

## Communications to the Editor

### Formation of $\text{BH}_6^+$ in the Gas Phase

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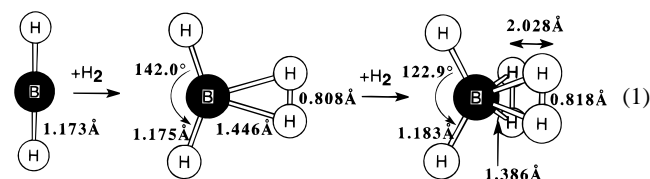
Recent matrix isolation experiments have shown that  $\text{BH}_5$ , the elusive neutral complex between  $\text{BH}_3$  and dihydrogen, has been prepared.<sup>1</sup> Computational studies support the  $\text{BH}_5$  assignment and provide additional insight into this molecule.<sup>2,3</sup> It is barely bound at liquid helium temperature in an argon matrix and is unstable toward dissociation to reactants above 25 K. We wish to report that its formal conjugate acid  $\text{BH}_6^+$ , better described as a complex between  $\text{BH}_2^+$  and two dihydrogen molecules, is readily produced at room temperature in the gas phase under the fairly high pressure conditions of the flowing afterglow-selected ion flow tube (FA-SIFT) apparatus.<sup>4</sup> Such an ion cannot survive the numerous collisions with the helium bath gas in the FA-SIFT unless it is bound by more than 8–10 kcal/mol. Indeed, our calculations predict a much stronger binding energy toward loss of a dihydrogen molecule for  $\text{BH}_6^+$ . The experimental observation of  $\text{BH}_6^+$  is also of note because of its isoelectronic relationship to  $\text{CH}_6^{2+}$  which has been considered in detail in two computational studies, one of  $\text{CH}_6^{2+}$  itself<sup>5</sup> and the other of  $\text{CH}_7^{3+}$ .<sup>6</sup>

When  $\text{B}_2\text{H}_6$  (5% in He) is introduced into the first flow tube of the FA-SIFT instrument a host of ions is formed by electron impact ionization and/or a series of ion–molecule reactions between the initially formed ions and diborane.<sup>7</sup> By tuning the first quadrupole to  $m/z$  13 we inject pure  $^{11}\text{BH}_2^+$ , uncontaminated by other ions or neutrals, into the second flow tube where its ion chemistry can be examined. In principle, an ion of  $m/z$  13 could be a mixture of  $^{11}\text{BH}_2^+$  and  $^{10}\text{BH}_3^+$ ; however, since no ions of  $m/z$  14 ( $^{11}\text{BH}_3^+$ ) are present in the spectrum,  $^{10}\text{BH}_3^+$

must also be absent. To confirm this, these mass selected  $m/z$  13 ions were injected at sufficiently high kinetic energies to strip them of hydrogens in collisions with helium;  $^{11}\text{B}^+$  but no  $^{10}\text{B}^+$  was observed.

When 0.04 to 0.1 Torr of ultrapure dihydrogen is added to the second flow tube at a helium buffer gas pressure of 0.75 Torr, ions of  $m/z$  15 ( $^{11}\text{BH}_4^+$ ) and  $m/z$  17 ( $^{11}\text{BH}_6^+$ ) are produced by three-body association reactions. The structural assignment of product ions is supported by several observations. Ions of these masses are not formed when  $^{11}\text{BH}_2^+$  is allowed to react with water, ammonia, or methane, each conceivable sources of other ions with the same mass-to-charge ratio. Injection of  $m/z$  12 ( $^{10}\text{BH}_2^+$ ) and its reaction with dihydrogen leads to the formation of the corresponding ions of  $m/z$  14 ( $^{10}\text{BH}_4^+$ ) and 16 ( $^{10}\text{BH}_6^+$ ). Another indicator of formation of  $\text{BH}_6^+$  is the reaction of  $^{11}\text{BH}_2^+$  with  $\text{D}_2$  to give ions of  $m/z$  23 ( $^{11}\text{BD}_6^+$ ), which result from H–D exchange in  $\text{BH}_2^+$ <sup>7</sup> and complexation of  $\text{D}_2$ . A peak at  $m/z$  19 ( $\text{H}_3\text{O}^+$ ) also has been observed in most such experiments due to ubiquitous traces of water that are present even in high-purity reagent gases. Ions of  $m/z$  19 ( $^{11}\text{BD}_4^+$ ) are also formed in the latter experiment, although  $\text{H}_3\text{O}^+$  also contributes to this peak.

Extensive *ab initio* molecular orbital calculations on these reactions at the MP2(fu)/6-311G(d,p)//MP2(fu)/6-311G(d,p) level of theory<sup>8</sup> have been carried out, and fully support the experimental observations. They predict  $\text{BH}_4^+$  to have a planar structure in which the dihydrogen molecule is bound by 14.5 kcal/mol, while  $\text{BH}_6^+$  is approximately tetrahedral with the second dihydrogen bound by 17.6 kcal/mol<sup>9</sup> (eq 1).



The  $^{11}\text{BH}_4^+$  and  $^{11}\text{BH}_6^+$  ions can be shown to be useful intermediates for the synthesis of complexes between  $\text{BH}_2^+$  and other neutrals. Although direct three-body association between  $\text{BH}_2^+$  and methane cannot be achieved because of a competing, fast, highly exothermic addition with loss of dihydrogen, adding methane to the second flow tube downstream of the formation of  $^{11}\text{BH}_4^+$  and  $^{11}\text{BH}_6^+$  yields a complex between  $^{11}\text{BH}_2^+$  and  $\text{CH}_4$  ( $m/z$  29). This complex is presumably formed by a switching reaction with  $^{11}\text{BH}_4^+$  and/or  $^{11}\text{BH}_6^+$ . The computations further suggest that methane is bound to  $\text{BH}_2^+$  in this complex by 33.4 kcal/mol. Complexes with dinitrogen and carbon monoxide have been made under similar experimental conditions. Thus,  $^{11}\text{BH}_2^+(\text{N}_2)$  and  $^{11}\text{BH}_4^+(\text{N}_2)$  as well as  $^{11}\text{BH}_2^+(\text{CO})$  and  $^{11}\text{BH}_2^+(\text{CO})_2$  have been observed. Computational studies suggest that dinitrogen in  $^{11}\text{BH}_2^+(\text{N}_2)$  is bound by 29.6 kcal/mol. Calculations suggest that the addition of a molecule of carbon monoxide to  $\text{BH}_2^+$  to form  $\text{BH}_2^+(\text{CO})$  is

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(2) Schreiner, P. R.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Chem. Phys.* **1994**, *101*, 7625–32.

(3) Watts, J. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 825–6.

(4) The FA-SIFT has been described previously (Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *81*, 85–100). For a general review of flow tube techniques see: Graul, S. T.; Squires, R. R. *Mass Spectrom. Rev.* **1988**, *7*, 263.

(5) Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Schleyer, P. v. R.; Simonetta, M. *J. Am. Chem. Soc.* **1983**, *105*, 5258–63.

(6) Olah, G. A.; Rasul, G. *J. Am. Chem. Soc.* **1996**, *118*, 8503–4.

(7) DePuy, C. H., et al. To be submitted for publication. The many positive ions which result from the ionization of diborane under conditions where the initial ions can react further with the neutral precursor were first noted by Dunbar in an ion-cyclotron resonance spectrometer (Dunbar, R. C. *J. Am. Chem. Soc.* **1968**, *90*, 5676–82). Under the reaction conditions he employed, however, the relative abundance of ions containing a single boron atom (e.g.  $\text{BH}_2^+$ ) was insignificant and cations with 2 to 6 boron atoms prevailed. A similar array of borohydride anions is produced simultaneously in a FA-SIFT (Krempf, M.; Damrauer, R.; DePuy, C. H.; Keheyian, Y. *J. Am. Chem. Soc.* **1994**, *116*, 3629–30). We have observed a series of ions ranging from  $^{10}\text{B}^+$  through  $^{11}\text{B}_5\text{H}_6^+$  and beyond, depending on the source conditions. The conventional mass spectrum of diborane contains peaks corresponding to cations from  $\text{B}^+$  to  $\text{B}_2\text{H}_5^+$ , the molecular ion being negligible.

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(9) Values are based on energies corrected for ZPVE and are at room temperature.

exoergic by 46.9 kcal/mol, and the addition of a second molecule of CO to form  $\text{BH}_2^+(\text{CO})_2$  is exoergic by 45.6 kcal/mol.

Complexes of electrophiles with hydrocarbons are of particular current interest because of their presumed intermediacy in many positive ion mass spectrometric processes,<sup>10</sup> but rational synthetic methods for their production are currently unavailable.

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In addition to their intrinsic interest,  $\text{BH}_4^+$  and  $\text{BH}_6^+$  promise to be useful in the synthesis of these elusive species.

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