ELSEVIER

Thermochimica Acta 342 (1999) 53–57

thermochimica acta

www.elsevier.com/locate/tca

A thermochemical study of 1,10-decanediol

Li Li, Zhi-Cheng Tan*, Shuang-He Meng, Yong-Ji Song

Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Academia Sinica, Dalian 116023, China

Received 16 March 1999; received in revised form 12 August 1999; accepted 17 August 1999

Abstract

A thermochemical study of 1,10-decanediol has been performed using adiabatic calorimetry and thermoanalytical techniques. The low-temperature heat capacities of 1,10-decanediol were determined precisely with a small sample automated adiabatic calorimeter in the temperature range from 80 to 370 K. A solid–liquid phase transition was found between 331 and 354 K and the temperature, enthalpy and entropy of the transition were determined to be 345.55 K, 44.2 kJ mol^{-1} and 127.9 J K^{-1} mol^{-1}, respectively. The melting point, enthalpy and entropy of fusion were also measured by DSC, respectively. The kinetic parameters of thermal decomposition of the compound were determined with the TG and DTG curves. The thermal conductivity and viscosity of the compound at various temperatures were also measured.

Keywords: 1,10-Decanediol; Heat capacity; Adiabatic calorimetry; Thermal decompositon; TG

1. Introduction

1,10-Decanediol (DDL) $C_{10}H_{22}O_2$, is an organic chemical, also named as decamethylene glycol. It is a white crystal with a needle crystalline shape. DDL is a kind of medicine intermediate, and it is widely used in the field of organic reactions. It is necessary to further understand its nature and improve its basic data.

Since heat capacity is a basic quantity for evaluation of thermodynamic properties, heat capacity measurements of this compound were carried out over the temperature range between 80 and 370 K with an automated adiabatic calorimeter [1]. The purity of DDL was determined by the adiabatic calorimeter. The melting temperature, the molar enthalpy and entropy of fusion were determined by DSC also. The kinetic parameters of the decomposition of DDL were determined with the TG and DTG curves.

The thermal conductivity and viscosity of the compound at various temperatures were also measured, which had not been reported in the literature before.

2. Experimental

2.1. Sample

The sample for this experiment was from Fluka Chemie AG CH-9471 Buchs, its purity was determined by GC analysis to be better than 95%.

---

*Corresponding author. Fax: +86-411-4671570.
E-mail address: tzc@ms.dicp.ac.cn (Z.-C. Tan)

PII: S0040-6031(99)00305-6

2.2. Adiabatic calorimetry

The heat capacity measurements were carried out by means of a small sample automatic adiabatic calorimeter over the temperature range from 80 to 370 K. The mass of the sample for experiments was 3.8001 g, which was equivalent to 21.8046 mmol. The adiabatic calorimeter used was described before in detail [1]. Briefly, a calorimeter cell was made of gold-plated copper 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 improve 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 entire experimental process. The miniature platinum resistance thermometer (IPRT No. 2 fabricated by Shanghai Institute of Industrial Automatic Meters, $R_0 = 100\Omega$) 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.

2.3. Differential scanning calorimetry (DSC)

A Du Pont TA 2000 Thermal Analysis system coupled with a personal computer loaded with the program for processing the obtained results was used. The DSC measurements were carried out using a differential scanning calorimeter with aluminum sample pans and sapphire reference material. Both the sample and sapphire were scanned at a heating rate of 5 K min^{-1}, under nitrogen atmosphere with a flow rate of 50 ml min^{-1}. The mass of the sample used for experiments was 3.50 mg.

2.4. Thermogravimetry (TG)

A thermal analysis system was equipped with a JF-2 thermobalance, a platinum wire furnace and platinum–rhodium thermocouples. The experiment was carried out with a sample of 9.5 mg, a nitrogen flow rate of 25 ml min^{-1} and a linear heating rate of 10 K min^{-1}, respectively.

2.5. Thermal conductivity and viscosity

The thermal conductivity of the sample was determined with KDR-1B instantaneous thermal conductometer in the temperature range from 273.15 to 373.15 K. Viscosity was measured with NDJ-1 viscosimeter in the temperature range from 348 to 353 K.

3. Result and discussion

3.1. Heat capacity

The low-temperature experimental molar heat capacities for 1,10-decanediol are shown in Fig. 1 and in Table 1. The $C_P - T$ curve in Fig. 1 indicates that there is no thermal anomaly from 80 to 330 K which means that the thermochemical property of 1,10-decanediol

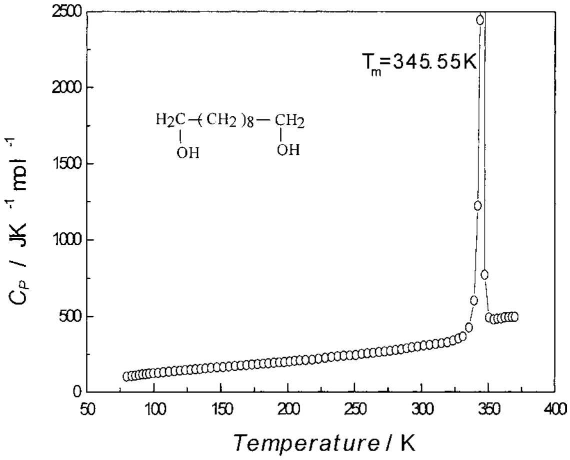

Fig. 1. C_P–T curve of 1,10-decanediol obtained by adiabatic calorimetry.

Table 1
Experimental molar heat capacities of 1,10-decanediol obtained by adiabatic calorimetry ($M = 174.28$ g mol^{-1})

T (K)	C_P (J K^{-1} mol^{-1})	T (K)	C_P (J K^{-1} mol^{-1})
79.69	102.3	142.54	158.7
83.29	106.2	147.15	162.2
86.07	109.2	151.68	165.2
88.78	111.9	156.14	168.5
91.43	115.9	160.53	171.0
93.99	118.7	164.85	174.9
96.49	121.1	169.12	177.0
99.53	124.0	173.32	181.0
103.08	127.1	177.45	183.6
106.98	130.7	181.54	186.1
111.21	134.4	185.57	189.0
115.34	137.7	189.55	192.2
119.37	141.1	193.49	195.1
123.31	144.0	197.38	198.2
127.18	146.9	201.23	200.9
130.98	150.0	205.04	204.9
134.71	152.9	208.80	207.5
138.39	155.6	213.16	211.1
218.13	213.1	296.99	299.9
223.03	218.9	301.55	306.7
227.83	224.9	306.40	311.6
232.54	230.5	310.47	317.5
237.17	235.0	314.84	322.2
241.72	240.4	319.17	328.5
246.24	240.7	323.42	340.0
250.72	244.3	327.56	354.0
255.14	251.0	330.86	367.9
259.50	254.9	335.44	426.3
263.83	258.9	353.79	478.7
268.11	263.3	356.58	483.9
272.35	267.1	359.34	486.8
276.54	271.7	362.08	494.1
280.67	276.8	364.80	494.4
284.75	281.6	367.52	497.1
288.77	288.3	369.88	496.8
292.73	294.9		

is stable in this temperature range. However, there is a phase transition in the temperature range 331–354 K. The heat-capacity measurements in the phase transition range were repeated for four times, and a very close agreement in the temperature and C_P values was obtained. This phase transition starts at 331.54 K and ends at 353.79 K, and its peak temperature is 345.55 K. The repeated heat-capacity measurements confirmed that this phase transition is reversible. The molar enthalpy and molar entropy of the transition were evaluated to be 44.2 kJ mol^{-1} and 127.9 K^{-1} mol^{-1}, respectively, based on the following thermodynamic relationships:

$$\Delta H_\mathrm{m} = \left[Q - n\int_{T_\mathrm{i}}^{T_\mathrm{m}} C_{P(S)}\,\mathrm{d}T - n\int_{T_\mathrm{m}}^{T_\mathrm{f}} C_{P(L)}\,\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} H_0\,\mathrm{d}T \right] / n \quad (\mathrm{kJ\,mol^{-1}}) \tag{1}$$

$$\Delta S_\mathrm{m} = \Delta H_\mathrm{m} / T_\mathrm{m} \tag{2}$$

where T_i in Eq. (1) is a temperature slightly below the starting transition temperature; T_f is a temperature slightly higher than the finishing transition temperature; Q is the total heat delivered to the colorimeter from temperature T_i to T_f; T_m is the melting point of the sample measured; n is the mole number of the sample; H_0 is the heat capacity of the empty container.

The phase transition is caused by the melting of 1,10-decanediol. The experimental molar heat capacities of this compound are also listed in Table 1 in temperature increment sequence so that the temperature increments can be deduced approximately from the adjacent mean temperatures.

From the DSC curve (Fig. 2) we can see that 1,10-decanediol starts to melt at 344.61 K, the peak temperature is 345.62 K, which accords well with the value described in [2]. The molar enthalpy and entropy

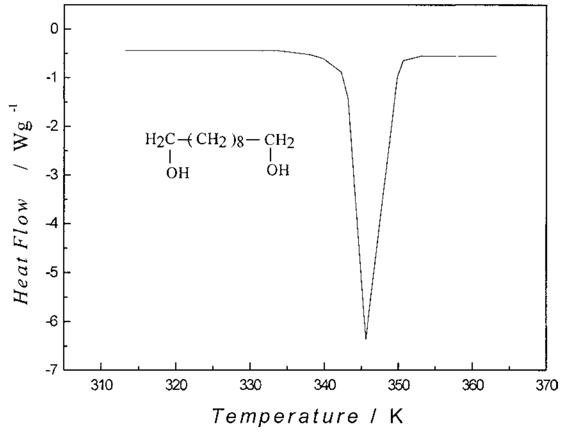

Fig. 2. DSC curve of 1,10-decanediol.

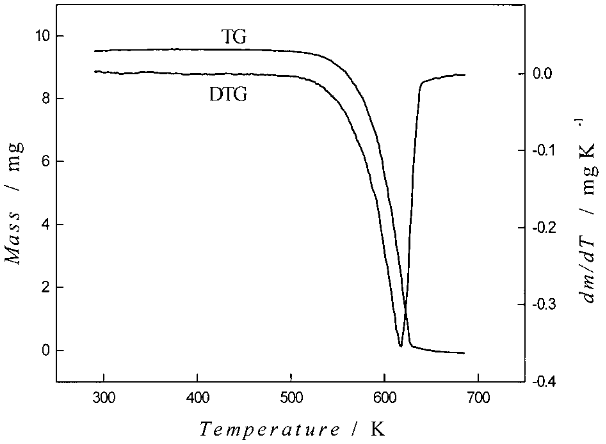

Fig. 3. TG and DTG curves of 1,10-decanediol.

of melting of DDL were determined by DSC being 43.50 kJ mol^{-1} and 126.23 J K^{-1} mol^{-1}, respectively.

3.2. Kinetic parameters

The TG and DTG curves of the DDL are shown in Fig. 3 and one can see that there is only one mass-lost field. It might be caused by the condensation and decomposition of DDL. The difference method [3] was used to calculate the kinetic parameters of the mass-lost process of DDL. The obtained kinetic parameters and the other main results from the TG and DTG curves of the sample are listed in Table 2.

3.3. Thermal conductivity and viscosity

The thermal conductivity λ(W m^{-1} K^{-1}) of DDL is described by the following relationships:

$$\text{Solid}(273\text{–}345\,\text{K}) \quad \lambda = 0.1532 + 0.0012983T$$
$$\text{Liquid}(345\text{–}373\,\text{K}) \quad \lambda = 0.2813\text{–}0.000194T$$

The experimental viscosity data of DDL are listed in Table 3.

Table 2
Kinetic parameters and other main results of thermal decomposition of 1,10-decanediol

Initial temperature (K)	531.15
Final temperature (K)	636.15
Temperature at DTG curve peak (K)	621.15
Apparent activation energy (kJ mol^{-1})	96.68
Reaction order	−0.024
Pre-exponential factor (s^{-1})	9.23×10^5

Table 3
Experimental viscosity of 1,10-decanediol

Temperature (K)	348	349	350	351	352	353
Viscosity($\times 10^3$) (Pa s)	22.0	21.3	20.0	19.5	18.8	17.5

3.4. Purity of the sample

The purity of the sample was determined during the determination of the melting curve. With experimental heat capacity data a series of equilibrium temperatures (T) at different melting fraction (F) of the sample are obtained during melting process [4]. All of the data are shown in Table 4 and Fig. 4 (the plot of T versus $1/F$),

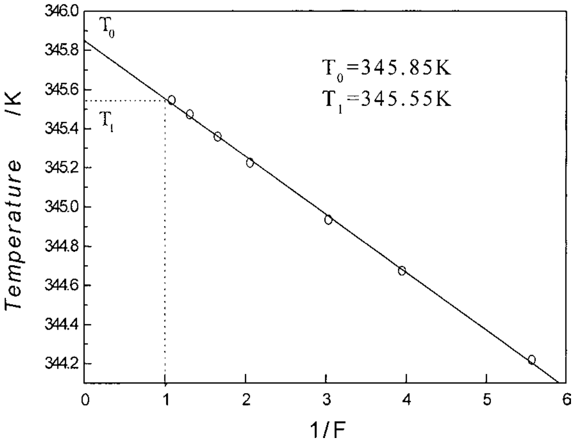

Fig. 4. Melting curve of 1,10-decanediol.

Table 4
The experimental results of melting fractions (F) and equilibrium temperatures (T) of 1,10-decanediol

1/F	5.5695	3.9506	3.0331	2.0562	1.6526	1.3081	1.0816
T (K)	344.2171	344.6743	344.9339	345.2242	345.3587	345.473	345.5466

which is a straight line. The meeting points of absolutely pure DDL and the sample can be obtained at $1/F = 0$ and $1/F = 1$, respectively. The results show that the melting points of pure DDL and the sample are 345.85 and 345.55 K, respectively. Finally, the purity of the sample is determined to be 98.69% (molar percent), according to the Van't Hoff equation.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China under the contract NSFC No.29773048. The authors are indebted to Ms. Ping Liang, Dalian University of Technology, for providing the DSC analysis.

References

[1] Zhi-cheng Tan, Guan-yu Sun, J. Therm. Anal. 45 (1995) 59.

[2] Z.Y. Zhang, M. Frenkel, K.N. Marsh et al., Landolt-Bornstein, Group IV, vol. 8, Thermodynamic Properties of Organic Compounds and their Mixtures, subvol. A, Springer, Berlin, 1995, p. 259.

[3] H.F. Joseph, A.W. Leo, J. Res. Natl. Bur. Standards A 70 (1966) 487–523.

[4] Zhi-cheng Tan, Jin-chunYe, An-xue Yin et al. Kexue Tongbao 32 (1987) 240–246.