THE THERMAL DECOMPOSITION OF AMMONIA BORANE

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ABSTRACT

The thermal decomposition of ammonia–borane has been studied by thermogravimetry, differential thermal analysis, and decomposition product measurements. Vigorous decomposition with hydrogen evolution begins near 120°C and proceeds in stages as the temperature is increased to 200°C leaving a white residue. The composition of the residue was approximately $BNH_{2.1}$ after heating to 170°C and $BNH_{(0.8-1.2)}$ after heating to 200°C. The i.. spectrum gave evidence of further slow hydrogen loss above that temperature.

INTRODUCTION

Ammonia–borane was first synthesized and characterized by Shore and Parry[1,2] who also reported some of its properties. The compound was found to be subject to slow hydrogen loss at room temperature accompanied possibly by conversion to the "diammoniate of diborane", $H_2B(NH_3)_2^+BH_4^-$. It was observed that a solid sample of $H_3N \cdot BH_3$ which was held in a dry atmosphere at 25° for a short period would not fully redissolve in ethyl ether, suggesting that a partial conversion to the insoluble "diammoniate" or some other insoluble substance may have occurred. Furthermore, ether solutions of $H_3N \cdot BH_3$ were observed to slowly precipitate an unidentified white solid.

During our investigations of the synthesis and properties of ammonia–borane[3], we have had an opportunity to make further observations on its thermal instability. As a part of these studies, thermogravimetric (TG) and differential thermal analysis (DTA) curves were obtained for $H_3N \cdot BH_3$ and its static pyrolysis was studied.

EXPERIMENTAL

TG and DTA measurements

The TG curves were obtained on a DuPont thermobalance, Model 950. A sample mass of about 10 mg was employed using a furnace heating rate of 5°C min^{-1} and a dynamic N_2 atm. DTA curves were obtained using open and sealed capillary tubes in an apparatus that has previously been described[4]. The furnace heating rate employed was 10°C min^{-1}.

Thermomanometry measurements

The pressure–temperature curves were obtained on an apparatus that has previously been described[5]. This apparatus was modified in that the pressure transducer employed consisted of a Validyne Model AP10, 0-1000 torr, connected to a Model C 23 digital readout meter rather than the change in resistance technique previously described. A furnace heating rate of $8\,°C\ min^{-1}$ was employed.

Preparation of $H_3N \cdot BH_3$.

Ammonia–borane was prepared and purified by a method described elsewhere[3].

Pyrolysis apparatus

The pyrolysis reactions were carried out either in a cylindrical tube fitted with a detachable O-ring joint or in a special vessel designed to minimize sublimation of the ammonia-borane. This vessel consisted of a pear-shaped approximately 100-ml bulb connected directly to a right angle Teflon vacuum valve (12 mm I.D.). The Teflon plug was fitted with an O-ring on the tip. The whole enclosed volume, including the lower part of the Teflon valve, was uniformly heated during the pyrolysis experiments so that ammonia-borane could not escape pyrolysis by subliming to a cool zone.

RESULTS AND DISCUSSION

TG, DTA and thermomanometry measurements

The TG and DTA curves are given in Figs. 1 and 2.

The rapid decrease in mass in the TG curve beginning at about 120°C and terminating near 133°C represented a mass-loss of about 31.6%. The total mass-loss up to 200°C was about 35%, the part above 133°C being lost in a very gradual manner.

The DTA curves obtained in both open and sealed capillaries exhibit sharp endothermic peaks beginning just above 112°C, which correspond to the observed melting temperature[6] of 112-114°C for purified $H_3N \cdot BH_3$. Near 117°C, a steep exothermic peak begins, reaching a maximum at about 130°C in the open tube. External observation of ammonia-borane samples in this temperature range revealed a rapid, frothing decomposition releasing copious quantities of gas. The sample held in a sealed capillary exploded in this interval but, up to this point, the curves from the sealed and open samples were nearly identical, suggesting that little, if any, sublimation occurs under these conditions. A final broad exothermic peak is observed beginning near 150°C and above 200°C the curve is featureless.

The thermomanometry curve of $H_3N \cdot BH_3$ is illustrated in Fig. 3.

Hydrogen evolution became evident near 120°C by the sharp pressure rise initiating at that temperature. This corresponds closely to the first exothermic peak in the DTA curve which accompanies the vigorous decomposition of the compound. When the temperature reached 145°C, a change in the rate of pressure increase was evident, probably reflecting a different hydrogen elimination reaction operative above that temperature. This change corresponds reasonably well with the onset of the
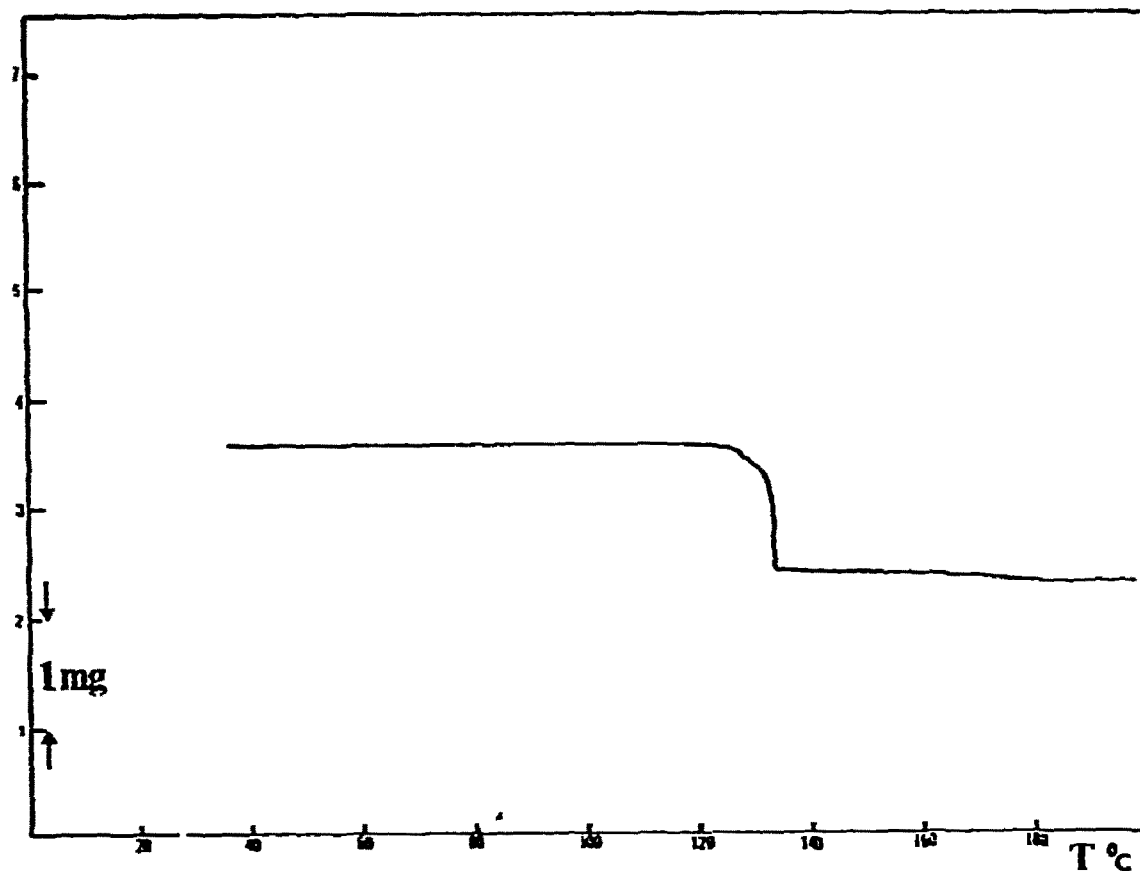
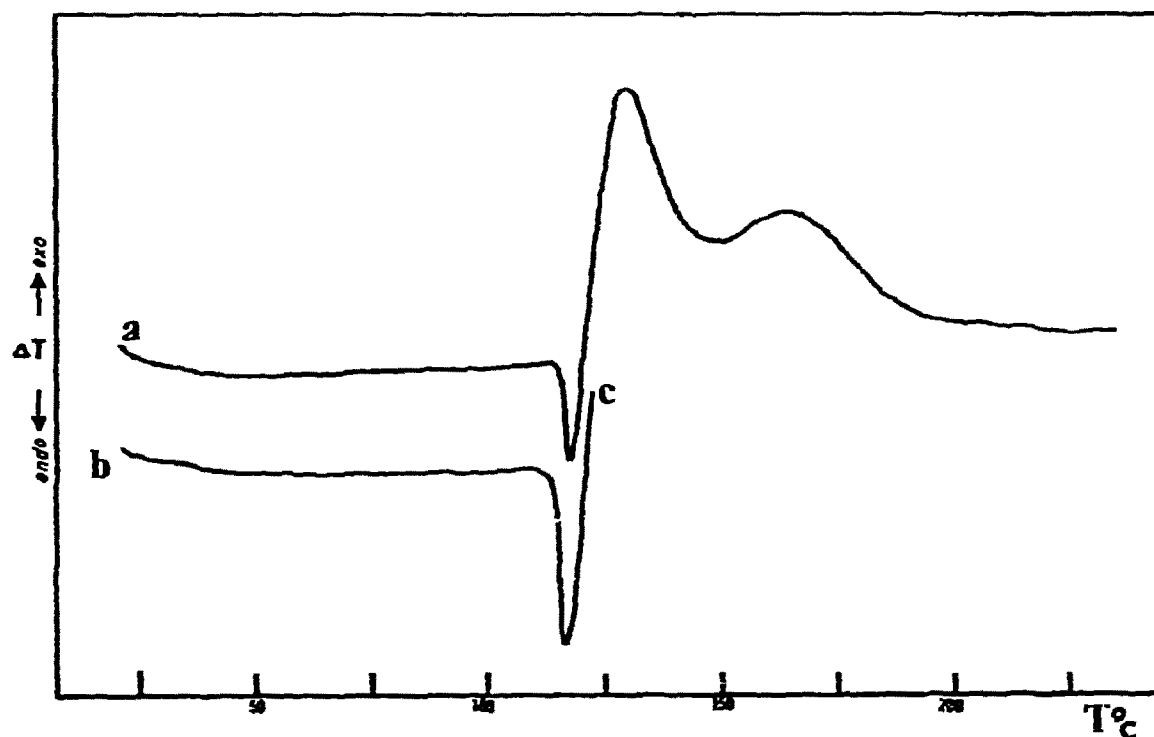Fig. 1. TG curve for ammonia–borane (heating rate = 5°C min⁻¹).

Fig. 2. DTA curves for ammonia–borane (heating rate –· 10°C min⁻¹). a = Open sample holder; b –· sample in sealed glass capillary; c = sample tube explodes.
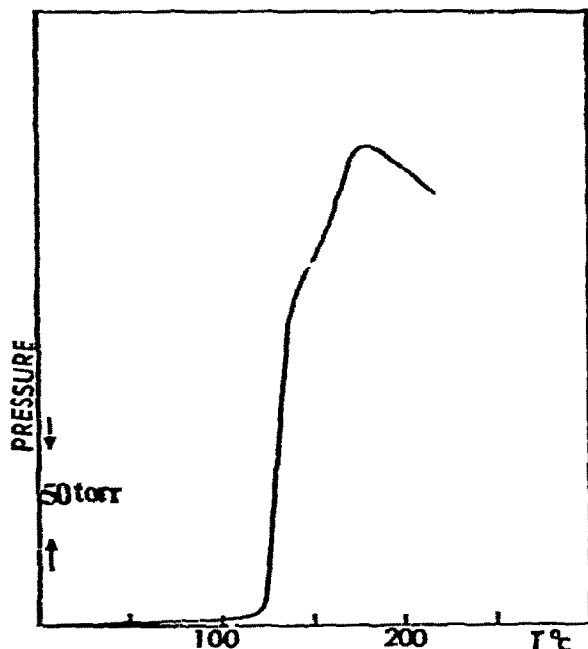
Fig. 3. Thermomanometric curve of ammonia–borane (heating rate $\sim$ 8°C min^{-1}).

second endothermic peak in the DTA curve. (The observed slow pressure decrease in the cell after $\sim$180° is believed to be an artifact of the instrument). It thus appears that the decomposition proceeds through two different hydrogen elimination steps with a rapid step beginning just above the melting point, and a slower step which occurs in the temperature range from 145 to 200°C.

Pyrolysis measurements

In order to learn more about the stoichiometry and other features of the decomposition, we subjected larger samples of ammonia-borane to pyrolysis at various temperatures in excess of its melting point. In one experiment the sample was placed in a cylindrical glass vessel under one atmosphere of N_2. The bottom of the tube was heated to 130°C over 15 min, held there for 10 min, and allowed to cool. The same foaming decomposition was observed beginning near 102°C and the volatile products were allowed to pass through a -196°C trap on the vacuum line. The only condensable product was a trace quantity of gas whose i.r. spectrum resembled that of B_2H_6[7]. A white solid, presumed to be ammonia–borane sublimed to the cooler areas of the reaction vessel.

In the second experiment a N_2 pressure of 618 torr was established in the pyrolysis tube over 31.9 mg (1.04 mmol) of $H_3N \cdot BH_3$. The vessel was heated to 170°C and maintained until no further change was evident. From the increase in the pressure in the system, it was estimated that 2.03 mmol H_2 was produced which corresponds to about 1.96 mmol H_2 per mmol $H_3N \cdot BH_3$ taken. Upon fractionation of the volatiles, a small quantity of borazine ($\sim$0.045 mmol) identified by its i.r. spectrum[8], along with a trace of B_2H_6 were found to be present. The nominal
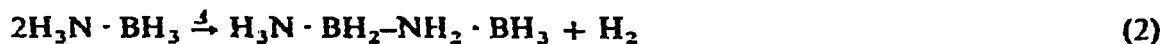
composition of the white solid residue was calculated to be $BNH_{2.1}$, but no elemental analyses were attempted.

A new vessel was designed to allow the entire enclosed volume of the pyrolysis bulb to be immersed in the oil-bath in order that no ammonia–borane escape pyrolysis through sublimation out of the heated zone. A typical pyrolysis started with 48.7 mg (1.58 mmol) $H_3N \cdot BH_3$ along with 381 torr of dry N_2. The vessel was heated to 200°C and held there for 15 min until no further change was noted. After cooling, there remained in the cell 31.9 mg of solid white residue, which corresponds to a weight loss of 34.5%. This agrees well with the TG results cited earlier. From the total non-condensable pressure in the system after pyrolysis, it was determined that 3.68 mmol H_2 was produced in the reaction indicating 2.33 mmol H_2 lost per mmol $H_3N \cdot BH_3$. A small quantity of condensable gas was separated in a trap held at $-196°C$. This substance contained a trace of B_2H_6 which was separated leaving 0.06 mmol of a compound with an average molecular weight of 77. The gas phase i.r. of this product matched very closely that reported for borazine[8] (MW = 80.4).

The i.r. spectrum of the solid residue exhibited N–H and B–H stretching absorptions at 3450 and 2500 cm^{-1}, respectively, which are somewhat increased compared to the corresponding frequencies in the $H_3N \cdot BH_3$ spectrum[9]. The composition of the solid residue as determined from mass balance on 200°C pyrolysis reactions was $BNH_{0.8}$ to $BNH_{1.2}$ although no elemental analyses were attempted.

One interpretation of the observations made in this investigation is that ammonia–borane undergoes thermally-induced hydrogen loss in two reaction steps. The first step involves hydrogen elimination in either an inter- or intramolecular step [eqns (1) and (2)]. We cannot distinguish

$$H_3N \cdot BH_3 \xrightarrow{\Delta} \frac{1}{X} (H_2N-BH_2)_x + H_2 \tag{1}$$

$$2H_3N \cdot BH_3 \xrightarrow{\Delta} H_3N \cdot BH_2-NH_2 \cdot BH_3 + H_2 \tag{2}$$

between these (limiting) situations but either could lead to condensed B–N structures including, ultimately, the borazine detected as a minor product in the 170 and 200°C pyrolyses.

Aminoboranes such as would be produced in eqn (1) are well known to associate[10] if steric factors do not interfere, whereas the adduct produced in eqn (2) could form extended B–N structures via further intermolecular H_2 elimination with additional $H_3N \cdot BH_3$ molecules. In both cases the ultimate result of this first stage of hydrogen loss is a material with BNH_4 composition. Earlier workers[11] have isolated and characterized several examples of such compounds including $(BNH_4)_2$ (cyclodiborazane), $(BNH_4)_3$ (cyclotriborazane), $(BNH_4)_5$ (cyclopentaborazane) and polymeric

$(BNH_4)_x$ using a different synthetic approach. The pyrolysis of these compounds was not systematically studied but it was observed that heating cyclopentaborazane to 120°C then slowly to 145°C results in the formation of cyclodiborazane along with hydrogen and apparently three different solid residues.

It is reasonable to suppose from these and other observations that $(BNH_4)_x$ materials may experience a second hydrogen loss step upon heating to higher temperatures eventually reaching the product composition shown in eqn (3). This corresponds well with the residue composition $(BNH_{2.1})$

$$\frac{1}{X} (H_2N-BH_2)_x \xrightarrow{\Delta} \frac{1}{X} (HNBH)_x + H_2 \qquad (3)$$
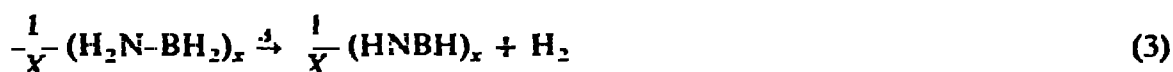
obtained in the 170°C pyrolysis reaction of ammonia–borane. Also the detection of borazine among the volatile pyrolysis products is further evidence that this stage of hydrogen loss is reached.

Pyrolysis of $H_2B(NH_3)_2^+ BH_4^-$ or ammonia and diborane has been used[12, 13] as a synthetic route to borazine in yields up to 40% but, to our knowledge, $H_3N \cdot BH_3$ has not been previously studied in this role. Very probably, it is involved as an intermediate in the synthesis of borazine from ammonium and tetrahydroborate salts[14]. The yields of these syntheses are low, most near 30%, suggesting that the major product(s) must be of a different sort.

The pyrolysis of borazine itself has been studied under various conditions[15] resulting in hydrogen, polynuclear borazines, and non-volatile residues. The empirical formula of the residue varied from $BNH_{0.8}$ to $BNH_{0.3}$ as temperatures and duration of pyrolysis increased. Although it seems unlikely that the ammonia–borane pyrolysis proceeds exclusively or even in a major way through a borazine intermediate, the same type of solid residue may well be involved.

The residue of 200°C pyrolysis of ammonia–borane in our studies is more hydrogen-rich than those obtained from borazine pyrolysis, but indications are that higher temperatures and prolonged heating will effect further H_2 elimination. It is difficult to propose a single structure to be associated with a composition approximating $(BNH)_x$. The presence of i.r. absorptions corresponding to both N–H and B–H stretching modes as well as a broad absorption near 1440 cm^{-1} similar to one in the borazine spectrum suggests condensed borazine structural features are present. The residue is amorphous by X-ray powder diffraction indicating the absence of long range order in the solid.

One sample which was pyrolyzed for a short period at 500–600°C showed i.r. absorptions at 1390 and 810 cm^{-1} corresponding closely to those reported[16] for boron nitride at 1372 and 815 cm^{-1}. In this residue, the N–H stretching band at 3450 cm^{-1} was attenuated and the B–H band had disappeared. It appears that hydrogen elimination is accompanied by the build-up of an extended B–N framework, leading eventually to the planar boron nitride structure.

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