Reactions of B Atoms with NH_3 To Produce HBNH, BNBH, and B_2N

Craig A. Thompson and Lester Andrews*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

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Laser ablation has proven to be valuable for studying boron atom reactions with small molecules such as O_2, H_2O, N_2, H_2, CH_4, and C_2H_2 to produce and characterize new molecules and to understand reaction mechanisms.[1−9] Boron−methane studies identified novel $HBCH_2$ and HBCH products of the insertion reaction followed by dehydrogenation; the reaction of a second boron atom gave HBCBH.[6,7] In the case of acetylene, boron atom C≡C addition and C−H insertion products were observed and characterized.[8,9]

The simplest iminoborane, HBNH, is isoelectronic with acetylene, and similar reactions with boron atoms are expected. However, HBNH is extremely reactive, and only two experimental observations of HBNH have been reported, a matrix photolysis of H_3BNH_3 and a gas phase discharge of B_2H_6/NH_3 mixtures.[10,11] The boron−methane studies predict that the elusive HBNH molecule will be a major product of the boron−ammonia reaction, and the boron−acetylene work suggests that further reactions will give linear and cyclic secondary reaction products, which will be reported here.

The pulsed-laser ablation matrix-isolation technique has been described.[1−4] Mixtures of argon/ammonia (1% and less) were codeposited with laser-ablated boron atoms onto a 10 ± 1 K optical window. Natural abundance ($^{14}NH_3$, 80.4% ^{11}B−19.6% ^{10}B) and isotopically enriched precursors ($^{15}NH_3$, ND_3, 93.8% ^{10}B−6.2% ^{11}B) were employed. Infrared spectra were recorded at 0.5 cm^{-1} resolution using a Nicolet 750 with MCT detector.

Figure 1 shows spectra of the major product absorptions in the diagnostic spectral regions. The sharp ^{n}B doublet at 1788.7, 1782.8 cm^{-1} and the weaker (1:4) counterpart at 1826.3, 1819.9 cm^{-1} (Figure 1c) are due to the B−N stretching fundamental of $H^{11}BNH$ and $H^{10}BNH$ in natural abundance site split by the matrix. Figure 1a shows spectra for the ^{10}B reaction, and the latter doublet is enhanced, but the former doublet is still observed owing to 6.2% ^{11}B in the ^{10}B-enriched sample. The spectrum for ^{10}B and $^{14}NH_3/^{15}NH_3$ is illustrated in Figure 1b, and new bands were observed at 1804.6, 1798.3 cm^{-1} for $H^{10}B^{15}NH$. Analogous bands were observed at 1766.2, 1760.3 cm^{-1} for $H^{11}B^{15}NH$ in a ^{n}B isotopic experiment. Stronger bands were observed at 3710.5, 3700.5 cm^{-1} (NH stretch) and 463.3, 461.0 cm^{-1} (NH bend) for HBNH in agreement with earlier work; the assignments are confirmed by ^{15}N shifts and ab initio frequency calculations.

The strongest feature in the spectrum exhibits a 1:8:16 triplet at 901.5, 891.1, 882.1 cm^{-1} with ^{n}B (absorbance 0.4−0.7) and a mixed $^{14}N/^{15}N$ doublet at 901.5, 881.8 cm^{-1} with ^{10}B (not shown). This band system has been produced from ablated BN and from ablated B + N_2 reactions and identified as the cyclic azadiboriridine radical B_2N with two equivalent B atoms.[3] A weaker 1:8:16 triplet at 1769.1, 1753.4, 1736.4 cm^{-1} is due to the linear BNB radical.[3] The weaker C and F bands are due to minor reaction products that will be identified in a complete experimental and theoretical report.

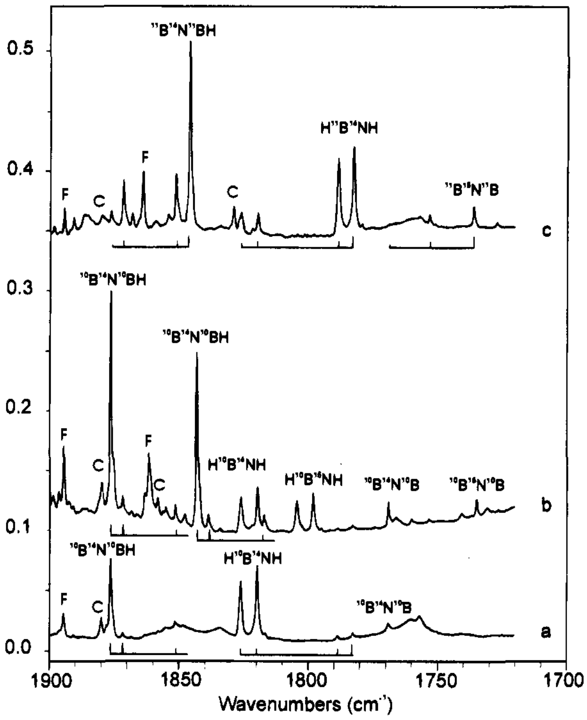

Figure 1. Infrared spectra in the B−N stretching region 1900−1725 cm^{-1} for pulsed-laser ablated boron atom−ammonia−argon samples condensed at 10 ± 1 K: (a) $^{10}B + {}^{14}NH_3$, (b) $^{10}B + {}^{14}NH_3/^{15}NH_3$, and (c) $^{n}B + {}^{14}NH_3$. Horizontal lines indicate boron isotopic multiplets (including site splittings for HBNH).

The next strongest band gives a new 1:4:4:16 quartet at 1876.4, 1871.8, 1851.5, 1846.3 cm^{-1} with ^{n}B (Figure 1c) denoting the vibration of two inequivalent B atoms; in the ^{10}B experiment (Figure 1a) the former three bands were observed as a 88:6:6 triplet with lower weights for the boron-10,11 isotopic species. A mixed $^{14}N/^{15}N$ doublet (Figure 1b) showed the involvement of a single N atom, and displacement with ND_3 verified the presence of hydrogen in this new species. Observed isotopic frequencies for this antisymmetric B−N−B stretching fundamental and weaker symmetric B−N−B stretching, B−H stretching and bending modes associated by common photolysis behavior (5% growth) are listed in Table 1.

The identification of linear BNBH from isotopic infrared spectra is confirmed by SCF calculations[12] of isotopic frequencies and intensities, which are also listed in Table 1. Typically SCF calculations produce frequencies that are about 10% higher than observed values as is the case for BNBH. However, the excellent agreement between observed and calculated isotopic frequencies is found in the observed:calculated frequency ratios given in the table for four isotopic BNBH molecules. First, note that the ratios are extremely close (0.928−0.941) for the three stretching modes (all isotopes) but slightly lower for the linear bending mode (0.881) as the latter mode is more anharmonic. Second, note that the deviation in isotopic frequency ratios for the N−H stretch (±0.0002) gives a ±0.6 cm^{-1} frequency fit. The deviations in ratios for the antisymmetric B−N−B stretch (±0.0004) and symmetric counterpart (±0.0007) show ±0.8 cm^{-1} frequency agreement. The deviation (±0.0003) in ratios for the N−H bending mode produces

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Scheme 1. Laser-Ablated Boron Plus Ammonia Reaction Mechanism

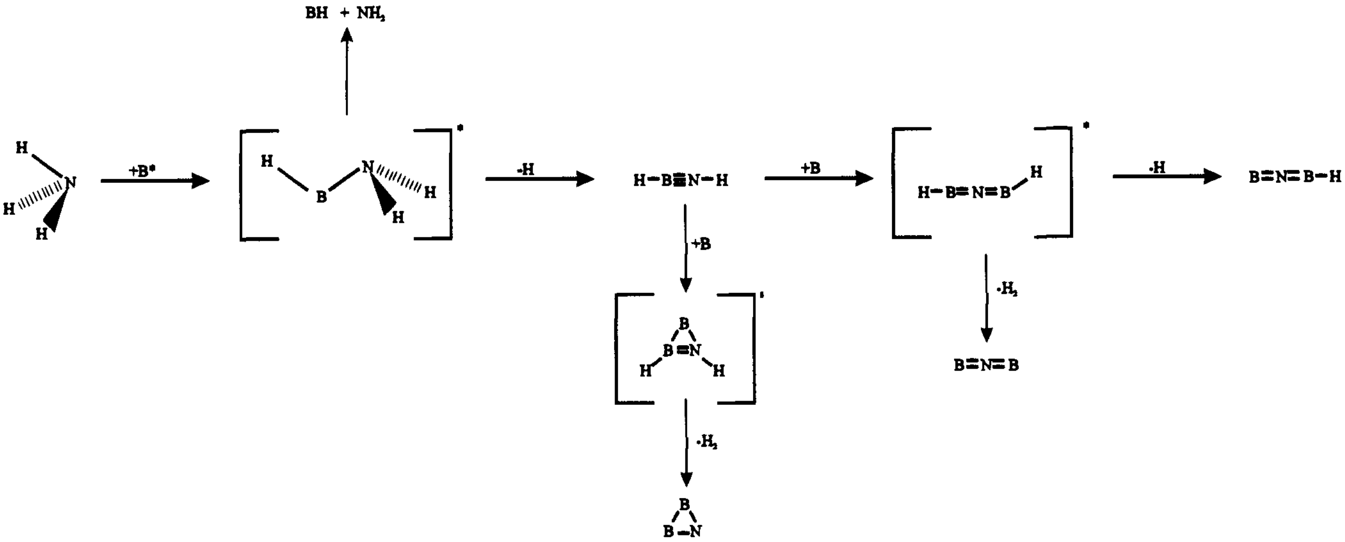

Table 1. SCF Calculated and Observed Isotopic Frequencies (cm^{-1}) for Linear BNBH

	ν(B−H)	ν_a(B−N−B)	ν_s(B−N−B)	δ(N−B−H)	δ(B−N−B)
$^{11}B^{14}N^{11}BH$	2981.4	1988.9	1159.3	847.0	158.2
observed	2805.6	1846.3	1089.3	746.2	
ratio	0.9410	0.9283	0.9396	0.8810	
I (km/mol)[b]	[94]	[947]	[118]	[2 × 24]	[2 × 0.3]
I (observed)[c]	[0.004]	[0.160]	[0.014]	[0.009]	
$^{10}B^{14}N^{11}BH$	2981.4	1993.9	1196.1	847.0	159.9
observed	2805.6	1851.5		746.2	
$^{11}B^{14}N^{10}BH$	3004.9	2016.0	1173.7	857.0	158.9
observed	2826.9	1871.4		754.5	
$^{10}B^{14}N^{10}BH$	3004.9	2020.5	1210.9	857.0	160.6
observed	2826.9	1876.4	1136.4	754.5	
ratio	0.9408	0.9287	0.9385	0.8805	
I (km/mol)	[114]	[957]	[133]	[2 × 26]	[2 × 0.3]
$^{11}B^{15}N^{11}BH$	2980.3	1951.1	1157.5	846.0	155.1
observed	2805.1	1812.3	1087.2	745.2	
ratio	0.9412	0.9289	0.9393	0.8809	
I (km/mol)	[88]	[903]	[121]	[2 × 24]	[2 × 0.3]
$^{10}B^{15}N^{11}BH$	2980.3	1956.0	1194.7	846.0	156.8
observed	2805.1	1817.2			
$^{11}B^{15}N^{10}BH$	3003.5	1979.5	1171.4	855.9	155.9
observed	2826.2	1838.8			
$^{10}B^{15}N^{10}BH$	3003.5	1983.9	1209.0	855.9	157.5
observed	2826.2	1843.3	1134.2	753.5	
ratio	0.9409	0.9291	0.9381	0.8804	
$^{11}B^{14}N^{11}BD$	2368.8	1833.3	1134.9	677.4	150.6
observed	2218.7	1717.6	1062.4	596.4	
ratio	0.9366	0.9369	0.9361	0.8804	
I (km/mol)	[447]	[615]	[97]	[2 × 25]	[2 × 0]
$^{10}B^{14}N^{11}BD$	2369.3	1839.7	1169.9	677.4	152.4
observed	2219.7	1723.8			
$^{11}B^{14}N^{10}BD$	2418.6	1837.5	1147.4	689.9	150.9
observed	2262.3	1723.2	1074.0		
$^{10}B^{14}N^{10}BD$	2419.1	1843.6	1182.8	689.9	152.6
observed	2263.2	1729.0			

[a] Using 6-311G* basis sets. [b] Using calculated infrared intensities. [c] Using observed band absorbances.

±0.3 cm^{-1} agreement. The observed band absorbances, relative to one another, agree well with the calculated infrared intensities except for the B−H stretch, which is weaker than predicted at the SCF level of theory. Finally, the observed:calculated frequency ratios for BNBD are slightly different owing to differences in anharmonicity and normal coordinate vibrational motion.

The matrix chemistry reported here is significant since the simplest and most reactive iminoborane, HBNH, and its further reactions with the simplest boron reagent, atomic B, have been examined. Scheme 1 outlines the major reactions observed here. The insertion of boron into a N−H bond requires activation energy provided by the hyperthermal ablated B atoms; the [$HBNH_2$]* species formed contains excess energy, which activates hydrogen elimination to give HBNH. Iminoborane, the acetylene analog, trimerizes to give borazine, $H_3B_3N_3H_3$, the benzene analog, under normal conditions,[13] but here the condensing argon matrix prevents this reaction. However, secondary reactions with B atoms proceed as expected following addition and insertion reactions with B + HCCH to give H_2C_2B and CCBH.[8,9] On the basis of band intensities the major secondary reaction is addition followed by H_2 elimination to give the azadiboriridine radical B_2N; no evidence was found for H_xB_2N ($x = 1, 2$) species absorbing near B_2N. In contrast the HCCH reaction yielded the borirene radical H_2C_2B and not C_2B; the latter has been observed from ablation of graphite/boron pellets.[14] The difference here is presumably the greater strength of C−H bonds compared to N−H and B−H bonds since the isoelectronic C_2B and B_2N rings should be of comparable stability.

The N−H insertion reaction followed by H and H_2 elimination produces the linear BNBH and BNB species. In contrast to HBCBH in the methane reaction,[6] there was no evidence for HBNBH; the former is a stable, allene-like species, whereas the latter is a radical precursor to the more stable BNBH molecule observed here. The yield of B_2N and BNBH in the present experiments is higher than the yield of H_2C_2B and CCBH in similar acetylene reactions,[8,9] on the basis of band intensities. Considering the obvious fact that HCCH reagent concentration in earlier work surely exceeded HBNH concentration here by at least 2 orders of magnitude, the reactivity of HBNH toward B atoms is substantially greater than the reactivity of HCCH. This is in accord with the ready formation of borazine from HBNH and the slow formation of benzene from HCCH. Iminoborane, HBNH, is clearly a stable but highly reactive molecule that can be formed in the exothermic reaction of B and NH_3 and trapped in a condensing argon matrix.

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