Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 414 (2004) 131–135
thermochimica acta
www.elsevier.com/locate/tca

Thermodynamic studies of monuron

Li-Guo Kong [a,c], Zhi-Cheng Tan [a,*], Jian-Ting Mei [b], Li-Xian Sun [a], Xin-He Bao [c]

[a] Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[b] Dalian Chemphy Chemicals Co. Ltd., 161 Zhongshan Road, Dalian 116011, China
[c] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Received 8 August 2003; received in revised form 12 December 2003; accepted 12 December 2003

Abstract

Monuron ($C_9H_{11}ClN_2O$; *N*,*N*-dimethyl-*N*′-(4-chlorophenyl) urea, CAS 150-68-5) was synthesized and the heat capacities of the compound were measured in the temperature range from 79 to 385 K with a high precision automated adiabatic calorimeter. No phase transition or thermal anomaly was observed in this range. The enthalpy and entropy data of the compound relative to the reference temperature 298.15 K were derived based on the heat capacity data. The thermodynamic properties of the compound were further investigated through DSC and TG analysis. The melting point, the molar enthalpy, and entropy of fusion were determined to be 447.6 ± 0.1 K, 29.3 ± 0.2 kJ mol^{-1}, and 65.4 J K^{-1} mol^{-1}, respectively.

Keywords: Monuron; Heat capacity; Thermodynamic property; Adiabatic calorimetry

1. Introduction

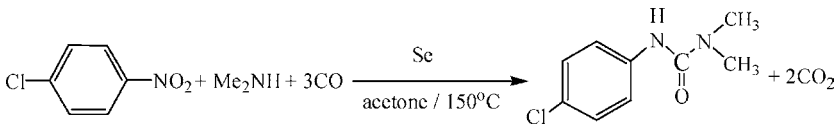
In the last 30 years compounds of unsymmetric ureas have been extensively investigated and synthesized due to their significant biological effects. Because of their effective function in the control of weeds, pests, and bacteria, these substances have been prepared and characterized through many methods [1,2]. In the present work, an important unsymmetric urea, monuron ($C_9H_{11}ClN_2O$; *N*,*N*-dimethyl-*N*′-(4-chlorophenyl) urea, CAS 150-68-5), was synthesized. Monuron is an effective and selective herbicide which has been widely used and investigated [3–7]. It has been used to remove weeds in wheat, soybean, corn, and rice etc. However, the data on thermodynamic properties of the compound are still insufficient. In order to improve the process of chemical synthesis and increase understanding of the properties of the compound, we measured some thermodynamic properties of the compound.

In the present study, the low-temperature heat capacities of this compound have been measured in the temperature range from 80 to 385 K. The enthalpy and entropy data of the compound were derived from the heat capacity data based on the reference temperature 298.15 K. In addition, the melting and evaporation behaviors of the compound were further investigated through TG and DSC analysis.

2. Experimental

2.1. Sample preparation and purity analysis

Instead of the synthesis processes by toxic phosgene, in the present work, monuron was prepared in a simple and convenient method described in literature [8]. The reaction is:



(1)

In the presence of Se (as a catalyst), monuron was synthesized in one step. This method is prior to the conven-

* Corresponding author. Tel.: +86-411-4379215; fax: +86-411-4691570.
E-mail address: tzc@dicp.ac.cn (Z.-C. Tan).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.12.007

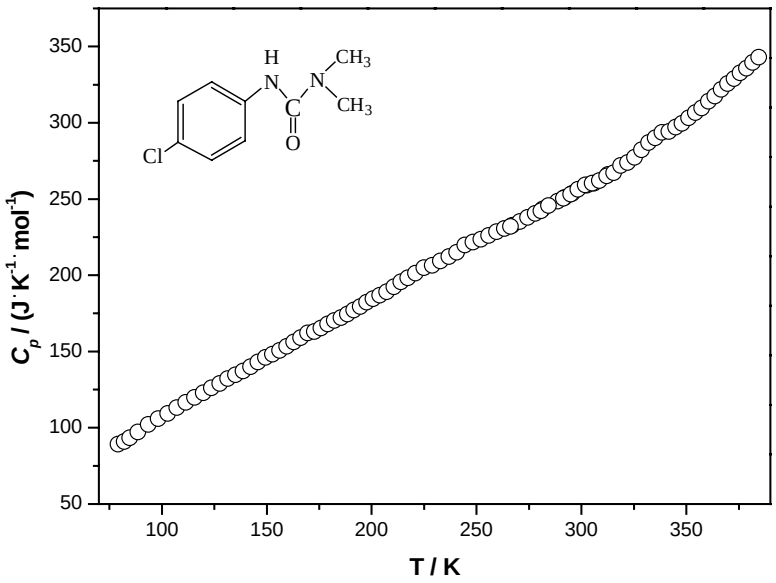


Fig. 1. Experimental molar heat capacity data of monuron as a function of temperature (T).

Table 1
The experimental molar heat capacity data of monuron ($M = 198.65\,\mathrm{g\,mol^{-1}}$)

T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
79.20	89.25	194.56	179.5	280.70	242.4
81.99	90.99	197.59	182.3	284.27	245.7
84.70	93.45	200.59	184.6	291.32	250.6
88.56	97.20	203.80	186.9	294.79	253.1
93.50	102.1	207.20	189.3	298.26	256.4
98.23	106.0	210.57	192.4	301.72	259.2
102.78	109.5	213.92	195.6	305.15	260.4
107.18	113.1	217.23	198.4	308.58	262.1
111.46	116.7	220.90	201.4	311.97	265.2
115.62	120.0	224.91	205.0	315.35	267.2
119.68	122.9	228.88	206.6	318.71	271.9
123.66	126.2	232.82	209.4	322.05	274.0
127.56	129.1	236.73	212.2	325.36	277.4
131.38	132.3	240.59	215.0	328.65	282.2
135.09	134.7	244.42	219.9	331.91	287.0
138.72	137.3	248.25	221.7	335.16	290.1
142.31	140.1	252.05	223.7	338.38	293.8
145.84	143.2	255.82	226.2	341.59	294.3
149.32	146.1	259.57	228.7	344.79	297.1
152.77	148.3	263.29	230.7	347.95	299.7
156.18	150.7	266.98	232.7	351.11	303.3
159.55	153.3	270.65	235.3	354.25	306.7
162.87	156.2	274.30	237.9	357.37	309.7
166.16	159.2	277.92	240.5	360.47	314.0
169.43	162.2	281.52	243.5	363.55	317.6
172.66	163.2	288.63	248.6	366.61	321.8
175.87	165.4	292.12	251.1	369.65	325.7
179.05	168.1	295.60	253.7	372.66	329.0
182.21	170.4	302.52	259.1	375.65	332.7
185.33	172.3	305.96	260.4	378.62	335.7
188.43	174.6	312.77	266.1	381.57	339.6
191.51	177.2	266.14	232.0	384.51	343.0

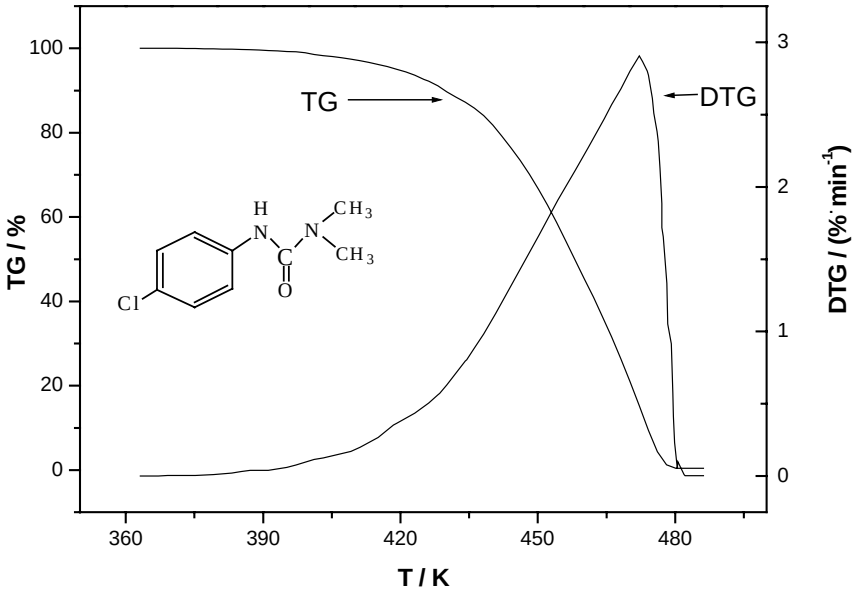


Fig. 2. TG–DTG curve of monuron.

tional ones, due to its low virulence, high security, and less demands to the devices. The structure and purity of the product were determined by IR, H^1NMR and C^{13}NMR and high-performance liquid chromatography (HPLC). The results of HPLC analysis demonstrate that the chemical purity of the sample is higher than 99.8 mol%.

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out in a high precision automated adiabatic calorimeter described in detail previously [9]. The sample amount used for heat capacity measurements is 2.6388 g, equivalent to 13.284 mmol, based on a molar mass of 198.65 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 reference standard material, α-Al_2O_3 . The deviations of our calibration results from there commended values reported by Ditmars et al. [10] of the former National Bureau of Standards are within of ±0.2% in the temperature range from 80 to 400 K.

2.3. TG–DTG and DSC analysis

TG–DTG and DSC measurements of the sample were carried out by a TG analyzer (Model: Setsys 16/18, SETARAM, France) and a DSC (Model: DSC 141, SETARAM, France) under high purity nitrogen (99.999%) with a flow rate of

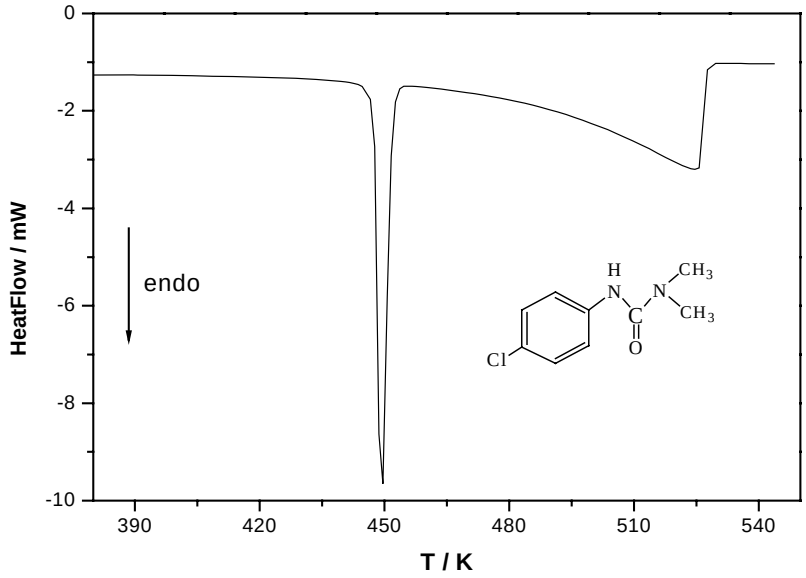


Fig. 3. DSC curve of monuron.

65 ml min^{-1}. For TG measurement the sample was put in an open alumina crucible with a volume of 100 μl; for DSC test the sample was held in a sealed aluminum pan with a volume of 30 μl. The mass of the sample used for TG and DSC analysis was 9.0 and 3.0 mg, respectively. The heating rate was 10 K min^{-1}.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacities of monuron are shown in Fig. 1 and tabulated in Table 1. The molar heat capacities were fitted to the following polynomial in reduced temperature (X), by means of least square fitting.

Over the temperature range from 80 to 385 K:

$$C_{p,m}(J\,K^{-1}\,mol^{-1}) = 208.02 + 108.78X - 5.9402X^2 + 18.54X^3 + 15.451X^4 \quad (2)$$

Where $X = (T - 232)/153$, and T is the absolute temperature. The correlation coefficient of the fitted curve, $r^2 = 0.99811$.

From Fig. 1. it can be seen that the heat capacities of the sample increases with temperature in a smooth and continuous manner from 79 to 385 K. No phase transition or thermal anomaly was observed in this range. Therefore, the sample is structurally stable in the temperature range from 79 to 385 K.

3.2. Thermodynamic functions of monuron

Through the polynomial of heat capacity and the relationship of thermodynamic functions, the thermodynamic function data relative to the reference temperature 298.15 K were derived in the temperature range from 80 to 385 K based on the heat capacity data. The values of thermodynamic function $H_T - H_{298.15}$, $S_T - S_{298.15}$ are listed in Table 2.

3.3. The results of TG–DTG and DSC analysis of monuron

TG and DTG curves of monuron are shown in Fig. 2. It can be seen that monuron begins to lose weight at 397 K and reaches the maximum rate of weight loss at 472 K. The sample completely loses its weight when the temperature reaches 480 K. The product collected during the heating until 500 K proves to be the same substance as the original sample judging from its color, melting point, and morphology. Thus we can deduce that monuron evaporates over the temperature range and completely changes into vapor at 480 K under the present experimental conditions.

The DSC curve is shown in Fig. 3. Two endothermic peaks appeared during the heating process, which are ascribed to melting and evaporation, respectively. The melting point is determined to be 447.6 ± 0.1 K, which coincides with the

Table 2
Calculated thermodynamic function data of monuron

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$H_T - H_{298.15}$ (kJ mol^{-1})	$S_T - S_{298.15}$ (J K^{-1} mol^{-1})
80	90.96	−38.20	−207.2
85	94.75	−37.74	−201.6
90	98.59	−37.25	−196.1
95	102.5	−36.75	−190.6
100	106.4	−36.23	−185.3
105	110.4	−35.69	−179.9
110	114.4	−35.12	−174.7
115	118.4	−34.54	−169.5
120	122.4	−33.94	−164.4
125	126.4	−33.32	−159.3
130	130.4	−32.68	−154.2
135	134.4	−32.01	−149.2
140	138.5	−31.33	−144.2
145	142.5	−30.63	−139.3
150	146.4	−29.91	−134.4
155	150.4	−29.17	−129.6
160	154.3	−28.40	−124.7
165	158.3	−27.62	−119.9
170	162.2	−26.82	−115.2
175	166.0	−26.00	−110.4
180	169.8	−25.16	−105.7
185	173.6	−24.30	−101.0
190	177.4	−23.42	−96.36
195	181.2	−22.53	−91.72
200	184.9	−21.61	−87.09
205	188.6	−20.68	−82.49
210	192.2	−19.73	−77.91
215	195.8	−18.76	−73.35
220	199.4	−17.77	−68.81
225	203.0	−16.76	−64.29
230	206.6	−15.74	−59.78
235	210.2	−14.70	−55.30
240	213.7	−13.64	−50.83
245	217.2	−12.56	−46.38
250	220.8	−11.46	−41.94
255	224.3	−10.35	−37.53
260	227.9	−9.221	−33.21
265	231.4	−8.073	−28.74
270	235.0	−6.907	−24.37
275	238.6	−5.723	−20.01
280	242.3	−4.521	−15.67
285	246.0	−3.300	−11.34
290	249.7	−2.061	−7.018
295	253.5	−0.802	−2.709
298.15	256.0	0.000	0.000
300	257.4	0.475	1.589
305	261.4	1.772	5.880
310	265.4	3.089	10.16
315	269.6	4.426	14.44
320	273.8	5.785	18.72
325	278.2	7.165	22.99
330	282.7	8.567	27.26
335	287.4	9.993	31.54
340	292.2	11.44	35.82
345	297.2	12.92	40.11
350	302.4	14.41	44.41
355	307.7	15.94	48.72
360	313.3	17.49	53.06
365	319.1	19.07	57.41
370	325.1	20.68	61.79
375	331.4	22.32	66.20
380	338.0	24.00	70.67
385	344.9	25.70	75.12

literature value, 447.88 K [11]. The molar enthalpy of fusion was determined to be $29.3 \pm 0.2\,kJ\,mol^{-1}$ through the integration of the area of the first peak, which is in good agreement with the literature value $29.46\,kJ\,mol^{-1}$ [12]. The molar entropy of fusion was derived to be $65.4\,J\,K^{-1}\,mol^{-1}$.

Acknowledgements

The authors greatfully acknowledge the National Natural Science Foundation of China for financial support to this work under Grant No. 20373072.

References

[1] R.J. Lewis, P. Camilleri, A.J. Kirby, C.A. Marby, A.A. Slawin, D.J. Williams, J. Chem. Soc., Perkin Trans. 2 (1991) 1625.
[2] Pesticide Manual, 9th Ed., 1991, No. 7520.
[3] L.H. Zhou, F.S. Li, X.J. Zhu, Contemp. Chem. Ind. (Chinese) 30 (2001) 242.
[4] B. Li, Y. Man, Z.J. Zhang, Pesticides (Chinese) 38 (1999) 16.
[5] R.J.C.A. Steen, B. Van Hattum, U.A.T. Brinkman, J. Environ. Monit. 2 (2000) 597.
[6] C. Richard, D. Vialaton, J.P. Aguer, F. Andreux, J. Photochem. Photobiol. 111 (1997) 265.
[7] V. Augugliaro, G. Marci, L. Palmisano, E. Pramauro, A. Biancoprevot, Res. Chem. Intermed. 19 (1993) 839.
[8] J.T. Mei, S.W. Lu, Prog. Chem. (Chinese) 14 (2002) 433.
[9] Z.C. Tan, G.Y. Sun, Y. Sun, A.X. Yin, W.B. Wang, J.C. Ye, L.X. Zhou, J. Therm. Anal. 45 (1995) 59.
[10] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. Rest, J. Rev. Natl. Bur. Stand. 87 (1982) 159.
[11] J.R. Donnelly, L.A. Drewes, R.L. Johnson, W.D. Munslow, K.K. Knapp, G.W. Sovocool, Thermochim. Acta 2 (167) (1990) 155.
[12] W.E. Acree Jr., Thermochim. Acta 189 (1) (1991) 37.