



Standard enthalpy of formation and heat capacities of 3,5-di-*tert*-butylsalicylic acid

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Abstract

The constant volume energy of combustion of crystalline 3,5-di-*tert*-butylsalicylic acid (*t*-BSA) in oxygen at 298.15 K was determined using combustion calorimeter to be $-8292.57 \pm 2.51 \text{ kJ mol}^{-1}$. The standard molar enthalpies of combustion and formation of 3,5-di-*tert*-butylsalicylic acid were derived, at $T = 298.15 \text{ K}$, $\Delta_c H_m^\ominus = -8302.48 \pm 2.51 \text{ kJ mol}^{-1}$ and $\Delta_f H_m^\ominus = -744.30 \pm 3.21 \text{ kJ mol}^{-1}$, respectively. The heat capacities of the compound were measured with an adiabatic calorimeter over the temperature range from 79 to 351 K. No indication of any phase transition or thermal anomaly was observed in this temperature range. The fusion and evaporation behavior of the compound were examined by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The molar enthalpy and entropy of fusion, $\Delta_{\text{fus}} H_m^\ominus$ and $\Delta_{\text{fus}} S_m^\ominus$, at $T = 437.5 \text{ K}$, were determined to be $22.92 \pm 0.55 \text{ kJ mol}^{-1}$ and $139.4 \pm 3.3 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively; and the molar enthalpy and entropy of evaporation, $\Delta_{\text{vap}} H_m^\ominus$ and $\Delta_{\text{vap}} S_m^\ominus$, at $T = 477.5 \text{ K}$, were obtained as $83.88 \pm 2.1 \text{ kJ mol}^{-1}$ and $341.7 \pm 8.4 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

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1. Introduction

3,5-Di-*tert*-butylsalicylic acid (*t*-BSA) (formula: $\text{C}_{15}\text{H}_{22}\text{O}_3$; molecular weight: 250.34; CAS registry number: 19715-19-6; molecular structure: see Fig. 1) is an important substance widely used as synthetic materials, such as pressure sensitive recording paper, agriculture chemicals, antioxidants, and so on. 3,5-Di-*tert*-butylsalicylic acid and its derivatives, both metal salts and complexes, possess interes-

ting triboelectrical properties. They are frequently used as charge control additives (CCAs) in dry xerographic toner at low concentrations (1–5 wt.%) to control the charging characteristic of toners [1–3].

Several compounds in the family of 3,5-di-*tert*-butylsalicylic acid and its derivatives have considerable commercial importance and no thermodynamic parameters of these materials were available till now. Knowledge of thermochemical properties of these materials would be useful for working out technological processes of synthesis and purification of the materials, and searching for energy-saving variants of the realization of these processes.

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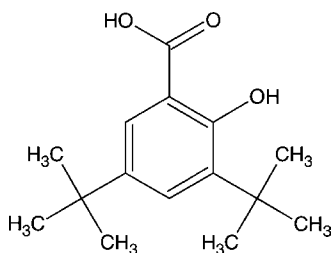


Fig. 1. Molecular structure of 3,5-di-*tert*-butylsalicylic acid.

Combustion calorimetry has been a classic method to obtain the standard enthalpy of formation for many organic compounds. These thermodynamic quantities are very important for production and utilization of fuels, quantum chemistry, computer-aided molecular designs for drugs and new materials, destruction of waste materials in incinerators, and so on [4–7]. Adiabatic calorimetry is an accurate method to obtain the heat-capacity data for many condensed matters. We are interested in determining thermodynamic properties of 3,5-di-*tert*-butylsalicylic acid and its derivatives.

In the present work, the constant-volume energy of combustion of the titled compound was determined by a rotating-bomb oxygen combustion calorimeter, and the standard molar enthalpy of combustion and formation of the compound were derived. Heat capacities of the compound from 79 to 351 K were measured using an adiabatic calorimeter. The fusion and evaporation behavior of the compound were examined by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

3,5-Di-*tert*-butylsalicylic acid (white crystalline powder), was purchased from commercial source and recrystallized from *n*-heptane for two times before use. The mole fraction purity of 3,5-di-*tert*-butylsalicylic acid was greater than 99.9% as determined by HPLC measurement. The FT-IR and ^1H NMR spectrum and elemental analysis of the sample showed no impurities in the sample.

2.2. Combustion calorimetry

The constant-volume energy of combustion of the compound were determined with a RBC-II type rotating-bomb combustion calorimeter constructed in Northwest University, Xi'an, PR China. More comprehensive descriptions and detailed procedure of the combustion calorimeter can be found in earlier papers [8–10]. The NIST Standard Reference Material 39i, benzoic acid, was used to calibrate the combustion calorimeter. The inaccuracy of the calorimeter was determined to be within $\pm 0.05\%$.

2.3. Adiabatic calorimetry

The heat-capacity measurements were carried out in a small sample adiabatic calorimeter over the temperature range from 79 to 351 K. The adiabatic calorimeter was described in detail elsewhere [11–13]. The apparatus was based on Nernst step heating method [14]. A temperature increment ΔT is caused by supplying a known quantity of electric energy ΔE , and the temperature of the calorimeter cell is measured when temperature disturbance in the cell due to the energy supply has subsided and thermal equilibrium at the new temperature is attained. The total heat capacity C of the cell plus sample is given as the ratio of the supplied electric energy to the temperature increment, namely as $C = \Delta E / \Delta T$. Heat capacity of the sample is obtained by subtracting the heat capacity of the empty calorimeter cell determined in a separate experiment from the total heat capacity.

In order to verify the reliability of the adiabatic calorimeter, the molar heat capacities of synthetic sapphire ($\alpha\text{-Al}_2\text{O}_3$, Standard Reference Material 720, the National Institute of Standards and Technology) were measured. The deviations of our experimental results from the smoothed curve were within $\pm 0.5\%$ compared with the recommended values of NIST in the entire temperature range of 77–380 K [15].

The sample mass for the heat-capacity measurement was 2.4623 g, which was equivalent to 9.8358 mmol, based on its molar mass of $250.34 \text{ g mol}^{-1}$.

2.4. Thermal analysis

The TG–DTA test was performed in a thermal analyzer, model Setsys 16/18 from Setaram, France

and under dynamic atmosphere of high purity N₂ (99.999%) with a flow rate of 60 ml min⁻¹ and a heating rate of 10 K min⁻¹. The DSC experiments were carried out in a differential scanning calorimeter, model DSC 141 from Setaram, France. The crucibles containing the sample and the empty crucibles used as the reference were made of aluminium. The samples were lightly pressed into the bottom of the pan to ensure good thermal contact. Open pans were used in the present experiments. The calibrations of the temperature and heat flux scales of the calorimeter were performed; the temperature scale was calibrated by measuring the melting temperatures of Hg, In, Sn, Pb, and Zn, at different heating rates, and the heat flux scale was calibrated by the Joule effect using the same standards. Measurements of the temperature of fusion and of the enthalpy of fusion of benzoic acid (NIST, Standard Reference Material 39i) were made in our laboratory to check the accuracy of the instrument. The experimental conditions were the following: temperature ramp rate, 10 K min⁻¹, nitrogen flow rate, 50 ml min⁻¹.

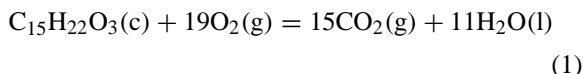
3. Results and discussion

3.1. The standard molar enthalpy of formation

The constant-volume energy of combustion of *t*-BSA, $\Delta_c U_m^\ominus$, determined by a rotating-bomb oxygen combustion calorimeter was -8292.57 ± 2.51 kJ mol⁻¹. The detailed values were summarized in Table 1.

The standard molar enthalpy of combustion of *t*-BSA, $\Delta_c H_m^\ominus$, refers to the combustion enthalpy

change of the following ideal combustion reaction at 298.15 K and 101.325 kPa.



The standard molar enthalpy of combustion of *t*-BSA was calculated from the experimental energy of combustion at 298.15 K by Eq. (2):

$$\Delta_c H_m^\ominus = \Delta_c U_m^\ominus + \Delta nRT \quad (2)$$

where n is the total amount (in moles) of gas present as products or reactants, $R = 8.314510$ J mol⁻¹ K⁻¹ [16], $T = 298.15$ K.

The standard molar enthalpy of formation of *t*-BSA, $\Delta_f H_m^\ominus$, is derived by Hess's law according to the following thermochemical equation:

$$\begin{aligned} \Delta_{f,t\text{-BSA}(\text{s})} H_m^\ominus &= [15\Delta_{f,\text{CO}_2(\text{g})} H_m^\ominus + 11\Delta_{f,\text{H}_2\text{O}(\text{l})} H_m^\ominus] \\ &\quad - \Delta_{c,t\text{-BSA}(\text{s})} H_m^\ominus \end{aligned} \quad (3)$$

where $\Delta_{f,\text{CO}_2(\text{g})} H_m^\ominus = -393.51 \pm 0.13$ kJ mol⁻¹, $\Delta_{f,\text{H}_2\text{O}(\text{l})} H_m^\ominus = -285.83 \pm 0.042$ kJ mol⁻¹ [17,18]. The standard molar enthalpy of combustion and formation of *t*-BSA are derived: $\Delta_c H_m^\ominus = -8302.48 \pm 2.51$ kJ mol⁻¹ and $\Delta_f H_m^\ominus = -744.30 \pm 3.21$ kJ mol⁻¹, at $T = 298.15$ K, respectively. The results are tabulated in Table 2.

The uncertainty for the $\Delta_f H_m^\ominus$ of *t*-BSA was calculated as follows:

$$\begin{aligned} s[\Delta_f H_m^\ominus(t\text{-BSA, cr})] &= \{[15s \Delta_f H_m^\ominus(\text{CO}_2, \text{g})]^2 + [11s \Delta_f H_m^\ominus(\text{H}_2\text{O, l})]^2 \\ &\quad + s[\Delta_c H_m^\ominus(t\text{-BSA, cr})]^2\}^{1/2} \end{aligned} \quad (4)$$

Table 1

Energy of combustion of 3,5-di-*tert*-butylsalicylic acid in oxygen at 298.15 K ($M = 250.34$ g mol⁻¹)^a

No.	m (g)	Q_c (J)	Q_N (J)	ΔT (K)	$\Delta_{c,t\text{-BSA}(\text{s})} U_m$ (kJ mol ⁻¹)
1	0.98420	12.60	39.17	1.8140	-8292.48
2	1.00741	12.60	39.50	1.8557	-8287.88
3	0.97236	12.60	38.99	1.7907	-8285.52
4	0.98305	12.60	39.41	1.8128	-8296.62
5	0.99002	12.60	39.33	1.8269	-8302.41
6	0.96685	12.60	38.41	1.7816	-8290.48
Mean					-8292.57 ± 2.51

^a m : mass of sample; Q_c : heat of combustion of igniting wire; Q_N : heat of formation of nitric acid; ΔT : temperature increment; $\Delta_{c,t\text{-BSA}(\text{s})} U_m$: energy of combustion of sample.

Table 2

Standard molar enthalpy of combustion and formation of 3,5-di-*tert*-butylsalicylic acid ($M = 250.34 \text{ g mol}^{-1}$)

Compound	$\Delta_{\text{c},t\text{-BSA(s)}}H_{\text{m}}^{\ominus} (\text{kJ mol}^{-1})$	$\Delta_{\text{f},t\text{-BSA(s)}}H_{\text{m}}^{\ominus} (\text{kJ mol}^{-1})$
3,5-di- <i>tert</i> -butylsalicylic acid	-8302.48 ± 2.51	-744.30 ± 3.21

where $s(\Delta_{\text{f}}H_{\text{m}}^{\ominus})$ represents the uncertainties in the enthalpies of formation of gaseous CO_2 , liquid H_2O , and $s(\Delta_{\text{c}}H_{\text{m}}^{\ominus})$ represents the uncertainty in the enthalpy of combustion of crystalline 3,5-di-*tert*-butylsalicylic acid.

3.2. Heat capacity

The experimental molar heat capacities of 3,5-di-*tert*-butylsalicylic acid over the temperature range from 79 to 351 K are listed in Table 3 and shown in Fig. 2. No indication of any phase transition or thermal anomaly was observed in this temperature range.

The experimental molar heat capacities are fitted to the following polynomial in reduced temperature (X), by means of the least square fitting:

$$C_{p,m} (\text{J K}^{-1} \text{mol}^{-1}) = 286.98622 + 183.46817X - 15.00522X^2 - 40.12048X^3 + 4.71481X^4 + 27.3303X^5 \quad (5)$$

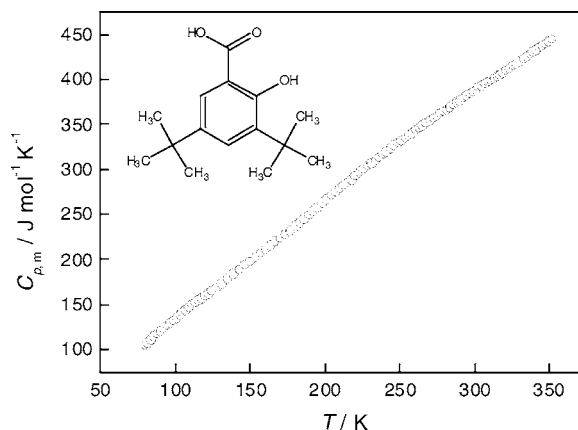


Fig. 2. Experimental molar heat capacities of 3,5-di-*tert*-butylsalicylic acid determined by adiabatic calorimetry.

where $X = (T - 215)/136$, and T is the absolute temperature. The correlation coefficient of the fitted curve, $R^2 = 0.99997$.

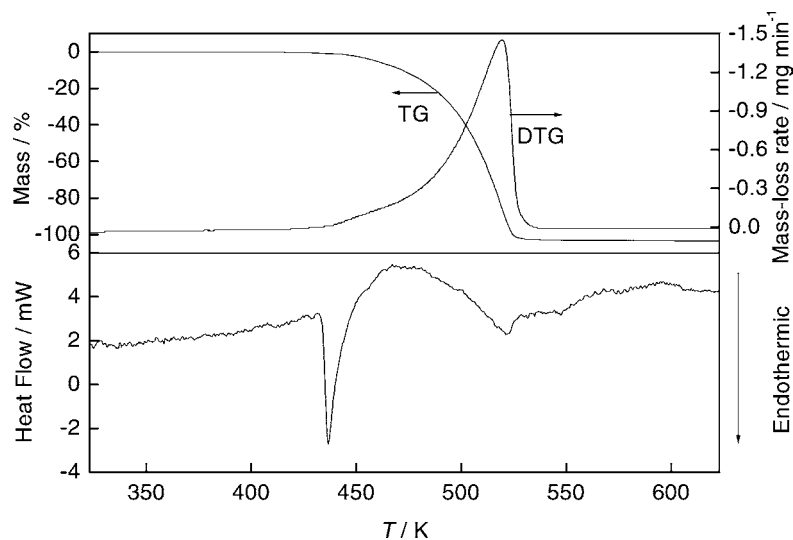


Fig. 3. TG–DTG–DTA curves of 3,5-di-*tert*-butylsalicylic acid.

Table 3

Experimental molar heat capacities of 3,5-di-*tert*-butylsalicylic acid ($M = 250.34 \text{ g mol}^{-1}$)

T (K)	C_p (J mol $^{-1}$ K $^{-1}$)	T (K)	C_p (J mol $^{-1}$ K $^{-1}$)	T (K)	C_p (J mol $^{-1}$ K $^{-1}$)
79.15	106.0	179.70	237.9	276.18	363.3
81.11	108.6	182.73	241.5	278.44	365.7
83.04	112.2	185.37	245.8	280.68	367.5
84.92	115.5	188.41	250.4	282.88	370.2
86.96	118.4	191.44	254.6	285.08	373.1
89.30	120.8	194.37	258.4	287.27	374.9
91.55	123.9	197.31	263.5	289.39	377.2
93.75	127.2	200.21	267.5	291.52	380.5
95.91	130.5	203.41	272.2	293.71	383.0
98.03	133.3	206.21	275.5	295.83	385.0
100.11	135.9	208.73	279.0	297.93	387.5
102.17	139.1	211.74	283.3	300.00	389.4
104.19	142.0	214.29	286.4	302.09	392.3
106.23	144.6	216.96	289.7	304.17	393.7
108.34	147.6	219.70	293.7	306.21	396.0
110.61	150.9	222.38	298.0	308.27	398.2
112.85	153.2	225.08	301.1	310.31	400.5
115.03	155.9	227.65	305.0	312.33	401.9
117.18	157.5	230.23	307.6	314.39	404.9
119.32	161.1	232.88	310.8	316.29	405.8
121.40	163.0	235.38	314.3	318.26	408.3
123.47	166.0	237.95	317.5	320.16	410.7
127.20	169.7	240.38	321.0	322.13	413.0
130.53	174.5	242.85	324.3	324.87	416.3
134.39	179.7	245.31	327.5	327.47	418.8
138.26	185.1	247.84	330.4	329.86	421.1
141.97	190.0	250.30	332.7	332.05	424.2
145.53	194.9	252.73	335.8	334.23	427.0
149.24	199.1	255.15	338.7	336.34	429.2
152.73	203.7	257.58	341.0	338.45	431.6
156.21	208.5	259.94	344.8	340.45	433.9
159.55	212.5	262.33	347.3	342.46	436.9
162.95	216.3	264.65	349.6	344.47	438.7
166.21	221.3	266.97	352.4	346.44	440.1
169.55	224.8	269.32	355.6	348.52	443.2
172.78	228.7	271.62	357.8	350.69	446.2
175.98	232.6	273.91	360.2		

3.3. Thermal analysis

The TG–DTA measurements were carried out in N_2 atmosphere. The TG–DTG–DTA results were presented in Fig. 3. It can be seen from the mass-loss curve that most of the activities occur in the temperature range from 443 to 533 K in a single step. No residue was founded in the crucible after the experiment was completed. Two obvious peaks were observed from the DTA curve, and the later one accorded with the mass-loss in the TG curve. So we consider

that the first peak in the DTA curve corresponded to the fusion of *t*-BSA, because no mass-loss founded in the TG curve. The FT-IR spectrums of the original sample of *t*-BSA and the product of vapor condensation of *t*-BSA were the same. So we consider that the second peak in the DTA curve and the mass-loss in the TG and DTG curves corresponded to the evaporation of *t*-BSA, instead of decomposition.

From the DSC curve (Fig. 4), the melting point of *t*-BSA was determined to be 437.5 ± 0.1 K, the melting peak temperature was 440.5 ± 0.4 K, and the molar

Table 4

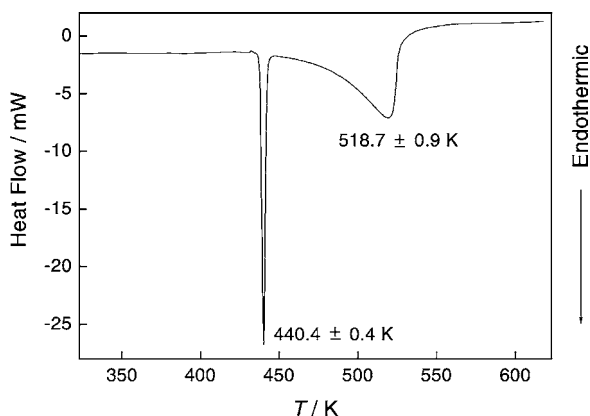
Fusion behavior of 3,5-di-*tert*-butylsalicylic acid determined by differential scanning calorimetry (DSC)

No.	<i>m</i> (mg)	Onset temperature (K)	Peak temperature (K)	$\Delta_{\text{fus}}H_{\text{m}}^{\ominus}$ (kJ mol ⁻¹)	$\Delta_{\text{fus}}S_{\text{m}}^{\ominus}$ (J mol ⁻¹ K ⁻¹)
1	4.1	437.43	440.20	23.387	53.465
2	4.0	437.43	440.91	23.053	52.701
3	4.4	437.64	440.14	22.319	50.999
Mean		437.5 ± 0.1	440.4 ± 0.4	22.92 ± 0.55	52.39 ± 1.26

Table 5

Evaporation behavior of 3,5-di-*tert*-butylsalicylic acid determined by differential scanning calorimetry (DSC)

No.	<i>m</i> (mg)	Onset temperature (K)	Peak temperature (K)	$\Delta_{\text{vap}}H_{\text{m}}^{\ominus}$ (kJ mol ⁻¹)	$\Delta_{\text{vap}}S_{\text{m}}^{\ominus}$ (J mol ⁻¹ K ⁻¹)
1	4.1	479.62	517.83	85.676	178.633
2	4.0	476.24	518.58	84.335	177.085
3	4.4	476.61	519.62	81.624	171.260
Mean		477.5 ± 1.9	518.7 ± 0.9	83.88 ± 2.06	175.66 ± 3.89

Fig. 4. DSC curve of 3,5-di-*tert*-butylsalicylic acid.

enthalpy and entropy of fusion were determined as 22.92 ± 0.55 kJ mol⁻¹ and 52.39 ± 1.26 J mol⁻¹ K⁻¹, respectively (Table 4). Evaporation of *t*-BSA started from 477.5 ± 1.9 K, the maximum rate of evaporation was at 518.7 ± 0.9 K, and the molar enthalpy and entropy of evaporation were obtained to be 83.88 ± 2.1 kJ mol⁻¹ and 175.66 ± 3.89 J mol⁻¹ K⁻¹, respectively (Table 5).

4. Conclusion

In this work, we report the standard molar enthalpy of formation, heat capacities from 79 to

351 K, and the fusion and evaporation behavior of 3,5-di-*tert*-butylsalicylic acid.

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