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THERMOCHEMICAL AND THERMAL ANALYSIS ON N-(*p*-METHYLPHENYL)-N'-(2-PYRIDYL)UREA

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Abstract

Low temperature heat capacities of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea were determined by adiabatic calorimetry method in the temperature range from 80 to 370 K. It was found that there was not any heat anomaly in this temperature region. Based on the experimental data, some thermodynamic function results were obtained. Thermal stability and decomposition characteristics analysis of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea were carried out by DSC and TG. The results indicated that N-(*p*-methylphenyl)-N'-(2-pyridyl)urea started to melt at ca. 426 K (153°C) and the melting peak located at 447.01 K (173.86°C). The melting enthalpy was 204.445 kJ mol^{-1} (899.6 J g^{-1}). The decomposition peak of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea was found at 499.26 K (226.11°C) from DSC curve. This result was similar with that from TG and DTG experiment, in which the mass loss peak was determined as 500.4 K (227.2°C).

Keywords: adiabatic calorimetry, N-(*p*-methylphenyl)-N'-(2-pyridyl)urea, thermal analysis, thermodynamic function

Introduction

Phenyl pyridylurea compounds are kinds of substances containing nitric heterocycles and peptide linkage. Its higher physiological activity has been pulling researchers attention [1]. It can initiate or promote cell division and cell differentiation, induce callus tissues to split into different organs, retard the senescence of leaves, regulate the transportation and distribution of the substances in plants, promote the development of lateral buds, and so on. These regulations stimulate plants growth and increase product yield. In addition, phenyl pyridylurea compounds, mixed with other ingredients proportionally are advanced selective high efficiency herbicides [2] with low toxicity to human, animal and insect.

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Traditionally, phenyl pyridylurea compounds are synthesized by isocyanate method [1, 3–5] or hydrazoate method [6–8]. These methods have disadvantage of high toxicity and environment pollution, rigorous reaction conditions and accurate technique. Since 70's last century a new method is developed [9] to synthesize phenyl pyridylurea compounds. Hereinto, the method of directly using carbon monoxide is efficient for synthesis of unsymmetrical urea [10]. This method is carbonylation reaction of $PhNO_2$ with amines as coreagents under selenium catalyzed.

Up to now, most of the researchers pay attentions to the study of synthesis, crystal structure and applications [11–13] of phenyl pyridylurea compounds. Less literature about thermal properties is reported. In present paper low temperature heat capacities of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea were determined by adiabatic calorimetry method. Thermal analysis was carried out to reveal its thermal stability and decomposition characteristics. This information may be helpful to the synthesis of phenyl pyridylurea compounds effectively.

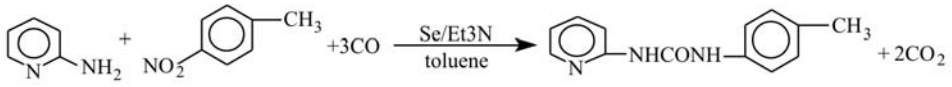
Experimental

Sample preparation

10 mmol *p*-methylnitrobenzene (AR), 10 mmol 2-aminopyridine (AR), 10 mmol triethylamine (AR) and 10 g methylbenzene (AR) were added to an autoclave 100 mL in volume. 0.5 mmol selenium powder (over 99% purity) was added in the autoclave as catalyzer. Sealed the autoclave, substitute the mixed gas by carbon monoxide (99.99% purity) and elevated pressure up to 3.0 MPa. Place the autoclave in an oil bath and make the temperature rise to 130 degree centigrade quickly. Keep stirring for 4 h. Then cooled down to room temperature and vent out the remaining gas. Filtrate the liquid mixture to obtain solid substance. Combine this solid with that obtained from the evaporation of the filtrated stock. Then recrystallize, dry the product and the sample was prepared.

The sample was characterized by melting point measurement, IR, ^{1}H NMR, ^{15}C NMR, HPLP and element analysis to identify its molecular structure. The results indicated that the sample was N-(*p*-methylphenyl)-N'-(2-pyridyl)urea($C_{13}N_3OH_{13}$; molecular mass is 227.262). Its melting point is 178–180°C ([6] reported as 172–173°C) and purity is 99%.

During above reaction process, selenium was catalyst and triethylamine was auxiliary catalyst and reaction was conducted as following



Low temperature calorimetry experiment

A low-temperature adiabatic calorimeter was used to measure the heat capacity of the sample. The calorimetric apparatus and measuring technique have been described in detail [14–18]. Briefly, it is an adiabatic calorimeter with intermittent energy inputs

and temperature equilibration after each input. The calorimeter cell, with an internal volume of ca. 6 mL, was made of gold plated silver with an Y-shape fin inside. Adhesive was used to seal the lid, which contained a copper capillary tube, to the loaded calorimeter. This assembly was evacuated through the capillary and then filled with helium gas in order to keep good thermal conductivity. The capillary was pinched off and soldered with tin. The outer wall of the sample cell was screened with brilliant aluminum foil to eliminate heat radiation.

The calorimeter-cell assembly was suspended inside an inner adiabatic shield, which was in turn surrounded by an outer adiabatic shield. All of these were housed in a high vacuum vessel. The temperature differences between the calorimeter cell and the inner shield and between the inner and outer shields were measured by means of two sets of eight junctions of chromel-constantan thermopiles installed between them. The amplified signals were used for automatic control of the shield heaters in a PID (proportional-integral-differential) mode during energy input and drift periods. The electrical energy supplied to the calorimeter cell and the temperature of the calorimeter of the cell were measured and processed automatically by a personal computer with a digital multimeter. Measurements of the heat capacities of α-alumina and *n*-heptane, two international accepted heat capacity standard reference materials, showed a precision of ±0.1% and agreed with those of the National Institute Science and Technology (formerly NBS) to within ±0.2 %.

In the present study, a sample of 0.8427 g was used to measure low temperature heat capacities in temperature region from ca. 80 to ca. 370 K.

DSC and TG measurements

To study the thermal stability, TG and DSC experiments were carried out. The thermogravimetric measurement was conducted on a DT-20B (Shimadzu, Japan) instrument with 1.500 mg sample at a heating rate of 10.0 K min^{-1} in nitrogen ambient. The DSC measurement was carried out by 7 Series Thermal Analysis System (Perkin Elmer Instruments). The sample mass was 2.3740 mg and heating rate was 10.0 K min^{-1}.

Results and discussion

Heat capacity

Heat capacity of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea sample at cooling rates of 0.1 and 10.0 K min^{-1} were measured from 370 to 80 K. Experiment results indicated that cooling rate of the sample had not obvious effect on heat capacity data. In measured temperature region, heat capacity curve is smooth and not any heat capacity anomaly is found. This result shows that there are no crystalline structure transition and melting process in the test temperature range. N-(*p*-methylphenyl)-N'-(2-pyridyl)urea has stable molecular and crystalline structures in the temperature from 370 to 80 K. The heat capacity experiment is drawn on Fig. 1 and listed in Table 1.

Table 1 Experimental data of heat capacities of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea (M=227.262 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}
79.9	109.1	159.2	192.6	255.3	258.9
81.6	111.5	161.5	194.3	257.1	260.3
83.3	114.1	163.8	195.9	259.0	261.8
85.0	116.6	166.1	197.5	260.9	263.1
86.7	119.1	168.4	199.0	262.7	264.5
88.4	121.4	170.6	200.6	264.5	265.9
90.1	123.7	172.9	202.1	266.3	267.1
91.7	126.2	175.1	203.6	268.1	268.6
93.2	128.0	177.3	205.1	269.9	270.0
94.8	130.1	179.5	206.6	271.7	271.4
96.3	132.0	181.7	208.0	273.5	272.8
97.8	134.0	183.9	209.5	275.3	274.1
99.3	135.9	186.0	210.8	277.1	275.5
100.7	138.1	188.2	212.3	278.9	276.9
102.2	139.5	190.3	213.7	280.7	278.3
103.6	141.2	192.4	215.1	282.5	279.7
105.0	142.9	194.5	216.4	284.2	281.0
106.5	144.6	196.6	217.8	286.0	282.4
107.8	145.8	198.7	219.2	287.8	283.8
109.2	147.8	200.8	220.6	289.5	285.2
110.6	149.4	202.8	222.0	291.3	286.5
112.0	150.9	204.9	223.4	292.7	287.7
113.3	152.3	207.0	224.8	294.1	288.8
114.7	153.8	209.0	226.1	297.4	291.4
116.0	155.2	211.1	227.5	300.7	294.0
117.3	156.6	213.1	228.9	304.0	296.6
118.6	158.0	215.1	230.3	307.3	299.3
120.0	159.4	217.1	231.7	310.6	302.0
121.4	160.8	219.2	233.0	313.9	304.8
122.9	162.3	221.2	234.4	317.2	307.6
124.4	163.8	223.1	235.8	320.5	310.3
125.9	165.2	225.1	237.1	323.8	313.2
127.4	166.6	227.1	238.5	327.1	316.0
128.8	167.9	229.0	239.9	330.3	319.0
130.3	169.3	230.9	241.2	333.6	322.0

Table 1 Continued

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}
131.9	170.8	232.9	242.6	336.8	325.1
133.4	172.1	234.8	243.9	340.0	328.2
135.5	174.0	236.7	245.3	343.2	331.4
137.6	175.7	238.6	246.7	346.3	334.8
140.1	177.8	240.4	248.0	349.4	338.2
142.6	179.9	242.2	249.3	352.6	341.9
145.0	181.8	244.1	250.7	355.7	345.6
147.4	183.7	246.0	252.0	358.8	349.5
149.8	185.6	247.8	253.4	361.8	353.6
152.2	187.4	249.7	254.8	364.8	357.8
154.5	189.1	251.5	256.2	367.7	362.6
156.9	190.9	253.4	257.6	370.7	366.9

Thermodynamic results

The data of heat capacities of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea were fitted with the following polynomial expression with least squares method.

$$C_p=238.083+95.783X-0.178X^2+30.876X^3$$

where $X=(T-224.5)/145.5$ and *T*/K is temperature. The definition of converted temperature *X* is

$$X=[T-(T_2+T_1)/2]/[(T_2-T_1)/2]$$

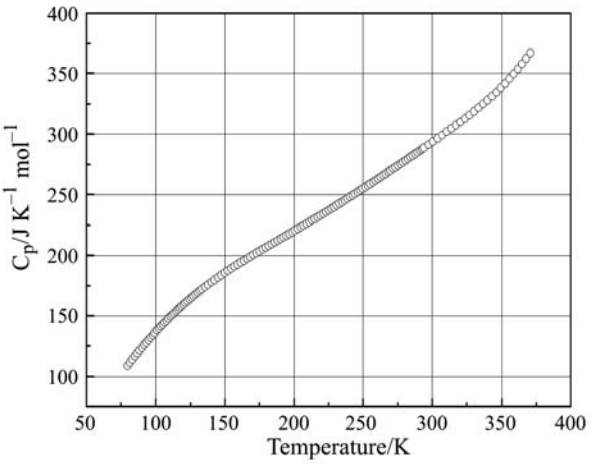


Fig. 1 Heat capacity curve of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea

where T_1 and T_2 are initial and end temperature of the test, respectively. Generally, T_1 and T_2 are rounded to integer. In present experiment, T_1 and T_2 are 79 and 370 K, respectively. The 3rd-order approximation gives standard deviation 1.29. The relativity coefficient of approximation expression is 0.999.

Based on above fitted polynomial expression and thermodynamic relationship, thermodynamic data of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea are calculated in the temperature range from 370 to 80 K, in which reference temperature is 298.15 K (standard state). The results are listed in Table 2.

Table 2 Calculated thermodynamic function results of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea

T/K	C_p/ J mol^{-1} K^{-1}	$[H_{(T)}-H_{(298.15)}]$/ J mol^{-1}	$[S_{(T)}-S_{(298.15)}]$/ J mol^{-1} K^{-1}	$[G_{(T)}-G_{(298.15)}]$/ J mol^{-1}
80	112.5	–58204	–252.1	–56551
85	118.9	–45256	–245.2	–24412
90	125.0	–44655	–238.4	–23203
95	130.9	–44020	–231.5	–22028
100	136.7	–43352	–224.6	–20888
105	142.2	–42652	–217.8	–19782
110	147.6	–41923	–211.0	–18710
115	152.7	–41166	–204.3	–17672
120	157.8	–40382	–197.6	–16667
125	162.6	–39572	–191.0	–15695
130	167.3	–38739	–184.5	–14756
135	171.9	–37883	–178.0	–13850
140	176.3	–37004	–171.6	–12976
145	180.7	–36105	–165.3	–12134
150	184.8	–35186	–159.1	–11323
155	188.9	–34248	–152.9	–10543
160	192.9	–33292	–146.9	–9793.4
165	196.8	–32317	–140.9	–9074.1
170	200.6	–31325	–134.9	–8384.6
175	204.3	–30316	–129.1	–7724.5
180	207.9	–29290	–123.3	–7093.6
185	211.4	–28247	–117.6	–6491.3
190	214.9	–27188	–111.9	–5917.5
195	218.4	–26112	–106.4	–5371.7
200	221.8	–25020	–100.8	–4853.8

Table 2 Continued

T/K	C_p/ J mol^{-1} K^{-1}	$[H_{(T)}-H_{(298.15)}]$/ J mol^{-1}	$[S_{(T)}-S_{(298.15)}]$/ J mol^{-1} K^{-1}	$[G_{(T)}-G_{(298.15)}]$/ J mol^{-1}
205	225.2	–23911	–95.35	–4363.4
210	228.5	–22785	–89.93	–3900.2
215	231.8	–21643	–84.55	–3464.0
220	235.1	–20484	–79.22	–3054.6
225	238.4	–19307	–73.94	–2671.7
230	241.7	–18113	–68.69	–2315.1
235	245.0	–16902	–63.48	–1984.7
240	248.3	–15672	–58.30	–1680.3
245	251.7	–14425	–53.15	–1401.7
250	255.0	–13159	–48.04	–1148.7
255	258.4	–11874	–42.95	–921.26
260	261.9	–10571	–37.90	–719.16
265	265.4	–9249.6	–32.89	–542.29
270	269.0	–7908.8	–27.85	–390.54
275	272.6	–6548.9	–22.86	–263.80
280	276.3	–5169.8	–17.89	–161.96
285	280.1	–3771.3	–12.94	–84.916
290	284.0	–2353.3	–8.003	–32.581
295	288.0	–915.78	–3.088	–4.862
298.15	290.5	0.000	0.000	0.000
300	292.1	541.51	1.811	–1.675
305	296.3	2018.7	6.694	–22.943
310	300.6	3516.1	11.56	–68.593
315	305.0	5034.0	16.42	–138.56
320	309.6	6572.7	21.27	–232.78
325	314.3	8132.8	26.11	–351.22
330	319.2	9714.9	30.94	–493.82
335	324.2	11320	35.76	–660.57
340	329.4	12949	40.59	–851.44
345	334.8	14602	45.42	–1066.5
350	340.4	16283	50.25	–1305.6
355	346.1	17992	55.10	–1569.0
360	352.1	19731	59.97	–1856.7
365	358.2	21504	64.86	–2168.7
370	364.6	23314	69.78	–2505.8

DSC and TG

The adiabatic calorimeter used in heat capacity measurement could only work under 380 K because of the limitation of heat insulating material. In order to understand the thermal activity of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea over 380 K, DSC and TG test were conducted. The results are drawn in Figs 2 and 3, respectively. The DSC experiment result shows that N-(*p*-methylphenyl)-N'-(2-pyridyl)urea began to melt at ca. 426 K (153°C) and the melting process ended at ca. 452 K (179°C). The melting peak

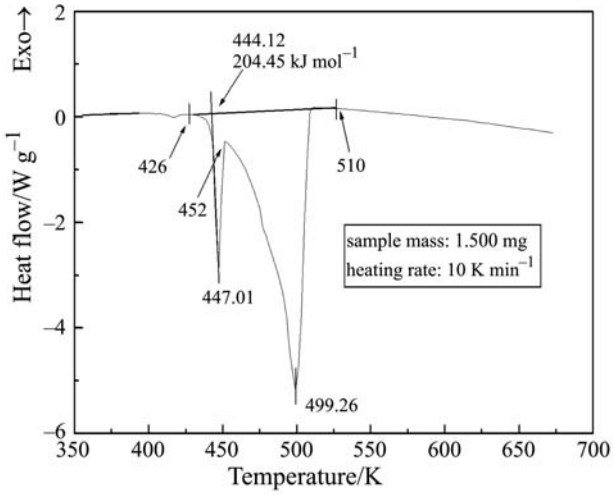


Fig. 2 DSC experimental result of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea

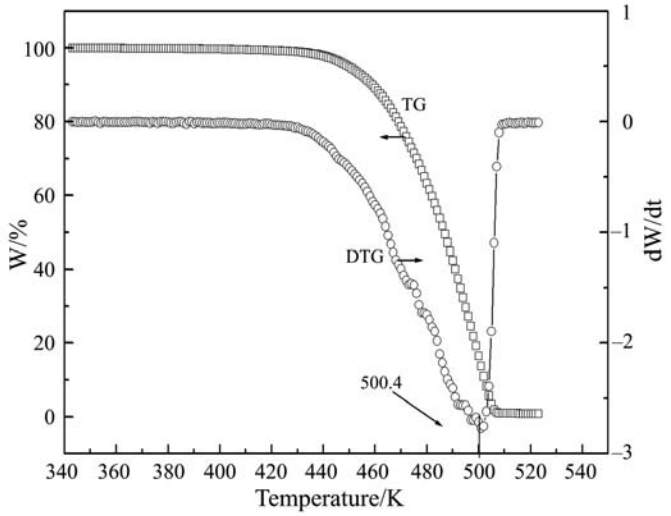


Fig. 3 TG and DTG experimental result of N-(*p*-methylphenyl)-N'-(2-pyridyl)urea

temperature is 447.01 K (173.86°C) and melting enthalpy is 204.445 kJ mol^{-1} (899.6 J g^{-1}). This fusing point value is similar to that (172–173°C) reported by [6], but has larger difference with that (178–180°C) measured by model X-4 binocular microscope melting point apparatus (made in China by Beijing Tech Instrument Co., Ltd).

N-(*p*-methylphenyl)-N'-(2-pyridyl)urea began to decompose close after the melting peak. Only one decomposition peak was found. The initial and final decomposition temperatures are 452 K (179°C) and 510 K (237°C), respectively. The decomposition peak temperature is 499.26 K (226.11°C).

Figure 3 is TG and DTG experiment results. It is shown that there is only one mass loss activity in the whole temperature range. The decomposition started from ca. 426 K (153°C) and ended at ca. 510 K (237°C). The decomposition peak temperature is ca. 500.4 K (227.2°C). These evidences are in accordance with the results derived from DSC test. However, the temperature started to decomposition is almost same with the initial melting temperature. The reason may be that the melting process and decomposition process happened almost at same time.

Conclusions

Low temperature adiabatic calorimetry experiment and thermal analysis on N-(*p*-methylphenyl)-N'-(2-pyridyl)urea revealed that there is no thermal anomaly in temperature range from 80 to 426 K. DSC test indicated that N-(*p*-methylphenyl)-N'-(2-pyridyl)urea starts to melt at 425 K. Its melting peak temperature is 447.86 K and its fusion enthalpy is 204.445 kJ mol^{-1} (899.6 J g^{-1}). A decomposition peak at 499.26 K, close adjacent to melting peak, started at ca. 451 K and stopped at ca. 237 K. TG and DTG investigation also shows similar results.

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