ELSEVIER

Thermochimica Acta 352–353 (2000) 117–120

thermochimica acta

www.elsevier.com/locate/tca

Thermal behavior of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$

Sun Lixia*, Hu Rongzu, Wu Shanxiang, Kang Bin

Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

Received 2 June 1999; received in revised form 10 September 1999; accepted 1 October 1999

Abstract

The thermal behavior and crystal transformation processes from I to II and from II to I for $Et_4N^{10}BH_4$ and from I′ to II′ and from II′ to I′ for $(Et_4N)_2B_{20}H_{18}$ are determined by DSC. The results show that their crystal transformation processes are reversible. The values of ΔH_{cr} and ΔS_{cr} are 101.0 J g^{-1} and 38.68 J mol^{-1} k^{-1} for $Et_4N^{10}BH_4$ and 148.4 J g^{-1} and 182.7 J mol^{-1} k^{-1} for $(Et_4N)_2B_{20}H_{18}$, respectively. The apparent activation energy (E) and pre-exponential constant (A) are 213.0 kJ mol^{-1} and $10^{17.7}$ s^{-1} for $Et_4N^{10}BH_4$, and E_1=105.4 kJ mol^{-1}, A_1=$10^{9.1}$ s^{-1}, E_2=180.2 kJ mol^{-1}, A_2=10^{15} s^{-1} for two exothermic processes of $(Et_4N)_2B_{20}H_{18}$, respectively.

Keywords: Crystal transformation; Decomposition; $Et_4N^{10}BH_4$; $(Et_4N)_2B_{20}H_{18}$; Kinetic parameters

1. Introduction

Ammonium tetraethylate of tetrahydroboracic acid ($Et_4N^{10}BH_4$) and ammonium tetraethylate of octabedahydro-eicosa boracic acid $(Et_4N)_2B_{20}H_{18}$ are two important intermediates of preparing the medicines used for curing the malignant tumour. However, their thermal behaviors under conditions of linear temperature increase have not been published. In the present work, their thermal behaviors are studied by means of differential scanning calorimeter (DSC) and polarization microscopy (PM).

2. Experimental

2.1. Materials

$Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ used in this work were prepared and purified by our Institute. Their purities were more than 99.9%. The standard material used for calibrating enthalpy value, α-naphthol and reference material, α-Al_2O_3 were of analytical purity.

2.2. Experimental equipment and conditions

All measurements were made with a Shanghai Balance Manufactures' CDR-1 differential scanning calorimeter. The conditions of DSC were as follows: heating rate, 5°C min^{-1} for determining the enthalpy of the crystal transformation and 1, 2, 5, 10, 20°C min^{-1} for determining the kinetic parameters of thermal decomposition; calorimetric sensitivity, ±20.92 mJ s^{-1}; paper speed, 20 mm min^{-1}; atmosphere, static air; sample mass, 3–5 mg; pan, sealed cell of aluminum. The above-mentioned heating rate was calculated according to the actual rising rate of temperature from 50°C to the temperature at the end of the reaction. The polarization microscope experiment were carried out on a model FP-5 melting point

* Corresponding author.

0040-6031/00/$ – see front matter
PII: S0040-6031(99)00448-7

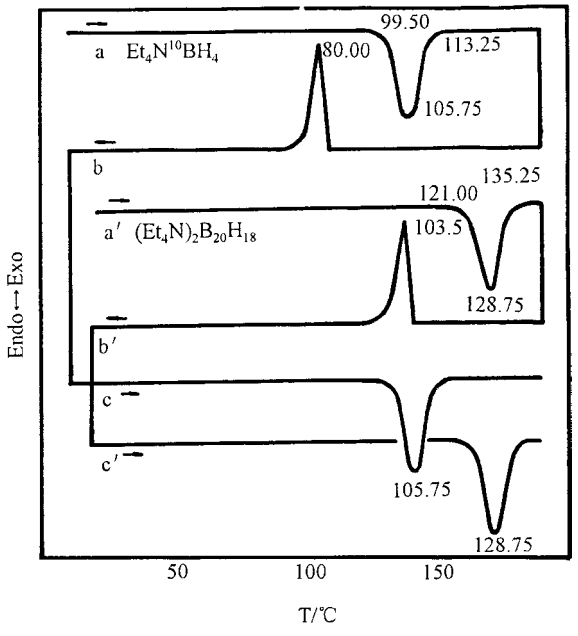

Fig. 1. DSC curves of the crystal transformation of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$. (a) and (a′) upon heating (5°C min^{-1}); (b′) upon cooling (5°C min^{-1}); (b) and (c′) upon heating once more (5°C min^{-1}).

analyzer made by the Metller company at a heating/cooling rate of 0.2°C min^{-1}.

3. Results and discussion

3.1. Crystal transformation of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$

The DSC curves of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ below 140°C under the condition of 5°C min^{-1} are shown in Fig. 1

The DSC curves in Fig. 1 show that (1) for $Et_4N^{10}BH_4$, the endothermic peak begins at 99.5°C, reaches its maximum 105.75°C and ends at 113.25°C, and (2) for $(Et_4N)_2B_{20}H_{18}$, its endothermic peak begins at 121.00°C, reaches its maximum 128.75°C and ends at 135.25°C. For verifying the assignation of above-mentioned two endothermic peaks, we made an experiment by the polarization microscope method. The results show that the endothermic peak in the temperature range 99.5–113.25°C is attributed to the crystal transformation of $Et_4N^{10}BH_4$ from I to II and the endothermic peak in the temperature range 121.00–135.25°C is attributed to the crystal transformation of $(Et_4N)_2B_{20}H_{18}$ from I′ to II′. On cooling, form II′ of $NH_4N^{10}BH_4$ will transform to form I′ when 80°C is reached, and form II′ of $(Et_4N)_2B_{20}H_{18}$will transform to form I′ when 103.5°C is reached. The above-mentioned two processes are exothermic. The curves (c) and (c′) obtained upon second heating is the same as curves (a) and (a′), respectively. This fact shows that the crystal transformation process for two compounds is reversible.

3.2. The enthalpy and entropy of crystal transformation of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$

To gain the accuracy enthalpy of crystal transformation of title compounds from DSC curve, we used a standard sample with known melting enthalpy (its melting temperature range closes to that of the crystal transformation of title compounds), α-naphthol, to run DSC experiments under the same conditions.

By substituting the data in Table 1 into Eq. (1) and [1]

$$\Delta H_{cr} = \frac{\Delta H_s (S_{cr}/m_{cr})}{S_s/m_s} \quad (1)$$

where ΔH_{cr} is the enthalpy of crystal transformation, J g^{-1}; ΔH_s is the melting enthalpy of standard sample. For α-naphthol, its value is 162.9 J g^{-1}; S_{cr} and S_s are the area under the DSC curve of title compounds and standard sample, respectively, mm^2; m_{cr} and m_s the mass of title compounds and standard sample, respectively, mg.

From Eq. (1), the enthalpy of crystal transformation of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ are obtained. The values of ΔH_{cr} for $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ are 101.6 and 148.4 J g^{-1}, respectively. By substituting the value of ΔH_{cr} and crystal transformation temperature into Eq. (2).

$$\Delta S_{cr} = \frac{\Delta H_{cr} M}{T_{cr}} \quad (2)$$

where ΔS_{cr} is the entropy of crystal transition of title compounds, J mol^{-1} k^{-1}; ΔH_{cr} the enthalpy of crystal transformation of title compounds, J g^{-1}; M the mass of 1 mol sample, g mol^{-1}; T_{cr} the crystal transformation temperature, K.

Table 1
DSC data of the crystal transformation processes of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$

Sample	Sample mass, m (mg)	Average peak area $\bar{S}^2$, (mm^2)	$\bar{S}/w$	$\sum_{i=1}^{n}(\bar{S}/w)/n$	Relative deviation (%)
α-naphthol	3.40	540.0	158.8	159.1	1.7
	3.36	526.8	156.8		1.4
	3.24	510.0	157.4		1.1
	3.40	545.0	160.3		0.8
	3.41	553.0	162.2		1.9
	3.65	360.0	98.6	98.6	0
$Et_4N^{10}BH_4$	3.65	363.3	98.5		0.9
	3.65	360.0	98.6		0
	3.65	350.0	95.8		2.8
	3.65	366.7	100.5		1.9
	3.66	330.9	90.4	89.8	0.6
$(Et_4N)_2B_{20}H_{18}$	3.66	321.7	87.9		2.1
	4.54	400.4	88.2		1.7
	4.54	410.0	90.3		0.6
	4.88	449.0	92.0		2.4

The entropies of crystal transformation of title compounds, ΔS_{cr} are obtained. The values of ΔS_{cr} for $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ are 36.68 and 182.7 J mol^{-1} k^{-1}, respectively.

3.3. Kintetic parameter of the thermal decomposition of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$

DSC curves of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ are shown in Fig. 2. The thermal decomposition of $Et_4N^{10}BH_4$ starts in 225.5°C and ends in 245.0°C with summit of 231.5°C. For $(Et_4N)_2B_{20}H_{18}$, there are two exothermic peaks of thermal decomposition at 210.25 and 258.0°C in the DSC curves.

In order to obtain the apparent activation energy (E) and pre-exponential constant (A) of thermal decomposition reaction for $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$, the Kissinger Eq. (1), i.e. Eq. (3) [2] is used

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{RA}{E}\right) - \frac{E}{RT_p} \tag{3}$$

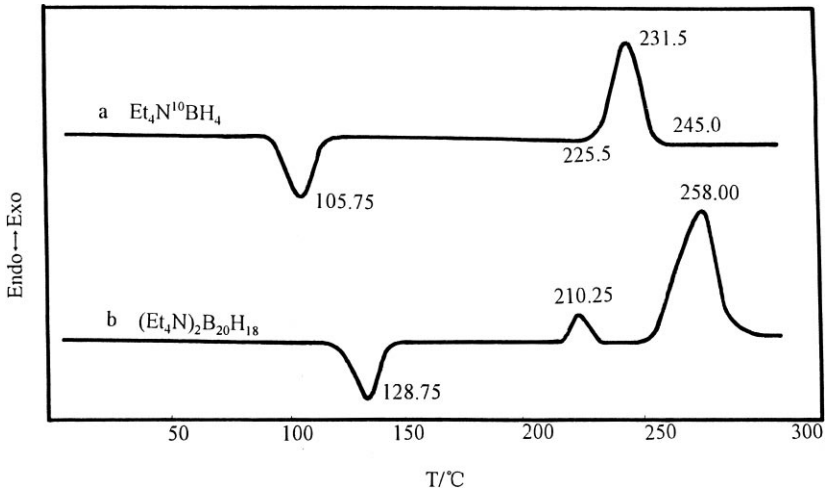

Fig. 2. The typical DSC curves of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ at a heating rate of 5°C min^{-1}.

where β is the heating rate, °C min^{-1}; T_p the maximum peak temperature, K; R the gas content, 8.314 J mol^{-1} k^{-1}.

From Eq. (3), the values of E of 213.0 kJ mol^{-1} and A of $10^{7.7}$ s^{-1} for the exothermic process of $Et_4N^{10}BH_4$, and E_1 of 105.4 kJ mol^{-1}, E_2 of 180.2 kJ mol^{-1}, A_1 of $10^{9.1}$ s^{-1} and A_2 of 10^{15} s^{-1} for two exothermic processes of $(Et_4N)_2B_{20}H_{18}$ are obtained.

4. Conclusions

The crystal transformation of $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$ occurs in the temperature range of 99.50–113.25°C and 121.00–135.25°C, respectively. Their crystal transformation processes are reversible.

Enthalpies and entropies of crystal transformation are 101.0, 148.4 J g^{-1} and 38.68, 182.7 J mol^{-1} k^{-1} for $Et_4N^{10}BH_4$ and $(Et_4N)_2B_{20}H_{18}$, respectively.

Their kinetic parameters of thermal decomposition reaction are as follows:

For $Et_4N^{10}BH_4$, E=213.0 kJ mol^{-1} $A=10^{17.7}$ s^{-1}; for $(Et_4N)_2B_{20}H_{18}$, E_1=105.4 kJ mol^{-1} $A_1=10^{9.1}$ s^{-1}; E_2=180.2 kJ mol^{-1} $A_2=10^{15}$ s^{-1}.

References

[1] Hu Rongzu, Liang Yanjun, Wu Shanxiang, Propellants Explosives 1 (1984) 14.
[2] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.