identical with unlabeled species: H, 52.1;[16] CH_3, 32.1;[16] C_2H_3, 65.3;[16] C_2H_4, 12.5;[16] C_2H_5, 25.4;[16] C_3H_5 (allyl), 30.0;[16] c-C_3H_6, 53;[3] C_3H_6, 4.88;[16] CH_3SH, −5.46;[17] C_2H_5SH, −10.99;[17] i-C_3H_7SH, −18.19;[17] CH_3SCH_3, −8.94;[17] $CH_3SC_2H_5$, −14.22;[17] n-$C_3H_7SCH_3$, −19.51;[17] $(C_2H_5)_2S$, −19.92;[17] $(CH_3S)_2$, −5.71;[17] $(C_2H_5S)_2$, −17.78.[17]

[16] R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

[17] H. Mackle and P. A. G. O'Hare, *Tetrahedron*, **19**, 961 (1963).

Ion–Molecule Chemistry of Diborane by Ion Cyclotron Resonance

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Abstract: Positive and negative ion–molecule chemistry of diborane has been investigated by ion cyclotron resonance. The production of a series of negative ions is described, and the reaction $BH_4^- + B_2H_6 \rightarrow B_2H_7^- + BH_3$ is studied in detail by double resonance: the three boron atoms in the reactants appear with equal probability in the neutral product. Several sulfur-containing negative ions are described, and an excited state of BH_4^- is shown to be produced from OH^-. A number of high-mass positive ions are found to be reactively formed by successive additions of B_2H_2 to ionic reactants.

Investigation of the chemistry of boron hydrides and related compounds has shown that their structure and behavior provide sharp contrasts to familiar organic systems.[1,2] However, except for the chemistry of several stable negative ions in solution, little is known of their ionic chemistry. Since ion cyclotron resonance (ICR) provides a powerful means of studying ion–molecule chemistry,[3–5] it is of interest to apply it to the study of boron-containing ions; the rapidly growing body of knowledge of a variety of ion–molecule reactions provides a valuable point of reference.[6] In general terms, the highly electron-deficient positive ions can be expected to show new patterns of structural and reactive behavior; on the other hand, many boron-containing negative ions are isoelectronic with organic systems, and it may be possible to interpret the chemistry of these ions using the methods and ideas of organic chemistry.

A preliminary study of diborane using single and double cyclotron resonance techniques is described in this paper. Previous work on gas-phase boron hydride ions has been done by conventional mass spectroscopic methods, using positive ions[7–9] produced by energetic electron impact, and more recently negative ions produced both by electron impact[10] and by high-energy Kr ions.[11] Aside from incidental observations,[8] ion–molecule reactions have been largely ignored. Ion cyclotron resonance spectrometry provides a convenient tool for examining ion–molecule reactions and in addition allows the production of ions by reactive mechanisms.

Experimental Section

Previous publications have described the ion cyclotron spectrometer used in this work and discussed its use in detecting positive ions and in identifying and characterizing the energy dependence of ion–molecule reactions.[12,13] The ionizing electron beam was normally run at 40 or 70 eV for low-pressure positive ion spectra (less than 10^{-6} torr); high-pressure positive ion spectra were taken using 17- or 18-eV electrons, except for the $B_2 \rightarrow B_3$ double resonance as discussed below. Negative ions were normally produced with about 8-eV electrons at pressures from 5×10^{-6} to 5×10^{-5} torr using an ionizing beam current of 3–10 μA. From the behavior of the spectra as a function of pressure, it is believed that some of the higher mass negative ions of diborane are formed from products of pyrolysis at the hot filament and accelerated into the analyzing cell by the electron beam accelerating potential. Thus the presence of a high-mass ion cannot be assumed, as is often done in the positive ion case, to be due to some ion–molecule reaction.

Diborane was synthesized by two methods. One sample was prepared by a convenient technique for which the author is indebted to Dr. William L. Jolly:[14] 1.6 g of KBH_4 (Metal Hydrides Inc.) was added slowly to a rapidly stirred sample of 30 ml of 85% phosphoric acid in an evacuated vacuum system, and the product was collected continuously by pumping through a Dry Ice–acetone trap into a liquid nitrogen trap. Several other samples were prepared by reduction of boron trifluoride etherate (Matheson Coleman and Bell, 47%) with $LiAlH_4$ in a flowing-nitrogen system.[15] All samples were purified by four to six passes through a CS_2 slush trap followed by pumping on the frozen sample. Frequent low-pressure spectra

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[1] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

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[11] G. Hortig, O. Mueller, K. R. Schubert, and E. Fluck, *Z. Naturforsch.*, **21b**, 609 (1966).

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[14] W. L. Jolly, private communication.

[15] S. G. Shore, K. W. Boddeker, and J. A. Patton, *Inorg. Syn.*, **9**, 4 (1967).

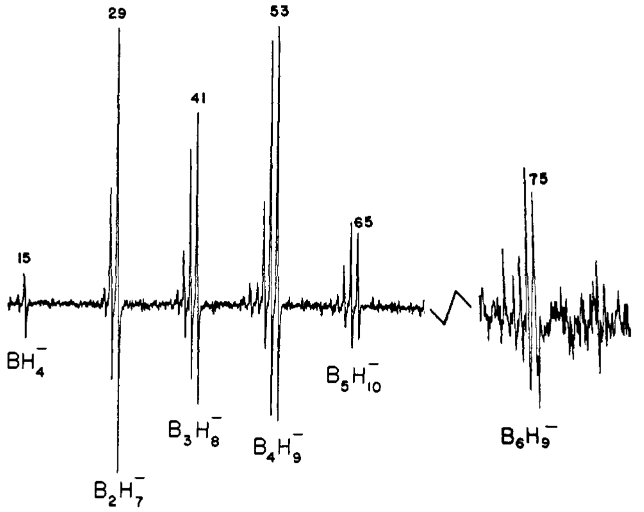


Figure 1. Negative ions. High-pressure single resonance spectrum of B_2H_6 at about 7 × 10^{-5} torr pressure and 8-eV ionizing energy. Each isotopic multiplet arises from the single species noted. All the spectra presented are reproduced from the original recorder tracings. The *m/e* 75 region is expanded × 10.

showed the samples to be free of measurable impurities, and even samples several weeks old showed no traces of contamination by higher hydrides. The H_2S was J. T. Baker CP grade used without further purification.

Results and Discussion

A. Negative Ions. Two processes apparently compete in the formation of negative ions: below about 5 × 10^{-6} torr the filament pyrolysis mechanism produces mainly higher species, with $B_4H_9^-$ predominating, while at higher pressures BH_4^- and $B_2H_7^-$ intensities increase sharply and the spectrum becomes quite insensitive to pressure. Figure 1 shows a typical spectrum taken at 5 × 10^{-5} torr pressure.

Each group of peaks in Figure 1 corresponds to a single ionic species: the splitting of the peaks is due to the normal isotopic distribution of ^{10}B (19%) and ^{11}B (81%). Six negative ions are readily identified. Of these, the three lightest, BH_4^-, $B_2H_7^-$, and $B_3H_8^-$, are well known in condensed-phase chemistry.[16] In addition to these, $B_4H_9^-$ and $B_5H_{10}^-$ have been obtained by impact of Kr^+ on higher boron hydrides.[11] The $B_6H_9^-$ ion has not been observed before. The spectrum in Figure 1 also suggests the possible presence of an ion such as $B_7H_8^-$, but the signal has always been too weak for reliable analysis of the isotopic multiplet. The structures of the three lowest ions are well characterized. Lipscomb has proposed structures for the other three conforming to his topological method,[17] but the present study offers no means of distinguishing between alternatives.

Weak double resonance signals are observed corresponding to reactions connecting many of the negative ions, but only the reaction

$$BH_4^- + B_2H_6 \longrightarrow B_2H_7^- + BH_3 \quad (1)$$

has been completely characterized by strong reproducible double resonance signals. As has been shown in other studies,[4,13] the irradiation and observation of the various isotopic species in such a reaction provides detailed and reliable information about the reaction mechanism. In particular, for a reaction such as (1) in which a small neutral fragment is eliminated, analysis of the double resonance of the various isotopically differing species permits the determination of which reactant is the source of the boron eliminated in the neutral. Appendix A outlines how this may be done for this simple case. Detailed analysis of the spectra for reaction 1 shows that both BH_4^- and B_2H_6 contribute boron atoms to the BH_3 product. Figure 2 shows the expected results for the case where the three boron atoms of the intermediate $B_3H_{10}^-$ are equivalent, leading to equal probability that any one of the boron atoms will be eliminated as BH_3. The excellent agreement of this calculated spectrum with the observed spectrum indicates that, in fact, the boron from the BH_4^- ion and the two borons from the neutral B_2H_6 are equivalent in the intermediate. This equivalence could arise either from high symmetry or rapid tautomerism. A possible $B_3H_{10}^-$ species has been suggested[18] in which the borons are made equivalent by a tautomerism process involving only small changes in geometry (Scheme I). In addition to undergoing rapid tautomerism, any such intermediate must be quite short-lived, since a species with a lifetime greater than about 10^{-4} sec would be expected to give an observable resonance peak.

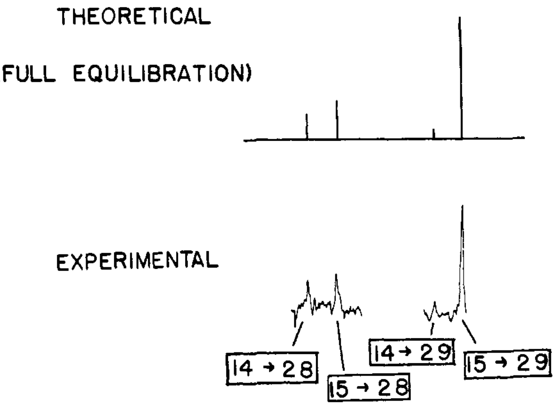
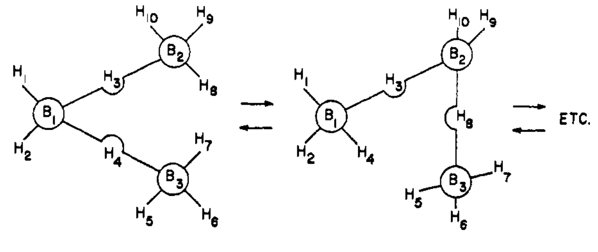


Figure 2. Double resonance for the reaction $BH_4^- + B_2H_6 \rightarrow B_2H_7^- + BH_3$, in which the $B_2H_7^-$ ion is observed while BH_4^- is irradiated. The theoretical spectrum is calculated assuming full equilibration of the three boron atoms.

Scheme I



Reactions with Other Molecules. The negative ion spectrum of a mixture of water and diborane was examined in the expectation that negative ions containing both boron and oxygen would be found. This was not the case, but, as shown in Figure 3, the spectrum indicates the presence of an ion at *m/e* 27, with isotopic satellites at 26 and 25 suggesting the $B_2H_5^-$ ion. Double

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(16) M. F. Hawthorne in ref 2, Chapter 5.

(17) Reference 1, Appendix A.

(18) W. N. Lipscomb, private communication.

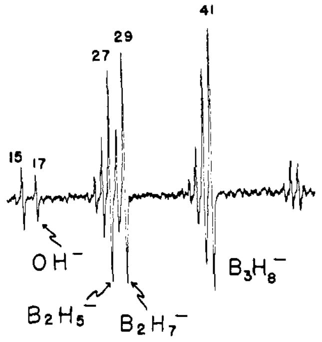

Figure 3. Negative ion single resonance spectrum at high pressure of a mixture of B_2H_6 and H_2O, showing the $B_2H_5^-$ ion, which is found to be formed *via* an excited BH_4^- ion by the sequence $OH^- \rightarrow BH_4^{-*} \rightarrow B_2H_5^-$.

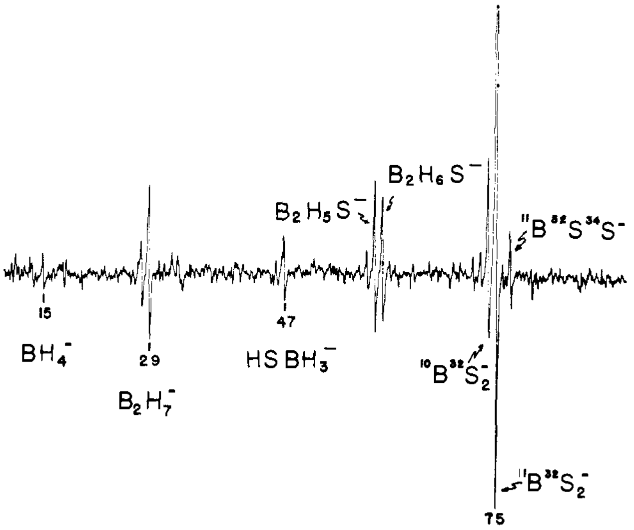

Figure 4. Negative ion single resonance spectrum of a mixure of B_2H_6 and H_2S, showing the predominance of the BS_2^- ion.

resonance shows that OH^- is *not* the parent of this ion, nor is $B_2H_7^-$ or $B_3H_8^-$, but that the reaction sequence is

$$OH^- + B_2H_6 \longrightarrow BH_4^- + \text{neutral products} \tag{2a}$$

$$BH_4^- + B_2H_6 \longrightarrow B_2H_5^- + BH_3 + H_2 \tag{2b}$$

$$ \longrightarrow B_2H_7^- + BH_3 \tag{2c}$$

Reaction 2a gives a double resonance peak barely resolved from noise, but reaction 2b yields a large peak. If, as seems reasonable to suppose, the sign of the double resonance peaks may be taken to have the same significance as in the positive ion cases previously studied,[12] then both of these reactions are exothermic. Since $B_2H_5^-$ has never been observed in pure diborane, it seems probable that the reaction $OH^- \rightarrow BH_4^-$ produces BH_4^- in an excited state, which makes accessible the reaction channel (2b) producing $B_2H_5^-$.

The energetics of reaction 2a make it clear why the BH_4^- may be produced in an excited state. The most stable neutral product is probably the $HOBH_2$ molecule. Using the experimentally determined values $\Delta H_f°(OH^-) = -39$ kcal,[19] $\Delta H_f°(B_2H_6) = 9$ kcal,[20] and $\Delta H_f°(HOBH_2) = -70$ kcal,[21] and the calculated value $\Delta H_f°(BH_4^-) = -23$ kcal,[22] the heat of reaction of reaction 2a may be estimated as $-\Delta H_f° = 63$ kcal. It may be easily supposed that some of this large heat of reaction is carried off as an internal excitation of the BH_4^- product.

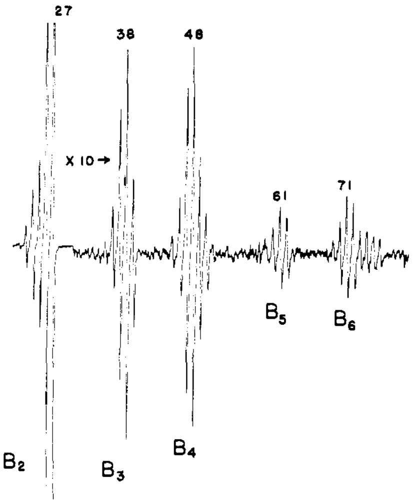

Figure 5. Positive ions. High-pressure single resonance spectrum of B_2H_6, with the pressure at about 3×10^{-5} torr and an ionizing voltage of 18 eV. Each group of peaks is composed of several different ionic species. These are corrected for the isotopic distribution in Table I.

A mixture of H_2S and diborane was also examined. At all pressures, the dominant peak is BS_2^-, as shown in Figure 4. This species is apparently formed near the filament by a pyrolysis mechanism, either reactively from the higher boron hydride negative ions or in competition with them, since these higher boron hydride peaks, which dominate the pure diborane spectra, are reduced to small intensities by addition of H_2S. In addition, three other sulfur-containing ions are obtained, $HSBH_3^-$, $B_2H_5SH^-$, and $B_2H_5S^-$.

BS_2^- and $HSBH_3^-$ are especially interesting, because they are isoelectronic with CS_2 and $HSCH_3$, respectively. The production of BS_2^- seems analogous to that of CS_2 from methane and H_2S under high-temperature conditions. This suggests that boron negative ion chemistry has a close relationship to neutral carbon chemistry; it is possible that ICR techniques can provide insights into the gas-phase reactions of simple carbon compounds, using B^- in the capacity of a *charge-labeled* carbon atom.

B. Positive Ions. Positive ion spectra are readily obtained at all pressures. The high-pressure spectra do not depend strongly on the ionizing electron energy and were taken at 17 or 18 eV. The higher mass products show a normal pressure dependence indicating that ion–molecule reactions are the mechanism of production, uncomplicated by any filament pyrolysis. Figure 5 shows a typical high-pressure positive ion spectrum of pure diborane. The correction of the observed spectra by subtracting out the contributions from the ^{10}B-containing ions is simple and straightforward, and Table I lists the ions observed at low and high pressures after applying this correction.

As is normal for positive ions, the spectra show a far greater variety of species than with the negative ions. All of these highly electron-deficient ions show a rel-

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[19] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Appendix.

[20] S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965), Appendix.

[21] R. F. Porter and S. K. Gupta, *J. Phys. Chem.*, 68, 2732 (1964).

[22] A. P. Altshuller, *J. Am. Chem. Soc.*, 77, 5455 (1955).

atively low hydrogen-to-boron ratio, lower than for the neutral hydrides. It is not surprising, in view of the unfamiliar binding patterns in these ions, that their compositions do not suggest any obvious structural patterns, and that in fact the existing topological theory[1] gives no hint as to the structures and geometries of the ions.

The B_1 species do not give significant peaks under any conditions, but there are substantial intensities for species containing from two to six boron atoms, and some very high-pressure spectra have indicated formation of hydride ions of still higher mass. It is interesting to compare the ICR spectra with conventional mass spectrometric data.[23] These spectra show the ions produced by electron impact on various boron hydrides, which lose varying numbers of hydrogens to form a series of ions ranging down in mass from the molecular ion. Table I includes a set of such data.

Table I. Relative Abundance of Positive Ions in Diborane[a]

	This work		
Species	Low pressure (70 eV)	High pressure (18 eV)	Mass spectroscopy[b,c]
B_2H^+	82	0	140
$B_2H_2^+$	1030	340	1460
$B_2H_3^+$	380	90	490
$B_2H_4^+$	870	850	1010
$B_2H_5^+$	1950[d]	1950	1950[d]
$B_3H_2^+$		4	
$B_3H_3^+$		5	
$B_3H_4^+$		11	
$B_3H_5^+$		117	
$B_3H_6^+$		59	
$B_4H_3^+$		5	25
$B_4H_4^+$		100[d]	100[d]
$B_4H_5^+$		48	21
$B_4H_6^+$		24	95
$B_4H_7^+$		8	9
$B_4H_8^+$		0	16
$B_5H_4^+$		3	4
$B_5H_5^+$		2	25
$B_5H_6^+$		6	2
$B_5H_7^+$		18	18[d]
$B_5H_8^+$		6	0
$B_5H_9^+$		0	20
$B_6H_4^+$		0	8
$B_6H_5^+$		0	1
$B_6H_6^+$		27	27[d]
$B_6H_7^+$		2	1
$B_6H_8^+$		8	12
$B_6H_9^+$		0	0
$B_6H_{10}^+$		11	10

[a] Corrected for presence of ions containing ^{10}B. [b] Reference 7. [c] Some small contributions at the low-mass end of each series have been omitted from this tabulation of the mass spectroscopy data. [d] Arbitrary normalization.

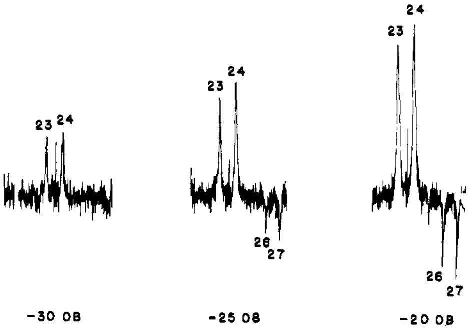


Figure 6. Typical double resonance spectrum for positive ions, observing *m/e* 47 and irradiating the B_2 species at the mass values indicated in the figure. Three different irradiating powers are shown in units of decibels down from an arbitrary level. Note that the endothermic peaks (negative peaks) become relatively more prominent at higher irradiating power. The narrow peak between *m/e* 23 and 24 is a commonly observed artifact arising because the irradiating frequency is a harmonic of the observing frequency, in this case the second harmonic.

The considerable similarity between the two types of spectra in the general pattern of ions produced is evident, but it can be seen that the mass spectrometric fragmentation products include a number of peaks which are not present, or present only at low intensity, in the ICR spectrum. This is not unexpected, because under the conditions of reactive ion formation in the cyclotron cell, higher ions may be produced only if they result by energetically allowed reaction channels from the available reactants.

As illustrated in the typical spectra of Figure 6, excellent double resonance spectra are obtained for all the B_3 through B_6 ions of reasonable intensity, except $B_6H_{10}^+$. (The $B_6H_{10}^+$ single resonance signal is not very strong, and it is not surprising that it gives no double resonance signals strong enough to observe.) The isotopic distribution of boron introduces considerable complications in the analysis of the double resonance spectra, owing to the occurrence at identical *m/e* values of ions of different chemical composition. However, as is detailed in Appendix B, the complex set of interrelated double resonance peaks may be analyzed exactly in the case where all of the boron atoms in the reactants are incorporated into the ionic product. This is found to be the case for all the reactions leading to the B_4, B_5, and B_6 series of ions. In the case of the reactions leading to the B_3 ions, which proceed with the elimination of a boron atom in a neutral product, no exact solution to the double resonance is possible, but Appendix B outlines an approximate method by which the data may be treated.

The double resonance signals for the B_4, B_5, and B_6 ions are strong and reproducible at an ionizing electron energy of 18 eV, with a sign of the double resonance indicating exothermic reactions in nearly all cases. The B_3 species, however, give anomalous results—no strong double resonance signals can be obtained with an ionizing beam energy of 18 eV; yet when the ionizing energy is raised to 20 eV, strong double resonance peaks are observed on irradiating the B_2 series, with a sign indicating endothermic reactions. This suggests that raising the ionizing energy from 18 to 20 eV may deposit sufficient internal energy in the B_2 reactant ions to change the mechanism of production of B_3 ions. This effect is reflected in the double resonance result.

The appearance of strong single resonance peaks for the B_3 series at 18 eV for which no precursors are revealed by double resonance is an unusual situation. The B_3 ions must be produced by some reaction, yet double resonance does not reveal any such reaction. These observations cast some doubt on a common tacit assumption in the interpretation of ICR results

(23) Reference 7, p 131.

Table II

Reaction	Reduced rel intensity[c]
A. Reactions where $dk/dT < 0$ (Exothermic)	
$B_2H_2^+ + B_2H_6 \rightarrow B_4H_4^+ + 2H_2$	10^d
$B_2H_3^+ + B_2H_6 \rightarrow B_4H_5^+ + 2H_2$	10
$B_2H_4^+ + B_2H_6 \rightarrow B_4H_6^+ + 2H_2$	2
$B_3H_5^+ + B_2H_6 \rightarrow B_5H_7^+ + 2H_2$	8
$B_4H_4^+ + B_2H_6 \rightarrow B_6H_6^+ + 2H_2$	10
$B_4H_6^+ + B_2H_6 \rightarrow B_6H_8^+ + 2H_2$	3
B. Reactions where $dk/dT > 0$ (Endothermic)	
$B_2H_5^+ + B_2H_6 \rightarrow B_4H_4^+ + 3.5H_2$	-0.5^a
$B_2H_5^+ + B_2H_6 \rightarrow B_4H_5^+ + 3H_2$	-0.5^a
$B_2H_5^+ + B_2H_6 \rightarrow B_4H_6^+ + 2.5H_2$	-0.2^a
C. $B_2 \rightarrow B_3$ ($dk/dT > 0$)	
$B_2H_5^+ + B_2H_6 \rightarrow B_3H_6^+ + BH_3 + H_2$	-2.5
$B_2H_5^+ + B_2H_6 \rightarrow B_3H_5^+ + BH_3 + 1.5H_2$	-4.5
$B_2H_5^+ + B_2H_6 \rightarrow B_3H_4^+ + BH_3 + 2H_2$	-6
$B_2H_4^+ + B_2H_6 \rightarrow B_3H_6^+ + BH_3 + H$	-3.5
$B_2H_4^+ + B_2H_6 \rightarrow B_3H_5^+ + BH_3 + H_2$	-6
$B_2H_4^+ + B_2H_6 \rightarrow B_3H_4^+ + BH_3 + 1.5H_2$	-6
$B_2H_4^+ + B_2H_6 \rightarrow B_3H_3^+ + BH_3 + 2H_2$	$+5^{b,e}$
$B_2H_3^+ + B_2H_6 \rightarrow B_3H_6^+ + BH_3$	-7.5
$B_2H_2^+ + B_2H_6 \rightarrow B_3H_5^+ + BH_3$	-10^d
$B_2H_2^+ + B_2H_6 \rightarrow B_3H_4^+ + BH_3 + H$	-5^b

[a] These values are consistent with those in part A, but comparison of exothermic and endothermic reactions has very doubtful validity. [b] The reduced relative intensities of these reactions are very uncertain due to the propagation of errors in the isotopic analysis. [c] Estimated uncertainty ±20%. [d] Arbitrary normalization. [e] $dK/dT < 0$.

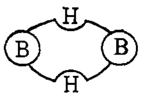
that any reaction which occurs with substantial rate may be observed by double resonance. Evidently such an assumption is not always warranted.

Table II lists all of the reactions which were observed by double resonance techniques. As shown in Appendix A, the double resonance intensity is proportional to the concentration of reactant ion. A measure of the values of dk/dT for the reaction in question may therefore be calculated by dividing the observed double resonance intensity by the reactant single resonance peak height. This number is termed the "reduced relative intensity" and is given for each reaction in Table II, along with an indication of whether the sign of the double resonance suggests an exothermic or an endothermic process. These numbers are consistent within each of the three groupings of the table, and, while in principle they should not be compared for different reactions possessing different values of dk/dT, they may still provide some indication of the relative rates of reactions of the same general type.

It seems significant that most of the exothermic reactions observed are of the form

$$(\text{ion})^+ + B_2H_6 \longrightarrow (\text{ion} + B_2H_2)^+ + 2H_2$$

This one general reaction appears to account for the formation of all of the B_4, B_5, and B_6 species (except that $B_6H_{10}^+$, which gives no observable double resonance, may be formed by some other process). This is suggestive of unusual stability for a fragment of structure



such that it is transferred intact in the course of the reaction.

There is no such striking feature common to the group of $B_2 \rightarrow B_3$ reactions. This is not surprising in view of their anomalous double resonance results. However, note that *every* reaction in this group may be written to give the highly favorable neutral product BH_3.

Conclusion

Primary, secondary, and higher order processes in the ion cyclotron produce a large variety of positive and negative ions from diborane. In contrast to direct electron bombardment processes, production of ions by an ion-molecule reaction process may be expected to produce only relatively stable ions. Therefore it is of interest to compare the observed ions with the predictions of the topological theory of Lipscomb and Dickerson.[1] Lipscomb predicts[24] stability of all of the observed negative ions except $B_2H_5^-$. In addition he predicts $B_4H_7^-$, which is not observed at all, and $B_6H_7^-$, which is not present as more than a small fraction of the $B_6H_9^-$ peak. The theory correctly predicts stability of $B_3H_6^+$, which is a major peak, but the predicted $B_6H_9^+$ and $B_6H_{11}^+$ ions give at best only minor peaks in the observed spectra. In fact, there is a surprising tendency toward greater abundance of odd-electron positive ions as opposed to the expected even-electron species. It appears therefore that the topological theory is useful in rationalizing the negative ion pattern but is not applicable to the positive ion case.

The exothermic reactions of the positive ions show a strikingly regular pattern, with the ionic product being larger than the reactant by a B_2H_2 unit. This regularity raises the hope that the chemistry of the positive boron hydride ions may be far simpler than would be suggested by the complicated single resonance spectra.

The observation of a large variety of negative ions including several containing sulfur indicates that boron-containing species may provide a far richer negative ion chemistry than other negative-ion systems previously investigated. Two ion-molecule reactions of BH_4^- have been verified in this study. It is hoped that boron-containing negative ions will be found to undergo a variety of other reactions analogous to the corresponding isoelectronic reactions of organic neutrals.

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Appendix A. Analysis of Double Resonance for a Single Reaction

Consider the single reaction

$$A^+ + N \longrightarrow B^+ + \text{neutrals} \qquad (A1)$$

where the reactant and product ion peaks are not confused by overlapping peaks from other species and are split into multiplets by a statistical distribution of iso-

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(24) W. N. Lipscomb, *J. Phys. Chem.*, **62**, 381 (1958).

topes. It is convenient to define the following quantities.

A_i^+ and B_j^+ are the isotopic species of the ions A^+ and B^+.

N_k's are isotopic species of the neutral reactant N.

$I(A_i^+)$ and $I(B_j^+)$ are the single resonance signals observed for ions A_i^+ and B_j^+. It is usual to assume that these signals are proportional to the total number of A_i^+ and B_j^+ ions present in the resonance region of the cell.

$\mathrm{DR}(i \rightarrow j)$ is the observed double resonance signal obtained by irradiating A_i^+ while observing B_j^+.

$[N_k]$ is the number density of neutral N_k.

$[A_i^+(0)]$ is the number density of A_i^+ ions at the electron beam, that is, the number density before depletion by any reaction.

K is the bimolecular rate constant for reaction A1.

$\pi(i, k \rightarrow j)$ is the probability that a reaction starting with reactants A_i^+ and N_k will yield the product B_j^+.

$P(i \rightarrow j)$ is the probability that a reaction starting with A_i^+ and a random neutral N will yield the product B_j^+.

$m(B_i^+)$ is the mass of ion B_i^+.

$T(A_i^+)$ is the average kinetic energy of the A_i^+ ions, which is assumed constant throughout the ICR cell.

It has been shown[12] that for reaction A1 in the absence of isotopic splitting

$$I(B^+) = \frac{C[A^+(0)]}{m(B^+)[N]K}\{[N]K(\tau' - \tau) - (e^{-[N]K\tau} - e^{-[N]K\tau'})\} \quad (A2)$$

where τ and τ' are respectively the times at which an ion enters and leaves the resonance region of the cell, and the constant C is an instrumental factor. If (A1) is written for reaction of specific isotopic species

$$A_i^+ + N_k \longrightarrow B_j^+ + \text{neutrals} \quad (A1')$$

then A2 may be written

$$I(B_j^+) = \sum_i\sum_k \frac{C[A_i^+(0)]}{m(B_j^+)[N_k]K\pi(i, k \rightarrow j)} \times \{[N_k]K\pi(i, k \rightarrow j)(\tau' - \tau) - (e^{-[N_k]K\pi(i,k\rightarrow j)\tau} - e^{-[N_k]K\pi(i,k\rightarrow j)\tau'})\} \quad (A2')$$

To facilitate the analysis assume that $\tau' \ll [N_k]K\pi(i, k \rightarrow j)$ (bearing in mind that $\tau < \tau'$). This implies that the experiment is performed under conditions for which the reaction does not seriously deplete the reactant B_j^+ over the length of the cell. This may always be achieved by working at low enough pressure.

Neglecting terms beyond second order, (A2′) then becomes

$$I(B_j^+) \cong \sum_i\sum_k \frac{C[A_i^+(0)]}{m(B_j^+)} \frac{[N_k]K\pi(i, k \rightarrow j)\Delta(\tau^2)}{2} \quad (A3)$$

where $\Delta(\tau^2) = \tau'^2 - \tau^2$. Since the double resonance experiment is concerned only with that part of $I(B_j^+)$ arising from the particular reactant A_i^+ which is irradiated, the summation over i may be conveniently dropped at this point. Then (A3) may be differentiated to give

$$\mathrm{d}I(B_j^+) = \sum_k \frac{C[N_k][A_i^+(0)]\Delta(\tau^2)}{2m(B_j^+)}[K\mathrm{d}\pi(i, k \rightarrow j) + \pi(i, k \rightarrow j)\mathrm{d}K] \quad (A4)$$

For practical calculations it is usually assumed that $m(B_j^+)$, $\Delta(\tau^2)$, and K are not significantly different for different isotopic species; these are expected to be good assumptions for isotopic species differing only a few per cent in mass. Moreover, it may be assumed that $\mathrm{d}\pi(i, k \rightarrow j)/\mathrm{d}T(A_i^+) = 0$, which implies that the detailed mechanism of the reaction is unaffected by heating of the reactant ion. Since the double resonance data of the reaction of diborane under consideration is fitted excellently without the use of a term in $\mathrm{d}\pi(i, k \rightarrow j)/\mathrm{d}T(A_i^+)$, this assumption is considered warranted in this case.

With these further assumptions, (A4) simplifies to

$$\mathrm{d}I(B_j^+) = C'\sum_k[N_k][A_i^+(0)]\pi(i, k \rightarrow j)\mathrm{d}K \quad (A5)$$

$$= C'[N][A_i^+(0)]P(i \rightarrow j)\mathrm{d}K \quad (A5')$$

where C' is now a constant characteristic of the reaction A1. The observed double resonance signal may be related to $\mathrm{d}I(B_j^+)$ to first order by

$$\mathrm{DR}(i \rightarrow j) \equiv \frac{\Delta I(B_j^+)}{\Delta T(A_i^+)} \cong \left.\frac{\mathrm{d}I(B_j^+)}{\mathrm{d}T(A_i^+)}\right|_{T(A_i^+) = kT}$$

so that

$$\mathrm{DR}(i \rightarrow j) \cong C'\sum_k[N_k][A_i^+(0)]\pi(i, k \rightarrow j) \times \mathrm{d}K/\mathrm{d}T(A_i^+) \quad (A6)$$

$$= C''[A_i^+(0)]P(i \rightarrow j)(\mathrm{d}K/\mathrm{d}T(A_i^+)) \quad (A6')$$

For the reaction $BH_4^- + B_2H_6 \rightarrow B_2H_7^- + BH_3$, the observed reactants are m/e 14 and 15, and the products are m/e 28 and 29 (27 being too low in intensity for good double resonance). Three possibilities may be considered: (1) the boron from BH_4^- is always retained in the ionic product; (2) this boron is always retained in the neutral product; (3) the three borons are completely scrambled in the reaction. The first two cases lead to readily identified patterns: in case 1, $P(14 \rightarrow 29) = \mathrm{DR}(14 \rightarrow 29) = 0$, while in case 2, $P(14 \rightarrow j) = P(15 \rightarrow j)$ so that (since $[14]/[15] \cong 1/4$) eq A6′ gives $\mathrm{DR}(14 \rightarrow j):\mathrm{DR}(15 \rightarrow j) \cong 1:4$. The experimental results clearly fit neither of these cases. Case 3 may be formalized by using the following probabilities, which result from randomization of the three borons (in the symbol $\pi(x, y \rightarrow z)$ the number x is the m/e value of the ionic reactant, z that of the ionic product, and y the molecular weight of the neutral reactant)

$$\pi(14, 26 \rightarrow 27) = \pi(15, 28 \rightarrow 29) = 1$$

$$\pi(14, 28 \rightarrow 28) = \pi(15, 26 \rightarrow 28) = \pi(14, 27 \rightarrow 28) = \pi(15, 27 \rightarrow 28) = 2/3$$

$$\pi(14, 28 \rightarrow 29) = \pi(15, 26 \rightarrow 27) = \pi(14, 27 \rightarrow 27) = \pi(15, 27 \rightarrow 29) = 1/3$$

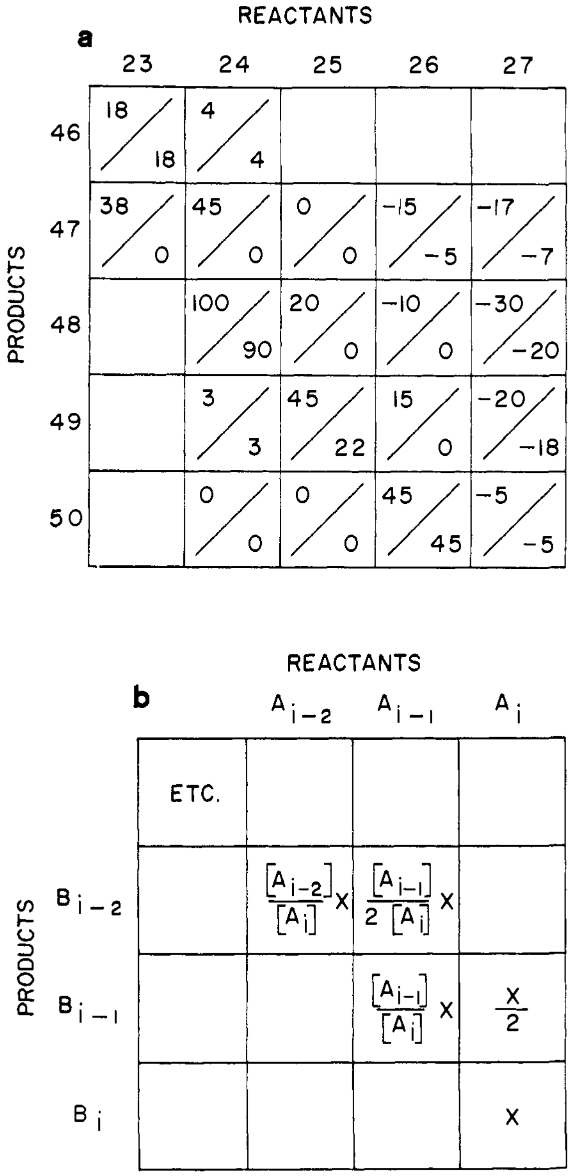
and the rest are zero. Using for the ratio of neutral diborane species [26]:[27]:[28] = 4:31:66 and for the ratio of BH_4^- species [14]:[15] = 19:81, eq A6 then yields for the double resonance signals

$\mathrm{DR}(14 \rightarrow 28) = 0.21$

$\mathrm{DR}(14 \rightarrow 29) = 0.07$

$\mathrm{DR}(15 \rightarrow 28) = 0.31$

$\mathrm{DR}(15 \rightarrow 29) = 1$ (arbitrary normalization)



PRODUCTS \ REACTANTS	23	24	25	26	27
46	18 / 18	4 / 4			
47	38 / 0	45 / 0	0 / 0	-15 / -5	-17 / -7
48		100 / 90	20 / 0	-10 / 0	-30 / -20
49		3 / 3	45 / 22	15 / 0	-20 / -18
50		0 / 0	0 / 0	45 / 45	-5 / -5

		A_{i-2}	A_{i-1}	A_i
	ETC.			
B_{i-2}		$\frac{[A_{i-2}]}{[A_i]}X$	$\frac{[A_{i-1}]}{2[A_i]}X$	
B_{i-1}			$\frac{[A_{i-1}]}{[A_i]}X$	$\frac{X}{2}$
B_i				X

Figure 7. (a) Illustrative grid for the reduction of overlapping double resonance data. The upper entry in each cell gives the signal obtained by observing a product peak (rows) while irradiating a reactant peak (columns). The lower entry is the value after the contribution from species containing ^{10}B atoms is subtracted. (b) Contribution to other cells of a reaction giving an observed signal X in the lower right-hand cell of the grid. The grid of (a) is reduced by successive subtraction of this pattern to calculate the corrected (lower) entries.

The excellent agreement of case 3 with the experimental results is clear in Figure 2.

Appendix B. Analysis of Double Resonance for Several Overlapping Reactions

The reactions producing the B_4, B_5, and B_6 positive ions all proceed without loss of boron in neutral products, making possible a complete analysis of the complicated double resonance pattern. The raw data are arranged in a grid, as illustrated in Figure 7 for a set of data on the $B_2 \rightarrow B_4$ reactions, and the data are reduced progressively. The entry at the lower right, which we may call X (see Figure 7b), plainly represents a single reaction R_1, since both reactant and product peaks consist of single species containing only ^{11}B. Now this same reaction contributes to the block directly above X by a reaction with a neutral $^{11}B^{10}BH_6$; since $[^{11}B^{10}BH_6]/[^{11}B^{11}BH_6] \cong 1/2$ this cell contains a contribution of about X/2 from R_1. Similar considerations show that the entry directly to the left of X has no contribution from R_1, but that the entry diagonal to X has a contribution$([A_{i-1}]/[A_i])$ X, where the [A]'s are reactant ion concentrations. In this manner the complete table of Figure 7b is constructed, and then all of these contributions are subtracted from the grid of Figure 7a; then the two blocks above and to the left of X will have been reduced to contributions from single reactions. This procedure is repeated progressively across the grid from lower right to upper left, and the real intensities for all the reactions are obtained successively. Finally the relative reduced intensity is found by dividing these intensities by the relative concentrations of the appropriate reactant ions, as is shown to be appropriate in Appendix A.

The reactions producing the B_3 positive ions are more difficult to analyze since one boron is eliminated in the neutral product. In principle there is not enough information for a ready solution of the grid; however, when calculations are made it is found that the double resonance pattern is relatively insensitive to whether the boron in the neutral product comes from the ionic or the neutral reactant, or both. Thus a qualitatively correct solution of the grid is feasible. The solution presented in Table II is based on equilibration of all the borons, but most of the relative reduced intensity values given would change by no more than 10 or 20% if the mechanism were different.