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Gas-Phase Ion Chemistry of Boron Hydride Anions

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We have found that we can produce a host of new, hitherto unknown, boron hydride anions including $B_2H_3^-$, $B_5H_8^-$, and $B_{10}H_{14}^-$ in the flowing afterglow source of our selected-ion flow tube (FA-SIFT). Several boron hydride ions which are known in solution[1,2] or have been produced previously in an ion cyclotron resonance experiment[3] (e.g., $B_2H_5^-$, $B_3H_8^-$, $B_4H_9^-$, and $B_{10}H_{13}^-$) are also observed. Certain of these anions have been mass selected from the complex mixture produced by the reaction of diborane and strong bases like amide and hydroxide in the source region of the FA-SIFT. Their reaction chemistry has been investigated under thermal conditions in a downstream (second) flow tube.[4–8] Collision-induced dissociation (CID) was also be carried out after ion purification, a process which led to the production of still other new ions.[6–8] Certain anions are also detected that have undergone both deprotonation and CID in the source region.

In the FA source, we produce amide ions by adding ammonia (0.07 Torr) to the helium carrier gas (0.3 Torr) (hydroxide ions are produced by adding trace amounts of N_2O and methane) and allowing the mixture to pass over an ionizer.[9,10] Just downstream from this ionizing filament, we add helium containing 5% B_2H_6. The resulting hot plasma is sampled into a quadrupole chamber where the precursor neutrals are removed by pumping, and the ions are mass selected and injected into the second flow tube, where neutral reagents are added.[4] Because of the complicating presence of two boron isotopes in appreciable amounts, we have not characterized all of the ionic products, but those mentioned clearly stand out.[11]

As an example, the ion $B_2H_3^-$ can be formed both by direct selection from the ion source and by CID upon injecting $B_2H_5^-$ at sufficiently high energies.[11] $B_2H_3^-$ is of particular interest because of its relationship to the intriguing and elusive neutral boron analog of ethylene, B_2H_4.[12] *Ab initio* calculations predict that bridged and nonbridged structures for the neutral are similar in energy.[13] We find a similar result for the anion: at the MP2/6-31++G(d,p)//6-31++G(d,p) level of theory,[14] the bridged structure I is 6.6 kcal/mol lower in energy than the open isomer structure II (see Table 1). This is in contrast to calculations carried out by Bigot and co-workers at lower levels of theory, where II was found to be the more stable isomer by 8.3 kcal/mol.[15]

$B_2H_3^-$ is relatively unreactive considering its presumed electron deficiency. It deprotonates pyrrole ($\Delta H^\circ_{acid} = 359 \pm 3$ kcal/mol) but not *tert*-butyl alcohol ($\Delta H^\circ_{acid} = 375 \pm 3$ kcal/mol), thus giving a bracketed ΔH°_{acid} at 367 ± 5 kcal/mol.[16] Most surprisingly, it fails to undergo hydrogen–deuterium exchange reactions with D_2O, CH_3OD, CD_3NO_2, CH_3CO_2D, and CF_3CO_2D (ranging in ΔH°_{acid} from 392 to 323 kcal/mol); evidently, protonation–deprotonation reactions of the anion are slow.[17] It undergoes interesting reactions with CO_2, COS, and CS_2 (eqs 1–3),the major products of which are $B_2H_3O^-$ or $B_2H_3S^-$ formed

$$[B_2H_3]^- + CO_2 \rightarrow [B_2H_3O]^- + CO \quad (77\%) \qquad (1a)$$

$$\rightarrow [BH_2CO]^- + HBO \quad (19\%) \qquad (1b)$$

$$\rightarrow [BO]^- + H_3BCO \quad (4\%) \qquad (1c)$$

$$[B_2H_3]^- + COS \rightarrow [B_2H_3S]^- + CO \quad (85\%) \qquad (2a)$$

$$\rightarrow [BH_2CO]^- + HBS \quad (10\%) \qquad (2b)$$

$$\rightarrow [B_2H_3O]^- + CS \quad (5\%) \qquad (2c)$$

$$[B_2H_3]^- + CS_2 \rightarrow [B_2H_3S]^- + CS \quad (100\%) \qquad (3)$$

by oxygen or sulfur extraction, respectively (eqs 1a, 2a, and 3). In the reaction with COS, where these two processes compete, sulfur atom extraction dominates over oxygen atom extraction by a large factor (eq 2a vs 2c). Another abundant and unusual pathway gives $[H_2BCO]^-$ from loss of HBO or HBS (eqs 1b and 2b). This anion, which is isoelectronic with the stable carbon monoxide/borane complex,[1a] is presumably formed by a nucleophilic attack of $B_2H_3^-$ at the carbon of CO_2 and COS.

A second unusual ion, $B_3H_6^-$, is the major CID product when $^{11}B_4H_9^-$ ($m/z = 53$) is injected at high energy. Small amounts of $B_4H_7^-$, $B_3H_4^-$, and BH_4^- are also produced. $B_3H_6^-$ is also rather unreactive, failing, for example, to undergo H/D exchange with CF_3COOD. It extracts sulfur from CS_2 with a low reaction efficiency of less than 0.6% compared with one of 18% for $B_2H_3^-$. While it does not react with propylene or acetonitrile, it adds to acrolein and acrylonitrile with loss of BH_3.

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(1) For an excellent general introduction to boron chemistry, see: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984; p 1543.

(2) For excellent up-to-date reviews of boron hydride chemistry, see: (a) *Chem. Rev.* **1992** *92*, (March/April). (b) *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991.

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(11) The natural abundance of boron is 19% ^{10}B and 81% ^{11}B. In studying $B_2H_3^-$, we can directly mass select the $m/z = 24$ ion containing one ^{10}B and one ^{11}B from the ion source to avoid any ambiguity about its structure and its reactivity. We have also prepared $^{11}B_2H_3^-$ by selecting $^{11}B_2H_5^-$ from the ion source and subjecting it to CID.

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(14) Both GAMESS and Gaussian were used for the *ab initio* computations. (a) GAMESS: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE BULL.* **1990**, *10*, 52–54. (b) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian90*, Revision J; Gaussian, Inc.: Pittsburgh, PA; 1990.

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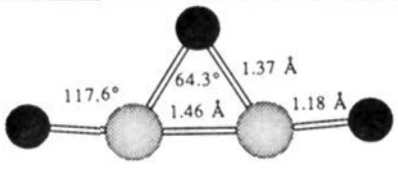
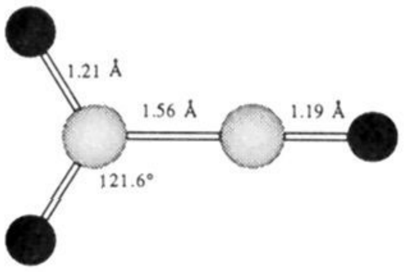
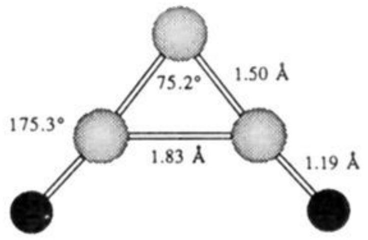
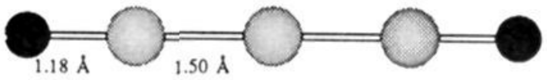
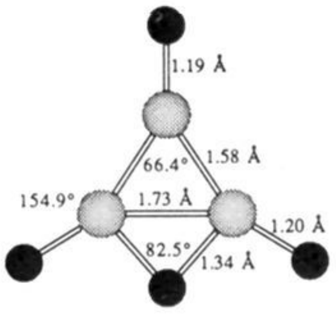
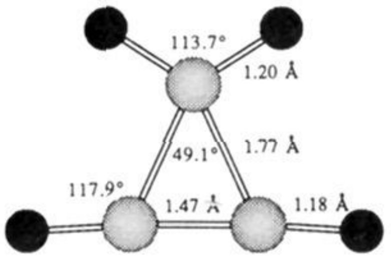
Table 1. *Ab Initio* Computations for $B_3H_2^-$ and $B_3H_4^-$ at the MP2/6-31++G(d,p)//6-31++G(d,p) Level

anion number	anion	MP2 energy (in Hartrees) (zero point correction)	relative energy (in kcal/mol)
I		−51.211 284 (0.029 344)	0
II		−51.200 571 (0.029 208)	6.6
III		−75.370 922 (0.026 772)	0
IV		−75.343 271 (0.026 892)	17.4
V		−76.604 276 (0.046 008)	0
VI		−76.596 448 (0.045 050)	4.4

All of the $B_nH_m^-$ ions that we have investigated so far undergo CID primarily by loss of H_2 and BH_3. Sequential loss of H followed by H_2 from the radical ion $B_{10}H_{14}^-$ generates $B_{10}H_9^-$, which resists further fragmentation under our relatively mild CID conditions. Sequential loss of BH_3 from $B_{10}H_{14}^-$ leads to $B_9H_{11}^-$, $B_8H_8^-$, and $B_7H_5^-$. Losses of H_2 followed by BH_3 from $B_{10}H_{14}^-$ generate $B_{10}H_{12}^-$, $B_9H_9^-$, and $B_8H_6^-$. It should be possible to study the gas-phase ion chemistry of many of these unusual species.

The origin of these anions in our FA sources is not fully understood at present, but they probably arise by pyrolysis of the B_2H_6 in the relatively hot ionization region of our source flow tube followed by deprotonation, other ion–molecule reactions, and, in some cases, subsequent collision-induced dissociation in the source region.[18] To show that they do not come from simple deprotonation of impurities in the B_2H_6, we injected HO^- and added the B_2H_6 in helium to the second flow tube. BH_4^- and $B_2H_5^-$ were the major ions observed, although traces of higher boron hydride ions were detected at quite high flows of B_2H_6. When $B_2H_5^-$ is injected and allowed to react with B_2H_6, only $B_3H_8^-$ is formed. Higher boron hydride ions were not observed when $B_3H_8^-$ or $B_5H_5^-$ was added to B_2H_6.

Some previous computational studies were carried out on boron hydride anions.[15,19] We are currently examining several boron hydride anionic structures that either have not been considered before or were studied using lower levels of theory and that we have observed in our gas-phase studies. These include $[B_3H_2]^-$ and $[B_3H_4]^-$, both of which are obtained by CID of higher boron hydride anions (e.g., $[B_4H_9]^-$). The two lowest energy isomers of these anions (**III–VI**) have been determined at the MP2/6-31++G(d,p)//6-31++G(d,p) level (Table 1).

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(18) Mass spectral analysis of the B_2H_6 used in these experiments revealed only small quantities of higher boron hydrides.

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