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Short communication

Heat capacity and thermodynamic properties of benzyl disulfide ($C_{14}H_{14}S_2$)

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Abstract

Heat capacities of benzyl disulfide have been measured with a high-precision automatic adiabatic calorimeter over the temperature range from 80 to 377 K. The melting point, molar enthalpy and entropy of fusion were determined to be 341.72 ± 0.07 K, 44965 ± 10 J mol^{-1} and 130.78 ± 0.11 J K^{-1} mol^{-1}, respectively. The thermal stability and the kinetics of thermal decomposition of the compound were investigated in air by means of thermogravimetry (TG) and differential thermal analysis (DTA). TG/DTA curves showed that the decomposition proceeded through one step. The activation energy and the reaction order for one-step decomposition was calculated to be 110.7 ± 12.3 kJ mol^{-1} and 1.2 ± 0.2 through Kissinger method.

Keywords: Benzyl disulfide; Heat capacity; Adiabatic calorimetry; Thermal decomposition; Activation energy

1. Introduction

Benzyl disulfide (formula: $C_{14}H_{14}S_2$; molecular weight: 246.39; CAS registry number: 150-60-7; molecular structure: see Fig. 1) has a harsh, burnt-caramel odor and is used in manufacturing corrosion inhibitors, fragrance compounds, high-pressure lubricant additives and other organic compounds.

The melting point of the compound has been reported to be 342 K [1]. However, no report about thermodynamic data and the kinetics of thermal decomposition was found in the literature.

In the present work, low-temperature heat capacity of the sample was measured from 80 to 377 K. The thermal stability and the kinetics of thermal decomposition of the compound were also investigated in air by means of thermogravimetry (TG) and differential thermal analysis (DTA).

2. Experimental

2.1. Sample

The benzyl disulfide (white crystalline powder) was purchased from MERCK-Schuchardt. The labeled mass fraction is >0.99. The sample was determined by HPLC analysis to be 99.4% mol fraction. The sample was used without further purification. Finally, the IR and ^{1}H NMR were employed to affirm the structure of the sample.

2.2. Adiabatic calorimetry

Heat capacity measurements were performed with a precision automatic adiabatic calorimetric system which has been described in detail [2]. The evacuated chamber was kept within ca. 1×10^{-3} Pa during the heat capacity measurement.

Before the heat capacity measurement of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material-α-Al_2O_3 (NBS SRM-720). The deviations of our calibration results from the recommended value reported by Ditmars et al. of the former National Bureau of Standards [3] are within ±0.2% in the temperature range of (80–400 K).

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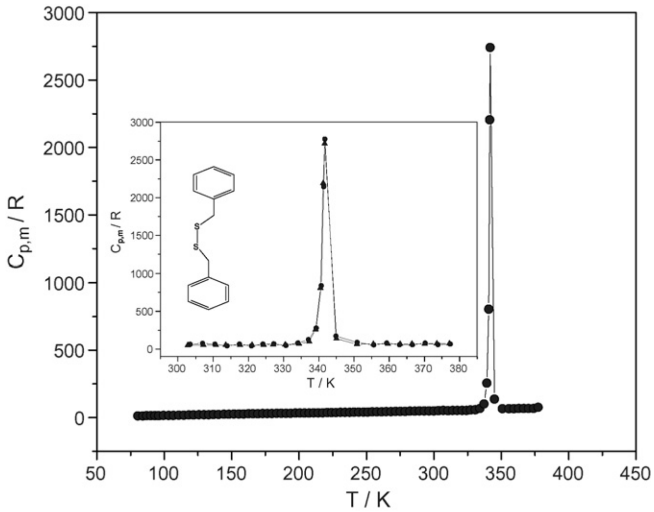

Fig. 1. Experimental molar heat capacities against temperature for benzyl disulfide.

2.3. Thermal analysis

Thermal analysis measurements (thermogravimetry, TG; differential thermal analysis, DTA) were carried out by means of a Henven HCT-1/2 thermal analyzer, China. Thermal analysis experiments TG/DTA were performed in air, at heating rates of 10, 20, 30, 40 °C/min.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacity of benzyl disulfide over the temperature range from 80 to 377 K are listed in Table 1 and shown in Fig. 1. The heat capacities of the sample increased with the temperature in the two regions of 80–303 K and 355–377 K. No phase transition or thermal anomaly was found, which indicated that the structure of the sample was stable in these temperature ranges. However, a thermal anomaly was observed in the temperature range from 303 to 355 K with a peak temperature at about 341.8 K. The evidence of fusion of the sample was found after the heat capacity measurement.

The molar heat capacities were fitted to the two following polynomial equations by least square fitting.

For the solid phase over the temperature range of (80–303 K):

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 270.2993 + 136.4588X - 2.8083X^2 + 77.6374X^3 - 32.1240X^4 - 54.6362X^5 + 32.9213X^6,$$

where X is the reduced temperature, and $X = \{T\,(\mathrm{K}) - 191.5\}/111.5$ and T is the absolute temperature. The correlation coefficient $R^2 = 0.9997$.

Table 1
Experimental molar heat capacities of benzyl disulfide ($M = 246.39\,\mathrm{g\,mol^{-1}}$) (The first series of measurements) ($R = 8.314472\,\mathrm{J\,mol^{-1}\,K^{-1}}$)[a]

T (K)	$C_{p,m}/R$
80.30	13.029
84.06	13.445
87.01	13.649
90.01	13.992
92.93	14.284
95.91	14.676
99.41	15.371
103.24	16.238
106.95	16.992
110.69	17.727
114.47	18.511
118.16	19.255
121.87	20.394
125.68	21.272
129.35	21.621
132.96	22.361
136.61	23.104
140.35	23.696
144.38	24.690
147.99	25.462
151.70	26.174
155.35	26.762
158.92	27.492
162.44	28.112
165.91	28.741
169.42	29.302
172.99	29.865
176.50	30.386
179.96	30.916
183.38	31.350
186.84	31.913
190.36	32.401
193.83	32.877
197.26	33.350
200.65	33.710
204.00	34.190
207.40	34.639
210.85	35.113
214.25	35.607
217.60	36.164
220.90	36.686
224.17	37.350
227.41	38.092
230.64	39.022
234.10	39.928
237.58	40.094
240.90	40.755
244.30	41.089
247.70	41.186
251.00	41.803
254.37	42.514
257.79	43.238
261.22	43.724
264.69	44.461
268.17	45.079
271.64	45.836
275.11	46.456
278.65	47.146
282.26	47.700
285.84	48.362
289.39	49.357
292.90	50.178
296.45	50.178

Table 1 (*Continued*)

T (K)	$C_{p,m}/R$
299.98	50.784
303.49	51.448
307.00	52.678
310.49	52.012
313.97	53.354
317.47	52.944
320.92	53.327
324.15	53.922
327.24	57.715
330.68	59.475
334.08	68.067
337.09	101.34
339.29	255.37
340.75	804.61
341.44	2204.1
341.77	2740.5
344.92	136.90
350.93	65.600
355.68	66.167
359.31	66.708
362.99	67.247
366.65	67.678
370.29	68.054
373.91	68.517
377.39	77.356

[a] Obtained from Ref. [4].

For the liquid phase over the temperature range of 355–377 K:

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 563.4018 + 17.0120X - 27.9875X^2 - 52.1764X^3 + 51.2029X^4 + 76.3749X^5,$$

in which $X = \{T\ (\mathrm{K}) - 366\}/11$. The correlation coefficient $R^2 = 0.9990$.

3.2. Melting point, molar enthalpy and molar entropy of fusion

Heat capacity measurements of the sample in the temperature range of phase change were made twice so that the repeatability of the fusion process was verified. The melting point was determined by a progressive approach with step-by-step heating. The molar enthalpy, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$, and molar entropy, $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$, of fusion can be calculated from the heat capacity data by following equations [5,6]:

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = \frac{Q - n\int_{T_\mathrm{i}}^{T_\mathrm{m}} C_{p,\mathrm{s}}\,\mathrm{d}T - n\int_{T_\mathrm{m}}^{T_\mathrm{f}} C_{p,\mathrm{l}}\,\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} H_0\,\mathrm{d}T}{n} \quad (1)$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}} = \frac{\Delta H_{\mathrm{m}}}{T} \quad (2)$$

The calculated results are listed in Table 2.

Table 2
Thermodynamic parameters of benzyl disulfide from heat capacity measurements

Thermodynamic parameters	Series 1	Series 2	Mean value	S.D.
T_m (K)	341.77	341.67	341.72	±0.07
$\Delta_{\mathrm{fus}}H_\mathrm{m}/(\mathrm{J\,mol^{-1}})$	44688	44702	44695	±9.9
$\Delta_{\mathrm{fus}}S_\mathrm{m}/(\mathrm{J\,K^{-1}\,mol^{-1}})$	130.70	130.86	130.78	±0.11

3.3. Thermodynamic functions of benzyl disulfide

According to the polynomial equation of heat capacity and thermodynamic relationship, the thermodynamic function data of the sample relative to the reference temperature 298.15 K were calculated in the temperature range 80–303 K and 355–375 K with an interval of 5 K. The thermodynamic relationships used for the calculation are as follows:

Before the melting of the sample,

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

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

After the melting of the sample,

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

$$S_\mathrm{T} - S_{298.15} = \int_{298.15}^{T_\mathrm{i}} \left[\frac{C_{p,m}(\mathrm{s})}{T}\right] \mathrm{d}T + \Delta_{\mathrm{fus}}H_\mathrm{m}/T_\mathrm{m} + \int_{T_\mathrm{f}}^{T} \left[\frac{C_{p,\mathrm{m}}(\mathrm{l})}{T}\right] \mathrm{d}T \quad (6)$$

in which T_i is the temperature at the start of the melt; T_f the temperature at the end of melt. $C_{p,\mathrm{m}}(\mathrm{s})$ and the $C_{p,\mathrm{m}}(\mathrm{l})$ are heat capacity of the solid sample and the liquid one, respectively.

The values of thermodynamic function $H_\mathrm{T} - H_{298.15}$, $S_\mathrm{T} - S_{298.15}$ are listed in Tables 3 and 4, respectively.

3.4. Thermal stability and the kinetics of thermal decomposition of benzyl disulfide

TG/DTA curves of benzyl disulfide in air at heating rate of 10 °C/min are shown in Fig. 2. Two obvious endothermic peaks appear in DTA curve; the first endothermic peak corresponds to the melting of benzyl disulfide with a peak temperature of 341.62 K. The second endothermic peak associated with decomposition appears in the temperature range from 509.4 to 569.6 K, with the peak temperature at 543.86 K. The TG curve shows that the thermal decomposition of this compound occurs in one step.

The activation energy (E_a) value of the one-step degradation for this compound in air was calculated by the Kissinger

Table 3
Calculated thermodynamic function data of benzyl disulfide in the solid phase

T (K)	$C_{p,m}/R$	$(H_T - H_{298.15})/R$ (K)	$(S_T - S_{298.15})/R$
80	13.088	−6.931	−36.48
85	13.403	−6.865	−35.68
90	13.953	−6.796	−34.89
95	14.685	−6.725	−34.11
100	15.555	−6.649	−33.34
105	16.524	−6.569	−32.55
110	17.558	−6.484	−31.76
115	18.630	−6.393	−30.96
120	19.718	−6.298	−30.15
125	20.805	−6.196	−29.32
130	21.876	−6.090	−28.49
135	22.923	−5.978	−27.65
140	23.937	−5.860	−26.79
145	24.915	−5.738	−25.94
150	25.855	−5.611	−25.07
155	26.758	−5.480	−24.21
160	27.624	−5.344	−23.34
165	28.457	−5.204	−22.48
170	29.261	−5.059	−21.62
175	30.041	−4.911	−20.75
180	30.802	−4.759	−19.90
185	31.549	−4.603	−19.04
190	32.288	−4.443	−18.19
195	33.024	−4.280	−17.34
200	33.762	−4.113	−16.50
205	34.507	−3.942	−15.66
210	35.262	−3.768	−14.82
215	36.030	−3.590	−13.98
220	36.815	−3.408	−13.15
225	37.618	−3.222	−12.31
230	38.440	−3.032	−11.48
235	39.280	−2.837	−10.64
240	40.139	−2.639	−9.81
245	41.014	−2.436	−8.97
250	41.904	−2.229	−8.13
255	42.806	−2.017	−7.29
260	43.717	−1.800	−6.45
265	44.633	−1.580	−5.60
270	45.551	−1.354	−4.76
275	46.467	−1.124	−3.92
280	47.379	−0.889	−3.07
285	48.282	−0.650	−2.23
290	49.175	−0.407	−1.38
295	50.057	−0.159	−0.53
298.15	50.607	0.000	0
300	50.928	0.094	0.31
303	51.446	0.248	0.83

method [7,8].

$$\ln\frac{\beta}{T_{max}^2} = -\frac{E_a}{R}\left(\frac{1}{T_{max}}\right) + \ln\frac{nAR(1-a_m)^{n-1}}{E_a} \quad (7)$$

Table 4
Calculated thermodynamic function data of benzyl disulfide in the liquid phase

T (K)	$C_{p,m}/R$	$(H_T - H_{298.15})/R$ (K)	$(S_T - S_{298.15})/R$
355	65.598	5.376	16.56
360	66.764	5.709	17.48
365	67.553	6.044	18.41
370	67.925	6.383	19.33
375	69.873	6.725	20.25

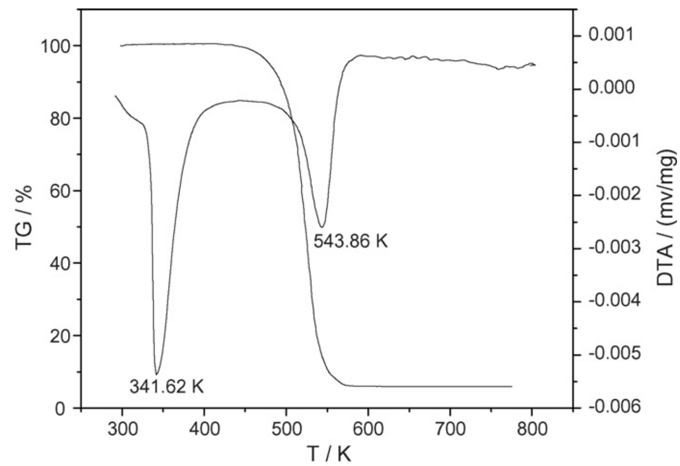

Fig. 2. TG/DTA curves of benzyl disulfide in air at heating rate of 10 °C/min.

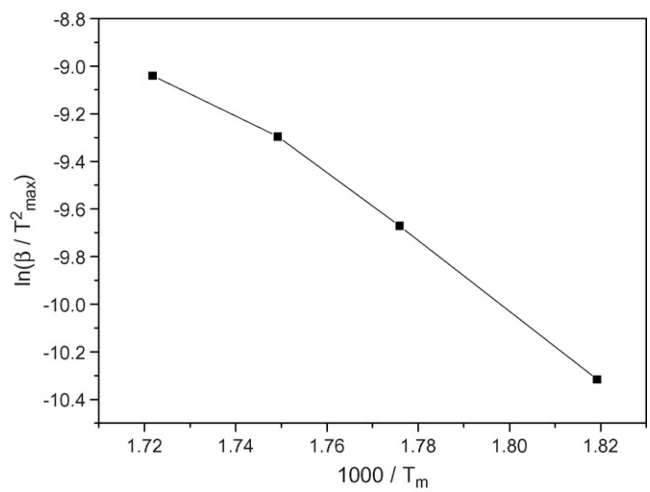

Fig. 3. Determination of activation energy for benzyl disulfide by Kissinger method.

where A is the pre-exponential factor, E_a the apparent activation energy of the degradation reaction, R the universal gas constant, and β is the heating rate. In this method, the activation energy is calculated from the T_{max}, the temperature at which the maximum degradation occurs for different heating rates by assuming that a_m or weight loss percentage at T_{max} is constant. Thus, the activation energy can be computed from the linear dependence of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$ plot (Fig. 3) for various heating rates and following the relationship of $E_a = -R \times$ slope. The E_a of benzyl disulfide was found to be 110.7 ± 12.3 kJ mol^{-1}.The reaction order obtained was 1.2 ± 0.2.

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References

[1] I.F. Trother, H.W. Thompson, J. Chem. Soc. 1946 (1946) 481.

[2] Z.C. Tan, G.Y. Sun, A.X. Yin, W.B. Wang, J.C. Ye, L.X. Zhou, J. Therm. Anal. 4 (1995) 59.
[3] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. Natl. Bur. Stand. 87 (1982) 159.
[4] J.M. Peter, N.T. Barry, J. Phys. Chem. Ref. Data 28 (1999) 1713.
[5] Y.Y. Di, Z.C. Tan, X.M. Wu, S.H. Meng, S.S. Qu, Thermchim. Acta 356 (2000) 143.
[6] B.P. Liu, Z.C. Tan, J.L. Lu, X.Z. Lan, L.X. Sun, F. Xu, P. Yu, J. Xing, Thermchim. Acta 397 (2003) 67.
[7] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[8] S. Montserrat, J. Malek, P. Colomer, Thermochim. Acta 313 (1998) 83.