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Heat capacities and thermodynamic properties of *N*-(tert-butoxycarbonyl)-L-phenylalanine ($C_{14}H_{19}NO_4$)

Z.-M. Zhao · L.-X. Sun · Z.-C. Tan

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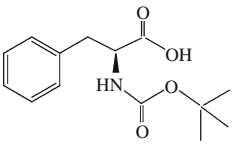
Abstract The heat capacities of *N*-(tert-butoxycarbonyl)-L-phenylalanine (abbreviated to NTBLP in this article), as an important chemical intermediates used to synthesize proteins and polypeptides, were measured by means of a fully automated adiabatic calorimeter over the temperature range from 78 to 350 K. The measured experimental heat capacities were fitted to a polynomial equation as a function of temperature. The thermodynamic functions, $H_T - H_{298.15K}$ and $S_T - S_{298.15K}$, were calculated based on the heat capacity polynomial equation in the temperature range of (80–350 K) with an interval of 5 K. The thermal stability of the compound was further studied using TG and DSC analyses; a possible mechanism for thermal decomposition of the compound was suggested.

Keywords Heat capacity · Thermodynamic property · *N*-(tert-butoxycarbonyl)-L-phenylalanine

Introduction

N-(tert-butoxycarbonyl)-L-phenylalanine (CAS: 13734-34-4, abbreviated to NTBLP in this article) is not only an important bio-nutrient, but also a useful raw material for synthesizing a variety of drugs. It can be used to synthesize body protein, anti-cancer drugs, antiviral drugs, vitamin B_6, and food and beverage additives.

The molecular formula of NTBLP is $C_{14}H_{19}NO_4$, the molar mass is 265.3 g mol^{-1} and the molecular structure is:



Molar heat capacities of materials at different temperatures are basic data in chemistry and engineering, from which many other thermodynamic properties such as enthalpy, entropy, and Gibbs free energy can be calculated, which are of importance to both theoretical and practical purposes [1].

However, till now, the fundamental thermodynamic data of NTBLP have not been reported in literatures. In order to improve the process of chemicals and medicine synthesis concerned with this compound, the study of thermodynamic property for this substance is necessary. In this study, the low-temperature heat capacities of this compound over the temperature range from 78 to 350 K were 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 thermal decomposition characteristics of this compound were investigated by TG and DSC.

Experimental section

The sample used for this calorimetric study was purchased from ACROS ORGANICS Company. The labeled chemical purity was higher than 0.99 in mass fraction.

Z.-M. Zhao · L.-X. Sun
Materials and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Dalian 116023, People's Republic of China

Z.-C. Tan (✉)
China Ionic Liquid Laboratory and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China
e-mail: tzc@dicp.ac.cn

DSC analysis was carried out in a TA MDSC-Q1000 differential scanning calorimeter. Prior to measurements of the sample, the calorimeter was calibrated with standard indium for the temperature and heat flow calibration. The sample mass about 0.00395 g was weighted and put into a closed aluminum pan, placed in the DSC cell and heated at the rate of 10 K min^{-1} under high purity nitrogen atmosphere (99.999%) with a flow rate of 50 mL min^{-1}. The temperature scale of the instrument was initially calibrated in the standard DSC mode, using the extrapolated onset temperatures of the melting of indium (429.75 K) at a heating rate of 10 K min^{-1}. The energy scale was calibrated with the heat fusion of indium (28.45 J g^{-1}).

TG analysis was performed on Thermo Cahn TG500 and calibrated by $CaC_2O_4{\cdot}H_2O$ (99.9%) before the test. A mass of 0.0310 g sample was placed in a 100 μL α-alumina crucible and heated from room temperature to 800 K with a rate of 20 K min^{-1} under high purity argon atmosphere (99.999%) with a flow rate of 60 mL min^{-1}.

A precision automatic adiabatic calorimeter was used to measure the heat capacity over the temperature range from 78 to 350 K. The calorimeter was developed in the Materials and Thermochemistry Laboratory. The principle and structure of the calorimeter were described in detail elsewhere [2–4]. The temperature increment for each experimental heat capacity point was usually controlled about 3 K during the whole experimental process. The sample mass used for calorimetric measurements was 2.67897 g, which is equivalent to 0.010098 mol based on the molar mass $M = 265.3$ g 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 deviations of the calibration results from those of the smoothed curve lie within ±0.2%, while the uncertainty is within ±0.3%, as compared with the recommended values reported by Archer [5] of NIST in the temperature range from 80 to 405 K.

Results and discussion

DSC and TG analysis

The TG-DTG technique was applied to determine thermostability of NTBLP. It can be seen from Fig. 1 that three mass-loss processes took place in the TG-DTG curves with increase of temperature.

The first mass loss took place over the temperature range from 421.95 to 498.97 K (the maximum differential mass-loss temperature in DTG was 439.37 K), and the experimental mass-loss percentage was 43.23%, which is in agreement with the theoretical percent content (44.15%) of

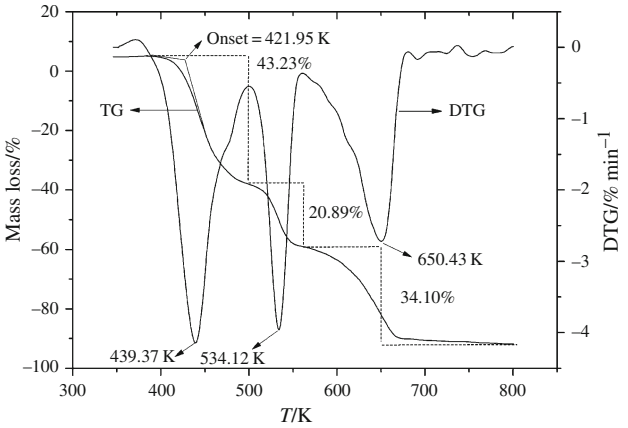
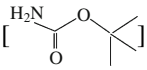
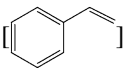


Fig. 1 TG-DTG curves of NTBLP

the part [] in NTBLP. The second mass-loss process happened over the temperature region from 498.97 to 562.54 K (the maximum differential mass-loss temperature in DTG was 534.12 K), and the actual mass-loss percentage was 20.89%, which approximately coincides with the theoretical percent content (17.34%) of this part [] in NTBLP. The last slow mass-loss process occurred over the range from 562.54 to 800 K with a real mass loss of 34.10%, which corresponds to the theoretical percent (37.31%) of the part [] in NTBLP.

Three distinct endothermic and one exothermic peaks were observed in DSC curve (Fig. 2). The first endothermic change without any considerable mass loss with a peak temperature of 361.63 K is attributed to a solid–liquid phase transition of NTBLP. The exothermic peak between 435.27 and 468.94 K corresponds to the first decomposition step in TG curve. The second endothermic peak

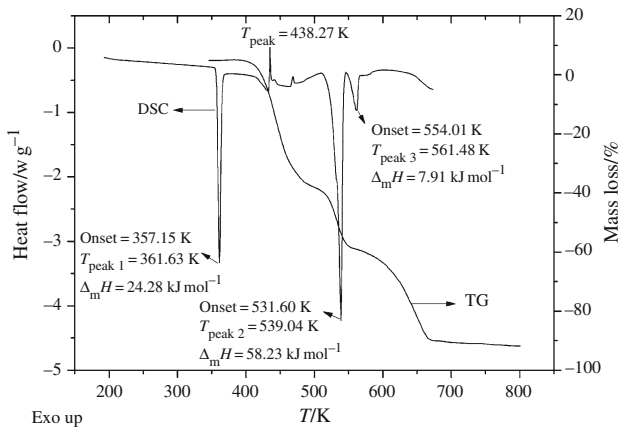


Fig. 2 DSC–TG curves of NTBLP

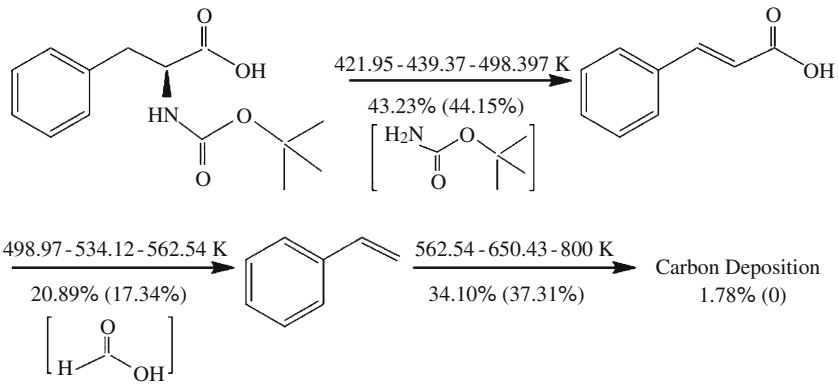
Table 1 Experimental molar heat capacities of NTBLP

T/K	$C_{p\cdot m}$/J K^{-1} mol^{-1}
78.370	128.5
81.053	130.7
84.326	132.5
87.214	135.0
90.046	138.7
92.912	140.7
95.762	143.7
98.608	146.9
102.577	150.6
106.520	154.9
109.325	157.5
112.185	160.4
115.040	163.4
117.900	165.7
120.755	168.5
123.618	171.6
126.484	174.1
129.353	177.0
132.230	180.2
135.114	182.4
138.003	185.4
140.857	188.1
143.722	189.8
146.593	192.2
149.435	195.1
153.131	198.5
156.799	201.8
159.618	204.6
162.474	208.0
165.307	211.2
168.178	214.2
171.083	216.9
173.967	220.1
176.828	222.9
179.666	225.6
182.545	228.3
185.457	233.1
188.352	235.0
191.225	237.3
194.079	240.0
196.970	242.4
199.904	244.2
203.476	249.1
207.005	253.8
209.853	257.0
212.767	260.1
215.736	263.1
218.685	264.9
221.622	269.5
224.542	273.7
227.447	276.5
230.299	280.2
233.240	287.8
236.247	282.9
239.172	289.3
242.621	295.2
246.146	293.3
249.129	295.1
252.099	297.7
255.057	300.9
258.001	304.4
260.935	306.0
263.851	308.1
266.756	311.6
269.646	315.0
272.502	316.8
275.445	318.3
278.402	319.8
281.252	317.4
284.075	319.0
286.883	324.4
289.777	329.8
292.741	334.1
295.690	334.7
298.652	337.3
301.604	341.9
304.545	345.9
307.478	349.6
310.404	354.4
313.325	358.1
316.235	360.8
319.138	363.4
322.029	365.9
324.909	370.6
327.876	373.3
330.932	373.8
333.976	378.1
337.010	382.7
340.030	387.4
343.032	391.2
346.017	395.3
348.969	403.5

corresponds to the decomposition process of [ ] in NTBLP with a mass loss of 20.89% from 498.97 to 562.54 K in TG curve.

The onset points, peak temperatures (T_{Peak}), and molar enthalpies of each endothermic process were shown in the Fig. 2.

According to the DSC and TG results, a possible mechanism for thermal decomposition of NTBLP was deduced as follows:



In above scheme, 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 NTBLP).

Heat capacity

The experimental molar heat capacities of NTBLP are listed in Table 1 and shown in Fig. 3.

The molar heat capacities are fitted to the following polynomial equation by the least square fitting. For the solid phase over the temperature range from 79 to 350 K:

$$C_{p\cdot m}/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 262.167 + 135.29836X - 16.04769X^2 - 21.12846X^3 + 20.44721X^4 + 23.50589X^5 \quad (1)$$

where X is the reduced temperature, and $X = [T - (T_{max} + T_{min})/2]/[(T_{max} - T_{min})/2]$, T is the experimental temperature (K). In this equation, T_{max} is the upper limit (350 K) and T_{min} is the lower limit (80 K) of experimental measurements, so $X = [(T/\mathrm{K} - 215)/135]$. Thus, it could make the value of X between +1 and −1. The correlation coefficient of the fitted curve $R^2 = 0.9996$.

Thermodynamic functions

The thermodynamic functions relative to the reference temperature of 298.15 K were calculated in the temperature range from 80 to 350 K with an interval of 5 K, using the polynomial equation of heat capacity and thermodynamic relationships as follows [6]:

Before melting of the sample,

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

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

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

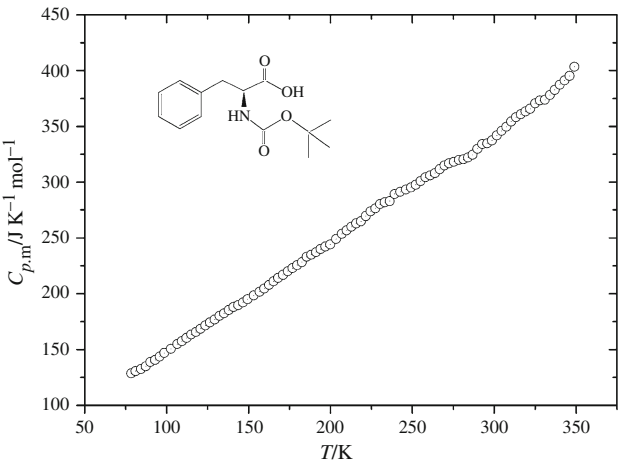


Fig. 3 Experimental molar heat capacity of NTBLP as a function of temperature

Table 2 Smoothed heat capacities and thermodynamic functions, $[H_T - H_{298.15K}]$ and $[S_T - S_{298.15K}]$, respectively of NTBLP

T/K	$C_{p\cdot m}$/ J K^{-1} mol^{-1}	$H_T - H_{298.15K}$/ kJ mol^{-1}	$S_T - S_{298.15K}$/ J K^{-1} mol^{-1}
80	128.9	−51.34	−279.71
85	134.0	−50.69	−271.74
90	138.9	−50.00	−263.94
95	143.8	−49.30	−256.30
100	148.6	−48.57	−248.81
105	153.3	−47.81	−241.45
110	158.0	−47.03	−234.21
115	162.6	−46.23	−227.09
120	167.3	−45.41	−220.07
125	172.0	−44.56	−213.14
130	176.8	−43.69	−206.30
135	181.6	−42.79	−199.54
140	186.4	−41.87	−192.84
145	191.2	−40.93	−186.22
150	196.2	−39.96	−179.65
155	201.1	−38.97	−173.13
160	206.1	−37.95	−166.67
165	211.1	−36.91	−160.25
170	216.2	−35.84	−153.87
175	221.3	−34.74	−147.53
180	226.4	−33.62	−141.22
185	231.6	−32.48	−134.95
190	236.7	−31.31	−128.71
195	241.8	−30.11	−122.49
200	247.0	−28.89	−116.30
205	252.1	−27.64	−110.15
210	257.1	−26.37	−104.01
215	262.2	−25.07	−97.90
220	267.2	−23.75	−91.82
225	272.1	−22.40	−85.76
230	277.0	−21.03	−79.73
235	281.8	−19.63	−73.72
240	286.6	−18.21	−67.74
245	291.3	−16.76	−61.78
250	295.9	−15.30	−55.85
255	300.5	−13.80	−49.94
260	305.1	−12.29	−44.06
265	309.6	−10.75	−38.21
270	314.0	−9.20	−32.38
275	318.5	−7.61	−26.58
280	322.9	−6.01	−20.80
285	327.4	−4.38	−15.04
290	331.9	−2.74	−9.30
295	336.6	−1.06	−3.59
298.15	339.5	0.00	0.00
300	341.3	0.63	2.11
305	346.1	2.35	7.79
310	351.1	4.09	13.45
315	356.4	5.86	19.11
320	361.9	7.66	24.77
325	367.8	9.48	30.42
330	374.0	11.33	36.08
335	380.7	13.22	41.76
340	387.9	15.14	47.45
345	395.8	17.10	53.17
350	404.2	19.10	58.92

Conclusions

The heat capacities of NTBLP were measured in the temperature range from 78 to 350 K by a high-precision automated adiabatic calorimeter. Based on the experimental heat capacities, one equation of heat capacity as a function of temperature was 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 350 K with temperature intervals of 5 K. The thermal stability of the compound was further studied using TG and DSC analyses and a possible mechanism for thermal decomposition was suggested.

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References

1. Tan ZC, Sun GY, Song YJ, Wang L, Han JR, 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;352–353:247–53.
2. Tan ZC, Shi Q, Liu BP, Zhang HT. A fully automated adiabatic calorimeter for heat capacity measurement between 80 and 400 K. J Therm Anal Calorim. 2008;92:367–74.
3. Tan ZC, Sun GY, Sun Y, Yin AX, Wang WB, Ye JC, et al. An adiabatic low-temperature calorimeter for heat capacity measurement of small samples. J Therm Anal. 1995;45:59–67.
4. Tan ZC, Sun LX, Meng SH, Li L, Zhang JB. Heat capacities and thermodynamic functions of p-chlorobenzoic acid. J Chem Thermodyn. 2002;341:1417–29.
5. Archer DG. Thermodynamic properties of synthetic sapphire (α-Al_2O_3), standard reference material 720 and the effect of temperature-scale differences on thermodynamic properties. J Phys Chem Ref Data. 1993;22:1441–52.
6. Di YY, Tan ZC, Sun XH, Wang MH, Xu F, Liu YF, et al. 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.