

D. F. Munro, J. E. Ahnell, and W. S. Koski

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Abstract

Questions of the role of negative boron hydride ions frequently arise in problems concerning energetics of electron impact processes, discharge tube reactions, and radiation chemistry. In view of the fact that the boron hydrides are electron deficient compounds, it might be expected that they are more prone to negative ion formation than hydrocarbons; however, very few studies of such ions have appeared in the literature. This paper gives some qualitative results obtained on boron hydride negative ions produced by electron bombardment of diborane, tetraborane, and pentaborane-9. A pulsed electron beam, a quadrupole mass analyzer, and an electron multiplier were used for this work. In diborane, the most intense ions observed were $B_2H_3^-$ and BH_4^- . Lower and varying intensities of $B_2H_4^-$, $B_2H_3^-$, $B_2H_2^-$, B_2H^- , B_2^- , BH_3^- , BH_2^- , BH^- , and B^- were also readily detectable. Similarly, the negative ions observed in tetraborane included the relatively high intensity $B_3H_7^-$ and lower intensities of $B_2H_5^-$, $B_2H_4^-$, BH_4^- , etc. In addition, indications were obtained for $B_4H_9^-$. Similar results were obtained with pentaborane-9.

Introduction

For many years, mass spectroscopists have dealt almost exclusively with processes involving positive ions; ionization, fragmentation, and ion-molecule reactions. Recently, however, despite problems of low intensity, an increasing amount of work has been done on negative ions. A number of species have been characterized,¹ and a few reactions have been studied.^{2,3} In addition, at least one investigation on the role of negative ions in flames has been carried out, using mass spectroscopic techniques.⁴

The boron hydrides are traditionally classified among the electron deficient compounds, and might well be expected to form negative ions. Furthermore, some work has been done with the boron hydrides in gaseous discharges and in radiation chemistry where these ions might conceivably play a role.⁵ Thus, it was of interest to us to study the negative ions of the boron hydrides with the eventual hope of providing information to permit the evaluation of the role these ions might play in discharges and other associated phenomena.

We have under construction in our laboratory a tandem mass spectrometer for the study of ion-molecule reactions. In the course of testing the first stage of the instrument, it became apparent that the spectrometer might be suited for the observation of negative ions. The ions from SF_6 and O_2 were detected with relative ease. It was decided to investigate what negative ions could be observed in the simpler boron hydrides; diborane, tetraborane, and pentaborane.

Because the spectrometer is still in the construction stage, some of the refinements normally found on conventional instruments are lacking, so that the results obtained are necessarily of a qualitative nature. Nevertheless, it was felt that the observations were sufficiently interesting to warrant reporting.

Experimental

The important features of the basic experimental arrangement are shown diagrammatically in Fig. 1. The gas to be analyzed flows from a bulb at room temperature into the ion source through a Granville-Phillips leak. The ion source, which is similar in design to one described by Von Zahn,⁶ has an electron beam energy

variable from 0 - 100 volts. There are no provisions for measuring pressure, temperature, or ionizing current in the ion source. The ions are focused and accelerated to 50 - 100 volts, and mass analyzed by a quadrupole mass filter with a length of 10.0 inches and an r_0 of 0.27 inches. Mass scanning is accomplished by varying the RF and DC voltages to the quadrupole. The resolution of the quadrupole is electronically variable. The ions are then accelerated to 600 volts and detected by a Bendix Channeltron continuous electron multiplier.

Because of the absence of slits in the mass spectrometer, the relatively open nature of the ion source, and the high sensitivity of the detector, it is necessary to reduce the background from scattered electrons reaching the detector. This is accomplished in two ways: first, by establishing a weak magnetic field to deflect the electrons but not the ions; and second, by pulsing the electron beam. The ionizing beam is pulsed at 10 kc by applying a 40 volt pulse to the first lens of the electron beam. The beam "on" time is 10 microseconds. After a delay of 5 microseconds, the second pulser sends a one volt pulse to turn on the transistorized "AND" gate for 20 - 30 microseconds. Only those pulses which arrive at the gate during this interval are sent on to the ratemeter. At the voltages used, most of the electrons arrive at the detector within one or two microseconds; the flight time of the negative ions, however, is of the order of 10 - 20 microseconds. Thus, the signal to the ratemeter is primarily due to ions, with a drastic reduction in the electron background. The output of the ratemeter is plotted versus the DC voltage on the quadrupole with an XY recorder. A signal of five ions per second can readily be observed. A typical plot, shown in Fig. 2, is the lower portion of the mass spectrum of the negative ions of pentaborane.

All the boron hydride samples were purified by distillation in a vacuum system. The diborane was trapped out at -154°C . The tetraborane was purified in three steps: pumping off hydrogen and diborane while trapped at -130 , passing through a trap at -95 to condense the pentaborane and the higher boron hydrides, and finally condensing at -196 . The pentaborane was similarly purified: pumping off diborane and tetraborane at -98 , passing through a trap at -79 , and final trapping at -196 .

Results and Discussion

The results are shown in the bar graph in Fig. 3. The narrow bars represent peaks which have been multiplied by a factor of ten. All measurements are for 70 volt ionizing electrons. The monoisotopic mass spectrum was computed assuming the natural B_{10}/B_{11} distribution of 20/80, and also assuming that there was no isotope effect in loss of hydrogen from B_{10} versus B_{11} . In nearly all cases, the peak heights from which the monoisotopic spectra were calculated were an average of at least three measurements, with separate measurements in agreement within 10%. In calculating the monoisotopic spectrum, the system is "over-determined," i.e., there are more equations than there are unknowns. This provides a means of checking the internal consistency of the results. For every case except two, the self-consistency deviation was less than 2%, and in all cases less than 10%. On the basis of these considerations, relative intensities within a group of peaks, e.g., B_5H_9 , $B_5H_8^-$, $B_5H_7^-$, etc., should be accurate to $\pm 10\%$. In comparing peaks between different groups, however, it is more difficult to assign limits of error, for the spectrometer may favor the observation of low masses over high masses in certain cases. One can observe this "discrimination" in the positive ion spectra, and it appears to be primarily a function of the resolution of the quadrupole. It is possible, however, that the continuous electron multiplier and the ion source also mass discriminate, perhaps differently for positive and negative ions. Since the signal from the multiplier is analyzed as pulses rather than current, mass discrimination by the detector should be minimized. The exit holes in our ion source are rather large, and it would be expected that discrimination here would also be negligible. Thus, if it is assumed that the discrimination effects are the same

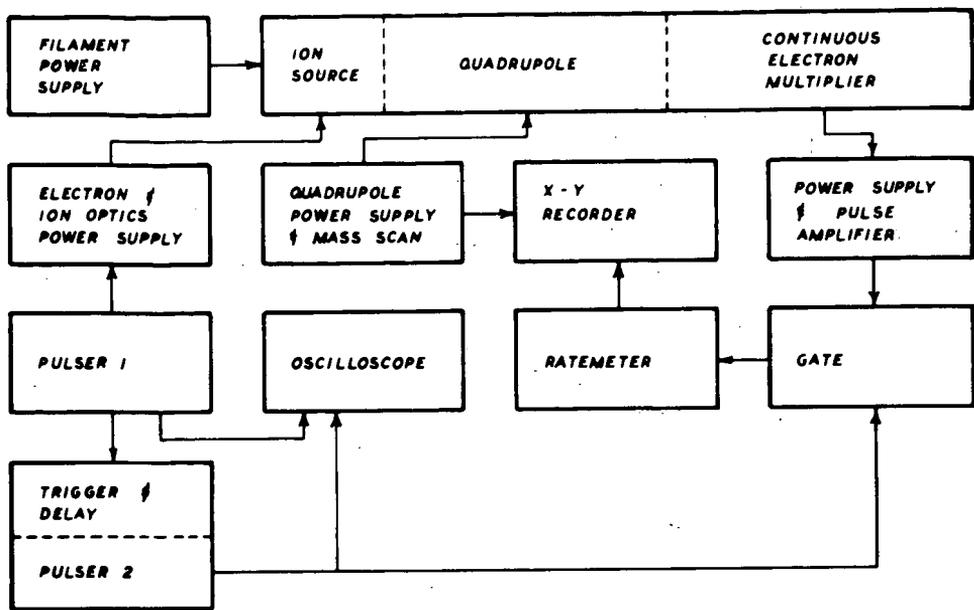


FIGURE 1

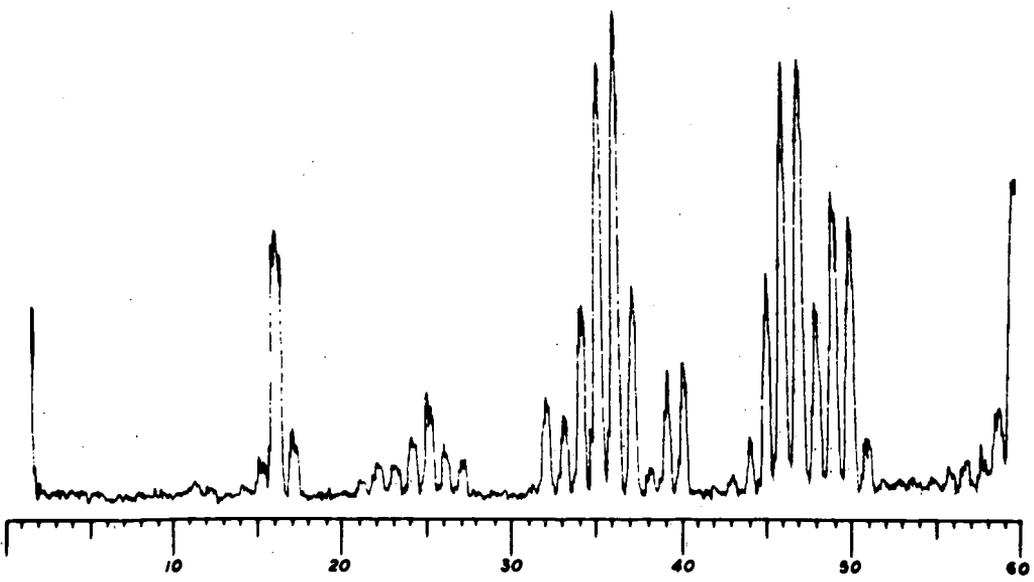


FIGURE 2

NEGATIVE IONS OF BORON HYDRIDES
MONOISOTOPIC RELATIVE INTENSITIES

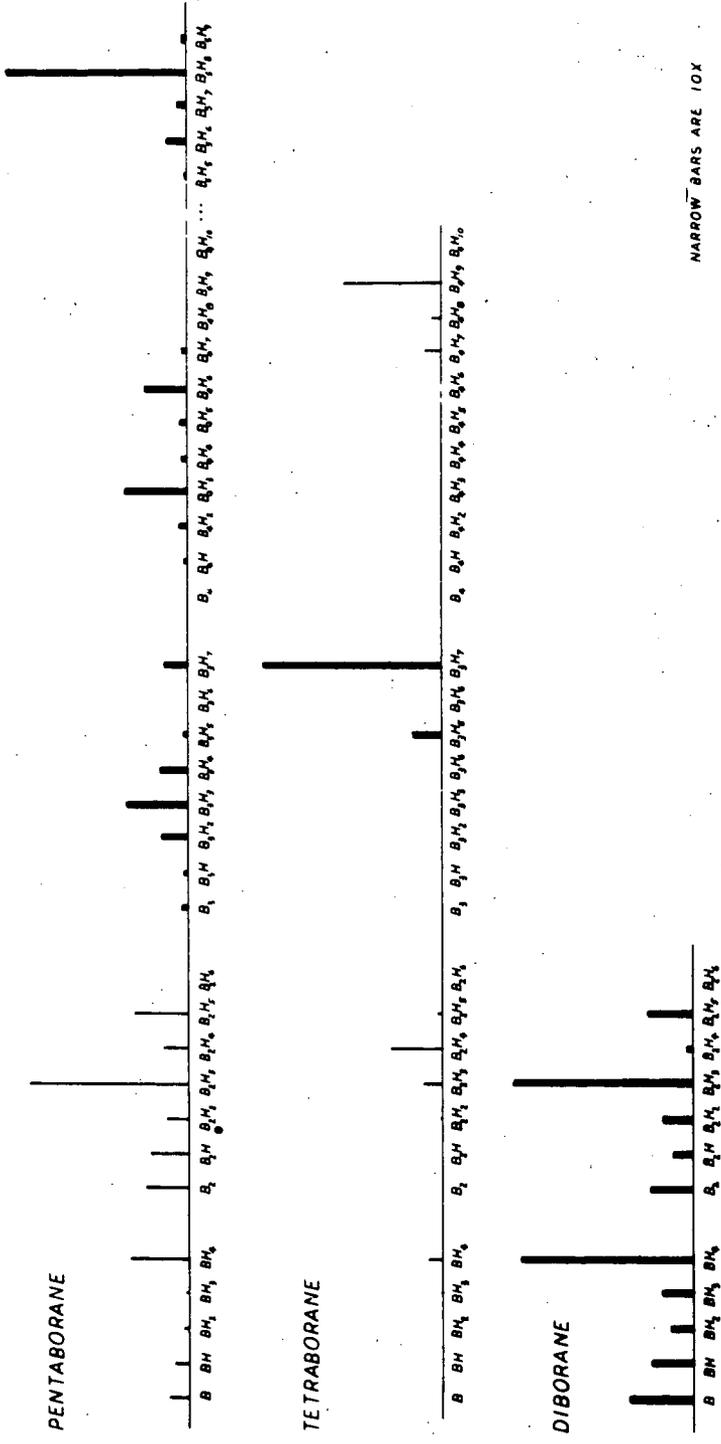


FIGURE 3

for positive and negative ions, approximate corrections can be made. At worst, the relative intensities throughout the whole spectra are probably correct within $\pm 25\%$.

Although reasonable precautions were taken to assure the purity of the sample in the diborane spectrum, peaks corresponding to $B_3H_7^-$ and $B_4H_9^-$ were observed. These could have arisen either from ion-molecule reactions, from pyrolysis of the diborane as the sample flowed into the source, or from impurities in the diborane. The latter is improbable, for in a positive ion spectrum of the same sample in the same spectrometer, the tetraborane peaks could be observed only with difficulty. It was estimated on the basis of the positive ion spectrum that the tetraborane impurity could be no greater than one part in five hundred. In the negative ion spectrum the peaks corresponding to $B_3H_7^-$ and $B_2H_3^-$ were of almost equal intensity. It should be noted, however, that in comparing the diborane and tetraborane samples, it was much easier to observe the negative ion peaks from tetraborane, which were larger by about two orders of magnitude.

There are several mechanisms by which negative ions can be formed. The traditional processes are as follows:

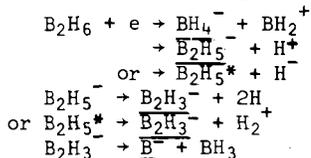
1. Ion pair formation: $XY + e \rightarrow X^+ + Y^- + e$
2. Resonance attachment: $XY + e \rightarrow XY^-$
3. Resonance attachment with dissociation: $XY + e \rightarrow X + Y^-$

In addition, a process somewhat like the third mentioned above can be imagined, in which the neutral species is left in an excited state which in turn decays to an ion pair. Also, a negative ion may fragment, giving rise to a neutral species and a new negative ion.

4. Excited state decay: $XYZ + e \rightarrow XY^* + Z^-$
 $XY^* \rightarrow X^+ + Y^-$
5. Fragmentation: $XY^- \rightarrow X + Y^-$

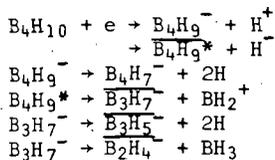
Using the above scheme, and assuming that the fragments most easily lost are BH_2^+ , BH_3 , and hydrogens, most of the more intense peaks in the negative ion boron hydride spectra can be accounted for rather well in the following manner.

Possible Modes of Fragmentation of Diborane



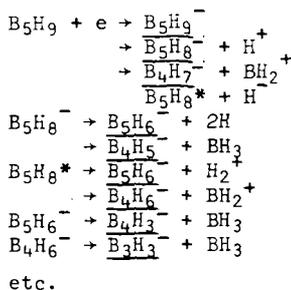
The underlined peaks are the four most intense in the diborane mass spectrum. The other peaks come from loss of hydrogens, either singly or in pairs, from the above species.

Possible Modes of Fragmentation of Tetraborane



This scheme accounts for all of the peaks with an observed intensity of greater than 1%, except for the B_2H_3 peak, whose intensity is 1.1%, and which could be due to a diborane impurity.

Possible Modes of Fragmentation of Pentaborane



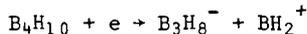
In support of the above mechanism, the data in Table 1 can be cited.

	Diborane ⁷	Tetraborane ⁸	Pentaborane ⁹
BH_2^+	19.1	7.0	12.2
BH_3^+	.59	.6	--

(These ion intensities were obtained with 70 volt electrons, and are given in percent relative to the most intense peak in the mass spectrum for the compound in question.)

Thus, it can be argued that the loss of BH_2^+ is much more likely than the loss of BH_3^+ . The loss of BH_3 , however, at least from neutral species, is fairly well established in a number of reactions.¹⁰ It should not be too surprising if BH_3 can also be readily fragmented from negative ions.

It is tempting to question the necessity of invoking the excited state decay process (4) described above. For example, can the formation of the B_3H_7^- not be simply written as a resonant attachment process with the dissociation of BH_3 ? Although this is certainly possible, one or two points argue against this mechanism. First, at the electron energies used, a resonant process of this type would not be expected to be of primary importance. Secondly, one might inquire why the pair ionization process,



is not observed, especially in view of the fact that the analogous process seems to be the predominant one in diborane. Indeed, the pair ionization process is the one which is expected; it is disturbing that it is not seen in view of the stability of B_3H_8^- in solution and in the solid phase. The structure of B_3H_8^- is known from x-ray work, and there is ample theoretical and experimental justification for its existence.¹¹ On the other hand, we have found no evidence in the literature for B_3H_7^- . The question arises as to whether an error can be made in the mass assignments. The marker compounds used were O_2 and H_2O , giving rise to the O_2^- , OH^- , and O^- peaks, which were always present in the background. Considerable care was taken in making the mass assignments, so that unless some unknown instrumental or chemical processes were occurring of which we are unaware, the given assignments are correct. Therefore, granting that the reported observations are valid, and accepting the notion that pair ionization should be the dominant process at higher electron energies, and further noting that the BH_2^+ ion is much more predominant than the BH_3^+ in the positive ion spectrum, it seems necessary to invoke some mechanism analogous to (4). Perhaps further weight can be given to this argument by noting that the parent peak is not observed in tetraborane, suggesting that a loss of hydrogen is a strongly favored process in the electron impact situation.

The present work suggests several further experiments which should be carried

out to answer some of the questions which have been raised here. An investigation of metastable negative ions on a magnetic sector instrument should prove useful in confirming or negating the fragmentation scheme postulated above. A careful study of the diborane spectrum, either in a tandem instrument, or with an ion source in which one could be sure that pyrolysis is not taking place would be necessary to remove the ambiguity in the observation of tetraborane—in the diborane sample; whether the peaks above diborane are due to impurities, or whether they do in fact result from ion-molecule reactions. Perhaps most useful initially would be an investigation of the boron hydride spectra at low electron energies, where resonance attachment becomes the dominant process. Ideally, one should study the spectra as a function of energy; the clastogram technique¹² might prove valuable in sorting out the various processes occurring. We made some attempt to work at low electron energies, but largely without success. Since we are unable to measure the ionizing current, i. e., keep it constant as a function of energy, we would have little confidence in an appearance potential measurement, particularly since the background from electrons again becomes a problem at low electron energies, when they can be pushed out of the ionization chamber by the repeller.

Reese, Dibeler, and Mohler have reported on the spectrum of pentaborane, in which they observed the resonant attachment process in the parent ion.¹³ Although their relative intensities are different from those which we observed, this is probably not surprising, in view of the different energies of the ionizing electrons in the two cases. Curiously, however, Dibeler does not report any of the lower fragments for pentaborane.

In conclusion, it is evident that the lower boron hydrides do form negative ions. In certain circumstances, the abundance of these ions may be great enough so that they would have to be taken into consideration in mass spectral, radiation, or gaseous discharge phenomena. It is also clear, however, that more than a mere qualitative study of these negative ions will be necessary for the complete understanding of their roles in these situations.

Acknowledgment- This work was done under the auspices of the United States Atomic Energy Commission.

Figure Captions

- Fig. 1. Block diagram of the mass spectrometer.
 Fig. 2. Lower portion of the mass spectrum of the negative ions from pentaborane.
 Fig. 3. The monoisotopic relative abundances for the negative ions from diborane, tetraborane, and pentaborane.

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