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Note

A TG– DSC STUDY OF THE THERMAL DISSOCIATION OF $(NH_2BH_2)_x$

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Even though the first report of polymeric NH_2BH_2, the inorganic analog of polyethylene, appeared over 40 years ago [1], the nature of $(NH_2BH_2)_x$ is still not fully characterized. Shore and co-workers prepared crystalline cyclic oligomers, $(NH_2BH_2)_n$ ($n = 2, 3, 4, 5$) [2] and an amorphous $(NH_2BH_2)_x$ apparently consisting of solvated linear chains with $x = 3$–5. An "inert white solid" identified as $(NH_2BH_2)_x$ on the basis of its infrared spectrum was produced by rf discharge in borazine vapor [3] and gas-phase pyrolysis of NH_3BH_3 [4].

A recent report describes the preparation of a similar or perhaps identical white solid from pyrolysis of NH_3BH_3 in the liquid phase under reduced pressure [5]. Elemental characterization indicated the empirical formula BNH_4 but the molecular weight could not be determined due to its low solubility. Mass spectra of volatiles above a heated sample showed ions representing $-NH_2BH_2-$ chains up to nine atoms in length along with various borazine derivatives thought to be thermal degradation products [6].

In order to characterize the thermal dissociation process further, we wish to report the results of a TG–DSC study of the compound.

EXPERIMENTAL

The TG curves were obtained using a Perkin–Elmer TGS-2 thermobalance. Sample sizes ranged in mass from 2 to 2.5 mg and were studied at a furnace heating rate of 10°C min^{-1} in a dynamic N_2 atmosphere. A special grade of high-purity nitrogen was used.

The DSC curves were obtained using a DuPont Model 990 system equipped with a DSC modular cell. The same conditions of pyrolysis, as used for TG, were employed.

The $(NH_2BH_2)_x$ was prepared as previously described [5]. Six different samples were prepared and studied by TG–DSC.

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RESULTS AND DISCUSSION

The TG–DSC curves of $(NH_2BH_2)_x$ are shown in Fig. 1. All of the six samples studied exhibited three mass-loss steps with associated TG features but the temperature ranges and the relative mass loss for each step varied considerably with sample history. In addition, most samples showed an initial mass loss starting from ambient temperature which was accompanied only by minor temperature changes. The magnitude of the initial loss was less for samples held in a dynamic vacuum at 30–50°C before running. These observations indicate that thermal desorption of substances adsorbed on the polymer is responsible for the initial mass loss. In other experiments, borazine impurities appeared in ^{11}B NMR spectra of solvent extracts of the polymer. Desorption of a volatile substance such as borazine could account for the initial mass losses observed in the TG curve.

Table 1 shows the total mass loss observed for four of the $(NH_2BH_2)_x$ samples up to 350°C. Sample **I** was freshly prepared according to the published procedure [5] and run within 12 h giving a total mass loss of 26%. Sample **II** was similarly prepared but held under dynamic vacuum overnight before running, resulting in a smaller mass-loss (22%) owing, we believe, to prior removal of some volatile adsorbates. Sample **III** was evacuated at 30–50°C for 5 h resulting in a total mass loss of only 13.5% up to 350°C and slightly more than 14% up to 450°C.

The TG results from **III** correspond closely to those expected for loss of the entire hydrogen content (14%) of an $(NH_2BH_2)_x$ polymer leaving boron nitride (eqn. 1).

$$(NH_2BH_2)_x \xrightarrow{\Delta} 2xH_2 + (BN)_x \qquad (1)$$

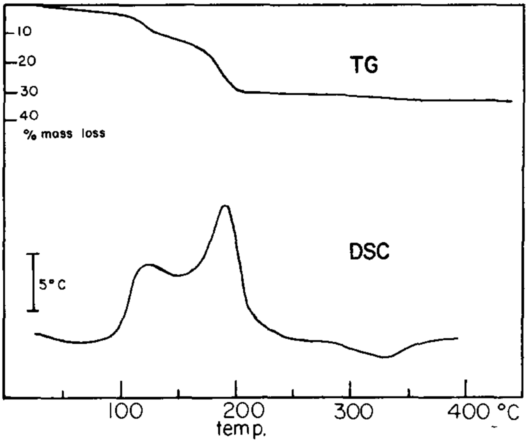

Fig. 1. TG–DSC curves of $(NH_2BH_2)_x$ in nitrogen at a heating rate of 10°C min^{-1}.

Sample **IV** was prepared like **III** but remained in a capped vial for two weeks before the TG and DSC curves were obtained. The TG curve is similar to that of sample **III** up to about 195°C (5 vs. 6% loss) but then a precipitous drop corresponding to a 25% mass loss occurs from 135 to 225°C. The total mass loss to 350°C is 32%. These results suggest that changes occur in the polymer as it ages such that instead of hydrogen alone, fragments containing boron and/or nitrogen are evolved during the heating process. The DSC curve shows much larger exothermic features for this region in **IV** than in **III**.

Since three steps were observed in the mass-loss curves of freshly prepared samples, we attempted to correlate these to progressive hydrogen loss steps (eqns. 2–4).

$$NBH_4 \rightarrow NBH_2 + H_2 \qquad (2)$$

$$NBH_2 \rightarrow NBH + \tfrac{1}{2}H_2 \qquad (3)$$

$$NBH \rightarrow NB + \tfrac{1}{2}H_2 \qquad (4)$$

Sample **III** showed about 7% loss from ambient to 150°C, 3% from 150 to 225°C and 4% from 250 to 400°C, roughly matching the values 6.9, 3.5 and 3.5% expected from eqns. (2)–(4). The mass-loss values for individual steps varied considerably even among samples prepared in the same way, however, so we believe processes other than stepwise hydrogen loss are involved to some degree in all of the samples examined in this study.

It is notable that the DSC curves show exothermic changes corresponding to two of the mass-loss regions. If the thermal reactions represent primarily H_2 loss, a rough measure of the enthalpy change can be obtained from eqn. (5).

$$\text{N–H} + \text{H–B} \rightarrow \text{H–H} + \text{N–B} \qquad (5)$$

for which

$$\Delta H_{rx} \cong D_{H-H} + D_{N-B} - D_{N-H} - D_{B-H}$$

Values for D_{H-H}, D_{N-H} and D_{B-H} are 432, 386 and 389(?) [7], respectively, leading to the conclusion that the lower limit on D_{N-B} is approximately 343

TABLE 1

Mass-loss data for $(NH_2BH_2)_x$ samples

Sample no.	Preparative history	Total mass loss (350°C) (%)
I	Freshly prepd. not evacuated	26
II	Evacuated overnight	22
III	Evacuated and heated 30–50°C, 5 h	13.5
IV	Evacuated and heated but stored 2 weeks	32

kJ, barring any other sizeable contributions to the reaction enthalpy. While this value is lower than that reported for the B–N bond in B-trichloroborazine [7], it is of reasonable magnitude given the approximate nature of this approach.

Finally, the characteristics of the TG curve of freshly prepared $(NH_2BH_2)_x$ which has been gently heated under dynamic vacuum suggest that heating the polymer in the appropriate temperature ranges (i.e., up to 150°C and near 200°C) may be an effective way to prepare more highly condensed structures with compositions near NBH_2 and NBH. We are currently studying those transformations.

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REFERENCES

1 H.I. Schlesinger, D.M. Ritter and A.B. Burg, J. Am. Chem. Soc., 60 (1938) 2297.
2 K.W. Böddeker, S.G. Shore and R.K. Bunting, J. Am. Chem. Soc., 88 (1966) 4396.
3 C.T. Kwon and H.A. McGee, Jr., Inorg. Chem., 9 (1970) 2458.
4 S.Y. Pusatcioglu, H.A. McGee, A.L. Fricke and J.C. Hassler, J. Appl. Polym. Sci., 21 (1977) 1561.
5 R. Komm, R.A. Geanangel and R. Liepin, Inorg. Chem., 22 (1983) 1684.
6 R.A. Geanangel and J.W. Rabalais, Inorg. Chim. Acta, 97 (1985) 59.
7 J.E. Huheey, Inorganic Chemistry, 3rd edn., Harper and Row, New York, 1983, Appendix E