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Thermochimica Acta 307 (1997) 11–15

thermochimica
acta

Heat capacity and thermal decomposition of dicyandiamide

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Received 13 August 1997; accepted 28 August 1997

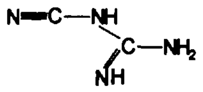
Abstract

A thermochemical study of dicyandiamide (DCD) has been performed using adiabatic calorimetry, differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The low-temperature heat capacity of DCD was determined with an automated adiabatic calorimeter in the range 80–370 K. A phase transition was found between 265 and 275 K, and the peak temperature, enthalpy and entropy of transition were determined to be 269.49 K, 2.98 kJ mol^{-1} and 11.07 JK^{-1} mol^{-1}, respectively. The high-temperature heat capacity of DCD was measured with a differential scanning calorimeter in the range 330–500 K. The DSC curve showed that DCD melts at 487.56 K and the enthalpy and entropy of melting were evaluated as 22.96 and 47.68 JK^{-1} mol^{-1}, respectively. The TG analysis of DCD was carried out in the range 300–850 K, from which it was found that decomposition starts at 521.20 K and ends at 659.62 K in three steps. © 1997 Elsevier Science B.V.

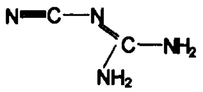
Keywords: Adiabatic calorimetry; Dicyandiamide; DSC; Heat capacity; TG

1. Introduction

Dicyandiamide (DCD) is an organic chemical, it is also named as cyanoguanidine and its formula is $C_2N_4H_4$. The structure of DCD [1,2] is:



Hughes [3] suggested that the structure of DCD should be:



DCD is white crystal with many crystalline shapes, such as needle, rhombus, scale, and so on. DCD has many important applications. For example, it is used as a raw material in medicine, plastics and pesticide, as an additive in chemical fertilizer, as a surface hardener in steel industry. In order to further understand its nature and perfect its basic data, a thermochemical study of DCD was performed in our thermochemistry laboratory.

Since heat capacity is a basic quantity for evaluation of thermodynamic properties, heat-capacity measurements of this compound were carried out in the low temperature range between 80 and 370 K with an automated adiabatic calorimeter [4]. In the range 300–800 K, the thermal behavior of DCD were investigated by a differential scanning calorimeter (DSC) and a thermobalance. The melting temperature, the

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PII S0040-6031(97)00323-7

molar enthalpy and molar entropy of melting and the decomposition temperature for DCD were determined by DSC and TG, respectively.

2. Experimental

2.1. DCD preparation

The DCD material used in the experiments was kindly supplied by Professor Guo-Xing Xing (State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Academia Sinica). DCD was systhensized according to the following route [5]:

$$Ca_2C + N_2 \rightarrow CaCN_2$$

$$CaN{-}CN + H_2O \rightarrow Ca(NHCN)_2 + Ca(OH)_2$$

$$Ca(NHCN)_2 + H_2O + CO_2 \rightarrow NH_2CN + CaCO_3$$

$$H_2N{-}CN + H_2N{-}CN \xrightarrow[\Delta]{74^{\circ}C} NC{-}NH$$

$$-C(NH){-}NH_2.$$

The DCD product of reaction was filtered, crystalled and separated for several times, and dried at last. The purity of DCD product finally obtained was >99.9% (mass) as determined by HPLC (Column: Bondpak G18).

2.2. Adiabatic calorimetry

The heat-capacity measurements were carried out by means of an automatic adiabatic calorimeter over the range 80–370 K. The mass of the sample amounted to 37.1688 g, which was equivalent to 0.4421 mol based on its molar mass of 84.080 g mol^{-1}. The equipment was based on the Nernst 'step heating' method and the main concepts of previous adiabatic calorimeters were adopted in Ref. [6]. The new calorimeter mainly consists of a calorimeter cell, a thermometer-heater assembly, an adiabatic shield, a guard shield, two sets of differential thermocouples, and a vacuum can. The adiabatic calorimeter was described before in detail [4] and only the new features of the equipment are described here.

The calorimeter cell was made of silver of 99.95% purity, 0.2 mm thick, gold-plated and polished. The main body was 33 mm in diameter and 60 mm high. The mass of the empty cell was about 50 g and its effective capacity was around 50 cm^3. In its center a tapered entrant well was provided for insertion of the thermometer-heater assembly. Onto the well's outer wall, eight L-shaped 0.15 mm thick radial silver vanes were brazed one by one by use of silver alloys. A space existed between the outer edges of the vanes and the cylindrical inner wall and four semi-circular vanes extended into the upper and the lower hemispherical spaces in the cell. A small amount of helium gas was introduced into the cell through a capillary copper tube, which was fitted on the silver lid of the cell, to promote the heat transfer. The cryostat of the adiabatic calorimeter included an adiabatic shield, a guard 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 shields. Each control circuit consisted of a modified DWT-702 precise temperature controller (made by No. 6 Automatic Instrument Manufacturing Co. of Shanghai, China) and a thermopile. When these control circuits were operating, the temperature difference between the calorimeter cell and its surroundings was maintained at 0.5 mK or less during the entire experimental process. A platinum-enclosed platinum resistance thermometer (No. 82021 4-lead, capsule-type, 25 Ω, 5 mm in diameter, 50 mm long) was used to measure the temperature of the adiabatic calorimeter cell. The thermometer was made by the Instrument Manufactory of Yunnan, China, and calibrated on the basis of the ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica, with an uncertainty of about 1 mK.

The energy introduced into the sample cell is supplied by a d.c. voltage supply with a stability of about 5 ppm. A computer-based on-line measuring system has been designed which can automatically measure the current through the calorimeter heater, the voltage across it, the duration of energy input, and subsequently computes the energy introduced. The system was composed of a main computer, I/O data channels, an A/D converter, a sample switch, the input interface, and clock signals. A Model 5000 Integrating Digital Multimeter (Sabtronics Instrument AG Switzerland) was used as A/D converter. The duration of heating was measured by means of a digitally displayed electronic timer-controller with an accuracy of 10^{-3} s. The temperature of the platinum thermometer in the calorimeter cell was also automatically measured by the above-mentioned system.

In order to verify the reliability of the calorimeter, the molar heat capacities of α-Al_2O_3 were measured from 80 to 400 K. The deviations of experimental results from the smoothed curve lie within ± 0.1%, while the inaccuracy was within ± 0.2% compared with those of the National Bureau of Standards [7] in the whole temperature range.

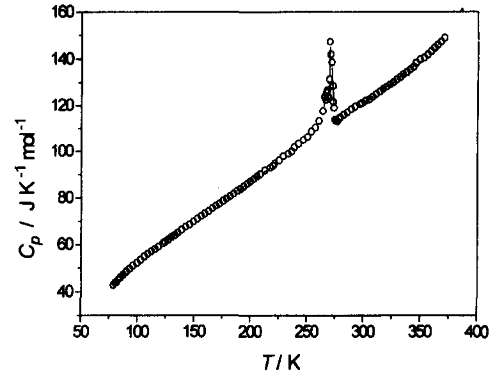

Fig. 1. The $C_p(T)$ curve of DCD obtained by adiabatic calorimetry.

2.3. *Thermal analysis*

A Du Pont TA 2000 thermal analysis system coupled with a personal computer loaded with a program for processing the obtained results, was used. The DSC measurements were carried out using a differential scanning calorimeter (Model 910) with aluminum sample pans and sapphire reference material. Both the sample and sapphire were scanned at a heating rate of 10 K min^{-1}, under nitrogen atmosphere with a flow rate of 150 ml min^{-1}. The mass of the sample used for experiments was 10.7600 mg. At the same time, the C_p measurements were performed under the same conditions as above in the range 300–500 K.

Thermogravimetric analysis was performed with a TG 951 thermobalance in the range 300–800 K. In the experiments, a DCD sample of 10.8870 mg, and a nitrogen flow rate of 150 ml min^{-1} were employed.

3. Results and discussion

The low-temperature experimental molar heat capacities for DCD are shown in Fig. 1. The deviation of the experimental points from the smoothed values in this region is within ± 0.2%. The heat-capacity measurements were repeated twice, and a very close agreement in the temperatures and C_p values was obtained. The $C_p(T)$ curve in Fig. 1 indicates that there is no thermal anomaly in the range 80–250 K which means that the thermochemical property of DCD is stable in this temperature range, and there is a phase transition in the range 250–280 K. This phase transition starts at 265 K and ends at 274 K, and its peak temperature is 269.45 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 2.98 kJ mol^{-1} and 11.07 J K^{-1} mol^{-1}, respectively, based on the following thermodynamic relationships:

$$\Delta H_m = \int C_{pm} dT \quad \text{and} \quad \Delta S_m = \int \frac{C_{pm}}{T} dT.$$

The phase transition may be caused by the change of DCD's crystalline structure. The experimental molar heat capacity of this compound is also listed in Table 1 in temperature increment sequence so that the temperature increments can be deduced approximately from the adjacent mean temperatures.

Owing to the need from both theoretical research and practical application for the heat capacity of higher temperature, the DSC heat-capacity measurements were carried out with sapphire reference material in the range 300–500 K. The accuracy of C_p determination is about ± 1%. The DSC results are shown in Fig. 2 and listed in Table 2. From Fig. 2, DCD is stable in structure below 500 K. For the comparison, the heat-capacity data obtained by adiabatic calorimetry are also plotted in Fig. 2, from which we can see that the two sets of the heat-capacity data accord well with each other. A DSC curve is shown in Fig. 3, from which we can see that DCD starts to melt at 481.59 K, the peak temperature is 487.56 K, which accords well with the value described in Ref. [2], The molar enthalpy and entropy of melting of DCD were determined by DSC being 22.96 kJ mol^{-1} and 47.68 J K^{-1} mol^{-1}, respectively. From Fig. 3, the decomposition reaction of DCD is rather complex,

Table 1

Molar heat capacities of DCD obtained by adiabatic calorimetry ($M = 84.080\ \mathrm{g\ mol^{-1}}$)

T (K)	C_p ($\mathrm{JK^{-1}\ mol^{-1}}$)	T (K)	C_p ($\mathrm{JK^{-1}\ mol^{-1}}$)	T (K)	C_p ($\mathrm{JK^{-1}\ mol^{-1}}$)
78.406	42.99	172.480	77.55	275.499	113.76
79.804	43.85	175.632	78.70	278.788	114.82
81.185	44.01	178.752	79.69	282.058	115.93
82.838	45.14	181.842	80.74	285.305	116.97
84.751	46.13	184.901	81.76	288.522	118.48
87.121	47.22	187.930	82.90	291.712	119.55
89.935	48.45	190.929	83.87	294.878	120.86
92.688	49.62	193.900	84.98	298.029	121.04
95.769	51.04	196.842	86.13	301.163	122.13
99.168	52.31	199.756	87.14	304.274	122.77
102.496	53.55	202.643	88.20	307.367	123.76
105.758	54.93	205.505	89.31	310.441	124.91
108.958	56.01	208.342	90.12	313.495	126.13
112.102	57.13	211.158	90.92	316.530	127.30
115.194	58.16	213.951	91.53	319.545	128.05
118.236	59.11	217.279	93.02	322.540	129.11
121.233	60.22	221.126	94.74	325.516	130.10
124.186	61.26	224.932	96.15	328.473	131.26
127.101	62.26	228.669	100.48	331.411	132.34
129.976	63.24	232.347	101.40	334.330	133.45
132.816	64.09	236.011	102.20	337.230	134.43
135.620	65.09	239.626	103.53	340.242	135.60
138.809	66.32	243.177	104.74	343.365	136.65
142.377	67.51	246.712	105.87	346.474	137.50
145.897	68.61	250.218	106.27	349.565	138.56
149.369	69.78	253.655	108.73	352.622	140.58
152.794	71.05	257.024	110.40	355.647	141.91
156.176	72.20	260.327	113.34	358.650	143.36
159.515	73.32	263.545	117.65	361.630	144.66
162.812	74.37	266.638	125.62	364.585	146.00
166.071	75.48	269.494	147.28	367.520	147.35
169.293	76.59	272.345	128.55	370.435	148.90

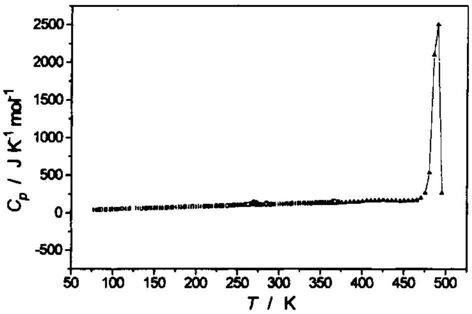

Fig. 2. Comparison of the heat capacities of DCD obtained by adiabatic calorimetry (ADC) and DSC. (○: ADC; ▲: DSC).

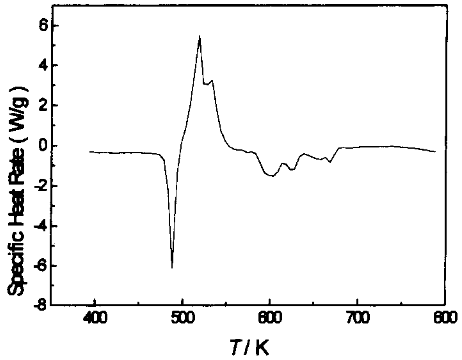

Fig. 3. DSC curve of DCD under nitrogen atmosphere.

Table 2
Molar heat capacity of DCD obtained by DSC

T (K)	C_p (JK^{-1} mol^{-1})	T (K)	C_p (JK^{-1} mol^{-1})	T (K)	C_p (JK^{-1} mol^{-1})
305.00	122.49	370.00	148.18	435.00	167.72
310.00	124.82	375.00	151.61	440.00	167.90
315.00	126.07	380.00	155.11	445.00	168.20
320.00	128.11	385.00	157.38	450.00	168.51
325.00	129.90	390.00	159.68	455.00	169.17
330.00	131.78	395.00	160.38	460.00	170.73
335.00	133.17	400.00	161.20	465.00	171.02
340.00	135.40	405.00	162.02	470.00	199.39
345.00	137.05	410.00	163.02	475.00	265.42
350.00	138.59	415.00	164.47	480.00	527.77
355.00	141.63	420.00	165.42	485.00	2093.93
360.00	143.45	425.00	166.77	490.00	2500.43
365.00	146.78	430.00	167.41	495.00	264.57

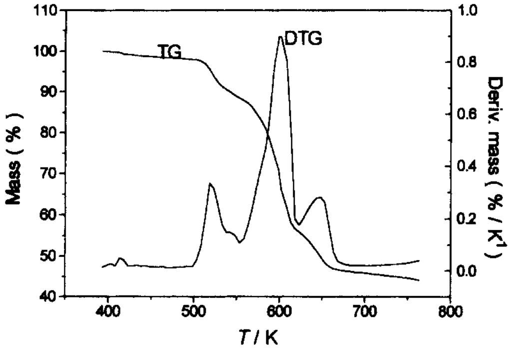

Fig. 4. TG–DTG plot of DCD in an atmosphere of flowing dry nitrogen at a heating rate of 10 K min^{-1}.

there are two strong exothermic peaks which means that DCD starts to decompose at about 495 K releasing a large amount of energy with two exothermic reactions, and there are three main endothermic peaks, but the absorbing energy of every peak is small.

The TG measurements were carried out in N_2 atmosphere. The results are presented in Fig. 4. As can be seen from the mass-loss curve, most activities occur in the range 500–700 K; the DCD undergoes three stages of decomposition and the mass loss of 2.3% below 520 K is due to the sublimation and evaporation of DCD. DCD starts to decompose at 521.20 K and ends at 659.62 K. These accord well with the results obtained by DSC. The decomposition products are complicated, but NH_3 and HCN might be two of those products. The decomposition temperature range in first stage is from 521 to 540 K and the peak temperature is at 530.29 K, the mass loss in this stage is 7.37%. The main decomposition reaction is in second step, the mass loss is 22.38% and the peak temperature is at 609.62 K. The third decomposition reaction takes place in the range 637–660 K, and the peak temperature and the mass loss in this stage are 649.16 K and 8.84%, respectively.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China for financial support to this work under Grant No. 29573133.

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