

Note

THE THERMAL DISSOCIATION OF NH_3BH_3

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Ammonia-borane, NH_3BH_3 , has been shown to undergo thermal decomposition upon melting [1,2]. The decomposition releases hydrogen forming a mixture of products including poly(aminoborane), $(\text{NH}_2\text{BH}_2)_x$, borazine and other substances. We have been interested in optimizing the synthesis of $(\text{NH}_2\text{BH}_2)_x$ by this route and have reported TG and DSC results on the reaction. In the present paper we wish to report DTA curves for NH_3BH_3 which better define the chemical steps in the decomposition reaction.

EXPERIMENTAL

The TG curves were obtained on a Perkin-Elmer TGS-2 thermobalance employing an *X-Y* plotter for data recording. The sample sizes ranged in mass from 1.5–2.0 mg and were studied at a furnace heating rate of 5 and $10^\circ\text{C min}^{-1}$ in a dynamic N_2 atmosphere (ca. 40 ml min^{-1}).

The DTA curves were obtained using a Deltatherm Model D8000 DTA instrument. Sample sizes ranged in mass from 2 to 3 mg and were heated at a furnace heating rate of 2, 5 or $10^\circ\text{C min}^{-1}$ in a dynamic N_2 atmosphere (ca. 40 ml min^{-1}).

The NH_3BH_3 was obtained from Callery Chemical Company and sublimed until the melting of a sample held in a closed capillary began at not less than 115°C when determined on a Melt Temp heated block set at 40 V. (Caution: Melting point capillaries should be sealed with a plug of modeling clay or wax; those sealed with a torch may shatter under the pressure developed during the decomposition.)

RESULTS AND DISCUSSION

The TG and DTA curves are shown in Fig. 1. Some difficulty was experienced in obtaining the TG curve of NH_3BH_3 . During the thermal decomposition process, the sample undergoes a voluminous swelling, causing contact to be made with the thermobalance furnace walls. Thus, an accurate

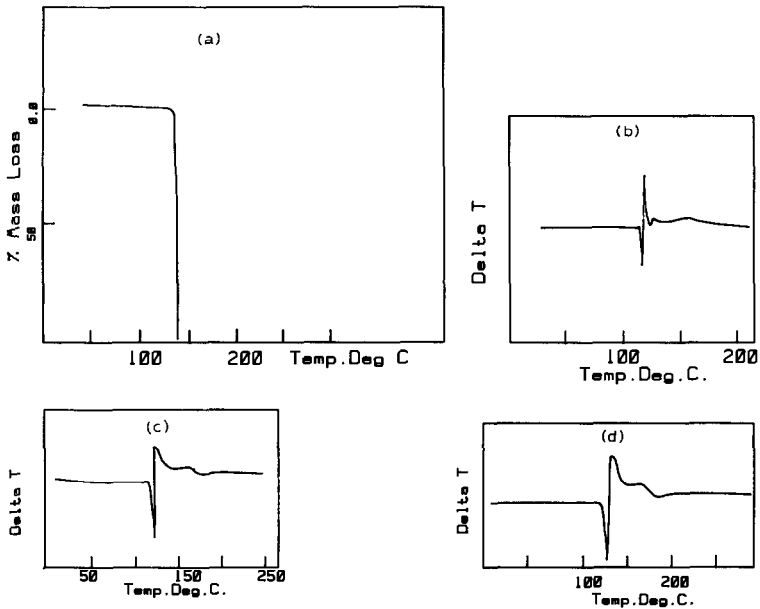


Fig. 1. TG and DTA curves of NH_3BH_3 . (a) TG; (b) DTA at 2°C min^{-1} ; (c) DTA at 5°C min^{-1} ; and (d) DTA at $10^\circ\text{C min}^{-1}$.

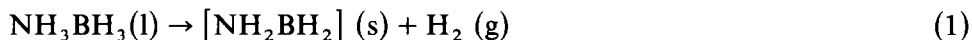
measurement of the sample mass after the thermal decomposition reaction could not be obtained. At heating rates of 5 and $10^\circ\text{C min}^{-1}$, a T_1 of 137°C was obtained for the compound. These results were obtained on a different instrument as reported earlier [1].

The DTA curves of NH_3BH_3 , at heating rates of 2, 5 and $10^\circ\text{C min}^{-1}$, respectively, as illustrated in Fig. 1, were characterized by a very narrow endothermic peak followed by a narrow exothermic peak. Apparently, the thermal decomposition reaction is initially endothermic but changes to exothermic as the reaction proceeds. As in the TG studies, the sample undergoes a voluminous swelling and completely fills the sample holder chamber during the thermal decomposition reaction.

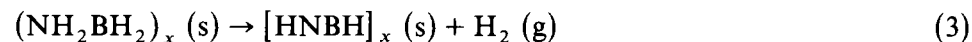
The DTA curve for NH_3BH_3 , obtained at a heating rate of $10^\circ\text{C min}^{-1}$, was reported earlier [1] and our current results at this heating rate are in qualitative agreement. At a heating rate of 2°C min^{-1} , however, the features of the DTA curve become considerably more distinct and four separate reactions can be discerned. The onset of the endothermic peak, which corresponds to melting of the solid, is at about 114°C at 2°C min^{-1} , some 5° lower than that found at $10^\circ\text{C min}^{-1}$. Depression of the melting point of NH_3BH_3 by slow heating is a characteristic we have observed independently; the solid phase begins to decompose, slowly releasing hydrogen approximately 30°C below the melting point of the compound. The thermal

effect of this solid-state reaction can be seen in the narrow increase of slope of the endothermic peak just before the onset of melting.

The exothermic peak following the melting endotherm results from the rapid evolution of hydrogen from the molten NH_3BH_3 , as given by the equation:



The exothermic character of the reaction is mainly attributable to the thermodynamic stability of H_2 , however, the actual chemical change is more complex than indicated by eqn. (1). The monomeric aminoborane $[\text{NH}_2\text{BH}_2]$ product, detected by its mass spectrum as a monomer in the gas phase [3], rapidly associated to a complex mixture of poly(aminoboranes) (eqn. 2). These in turn undergo thermal decomposition [4] in this temperature range, releasing additional hydrogen along with borazine (eqn. 3) and other products.



↓
borazine + other products

We suggest that the two exothermic DTA peaks near 125 and 155°C are associated with the spontaneous poly(aminoborane) formation from NH_2BH_2 (eqn. 2) and the ensuing decomposition of poly(aminoborane), respectively. We cite as evidence supporting this assignment theoretical studies of the formation of $(\text{NH}_2\text{BH}_2)_2$ from NH_2BH_2 which indicate that the dimer is only about 13 kJ more stable than two unbonded monomers [5]. It follows that the association of NH_2BH_2 to poly(aminoborane) may only be mildly exothermic, in agreement with the small magnitude of the 125°C DTA peak. Further support for this comes from a band structure calculation on poly(aminoborane) which found it to be characteristic of a weakly bonded polymer [6].

Hydrogen loss from $(\text{NH}_2\text{BH}_2)_x$ is known to begin near 100°C and to continue in steps over a broad temperature range [1]; thus the broad DTA peak centered near 155°C appear to represent this decomposition process. The loss of the last residual hydrogen, forming boron-nitride, was shown earlier to require temperatures in excess of 500°C [1].

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