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LOW-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF CRYSTALLINE ISOPROTURON

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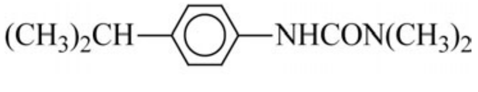
Abstract

Isoproturon [N'-(*p*-cumenyl)-N,N-dimethylurea] was synthesized, and the low-temperature heat capacities were measured with a small sample precise automatic adiabatic calorimeter over the temperature range from 78 to 342 K. No thermal anomaly or phase transition was observed in this temperature range. The melting and thermal decomposition behavior of isoproturon was investigated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The melting point and decomposition temperature of isoproturon were determined to be 152.4 and 239.0°C. The molar melting enthalpy, and entropy of isoproturon, ΔH_m and ΔS_m, were determined to be 21.33 and 50.13 J K^{-1} mol^{-1}, respectively. The fundamental thermodynamic functions of isoproturon relative to standard reference temperature, 298.15 K, were derived from the heat capacity data.

Keywords: adiabatic calorimetry, DSC, heat capacity, isoproturon, TG, unsymmetric ureas

Introduction

Compounds of asymmetric ureas have been extensively investigated and synthesized due to their significantly biological effects in the last 30 years [1, 2]. Because of their effective role in the control of weeds, pests, and bacteria, these substances have been prepared and characterized through many methods [3, 4]. In the present work, an important unsymmetry urea, isoproturon, was synthesized. The chemical formula and molecular structure of isoproturon are as follows: $C_{12}H_{18}N_2O$ and



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Isoproturon is an effective and selective herbicide. It was first synthesized in 1972 by Farbwerke Hoechst A. G. [5]. Isoproturon can be used to remove weeds in wheat, soybean, corn, rice, etc. [6]. It is produced in amount of 7000 ton every year in the world, and in the developed countries, it has been used widely because of it's a virulence and little residue. In order to improve the process of chemical synthesis of this asymmetry urea, and carry out relevant application and theoretical research, the thermodynamic properties of this compound are of vital importance both in agrochemical science and technology. However, so far no thermodynamic study of this asymmetry urea has been reported in literature.

Heat capacity is one of the fundamental thermodynamic properties of substances. It is closely related to the energetic structure, and is sensitive to the variations in other properties of substances. In the present work, the low-temperature heat capacity measurements and thermal decomposition test of isoproturon sample synthesized in our laboratory were carried out over the temperature range from 78 to 342 K and 323.15 to 623.15 K, respectively. The fundamental thermodynamic functions of the compound were calculated on the basis of low-temperature heat capacity measurements.

Experimental

Sample preparation

Instead of the synthesis processes by toxic phosgene, in the present work, isoproturon was prepared in a simple and convenient method described in literature [7].

The reaction is:

$$(CH_3)_2CHC_6H_4NO_2+Me_2NH+3CO \xrightarrow{Se} (CH_3)_2CHC_6H_4NHCONMe_2+2CO_2 \quad (1)$$

In the presence of Se (as a catalyst), isoproturon was synthesized in one step. This method is prior to the conventional ones, due to its virulence, security and less demands to the devices. The structure of this product was determined by infrared (IR), hydrogen-1 nuclear magnetic resonance (H^1 NMR), carbon-13 nuclear magnetic resonance (C^{13} NMR) and high-performance liquid chromatography (HPLC). The results of these analyses demonstrate that the chemical purity of the sample is higher than 99.0 mass%.

Adiabatic calorimetry

Heat-capacity measurements were carried out in a precision automatic adiabatic calorimetric system described in detail previously [8]. In brief, it is an adiabatic calorimeter with intermitted energy inputs and temperature equilibrium after each energy input. The calorimeter consists mainly of a sample cell, an adiabatic (or inner) shield, a guard (or outer) shield, two sets of differential thermocouples and a high vacuum can. Liquid nitrogen was used as the cooling medium. The evacuated chamber was kept within $1\cdot10^{-3}$ Pa during the heat capacity measurements so as to eliminate the heat leakage owing to gas convection.

The sample cell was a gold-plated copper container with an internal volume about 6 cm^3. The temperature of the cell was determined by a miniature platinum resistance thermometer. The thermometer was made by the No. 3 Shanghai Institute of Industrial Automatic Meters, China and calibrated on the basis of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica. The temperature and energy data for heat capacity measurements are automatically collected by use of the Data Acquisition/Switch Unit (Model: 34970A, Agilent, USA) and processed on line by a computer.

In the present study, the mass of isoproturon sample used for heat capacity measurement was 1.3016 g, which was equivalent to 6.312 mmol, based on its corresponding molar mass of 206.2 g mol^{-1}.

The molar heat capacities of α-Al_2O_3 used as the reference standard material were measured in the same temperature range as that of the sample measurement in order to confirm the reliability of the calorimeter. The deviation of our calibration results from the recommended values reported by Ditmars *et al*. of the former National Bureau Standard [9] is within ±0.2% in the whole experiment temperature range.

TG-DTG and DSC analyses

The TG-DTG, 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 65 mL min^{-1}. For TG measurement the sample was put in alumina crucible with a volume of 100 μL; for DSC test the sample was sealed in aluminum pan with a volume of 30 μL. The mass of the sample used for TG and DSC analyses was about 9.0 and 5.0 mg, respectively. The heating rate was 10°C min^{-1}.

Results and discussion

Heat capacity

The experimental molar heat capacities of the sample are shown in Fig. 1, and tabulated in Table 1. Figure 1 indicates that the heat capacities of the sample increase

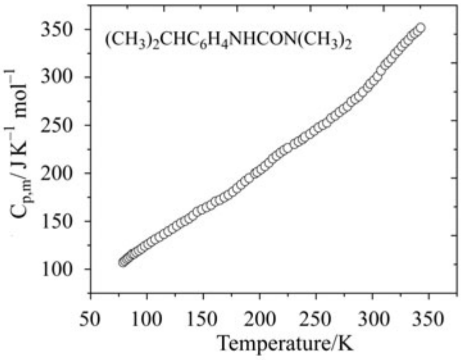

Fig. 1 Experimental molar heat capacities $C_{p,m}$ of isoproturon as a function of temperature

Table 1 The experimental molar heat capacities of isoproturon (molar mass: M=206.2 g mol^{-1})

T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}
78.765	107.16	160.784	170.63	259.674	252.70
80.457	108.79	164.680	172.13	263.370	257.38
82.108	110.62	168.537	175.08	267.025	360.03
83.726	112.19	172.345	177.40	270.668	263.73
85.313	113.65	176.102	180.61	274.241	266.90
86.871	115.62	179.813	184.33	277.777	269.68
88.616	115.96	183.480	188.16	281.269	274.71
90.544	117.76	187.105	191.71	284.730	277.39
92.725	119.34	190.688	194.83	288.139	280.18
95.337	121.47	194.237	196.36	291.477	284.80
98.078	124.07	197.779	201.21	294.744	287.30
100.975	126.15	201.283	204.11	298.034	293.32
104.018	128.60	204.746	207.49	301.278	296.74
107.269	131.18	208.179	210.95	304.461	299.84
111.037	133.53	211.576	215.22	307.634	303.74
115.026	136.68	214.914	218.11	310.776	309.78
118.927	139.51	218.253	221.38	313.879	312.50
122.742	142.40	221.520	224.07	316.950	319.38
126.481	145.25	224.787	226.29	319.987	324.55
130.151	148.25	230.611	232.06	322.999	327.85
133.758	150.26	234.375	233.02	325.994	332.15
137.300	152.80	237.926	235.43	328.906	335.81
140.788	155.80	240.057	237.93	331.789	338.92
144.604	159.82	244.602	240.92	334.611	344.39
148.744	162.13	248.366	244.28	337.358	345.72
152.817	164.45	252.168	247.68	339.986	348.22
156.831	166.98	255.940	250.38	342.756	351.50

smoothly with temperature in the range from 78 to 342 K. In this temperature range, no phase transition or thermal anomaly was observed. Therefore, isoproturon is stable in this temperature range.

The molar heat capacities are fitted to the following polynomial of heat capacities *vs*. reduced temperatures (X), by means of the least square method.

For the solid compound, over the temperature range of 78 to 342 K:

$$C_{p,m}(\mathrm{J\ k^{-1}\ mol^{-1}}) = 213.01987 + 111.99042X - 17.75328X^2 + \\ + 0.44775X^3 + 87.8848X^4 + 12.03838X^5 - 53.97641X^6 \quad (2)$$

where $X=(T-210.5)/132.5$ and T is the absolute temperature. The correlation coefficient of the fitted curve, $R^2=0.99969$.

The results of TG-DTG, and DSC analyses of the isoproturon sample

The DSC and TG-DTG curves of the isoproturon sample are shown in Figs 2 and 3, respectively. From Fig. 2 a sharply endothermic peak in the range from 150 to 160°C with a peak temperature of 155.7°C was observed, which corresponds to the melting process of isoproturon. Based on the DSC curve, the melting point of isoproturon was determined to be 152.4°C, which is slightly higher than the value (151°C) reported in the literature [10]. The molar enthalpy of melting, ΔH_m, and the molar entropy of melting, ΔS_m, of isoproturon were determined to be 21.33 and 50.13 J $\mathrm{mol^{-1}\ K^{-1}}$, respectively, according to the integral of DSC curve. Following the melting, the sample begun to decompose. The initial temperature of decomposition was 239.0°C, and peak temperature was 271.8°C. At approximate 300°C, the decomposition finished.

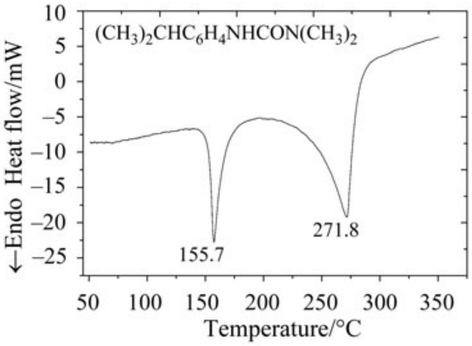

Fig. 2 DSC curve of isoproturon under nitrogen atmosphere

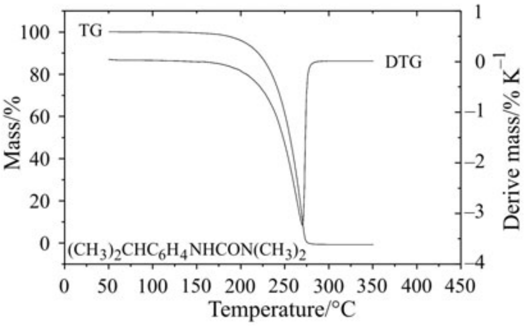

Fig. 3 TG-DTG curves of isoproturon under nitrogen atmosphere

It can be seen from the TG-DTG curves that the thermal decomposition taken place in one step. The starting temperature of mass loss was about 150°C, and the end temperature of mass loss was approximately 300°C with the peak temperature of mass loss rate 272°C. The mass loss occurred even when the melting course had just begun owing to the possible evaporation of the sample. The temperatures of decomposition process measured by TG were in agreement with those determined by DSC.

The calculated thermodynamic functions of isoproturon

According to the following thermodynamic equations:

$$\Delta H = H_{\mathrm{T}} - H_{298.15} = \int_{298.15}^{\mathrm{T}} C_{\mathrm{p}} \mathrm{d}T$$

$$\Delta S = S_{\mathrm{T}} - S_{298.15} = \int_{298.15}^{\mathrm{T}} C_{\mathrm{p}} / T \mathrm{d}T$$

and by using the fitted polynomials (2), the fundamental thermodynamic functions of isoproturon relative to the standard reference temperature 298.15 K were calculated and tabulated in Table 2.

Table 2 Calculated thermodynamic functions of isoproturon

T/K	C_p/J K^{-1} mol^{-1}	H_T–$H_{298.15}$/J mol^{-1}	S_T–$S_{298.15}$/J K^{-1} mol^{-1}
80	107.318	–39851.6	–220.205
85	113.224	–39303.9	–213.567
90	118.260	–38729.9	–207.006
95	122.637	–38133.4	–200.557
100	126.533	–37517.4	–194.238
105	130.100	–36883.8	–188.056
115	136.717	–35569.3	–176.102
120	139.949	–34889.7	–170.318
125	143.217	–34195.4	–164.650
130	146.565	–33486.3	–159.088
135	150.026	–32762.1	–153.622
140	153.616	–32022.4	–148.242
145	157.345	–31266.5	–142.937
150	161.210	–30494.0	–137.700
155	165.206	–29704.4	–132.522
160	169.318	–28897.3	–127.397
165	173.529	–28072.2	–122.320

Table 2 Continued

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
170	177.821	–27229.0	–117.286
175	182.172	–26367.5	–112.291
180	186.560	–25487.6	–107.334
185	190.966	–24589.4	–102.413
190	195.370	–23673.1	–97.526
195	199.756	–22738.9	–92.673
200	204.108	–21787.2	–87.854
205	208.418	–20818.3	–83.069
210	212.677	–19832.8	–78.319
215	216.885	–18831.0	–73.605
220	221.042	–17813.5	–68.927
225	225.155	–16780.8	–64.285
230	229.234	–15733.2	–59.681
235	233.295	–14671.3	–55.113
240	237.355	–13595.2	–50.582
245	241.438	–12505.2	–46.087
250	245.567	–11401.3	–41.627
255	249.771	–10283.7	–37.201
260	254.079	–9151.9	–32.805
265	258.521	–8005.9	–28.439
270	263.126	–6845.1	–24.100
275	267.924	–5668.9	–19.784
280	272.940	–4476.8	–15.488
285	278.198	–3267.6	–11.208
290	283.714	–2040.7	–6.939
295	289.499	–794.9	–2.681
298.15	293.283	0.000	0.000
300	295.555	470.6	1.573
305	301.875	1757.1	5.826
310	308.439	3065.2	10.080
315	315.214	4395.9	14.338
320	322.149	5749.8	18.602
325	329.177	7127.1	22.873
330	336.209	8527.7	27.149
335	343.133	9951.0	31.430
340	349.813	11395.9	35.712

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