	283.119	314.7	380.134	557.1
174.160	201.1	286.092	319.9	383.207	558.5
177.160	206.1	289.048	323.8	386.327	560.8
180.144	209.9	291.975	326.7	389.430	562.4
183.108	211.4	295.014	330.1	392.554	563.6
186.048	211.8	298.060	333.0	395.546	564.8
188.969	218.1	301.112	336.5		

Heat Capacity. The experimental molar heat capacities of NBLP are tabulated in Table 1 and shown in Figure 3. The molar heat capacities are fitted to the two following polynomial equations by the least-squares fitting. For the solid phase over the temperature range from (79 to 345) K

$$C_{p,\mathrm{m}}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 236.857 + 124.005X - 0.172X^2 + 11.464X^3 + 34.905X^4 + 1.898X^5 - 25.153X^6 \tag{1}$$

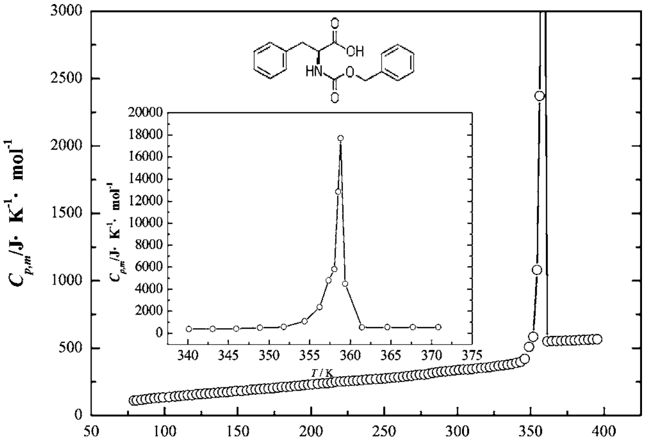


Figure 3. Experimental molar heat capacity $C_{p,\mathrm{m}}$ of *N*-benzyloxycarbonyl-L-3-phenylalanine as a function of temperature.

where X is the reduced temperature and $X = [T - (T_{\max} + T_{\min})/2]/[(T_{\max} - T_{\min})/2]$; and T is the experimental temperature. In this equation, $T_{\max}$ is the upper limit (345 K), and $T_{\min}$ is the lower limit (80 K), so $X = [(T/\mathrm{K} - 212.5)/133.5]$. Thus, it could make the value of X between +1 and −1. The correlation coefficient of the fitted curve $R^2 = 0.9992$.

For the liquid phase over the temperature range from (365 to 400) K

$$C_{p,\mathrm{m}}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 556.931 + 7.2351X + 6.351X^2 + 4.008X^3 - 11.465X^4 - 11.267X^5 + 6.747X^6 + 6.747X^7 \tag{2}$$

where $X = [(T/\mathrm{K} - 380)/16]$ and $R^2 = 0.9982$.

Thermodynamic Functions. The thermodynamic functions relative to the reference temperature of 298.15 K were calculated in the temperature range from (80 to 345) K and from (365 to 400) K with an interval of 5 K, using the polynomial equations of heat capacity and thermodynamic relationships as follows.[10]

Before melting of the sample

$$H_\mathrm{T} - H_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}}(\mathrm{s})\mathrm{d}T \tag{3}$$

$$S_\mathrm{T} - S_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}}(\mathrm{s})T^{-1}\mathrm{d}T \tag{4}$$

After melting of the sample

$$H_\mathrm{T} - H_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T_\mathrm{i}} C_{p,\mathrm{m}}(\mathrm{s})\mathrm{d}T + \Delta_\mathrm{fus}H_\mathrm{m} + \int_{T_\mathrm{f}}^{T} C_{p,\mathrm{m}}(\mathrm{l})\mathrm{d}T \tag{5}$$

$$S_\mathrm{T} - S_{298.15\mathrm{K}} = \int_{298.15\mathrm{K}}^{T_\mathrm{i}} [C_{p,\mathrm{m}}(\mathrm{s})T^{-1}]\mathrm{d}T + \Delta_\mathrm{fus}H_\mathrm{m}T_\mathrm{m}^{-1} + \int_{T_\mathrm{f}}^{T} [C_{p,\mathrm{m}}(\mathrm{l})T^{-1}\mathrm{d}T] \tag{6}$$

The values of thermodynamic function $[H_\mathrm{T} - H_{298.15\mathrm{K}}]$ and $[S_\mathrm{T} - S_{298.15\mathrm{K}}]$ are listed in Table 2.

Temperature, Molar Enthalpy, and Entropy of Fusion. The molar enthalpy $\Delta_\mathrm{fus}H_\mathrm{m}$ and entropy $\Delta_\mathrm{fus}S_\mathrm{m}$ of fusion of NBLP were calculated from the following equations

$$\Delta_\mathrm{fus}H_\mathrm{m} = [Q - n\int_{T_\mathrm{i}}^{T_\mathrm{m}} C_p(\mathrm{s})\mathrm{d}T - n\int_{T_\mathrm{m}}^{T_\mathrm{f}} C_p(\mathrm{l})\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} \overline{H_0}\mathrm{d}T]/n \tag{7}$$

$$\Delta_\mathrm{fus}S_\mathrm{m} = \Delta_\mathrm{fus}H_\mathrm{m}/T_\mathrm{m} \tag{8}$$

where T_i is the temperature slightly lower than the initial melting temperature; T_f is the temperature slightly higher than the final melting temperature; Q is the total energy introduced to the sample cell from T_i to T_f; $C_p(\mathrm{s})$ is the heat capacity of the sample in the solid phase from T_i to T_m; $C_p(\mathrm{l})$ is the heat capacity of the sample in liquid phase from T_m to T_f; and $\bar{H}_0$ is the heat capacity of the empty sample cell at temperature $(T_\mathrm{i} + T_\mathrm{f})/2$.

The results of the melting point, molar enthalpy, and entropy of fusion obtained from the heat capacity measurements are listed in Table 3.

Table 2. Smoothed Heat Capacities and Thermodynamic Functions of *N*-Benzyloxycarbonyl-L-3-phenylalanine

T	$C_{p,m}$	$H_T - H_{298.15\,K}$	$S_T - S_{298.15\,K}$
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
80	110.4	−46.94	−258.0
85	116.7	−46.37	−250.5
90	122.6	−45.77	−243.2
95	128.0	−45.15	−236.0
100	133.2	−44.50	−229.0
105	138.1	−43.83	−222.2
110	142.8	−43.13	−215.5
115	147.5	−42.41	−208.9
120	152.0	−41.67	−202.4
125	156.5	−40.89	−196.0
130	161.0	−40.10	−189.7
135	165.4	−39.29	−183.5
140	169.9	−38.45	−177.4
145	174.4	−37.58	−171.4
150	179.0	−36.70	−165.4
155	183.5	−35.79	−159.4
160	188.1	−34.86	−153.5
165	192.7	−33.90	−147.6
170	197.3	−32.93	−141.8
175	202.0	−31.93	−136.0
180	206.6	−30.90	−130.3
185	211.3	−29.86	−124.6
190	215.9	−28.79	−118.9
195	220.6	−27.70	−113.2
200	225.2	−26.58	−107.6
205	229.9	−25.44	−102.0
210	234.5	−24.28	−96.37
215	239.2	−23.10	−90.80
220	243.8	−21.89	−85.24
225	248.5	−20.66	−79.71
230	253.1	−19.41	−74.19
235	257.8	−18.13	−68.69
240	262.6	−16.83	−63.21
245	267.3	−15.50	−57.74
250	272.1	−14.16	−52.29
255	277.0	−12.79	−46.84
260	282.0	−11.40	−41.41
265	287.1	−9.979	−35.99
270	292.2	−8.539	−30.58
275	297.5	−7.076	−25.16
280	302.9	−5.590	−19.75
285	308.5	−4.081	−14.33
290	314.2	−2.548	−8.895
295	320.0	−0.992	−3.445
298.15	323.7	0.000	0.000
300	326.0	0.587	2.029
305	332.1	2.189	7.535
310	338.3	3.815	13.08
315	344.6	5.463	18.68
320	351.0	7.136	24.34
325	357.5	8.831	30.07
330	363.9	10.55	35.89
335	370.3	12.29	41.81
340	376.6	14.06	47.85
345	382.6	15.85	54.03
350	phase transition	\	\
355	phase transition	\	\
360	phase transition	\	\
365	552.0	49.22	148.0
370	553.2	51.68	154.7
375	554.7	54.14	161.3
380	556.2	56.61	167.9
385	558.3	59.08	174.3
390	561.2	61.57	180.7
395	563.3	64.07	187.1
400	565.3	66.58	193.4

Table 3. Thermodynamic Parameters of Solid−Liquid Phase Transition of *N*-Benzyloxycarbonyl-L-3-phenylalanine Obtained from Heat Capacity Measurements

	T_m	$\Delta_{fus}H_m$	$\Delta_{fus}S_m$
thermodynamic properties	K	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
	358.80	31.77	88.59

Table 4. Experimental Results of Melting Fractions and Equilibrium Temperatures of *N*-Benzyloxycarbonyl-L-3-phenylalanine

q/J	F	1/F	T/K
26.526	0.1716	5.8263	356.227
45.371	0.2936	3.4064	357.328
65.175	0.4217	2.3713	358.031
87.812	0.5682	1.7600	358.520
111.174	0.7193	1.3902	358.799

Purity Determination. The purity of the sample was determined by a set of equilibrium melting temperatures and melted fractions corresponding to these temperatures. The principium was described in detail in the literature.[11−13] The experimental equilibrium melting temperature T and melted fraction F corresponding to the temperature are listed in Table 4. The equilibrium melting temperature T is plotted against the reciprocal of the melted fractions 1/F as shown in Figure 4. The melting points of the absolute pure sample, $T_0 = 359.479$ K, and that of the sample, $T_1 = 358.904$ K, can be obtained at $1/F = 0$ and $1/F = 1$, respectively, from Figure 4.

According to ideal solution law, the molar fraction of a small amount of impurities, N, can be calculated from the following equation[7]

$$N = \frac{\Delta_{fus}H_m(T_0 - T_1)}{RT_0^2} \tag{9}$$

Putting the values of T_0, T_1, and $\Delta_{fus}H_m$ (listed in Table 3) into the above equation, the molar fraction of impurities, $N = 0.017$, was obtained, and then the molar fraction purity of the sample was determined to be 0.9830.

Standard Molar Energy, Enthalpy of Combustion, and Enthalpy of Formation. The standard molar energy of combustion of NBLP, $\Delta_c U_m^0$, can be calculated from the equation[10]

$$\Delta_c U_m^0 = (\varepsilon_{calor}\Delta T - Q_{Ni} - Q_{HNO_3} - \Delta U_{washburn})M/W \tag{10}$$

where ε_{calor}/J·K^{-1} is the energy equivalent of the oxygen bomb calorimeter; ΔT is the corrected temperature rise; M is the molar

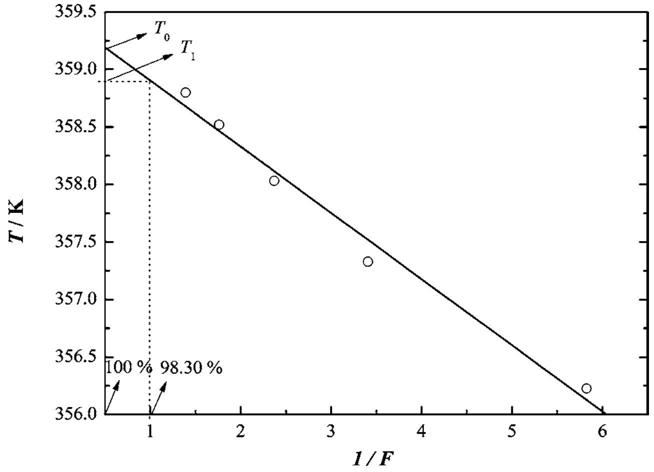


Figure 4. Melting curve (T vs 1/F) of *N*-benzyloxycarbonyl-L-3-phenylalanine during the fusion process.

Table 5. Experimental Results of the Combustion Energies of *N*-Benzyloxycarbonyl-L-3-phenylalanine Obtained from the Oxygen-Bomb Combustion Calorimetry at T = 298.15 K and P^0 = 0.1 MPa[a,b]

	1	2	3	4	5
$m_{\text{substance}}$/g	0.59136	0.57730	0.63018	0.58550	0.47559
$n\text{HNO}_3 \cdot 10^5$/mol	33.16	26.65	33.16	31.38	26.64
ΔT_c/K	1.1704	1.1409	1.2444	1.1573	0.9397
Q_{ign}/J	38.660	39.832	36.610	39.539	38.953
ΔU_{HNO_3}/J	19.84	15.94	19.84	18.78	15.94
$\Delta U_{\text{washburn}}$/J	12.35	12.10	13.18	12.24	9.99
$-\Delta_c U^0$/J·g^{-1}	27809.38	27768.89	27753.74	27771.83	27745.92
$-\Delta_c U_m^0$/kJ·mol^{-1}	8320.21	8308.16	8303.30	8309.00	8301.92
mean	$\Delta_c U_m^0(\text{s}) = \Delta_c \bar{U}_m^0 \pm \sigma_a{}^b = -(8308.52 \pm 3.22)$ kJ·mol^{-1}				

[a] ΔU_{HNO_3}, $\Delta U_{\text{washburn}}$, Q_{ign} are the energy correction of the nitric acid formation, the washburn correction, and the energy of combustion of the nickel fuse, respectively. [b] $\sigma_a = [\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)]^{1/2}$, in which n is the experimental number (n = 5); x_i is a single value of combustion energies; and $\bar{x}$ is the mean value of combustion energies.

Table 6. Experimental Results of DSC during the Different Heating Rate of *N*-Benzyloxycarbonyl-L-3-phenylalanine[a]

	first peak			second peak		
β	T_{onset}	T_{Peak}	$\Delta_{\text{fuse}}H$	T_{onset}	T_{Peak}	$\Delta_{\text{dec}}H$
K·min^{-1}	K	K	J·mol^{-1}	K	K	J·mol^{-1}
5	357.62	358.47	26.18	483.63	524.04	34.28
10	357.75	358.80	26.51	496.15	536.25	34.86
15	358.01	359.11	27.04	503.64	546.47	35.23
20	358.48	359.58	27.89	509.13	550.84	35.77
25	358.31	359.63	28.92	506.14	554.90	40.50

[a] β is the heating rate; T_{onset} is the onset temperature; T_{Peak} is the peak temperature; $\Delta_{\text{fuse}}H$ is the enthalpy of fusion; and $\Delta_{\text{dec}}H$ is the enthalpy of decomposition obtained from DSC curves.

mass of the sample; and W is the mass of the sample. The results calculated by the equation are listed in Table 5.

The standard molar enthalpy of combustion of NBLP, $\Delta_c H_m^0$, referred to the combustion enthalpy change of the following reaction at T = 298.15 K and P^0 = 100 kPa based on the definition of the combustion enthalpy about the organic compound

$$C_{17}H_{17}NO_4(s) + 77/4O_2(g) = 17CO_2(g) + 17/2H_2O(l) + 1/2N_2(g) \quad (11)$$

The standard molar enthalpies of combustion can be derived from the standard molar combustion energy by the following formula

$$\Delta_c H_m^0 = \Delta_c U_m^0 + \Delta n \cdot RT \quad (R = 8.314\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \quad (12)$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g}) \quad (13)$$

where $\sum n_i$ is the total molar amount of the gases in products or reactants. From formulas11 and 13, $\Delta n = -1.75$.

The standard molar energy of combustion, $\Delta_c U_m^0$, can be obtained from Table 5

$$\Delta_c U_m^0 = (\overline{\Delta_c U_m^0} \pm \sigma_a) = -(8308.52 \pm 3.22)\ \text{kJ}\cdot\text{mol}^{-1}$$

The standard molar enthalpy of combustion of NBLP is calculated

$$\Delta_c H_m^0 = -(8304.18 \pm 3.22)\ \text{kJ}\cdot\text{mol}^{-1}$$

The standard molar enthalpy of formation of the organic compound, $\Delta_f H_m^0$, is calculated by a designed Hess thermochemical cycle according to the following reaction

$$\Delta_f H_m^0(C_{17}H_{17}NO_4, s) = 17\Delta_f H_m^0(CO_2, g) + 17/2\Delta_f H_m^0(H_2O, l) - \Delta_c H_m^0(C_{17}H_{17}NO_4, s) \quad (14)$$

In the above formula, the standard molar enthalpies of formation of CO_2(g) and H_2O(l), recommended by CODATA,[14] $\Delta_f H_m^0(CO_2, g) = -(393.51 \pm 0.13)$ kJ·mol^{-1}, and $\Delta_f H_m^0(H_2O, l) = -(285.83 \pm 0.04)$ kJ·mol^{-1}, are employed in the calculation of $\Delta_f H_m^0(C_{17}H_{17}NO_4, s)$ values. On the basis of these values and the standard molar enthalpy of combustion, the standard molar enthalpy of formation of NBLP can be calculated: $\Delta_f H_m^0(C_{17}H_{17}NO_4, s) = -(815.05 \pm 0.67)$ kJ·mol^{-1}.

Conclusions

The heat capacities of NBLP were measured in the temperature range from (79 to 395) K by a high-precision automated adiabatic calorimeter. On the basis of the experimental heat capacities, two equations of heat capacity as a function of temperature were obtained. The thermodynamic functions ($H_T - H_{298.15K}$) and ($S_T - S_{298.15K}$) were derived from the equations in the range from (80 to 400) K with temperature intervals of 5 K. The thermodynamic properties of the fusion process were completely studied through heat capacity measurements: the melting temperature and the standard molar enthalpy and entropy of fusion were determined, respectively. The molar fraction purity was calculated in terms of the Van't Hoff equation. The standard molar enthalpy of formation of NBLP was determined with a precision oxygen bomb combustion calorimeter. The thermal stability of the compound was further studied using TG and DSC analyses, and a possible mechanism for thermal decomposition was suggested.

Literature Cited

(1) Nguyen, V. A.; Willis, C. L.; Gerwick, W. H. Synthesis of the marine natural product barbamide. *Chem. Commun.* **2001**, *19*, 1934–1935.

(2) Oh, E. S.; Kim, D. S.; Kim, J. H. Enzymatic properties of a protease from the hepatopancreas of shrimp, Penaeus orientalis. *J. Food Biochem.* **2000**, *24*, 251–264.

(3) Darkins, P.; Groarke, M.; McKervey, M. A.; Moncrieff, H. M.; McCarthy, N.; Nieuwenhuyzen, M. Enantiopure N-protected alpha-amino glyoxals 1. Synthesis from alpha-amino acids and some condensation reactions with amines. *J. Chem. Soc., Perkin Trans.* **2000**, *1*, 381–389.

(4) Tan, Z. C.; Sun, G. Y.; Song, Y. J.; Wang, L.; Han, J. R.; Wang, M. An adiabatic calorimeter for heat capacity measurement of small samples---The heat capacity of nonlinear optical materials $KTiOPO_4$ and $RbTiOAsO_4$ crystals. *Thermochim. Acta* **2000**, *352*, 247–253.

(5) Tan, Z. C.; Shi, Q.; Liu, B. P.; Zhang, H. T. A Fully Automated Adibatic Calorimeter for Heat Capacity Measurement between 80 and 400 K. *J. Therm. Anal. Calorim.* **2008**, *92*, 367–374.

(6) Tan, Z. C.; Sun, G. Y.; Sun, Y.; Yin, A. X.; Wang, W. B.; Ye, J. C.; Zhou, L. X. An adiabatic low-temperature calorimeter for heat capacity measurement of small samples. *J. Therm. Anal.* **1995**, *45*, 59–67.

(7) Tan, Z. C.; Sun, L. X.; Meng, S. H.; Li, L.; Zhang, J. B. Heat capacities and thermodynamic functions of p-chlorobenzoic acid. *J. Chem. Thermodyn.* **2002**, *341*, 417–1429.

(8) Archer, D. G. Thermodynamic properties of synthetic sapphire (alpha-Al_2O_3), standard reference material 720 and the effect of temperature-scale differences on thermodynamic properties. *J. Phys. Chem. Ref. Data* **1993**, *22*, 1441–1452.

(9) Zhang, L. M.; Tan, Z. C.; Wang, S. D.; Wu, D. Y. Combustion calorimetric and thermogravimetric studies of graphite and coals dopes with a coal-burning additive. *Thermochim. Acta* **1997**, *299*, 13–17.

(10) Di, Y. Y.; Tan, Z. C.; Sun, X. H.; Wang, M. H.; Xu, F.; Liu, Y. F.; Sun, L. X.; Zhang, H. T. Low-temperature heat capacity and standard molar enthalpy of formation of 9-fluorenemethanol ($C_{14}H_{12}O$). *J. Chem. Thermodyn.* **2004**, *36*, 79–86.

(11) Wu, X. M.; Tan, Z. C.; Meng, S. H.; Sun, C. X.; Wang, F. D.; Qu, S. S. Study on thermodynamic properties of polypyromellitimide molding power. *Thermochim. Acta.* **2000**, *359*, 103–107.

(12) Badley, J. H. The Calorimetric Determination of Purity—Theory and Calculation Methods. *J. Phys. Chem.* **1959**, *63*, 1991–1996.

(13) Tan, Z. C.; Ye, J. C.; Yin, A. X.; Chen, S. X.; Wang, W. B. Heat capacity and thermodynamic properties of 2-chloro-6-(trichloromethyl) pyridine. *Chin. Sci. Bull.* **1987**, *32*, 240–246.

(14) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp: New York, 1989.

Received for review April 27, 2010. Accepted August 17, 2010.

JE1004092