

# Positive and Negative Ions and Ion-Molecule Reactions of Several Boron Hydrides Studied by Ion Cyclotron Resonance

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**Abstract:** Ion cyclotron studies were made of positive and negative ions and ion-molecule reactions in  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_5H_{11}$ , and  $B_6H_{10}$ . The results for negative ions were found to support the classification of the boron hydrides into  $B_nH_{n+4}$  and  $B_nH_{n+6}$  series. The  $B_nH_{n+4}$  hydrides strongly favored formation of the  $(M - 1)^-$  ion, especially at low electron energy; the  $B_nH_{n+6}$  hydrides were characterized by loss of  $BH_3$  to form  $(M - BH_3)^-$  ions, and by successive addition of  $BH$  units to the parent negative ion. No "unsymmetrical" cleavage of unstable hydrides was observed. The fragmentation and reaction products in the positive-ion spectra indicated that odd-electron (radical ion) positive ions are much more readily formed than even-electron ions. A number of ion-molecule condensation reactions of positive ions were observed by double resonance. The compositions of the condensation products are successfully predicted by assuming that the product ion from such a condensation is likely to contain only the boron atoms and the bridge hydrogens from the reactants, with loss of all terminal hydrogens.

A previous publication described some of the features of the positive- and negative-ion chemistry of diborane in the vapor phase, studied by the ion cyclotron resonance (icr) method.<sup>1</sup> The icr technique was found to have some unique features which make it particularly well suited to studying the reactive and elusive boron hydride ions. In investigating the negative-ion species, conditions in the icr spectrometer are such that the formation of the more stable negative ions seems to be favored, and many of the exotic negative ions observed in other types of gas-phase techniques are avoided entirely. This suggests strongly that the information obtained from such spectra may have more relevance to condensed-phase chemistry than mass spectra obtained by energetic electron or ion bombardment. In studying the positive ions, double-resonance methods of elucidating the ion-molecule reaction patterns were found invaluable in revealing very simple and suggestive regularities in reaction patterns.

It has long been recognized that many stable boron hydrides fall into two more or less distinct series, having empirical formulas  $B_nH_{n+4}$  and  $B_nH_{n+6}$ ;<sup>2,3</sup> these series are often called "stable" and "unstable," respectively. The boron frameworks of the stable hydrides are more closed and compact than the corresponding unstable hydride frameworks, the unstable hydrides normally have terminal  $BH_2$  groups which are lacking in the stable hydrides, and a neutral unstable hydride loses hydrogen more readily than the corresponding stable hydride.

One of the principal goals of the present study was to compare the behavior of ionized boron hydrides derived from both of these two classes. The extent to which the stable-unstable classification scheme is valid for the cations and the anions of different boron hydrides should provide a measure of how the ionized species differ from the neutrals, and may provide a basis for understanding their chemical behavior.

In order to investigate the ionic chemistry of the higher hydrides in the gas phase and to have a sufficient variety of behavior to provide meaningful comparison, the four lowest known hydrides above diborane were obtained and investigated. Two of these, tetraborane and pentaborane-11, are unstable hydrides, and two, pentaborane-9 and hexaborane-10, are stable hydrides.

## Experimental Section

Since the reduction of positive-ion spectra and double-resonance spectra from the normal boron isotopic form to monoisotopic form becomes rapidly more difficult with increasing numbers of borons in the ions, it was essential to use isotopically enriched compounds to get useful spectra. Accordingly tetraborane, pentaborane-11, and hexaborane-10 were obtained in 96%  $^{10}B$  enrichment. Adequate results were obtained with normal pentaborane-9.

$^{10}B_2H_6$ . Normal diborane was prepared as described in ref. 1.

$^{10}B_5H_9$ . Normal  $B_5H_9$  was purchased from Callery Chemical Corp. and used with no purification except degassing at  $-196^\circ$ .

$^{10}B_5H_6$ . Diborane (96%  $^{10}B$ ) was prepared by reduction of  $^{10}BF_3 \cdot Et_2O$  with  $LiAlH_4$  and purified by distillation through a trap at  $-126^\circ$ .

$B_4H_{10}$ . Tetraborane (96%  $^{10}B$ ) was kindly provided by Professor Riley Schaeffer. Normal  $B_4H_{10}$  was prepared by addition of  $KB_3H_8$  to polyphosphoric acid. All tetraborane was purified by distillation through a  $-95^\circ$  trap into a  $-135^\circ$  trap.

$^{10}B_5H_{11}$ . Isotopically labeled pentaborane (96%  $^{10}B$ ) was prepared from  $^{10}B_2H_6$  by pyrolysis for 24 hr in a continuously flowing closed glass pyrolysis system. The pyrolysis was carried out at about  $165^\circ$ , and the products were trapped by passage through a trap at  $-78^\circ$ . The pentaborane-11 was purified by fractionation on a low-temperature glass vacuum fractionating column.<sup>4</sup>

$^{10}B_6H_{10}$ . Hexaborane was prepared via  $B_9H_{15}$  using the same circulating pyrolysis system as was used for  $B_5H_{11}$ . Diborane was pyrolyzed for 24 hr under conditions suitable for  $B_5H_{11}$  formation, after which more diborane was introduced, the trap was raised to  $0^\circ$ , and  $B_9H_{15}$  was obtained by copyrolysis of diborane and pentaborane for about 24 hr more. The  $B_9H_{15}$  was hydrolyzed to  $B_6H_{10}$  by addition of a roughly stoichiometric amount of water,<sup>5</sup> and the  $B_6H_{10}$  was purified on the low-temperature vacuum fractionating column.<sup>4</sup>

The same icr instrumentation and instrumental techniques were used in this study as were used in the investigation of diborane.<sup>1</sup>

## Results and Discussion

**A. Negative Ions.** Negative-ion spectra of all the hydrides were taken under similar conditions—the

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(1) R. C. Dunbar, *J. Amer. Chem. Soc.*, **90**, 5676 (1968).

(2) A. Stock "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(3) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).

(4) J. E. Dobson, Ph.D. Thesis, Indiana University, 1967.

(5) R. O. Schaeffer, private communication.

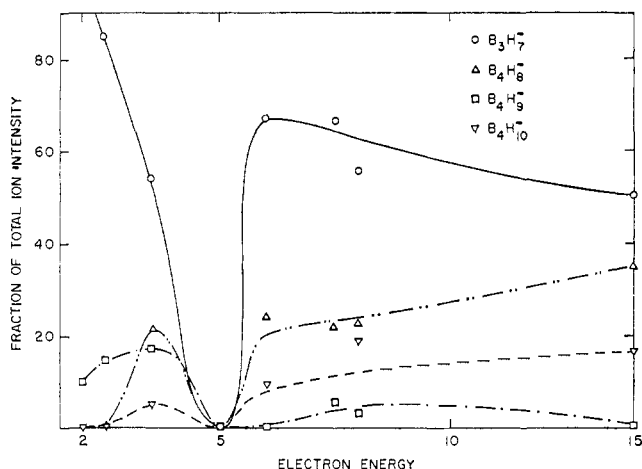


Figure 1. Variation in relative abundance of the major fragment ions in tetraborane negative-ion spectra with energy of the bombarding electrons. The two regions of ion production separated by the sharp minimum near 5 eV are characteristic of all the boron hydrides.

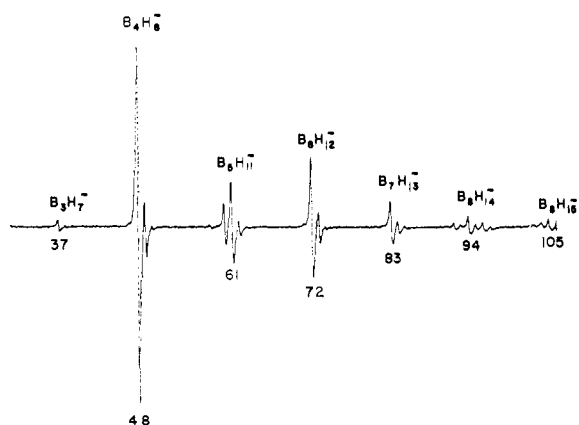


Figure 2. High-pressure negative-ion spectrum of  $B_5H_{11}$  containing 96%  $^{10}B$ . The principal peak at  $m/e$  48 is the symmetrical cleavage product, and the peaks at  $m/e$  72 and above are products of reactive processes. This spectrum in monoisotopic form is included in Figure 3.

pressure was around  $10^{-5}$  Torr, and the drift and trapping settings were arranged for good line shapes. All of the hydrides (including diborane) show a similar pattern of ion formation *vs.* bombarding electron energy. There is a region of ion formation around 3–4 V, often extending downward undiminished to the instrumental cutoff at about 2 V; the ion formation shows a sharp minimum around 5 V, rises to a peak around 8 V, and extends on upward into the high-energy regions which have been studied by other methods. Most ions are formed in both of the voltage ranges, but some of the more highly fragmented species are not formed in the low-voltage range. Figure 1 shows this pattern very clearly for several tetraborane negative ions, and in particular shows that  $B_3H_7^-$  becomes dominant at the lowest electron energies. A typical negative-ion spectrum, that of  $B_5H_{11}$ , is shown in Figure 2.

The spectra obtained are displayed in graphical form in Figure 3. The spectra are shown in monoisotopic ( $^{10}B$ ) form. The highest peak is normalized to the

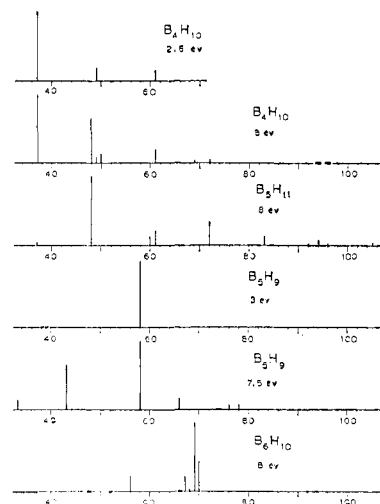


Figure 3. High-pressure negative-ion spectra of the boron hydrides studied, reduced to  $^{10}B$  monoisotopic form.

same height in each case, and no attempt has been made to report the results as fractions of total ions; nor was any attempt made to correct the peak heights for any of the mass dependent discrimination effects which are known in *icr*.<sup>6</sup> Hence the spectra should only be taken to show relative peak heights within one spectrum, and comparison of peak heights at widely different masses is very uncertain.

A number of features are of interest in examining and comparing the spectra of Figure 3. None of the hydrides seems to favor the very well-defined series of negative ions which was observed in diborane,<sup>1</sup> but rather each hydride shows its own set of ions. This is surprising, since the diborane series of ions seemed to represent the ion of greatest stability at each number of borons. This observation suggests instead that the structural identity of a boron hydride is maintained to a considerable extent when negative ions are formed.

The distinction between the stable hydrides  $B_5H_9$  and  $B_6H_{10}$ , and the unstable hydrides  $B_4H_{10}$  and  $B_5H_{11}$  provides a valid and useful basis for looking at the spectra.

**Stable Hydrides.** The most abundant ion in both of these hydrides is the  $(M - 1)^-$  peak,  $B_5H_8^-$  and  $B_6H_9^-$ . In addition to the  $M - 1$  peak, each of these hydrides forms a major ion with one less boron,  $B_4H_8^-$  for pentaborane, and  $B_5H_6^-$  for hexaborane, which seems to be unique and characteristic for each molecule, but has no obvious structural justification. The  $B_3H_3^-$  ion in pentaborane is similarly difficult to relate to the neutral hydride structure, and the higher mass ions formed in pentaborane at 8 V, such as  $B_6H_6^-$  and  $B_7H_8^-$ , also look strange and may possibly be due to impurities or filament pyrolysis. It appears that in these two hydrides the  $M - 1$  ion is a very stable species which has little propensity to make new ions either by eliminating neutral fragments or by ion-molecule condensations and that when the  $M - 1$  ion is formed with too much excess energy, it normally eliminates a fragment to form one specific smaller ion also of low reactivity.

The spectrum of pentaborane at low electron energy shows that in the low-energy region even the limited fragmentation observed at higher energy did not occur,

(6) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1968.

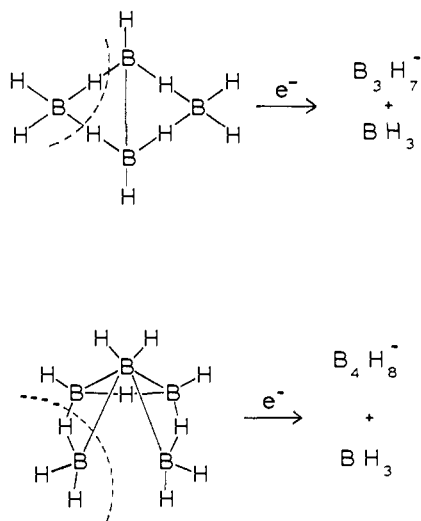


Figure 4. Postulated symmetrical cleavage of tetraborane and pentaborane-11 by an electron in the source region of the icr cell. No unsymmetrical cleavage product was observed.

and the  $B_3H_8^-$  ion was the only ion formed. Similar behavior was observed for  $B_6H_{10}$ , with all of the fragment ions except  $B_6H_9^-$  disappearing at 3 eV. These low-energy results further support the conclusion that the  $(M - 1)^-$  ion in these stable hydrides is readily formed and unless formed with considerable internal excitation is stable with respect to further fragmentation or reaction with the parent neutral.

**Unstable Hydrides.** These two hydrides form a group of relatively small peaks near the molecular weight. Figure 1 shows the variation of this group of peaks with electron energy for tetraborane, and shows how the relative magnitude of these peaks depends rather strongly on the exact conditions of formation. For both of the unstable hydrides, however, the major peak is the  $(M - BH_3)^-$  ion, corresponding to the cleavage of  $BH_3$  from the parent molecule giving the  $B_3H_7^-$  and  $B_4H_8^-$  ions for the two hydrides. This is the well-known symmetrical cleavage reaction which is effected in tetraborane and pentaborane-11 in solution by a variety of strong Lewis bases<sup>3,7,8</sup> and can be drawn schematically as in Figure 4.

There has been some uncertainty as to whether the initial step in these cleavage reactions in solution is in fact symmetrical. It is interesting that an unsymmetrical cleavage to give  $B_3H_8^-$  was not observed in tetraborane in the gas phase, although it has been suggested that such an unsymmetrical cleavage is the first step in cleavage of tetraborane by strong Lewis bases.<sup>7</sup> In the present experiments in the gas phase at low pressure, the cleavage mechanism suggested in ref 7, consisting of unsymmetrical cleavage followed by hydride transfer, can plainly not be invoked as a two-step process, since in the gas phase the products of the initial cleavage separate at once. This observation indicates that the cleavage of tetraborane by an electron proceeds directly through a symmetrical mechanism without initial formation of triborohydride ion.

(7) R. O. Schaeffer, T. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

(8) R. W. Parry, R. W. Rudolph, and D. F. Shriver, *ibid.*, **3**, 1479 (1964).

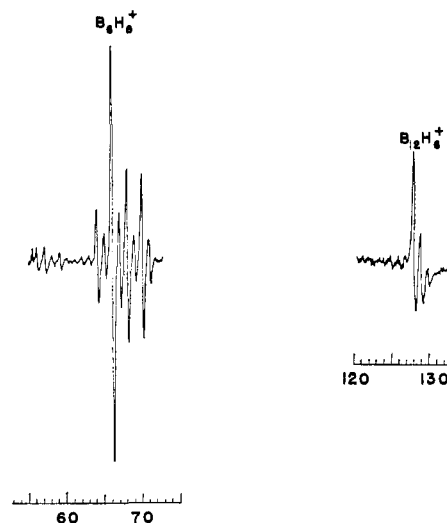
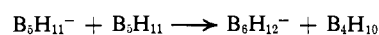
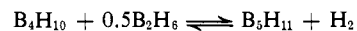


Figure 5. High-pressure positive-ion spectrum of  $B_6H_{10}$  containing 96%  $^{10}B$ , showing both the primary-ion region and the region of condensation products. This spectrum in monisotopic form is included in Figure 6.

In addition to the elimination of  $BH_3$ , the unstable hydrides show another striking feature in their spectra. This can be formally described as the successive addition of  $BH$  units to the molecular ion. This gives the  $B_3H_{11}^-$  and  $B_6H_{12}^-$  ions in tetraborane, and a series  $B_6H_{12}^-$ ,  $B_7H_{13}^-$ ,  $B_8H_{14}^-$ ,  $B_9H_{15}^-$  in pentaborane-11. (The  $B_9H_{15}^-$  ion in pentaborane-11 may not be the highest ion formed, but simply represents the point at which the spectrum was cut off.) It may be noted that this series of ions consists simply of the molecular negative ions of the series of unstable neutral hydrides, and suggests that for the  $B_nH_{n+6}$  hydride series the molecular negative ion is very stable. The reaction of negatively charged unstable hydrides through condensation reactions resulting in addition of  $BH$  units, for which a typical formulation would be



is reminiscent of the neutral hydrides, as exemplified by the well-known equilibrium<sup>9</sup>



It seems likely that in the unstable series of hydrides the presence of a negative charge does not have a great effect on the determination of the most stable ions or on the pattern of reaction with neutral hydrides.

In summary, the negative-ion behavior of the hydrides shows very striking differences between the stable and the unstable hydrides. The principal features of the stable hydrides are (1)  $(M - 1)^-$  is the major ion, (2) at high electron energy lower fragment ions and possibly higher reaction products are formed which cannot be easily rationalized, and (3) at low electron energy there appears to be little or no fragmentation or reaction beyond the  $(M - 1)^-$  ion. The principal features of the unstable hydrides are (1) the  $(M - BH_3)^-$  ion corresponding to symmetric

(9) E. L. Muetterties, Ed., "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967.

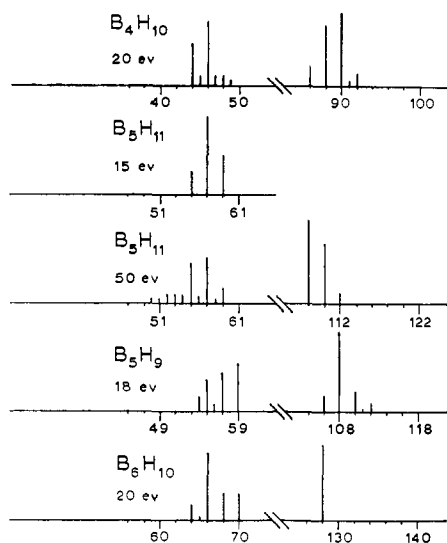


Figure 6. High-pressure positive-ion spectra of the boron hydrides studied, reduced to  $^{10}\text{B}$  monoisotopic form. In the low-mass region the spectra are aligned according to the molecular weight, and in the high-mass region according to twice the molecular weight.

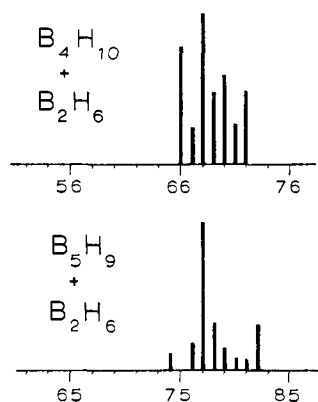


Figure 7. High-pressure positive-ion spectra of mixtures of tetraborane and pentaborane-9 with diborane, reduced to monoisotopic  $^{10}\text{B}$  form.

$\text{BH}_3$  cleavage is the dominant product at all electron energies and (2) a series of ions  $(\text{M} + n\text{BH})^+$  is formed where  $n$  can be at least 4 (for  $\text{B}_5\text{H}_{11}$ ).

**B. Positive Ions. Formation.** Positive-ion spectra were taken of the four hydrides at low and high pressures, and for mixtures of tetraborane and pentaborane-9 with diborane, using bombarding electron energies in the 15–20-eV range. The low-pressure spectra showed the samples were of reasonable purity. Figure 5 shows a typical high-pressure spectrum, that of  $\text{B}_6\text{H}_{10}$ . Figures 6 and 7 show the high-pressure spectra of the pure hydrides and the diborane mixtures in graphical form, including both the primary-ion region and the high-mass dimeric-product region. All of the spectra have been reduced to monoisotopic ( $^{10}\text{B}$ ) form by the usual methods.

A comparison of the products of primary ionization of the four hydrides with the 70-eV low-pressure spectra presented in ref 10 shows that the spectra are qualita-

(10) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, *Advan. Chem. Ser.*, No. 32, 127 (1961).

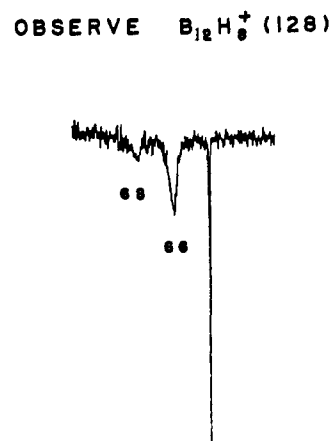


Figure 8. Typical double-resonance spectrum for boron hydride positive-ion condensation reactions, showing here the reaction  $\text{B}_6\text{H}_6^+ + \text{B}_6\text{H}_{10} \rightarrow \text{B}_{12}\text{H}_8^+ + 4\text{H}_2$ , with a small contribution from the similar reaction with  $\text{B}_5\text{H}_9^+$ . The harmonic peak at half the observed ion mass serves as a convenient check on the mass assignments.

tively similar. This suggests that neither the lower electron energy nor the presence of ion-molecule reactions has a drastic effect on the ionization patterns. For  $\text{B}_5\text{H}_{11}$  a spectrum was also taken at 50 eV, and a comparison with the 15-eV spectrum shows that, as expected, the center of gravity of the spectrum is shifted to lower mass, indicating more fragmentation, but that the qualitative features of the spectrum are not greatly distorted.

The primary-ion spectra show the strong tendency of boron hydrides to lose hydrogen in units of  $2\text{H}$ , with loss of  $2\text{H}_2$  often being favored.

As was found for diborane,<sup>1</sup> the principal mode of ion-molecule reaction was found to be the condensation in which all the boron atoms are retained and large numbers of H's are eliminated. This is reflected in the spectra in the 2M region shown in Figure 6. In view of the number of primary ions found for each hydride, the small number of different dimerization ions observed is rather unexpected, and suggests that the ion-molecule reaction paths are rather specific; it will be seen below that the double resonance bears this out. The dimerization products of the two stable hydrides and the products of the  $\text{B}_5\text{H}_9$ - $\text{B}_2\text{H}_6$  mixture are noteworthy. In each case there is only *one* major ion.

**C. Positive Ions. Reactions.** The icr double-resonance technique<sup>1</sup> was used to identify the specific reactions leading to the condensation products in the positive-ion spectra. Good double-resonance signals were observed for the positive-ion reactions in all of the hydrides, and a typical spectrum is displayed in Figure 8. All the major reactions had a negative double-resonance sign, indicating exothermic reaction. The reduction of the double-resonance spectra to monoisotopic form was carried out using the reduction methods described in ref 1.

Table I summarizes the ion-molecule reactions observed. It will be seen that each major condensation product was found to have at least one corresponding reaction, but that in most cases there are only one or two significant reactions giving each observed product. The variety of reaction types is wider than with diborane, but is still remarkably small.

Table I

Reaction	Reduced relative intensity
$B_4H_4^+ + B_4H_{10} \rightarrow B_8H_8^+ + 3H_2$	100 <sup>a</sup>
$B_4H_6^+ + B_4H_{10} \rightarrow B_8H_{10}^+ + 3H_2$	83
$B_4H_7^+ + B_4H_{10} \rightarrow B_8H_{11}^+ + 3H_2$	67
$B_4H_7^+ + B_4H_{10} \rightarrow B_8H_{13}^+ + 2H_2$	39
$B_4H_4^+ + B_4H_{10} \rightarrow B_8H_6^+ + 4H_2$	33
$B_4H_5^+ + B_4H_{10} \rightarrow B_8H_{11}^+ + 2H_2$	28 <sup>b</sup>
$B_4H_6^+ + B_4H_{10} \rightarrow B_8H_{12}^+ + 2H_2$	22
$B_5H_7^+ + B_5H_{11} \rightarrow B_{10}H_{10}^+ + 4H_2$	100 <sup>a</sup>
$B_5H_7^+ + B_5H_{11} \rightarrow B_{10}H_{12}^+ + 3H_2$	50
$B_5H_5^+ + B_5H_{11} \rightarrow B_{10}H_8^+ + 4H_2$	43
$B_5H_5^+ + B_5H_9 \rightarrow B_{10}H_8^+ + 3H_2$	100 <sup>a</sup>
$B_5H_7^+ + B_5H_9 \rightarrow B_{10}H_{10}^+ + 3H_2$	60
$B_5H_5^+ + B_5H_9 \rightarrow B_{10}H_7^+ + 3.5H_2$	50
$B_5H_7^+ + B_5H_9 \rightarrow B_{10}H_{13}^+ + 2H_2$	25
$B_5H_9^+ + B_5H_9 \rightarrow B_{10}H_{12}^+ + 3H_2$	5
$B_6H_6^+ + B_6H_{10} \rightarrow B_{12}H_8^+ + 4H_2$	100 <sup>a</sup>
$B_6H_8^+ + B_6H_{10} \rightarrow B_{12}H_8^+ + 5H_2$	54
$B_4H_6^+ + B_2H_6 \rightarrow B_6H_8^+ + 2H_2$	100 <sup>a</sup>
$B_4H_4^+ + B_2H_6 \rightarrow B_6H_6^+ + 2H_2$	90
$B_4H_6^+ + B_2H_6 \rightarrow B_6H_{10}^+ + H_2$	56
$B_4H_4^+ + B_2H_6 \rightarrow B_6H_7^+ + 1.5H_2$	~40
$B_4H_6^+ + B_2H_6 \rightarrow B_6H_9^+ + 1.5H_2$	38
$B_4H_6^+ + B_2H_6 \rightarrow B_6H_{11}^+ + 0.5H_2$	28
$B_5H_5^+ + B_2H_6 \rightarrow B_7H_7^+ + 2H_2$	100 <sup>a</sup>
$B_2H_2^+ + B_3H_9 \rightarrow B_7H_7^+ + 2H_2$	100 <sup>a</sup>
$B_2H_3^+ + B_3H_9 \rightarrow B_7H_7^+ + 2.5H_2$	72
$B_2H_4^+ + B_3H_9 \rightarrow B_7H_8^+ + 1.5H_2$	36
$B_2H_2^+ + B_3H_9 \rightarrow B_7H_6^+ + 2.5H_2$	14
$B_2H_4^+ + B_3H_9 \rightarrow B_7H_8^+ + 3.5H_2$	7

<sup>a</sup> Arbitrary normalization. <sup>b</sup> Very uncertain value.

It is clear from the experimental results that in contrast to diborane the higher hydrides show no features in their positive-ion behavior which can be generalized into a strict rule of reliable predictive value. However, given that it is necessary to treat these reactions in terms of the relative probabilities of various competing processes, and that general statements can only be made about the most likely patterns of behavior, it is possible to draw some interesting conclusions from the data presented here.

A striking feature of the boron hydride positive ions in contrast to hydrocarbon ion chemistry is the marked preference for formation of odd-electron ions. As can be seen from Figures 6 and 7, the primary ionization favors the formation of odd-electron ions, and only a small fraction of the condensation ions are even-electron species. Apparently a general feature of the boron hydride systems is that an unpaired electron is more readily supported as a positive radical ion than as a neutral radical fragment.

It is interesting to note that a simple prescription predicts the composition of one of the principal dimerization product ions for each of the hydrides: the predicted ion, which may be called the fully condensed dimer ion, is found by combining two neutral hydride molecules, retaining all the boron atoms and all the bridging hydrogen atoms, and eliminating all the terminal hydrogen atoms. For the "stable" hydrides this procedure predicts the ions  $B_{10}H_8^+$  (from  $B_5H_9$ ) and  $B_{12}H_8^+$  (from  $B_6H_{10}$ ), and these are seen from Figure 6 to be the predominant product dimer ions. The fully condensed product for  $B_4H_{10}$  is  $B_8H_8^+$ , while for  $B_5H_{11}$  it seems reasonable to consider one of the apical hydrogen

atoms as bridging<sup>11</sup> to give  $B_{10}H_8^+$  as the predicted fully condensed ion. In the case of the two unstable hydrides both the fully condensed ion and the ion two mass units larger are major peaks, but in none of the hydrides is an ion smaller than the fully condensed species an important product.

In the reaction of  $B_4H_{10}$  with diborane, the products can be understood in the same term: the fully condensed ion  $B_8H_6^+$  is the lowest mass ion and is a major product, and the ion two mass units larger,  $B_8H_8^+$ , is also a major product; the other ions have lower abundance than these two. Applied to the products of  $B_5H_9$  reacting with diborane these concepts lead to the prediction of even-electron ions, and may therefore not apply; and as Figure 7 shows, the major product is  $B_7H_7^+$ , which is one mass unit higher than the fully condensed ion, but which is an odd-electron ion, and therefore more likely to be a major product.

Re-examination of the earlier diborane results<sup>1</sup> shows that a similar conclusion can be reached here: among the  $B_4$  positive ions, corresponding to dimerization of diborane, and  $B_6$  positive ions, corresponding to the trimerization of diborane, the most abundant species are respectively  $B_4H_4^+$  and  $B_6H_6^+$ , which are seen to be the fully condensed ions predicted by this same prescription.

It may also be noted from Table I that the reactions of tetraborane and pentaborane-9 with diborane follow the earlier rule for condensation products. It was found in ref 1 that when neutral diborane condenses with a boron hydride positive ion the product can be written as the result of adding  $B_2H_2$  to the ion. This successfully predicts the fastest reactions in Table I, although there are several slower reactions which do not follow the rule.

## Conclusions

The classification of the neutral boron hydrides into stable and unstable series provides a very convincing basis for interpreting the patterns of negative-ion formation under icr conditions. The similarity of behavior of the hydrides within the two classifications and the striking differences between the two types of hydride suggest that for the negative ions this classification scheme is of fundamental importance, and that the presence or absence of terminal  $BH_2$  groups is the dominant factor in the negative-ion chemistry.

The very distinctive patterns of negative-ion formation for each of the boron hydrides investigated suggest that negative-ion icr would be an exceptionally convenient and specific tool for identifying and characterizing extremely small quantities of unknown boron hydrides. For instance, the icr spectra of the two pentaboranes are entirely different and distinctive, and icr would be a convenient means of distinguishing these two compounds in microgram quantities.

The very ready formation of the  $B_5H_8^-$  and  $B_6H_9^-$  anions from pentaborane and hexaborane in the gas phase is in accord with the recent generation of these

(11) The position of one of the apical hydrogens of pentaborane-11 deep inside the boron framework of the molecule makes it seem likely that this hydrogen would behave in a similar manner to the basal bridging hydrogens, and in fact this hydrogen atom has been postulated to participate in multicenter bonding (see ref 9).

ions in solution by reaction of the boranes with proton acceptors.<sup>12</sup> In solution it is believed that a bridge proton is abstracted in forming these anions, and it should be possible to determine by icr experiments on specifically deuterated boranes whether the gas-phase process also involves elimination of a bridge proton.

Munro, Ahnell, and Koski have reported the results of negative-ion formation in diborane, tetraborane, and pentaborane by bombardment with 70-eV electrons.<sup>13</sup> For tetraborane and pentaborane they find much less specific behavior, and observe many minor ions and a few major ions not observed in the icr experiments, but in general terms the same major ionic fragments are observed by both techniques. (Of course, conventional mass spectroscopic methods do not observe the higher reaction products found with icr.) However, in interpreting their tetraborane results they conclude that  $B_3H_7^-$  is not formed by resonant dissociative attachment, but rather by pair formation. The present results show that  $B_3H_7^-$  is the predominant ion at electron energies far too low to permit any pair process, and thus indicate that  $B_3H_7^-$  is readily formed by dissociative attachment. This of course does not rule out a transition to a pair-production mode of formation at energies above 10 eV. The structure of fragmentation patterns such as Figure 1 suggests that there are two distinct types of dissociative attachment processes involved depending on the electron energy, but it is not obvious what these are and why they lead to such a sharp minimum in ion production around 5 eV.

Much of the positive-ion chemistry of the boron hydrides which have been investigated leads to the general conclusion that following the initial production of the parent positive ion, a number of fragmentation and ion-molecule condensation processes are possible, usually resulting in the formation of an odd-electron ion and one or more even-electron neutral products. The ion-molecule reactions observed are all condensations in which the reactant ion couples with a neutral molecule with retention of all the borons and extensive elimination of hydrogen, and the rather small number and specific nature of these reactions suggests that there may

(12) G. L. Brubaker, M. L. Denniston, S. G. Shore, J. C. Carter, and F. Swicker, *J. Amer. Chem. Soc.*, **92**, 7216 (1970); D. F. Gaines and T. V. Iorns, *ibid.*, **89**, 3375 (1967).

(13) D. F. Munro, J. E. Ahnell, and W. S. Koski, *J. Phys. Chem.*, **72**, 2682 (1968).

be very specific mechanistic patterns in these reactions which are yet to be elucidated.

It is a suggestive discovery that the most favored positive-ion condensation products have the composition predicted by retaining bridge hydrogens and eliminating terminal hydrogens (with the provision that this product must be an odd-electron ion). It should be emphasized that no conclusions regarding the structure of the product ions can be drawn from these data, and the actual structures of the ions and the site of origin of their retained hydrogen remain open questions. Existing theories of boron hydride bonding<sup>14</sup> have been notably unsuccessful in predicting features of gas-phase position-ion compositions, structures, and reactions, and are probably not useful in this case. The extensive loss of hydrogen in these condensation reactions suggests that the presence of the positive charge reduces the B-H bond strength to the point where little energy is required to disproportionate B-H bonds into H-H and B-B bonds. It is an attractive hypothesis that it is the terminal B-H bonds which are broken in this fashion, but a test of this hypothesis will await the results of experiments with selectively deuterated boranes.

The classification of the parent neutral hydrides into stable and unstable appears to have little value in the interpretation of either the ionization patterns or the ion-molecule reactions for these positive ions. The extra two hydrogen atoms of the unstable hydrides appear to be lost immediately on ionization or reaction, and to have little or no effect on the fragmentation and reaction patterns.

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(14) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.