Molecular Beam Mass Spectrometric Investigation of Ammonia Borane and Aminoborane Vapors[1a]

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Abstract: The vapors above ammonia borane solid at room temperature include the ammonia borane molecule, BNH_6, plus aminoborane, BNH_4, and diborane, B_2H_6, from solid-state decomposition. Direct mass spectrometric observation of the effluent of a flow reactor in which these vapors were pyrolyzed at 5×10^{-5} torr gives no evidence for further formation of aminoborane, nor for iminoborane, BNH_2. Surprisingly, aminoborane is much more thermally stable than ammonia borane at these low pressures. Pyrolysis data for the hemideuterio compound, BH_3ND_3, are consistent with an ethylene-like structure, BH_2NH_2, for aminoborane rather than the asymmetric structure $BHNH_3$.

Pyrolysis of boron–nitrogen compounds at densities corresponding to 10^1 torr and above leads to polymeric materials such as $(BH_2NH_2)_n$, borazines, condensed borazines, and ultimately $(BN)_\infty$.[2-4] Because of the high collision frequencies at these pressures, the primary species resulting from the pyrolysis are not detected. On the other hand, direct mass spectrometric identification of reactive species such as BH_3 and B_4H_8 has been successfully carried out at low pressures (10^{-5} to 10^{-1} torr).[5,6] Consequently, the present study was undertaken of the vapors above ammonia borane, BH_3NH_3, and the pyrolysis of these vapors. The goal of these studies was to obtain evidence for BH_2NH_2 and BHNH, the B–N analogs of ethylene and acetylene.

When this work was initiated there were no reports of BH_2NH_2 or BHNH; however, substituted analogs of the former were known.[7] Before our first successful experiments were completed, Böddeker, Shore, and Bunting reported the isolation of a BNH_4 species as a pyrolysis product of cyclodiborazane $(BH_2NH_2)_2$.[8] They found that the BNH_4 was unstable at room temperature and ordinary pressures. Although this precluded thorough characterization they gave convincing evidence for its existence.

Experimental Section

Materials. A preparative high-vacuum line and nitrogen-flushed glove bags were employed in all hydride syntheses. Organic solvents were dried over CaH_2 or $LiAlH_4$ and transferred by trap-to-trap distillation. Nitrogen gas, used in the preparation of magnesium nitride and as an inert gas, was purified by passage through a train of tubes containing copper–oxygen scavenger (BTS catalyst), $MgClO_4$, silica gel, and CaH_2. When BF_3 was manipulated, stopcocks were lubricated with Kel-F 90. Before deuterio compounds were handled, the vacuum line was conditioned by exposure to D_2O vapor followed by evacuation. This was carried out twice, after which the glassware was flamed under high vacuum.

Ammonia borane was prepared by the interaction of ammonia with the borane–tetrahydrofuran adduct.[9] For mass spectrometric work the ammonia borane was introduced directly into the sample tube on the vacuum line and was stored at −78° when measurements were not being taken. The X-ray powder pattern agreed with that published for BH_3NH_3,[9] and the mass spectrum revealed no impurities.

Hexadeuterio- and N-trideuterioammonia borane were prepared by the same procedure. For these reactions, ND_3 was synthesized from D_2O and freshly prepared Mg_3N_2, while B_2D_6 was prepared by the reaction of boron trifluoride ethereate with $LiAlD_4$ (Alfa Inorganics) in diethyl ether.[10] The infrared spectra of the deuterioammonia[11] and of the B_2D_6[12] indicated virtually no protium content. The mass spectrum of BD_3ND_3 showed the presence of only 3% protium. The infrared spectrum[13] of BH_3ND_3 which was taken from the mass spectrometer sample tube after all data had been collected showed that no detectable H–D scrambling had occurred.

Mass Spectrometer. The mass spectrometer[5,14] and flow reactor system[5] were those used previously for studies of the boron hydride systems. The sample was distilled in the usual way into the reactor from a tube kept at or below room temperature. From an upper limit of 1 μ for the vapor pressure[16] of BH_3NH_3 at room temperature, and the estimated[17] conductance of the inlet system and reactor, the maximum sample pressure in the flow reactor was calculated to be 5×10^{-5} torr.

The molecular beam effusing from the reactor usually was ionized by 70-eV electrons. The ions formed were accelerated through 4000 V, mass analyzed, accelerated through an additional 3900 V, and detected by a 16-stage Cu–Be secondary electron multiplier.

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The detectability limit was better than 10^{-6} torr partial pressure of species in the reactor.

The resolution of the mass spectrometer, which permitted separation of, *e.g.*, $^{11}B_2H_5^+$ from $^{11}B^{14}NH_2^+$ which are both at *m/e* 27, has been illustrated elsewhere.[18] The apparatus for time averaging the intensity at a given mass peak, digitizing it, and recording it on perforated tape, as well as the automatic ionization efficiency curve recorder, also have been described.[19]

Results and Discussion

Mass Spectra. With the flow reactor at or below room temperature, studies were made on the vapors coming from BH_3NH_3, BD_3ND_3, and BH_3ND_3 solids. The ions observed and their neutral progenitors were identified by mass defect, isotope ratios, shutter profile, and percentage shutter effect.[5,18] Only those ions due to molecular beam species are considered.

Ion peaks of low intensity were observed at masses higher than that of the parent peak and up to *m/e* 90. The intensities of these peaks varied from run to run, were not sensibly shifted for the hexadeuterio compound, and did not match the known mass spectra of borazine[20] nor of the solvents diethyl ether and tetrahydrofuran.[21] The intensities were sufficiently small to indicate that fragmentation of the progenitors of these peaks would not interfere with observation of the peaks of interest.

The presence of diborane was indicated by ion intensities with relatively low percentage shutter effects at *m/e* 20 to 24. This was confirmed by examination of the mass spectrum of BD_3ND_3. For this molecule the bulk of the ion intensity should fall at odd mass peaks corresponding to $^{11}B^{14}ND_x^+$, whereas for diborane it should fall at even peaks, $^{11}B_2D_x^+$ (isotopic abundances: ^{11}B, 80%; ^{10}B, 20%; ^{14}N, 99.6%).

While the ratio of the parent ion, p, intensity at *m/e* 31 for the protio compound to that of p − 1 was constant at about 1:11, the intensities of peaks of lower mass varied with time over a period of several weeks. In a second set of runs taken 4 months after the first, these lower mass peaks were relatively more intense. Furthermore, the percentage shutter effect was lower for peaks 20–29 (15–20%) than for 30 and 31 ($\sim$80%). This difference was particularly noticeable for the doubly charged ion peaks BNH_2^{2+} at *m/e* 13.5 and BNH_4^{2+} at 14.5, for which the shutter effects were respectively 16 and 91%. (Note that several studies[5,22] of diborane report no doubly charged ion at *m/e* 13.5.) A peak with 80% shutter effect was observed at *m/e* 18 for BH_3NH_3 and at *m/e* 22 for BD_3NH_3. These are attributed to NH_4^+ and ND_4^+, respectively.

These observations and the observation by Shore and Parry[23] that BH_3NH_3 decomposes slowly at room temperature with evolution of hydrogen lead to the conclusion that the vapors above the solid ammonia borane at $\sim$20° are composed of (1) a discrete molecule, BH_3NH_3,[24] that is relatively unstable with respect to collisions with the walls of the vacuum envelope; (2) diborane and ammonia (by inference, since fragmentation of ammonia borane could give rise to NH_x^+ ions); and (3) the neutral species aminoborane, BNH_4, which grows in through a slow decomposition probably occurring in the ammonia borane solid.

A partial mass spectrum of the vapors above solid hemideuterioammonia borane, BH_3ND_3, is shown in Table I. The contributions of ^{10}B to the ion intensities have been stripped out. Since no measurable scrambling had occurred, the three peaks listed could arise only from ammonia borane. The ion intensity at *m/e* 32 could arise, furthermore, only by fragmentation of H_2 from the B atom or of D from the N atom in ammonia borane. The importance of H_2 elimination could not be determined; consequently $I(32^+)$ gives an upper limit for the fragmentation of D from the N atom. Fragmentation from the B atom is thus at least one and one-half times as important as from the N. Similar observations regarding B–X and N–X bond rupture were made for the borazines[25,26] and are consistent with the idea that the B–X bond is weaker than the N–X bond.

Table I. Mass Spectrum of Vapors above BH_3ND_3[a] Stripped of the ^{10}B Contributions (Arbitrary Units)

m/e	Intensity	Possible assignment
34 p[b]	11	$^{11}BH_3ND_3^+$
33	103	$^{11}BH_2ND_3^+$
32	66	$^{11}BH_3ND_2^+ + {}^{11}BHND_3^+$

[a] An infrared spectrum taken after the experiments were made gave no evidence for any scrambling. [b] p = parent.

Pyrolysis Studies. During the pyrolysis runs, no evidence for polymeric species containing B, N, and H or D could be found.

The absolute ion intensities of $^{11}BNH_5^+$ and $^{11}BNH_4^+$ are shown in Figure 1 as a function of reactor temperature for two different runs taken 5 months apart. Since the ion currents were small and each peak had to be individually shuttered, the mass spectra at only one or two different temperatures could be recorded on a given day. Consequently, there are small changes in spectrometer sensitivity from temperature to temperature. In addition, there was a large change in sensitivity, due mostly to a change in secondary electron multiplier gain, between the two runs. The data for the run 6609 were normalized so that the point for $I(BNH_5^+)$ at 30° agrees roughly with run 6604 (circles). The sharp decrease in this ion intensity at about 200° indicates pyrolysis of the ammonia borane. The intensity is almost zero at 400°; pyrolysis is almost complete.

The points for $I(^{11}BNH_4^+)$, on the other hand, decrease slowly with temperature, but still are quite high at 600°.

Similar data are shown in Figure 2 for *m/e* 14.5, BNH_4^{2+}, and *m/e* 13.5, BNH_2^{2+}. The former drops rapidly with temperature, while the latter remains

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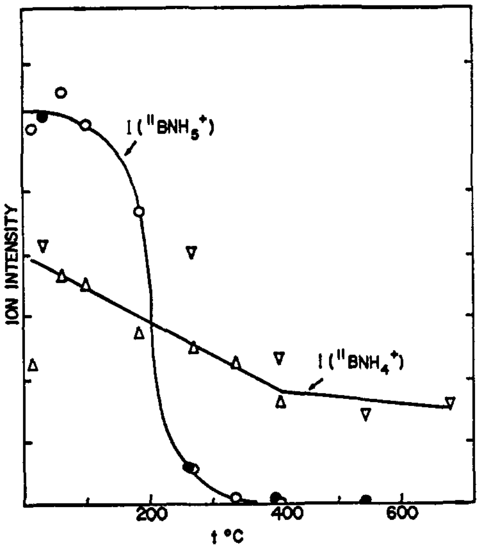

Figure 1. Pyrolysis of the vapors above ammonia borane; absolute ion intensities of molecular beam species coming from flow reactor *vs.* reactor temperature. For *m/e* 30, $^{11}BNH_5^+$: ○, run 6604 (the first point is at 12.0 mV); ●, run 6609 with intensities normalized to those of 6604 (the first point is at 2.37 mV ion intensity). For *m/e* 29, $^{11}BNH_4^+$: △, run 6604; ▽, 6609 (same scales as for *m/e* 30).

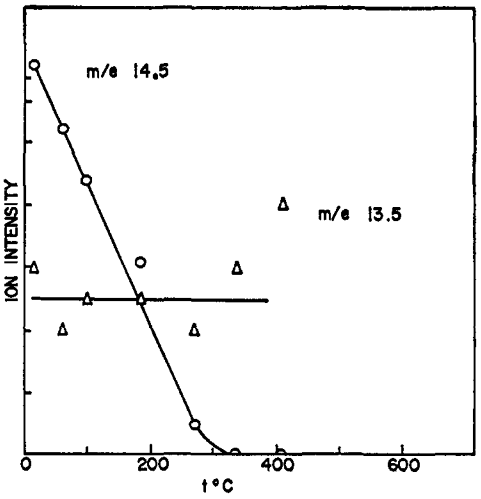

Figure 2. Absolute ion intensities of *m/e* 14.5, $^{11}BNH_4{}^{2+}$ (○), and *m/e* 13.5, $^{11}BNH_2{}^{2+}$ (run 6604). One scale division equals 0.1 mV ion intensity for *m/e* 14.5 and 0.02 mV for 13.5. With the secondary electron multiplier used, 0.02 mV is equivalent to about 10^{-18} A ion current.

essentially constant. (The largest ion current of $BNH_2{}^{2+}$ shown is about 4×10^{-18} A). Similarly, the peak due to $NH_4{}^+$ decreases rapidly with temperature.

The intensities of $BNH_x{}^+$ ions containing one, two, three, and four hydrogens relative to $I(BNH_5{}^+)$ are shown in Figure 3. This plot tends to eliminate effects of the day-to-day variation of mass spectrometer sensitivity and shows more effectively the change in mass spectrum with reactor temperature.

These changes in both the relative and absolute intensities could be due to a number of causes. The most likely are change in fragmentation pattern or the change in relative concentration of two or more neutrals giving rise to the peaks. The very large change in the relative intensities, as well as the difference in percentage shutter effect between the group of peaks at *m/e* 30, 31, 18, and 14.5 (~80%) and the lower peaks, including 13.5 (15–20%), indicate that two neutral species are present. The changes in mass spectra due to deuteration and/or reactor temperature indicate that the species are gaseous ammonia borane and aminoborane, BNH_4. The ion $BNH_4{}^{2+}$ is taken to arise almost exclusively from ammonia borane, and $BNH_2{}^{2+}$ from aminoborane. The ion $NH_4{}^+$ is attributed to a rearrangement process in ionized ammonia borane. Both the temperature dependence of the mass spectra and the percentage shutter effect indicate that aminoborane is more stable with respect to decomposition on the walls than ammonia borane.

In previous work of this type none of the high-temperature species (*e.g.*, BH_3 or B_4H_8) was present in the vapors effusing from the reactor at room temperature.[5,6,18] These species were formed in the reactor and had high percentage shutter effects, indicating that they were rapidly decomposed on the cold walls of the vacuum chamber. Furthermore, the absolute intensities of the ions attributable to the monoborane intermediate increased in the region where the relative intensities increased.

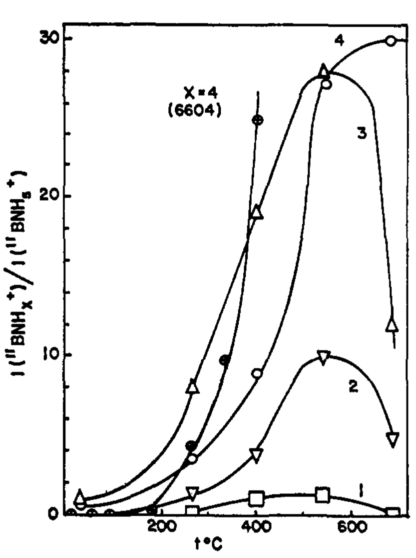

Figure 3. $I(^{11}BNH_x{}^+)/I(^{11}BNH_5{}^+)$ *vs.* flow reactor temperature. Run 6609: ○, $x = 4$; △, $x = 3$; ▽, $x = 2$; □, $x = 1$. Run 6604: ⊕, $x = 4$ (×0.5).

The present case is quite different. The data indicate that the aminoborane vapor is present initially in varying amounts, depending on sample purity or age. As the reactor is heated, the ammonia borane is decomposed, leaving only the aminoborane and causing the ion intensity ratios plotted in Figure 3 to increase as shown. The absolute intensities of ion peaks (Figure 1) due to aminoborane (*e.g.* $BNH_2{}^{2+}$, $BNH_4{}^+$) decrease slowly in such a way as to preclude any but small amounts of additional BNH_4 being formed in the reactor.

Attempts were made to adduce evidence for iminoborane, BNH_2. The small ion currents available (generally 10^{-16} A or less), instrumental instabilities caused by the reactivity of the sample, and the possibility that three neutral species (BNH_6, BNH_4, BNH_2) contribute to BN containing ions at peaks 25^+ to 27^+ greatly complicated these efforts. No positive evidence for or against neutral BNH_2 could be obtained.

Diborane was present in small quantities (10–20%) with the reactor at room temperature. No significant increase in the absolute intensities of mass peaks 22–24 (B_2^+, B_2H^+, $B_2H_2^+$) was observed with increasing reactor temperature. No more than 4–8% of the ammonia borane that decomposed in the reactor under these conditions could have formed diborane. A very weak ion peak with high percentage shutter effect did grow in on the high mass side of *m/e* 14 and was attributed to BH_3 neutral. This borane intensity could be accounted for completely by pyrolysis of the diborane.[5]

Pyrolysis of Hemideuterioammonia Borane, BH_3ND_3. When the vapors from the hemideuterio compound were pyrolyzed at 223°, with the particular reactor used, $I(H_2{}^{11}BND_3^+/H_3{}^{11}BND_3)$ was reduced to ~0.5% of its value at 30°. For measurements made at 223, 338, and 464°, the relative intensities of mass peaks 32, 31, and 30 were sensibly constant and in the ratio shown in the bottom line of Table II.

Shore and coworkers[2] found that for ionization of BNH_4, $I(^{11}BNH_4^+):I(^{11}BNH_3^+) \cong 1:3$. The ion intensity ratios predicted on this basis for aminoborane molecules with the structures $H-{}^{11}BN-D_3$, H_2-D_2, and H_3-D also are shown in Table II. The observed intensities can be explained on the basis of a small amount of H–D scrambling in the pyrolysis reactor giving rise to the intensity at *m/e* 32 plus ionization of a molecule with the symmetrical, ethylene-like structure, BH_2-ND_2. For lack of data at *m/e* 29, the structure BH_3ND cannot be excluded. It is, however, unlikely since the B–H bond is believed to be weaker than N–H.

Table II. Predicted[a] and Observed Ion Intensity Ratios for Aminoboranes of Different Structures Arising from Pyrolysis of BH_3ND_3

Possible structure	*m/e* 32	31	30	29
$^{11}BHND_3$	1	3		
$^{11}BH_2ND_2$		1	3	
$^{11}BH_3ND$			1	3
Observed[b]	1	7.5	26	

[a] Predicted on the basis of $I(^{11}BNH_4^+):I(^{11}BNH_3^+) \cong 1:3$ observed for neutral aminoborane by Shore, *et al.*[8] [b] Observed at 223, 338, and 464°. At these temperatures the ammonia borane ion intensities were less than 0.5% of their value at 30°.

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