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Appearance and Ionization Potentials of Selected Fragments from Isotopically Labeled Pentaboranes^{1a}

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This paper presents appearance potentials of isotopically labeled pentaboranes, B¹¹₅H₉ and B¹¹₅D₉, and some of their fragment ions as determined by mass spectrometric electron impact measurements. A set of apparently self-consistent ionization potentials for the pentaboranes and various fragments was calculated from these appearance potentials using what little thermochemical bond energy data are available combined with the authors' interpretation of the processes taking place on ionization and fragmentation. $A(\text{B}_5\text{H}_9) > A(\text{B}_5\text{D}_9)$ is compared to $A(\text{B}_2\text{H}_6) < A(\text{B}_2\text{D}_6)$ and possible reasons for the reversal of ionization potential differences are discussed. Using an IBM 7090 computer program, monoisotopic fragmentation patterns for normal and deuteriated pentaboranes were calculated from the mass spectra of these compounds at 70 e.v.

This paper presents appearance potentials of isotopically labeled pentaboranes, B¹¹₅H₉ and B¹¹₅D₉, and some of their fragment ions as determined by mass spectrometric electron impact measurements. A set of apparently self-consistent ionization potentials for the pentaboranes and various fragments was calculated from these appearance potentials using what little thermochemical bond energy data are available combined with the authors' interpretation of the processes taking place on ionization and fragmentation.

The cracking pattern data were obtained by electron impact of B¹¹₅H₉ and B¹¹₅D₉, and subsequent measurement of the relative intensities of the molecule ions and fragment ions formed. A program for calculating monoisotopic fragmentation patterns from mass spectral raw data was written for an IBM 7090. Using this program the monoisotopic fragmentation patterns for B₅H₉ and B₅D₉ were calculated.

Experimental

The instrument used to measure the appearance potentials of the pentaboranes and their fragment ions has been previously described.^{1b}

As an internal standard for B¹¹₅H₉, krypton was used. Since it would have been extremely tedious to match the signals at 70 e.v. from the krypton calibrating gas and the numerous fragment ions from B¹¹₅H₉ exactly, a method was devised to approximate matching Kr values. Data were obtained for various isotopic krypton ions of m/e 80, 82, 83, 84, and 86, at a number of different pressures. In each series of runs, the krypton values were plotted against the ionizing voltage and the average ion current at each voltage was determined for the five krypton ions in terms of per cent of value at 70 e.v. From these percentages, values for krypton matching the various ions were estimated. For B₅D₉ fragments, xenon was used as the internal standard. (Fig. 1.)

The resulting estimated krypton curves were then plotted with the curves of the respective ions from pentaborane on a semilog

plot of ion current *versus* apparent ionizing voltage. Using known spectroscopic values for the internal standard, a correction was determined and applied to the unknown, giving its appearance potential. The accuracy of this method was verified by measuring the appearance potential of C₂H₆⁺ from C₂H₆ which checked to within 0.4 e.v., higher than the spectroscopic value (the appearance potentials of ions are usually 0.2–0.3 e.v. higher than spectroscopic ionization potentials). The appearance potential of C₂H₆⁺ was also measured relative to xenon which was used as the internal standard for the B₅D₉ measurements. The extrapolated appearance potentials for C₂H₆⁺ relative to either krypton or xenon checked each other to within experimental error.

TABLE I
B¹¹₅H₉ APPEARANCE POTENTIAL DATA

Ion if B ¹¹ _x H _n ⁺	m/e	Method 1 A_1 (e.v.)	Method 2 A_1 (e.v.)	70 e.v. value, %
B ¹¹ ₅ H ₉	64	10.3 ₈ ± 0.05	10.3 ₉	(1)
B ¹¹ ₅ H ₈ (B ¹¹ ₄ B ¹⁰ H ₉)	63	10.5 ₀ ± .1	10.5 ₄	(1)
B ¹¹ ₅ H ₇	62	11.4 ₃ ± 0.1	11.4 ₄	(1)
B ¹¹ ₄ H ₆	61	12.1 ₃ ± .3	12.4 ₈	(1)
B ¹¹ ₃ H ₅	60	12.6 ₇ ± .03	12.6 ₉	(1)
B ¹¹ ₃ H ₄	59	13.0 ₁ ± .3	13.2 ₀	(1)
B ¹¹ ₄ H ₆	50	12.2 ₅ ± 0.2	12.2 ₀	(10)
B ¹¹ ₄ H ₅	49	15.0 ₇ ± .3	14.5 ₀	(1)
B ¹¹ ₄ H ₄	48	14.0 ₆ ± .1	14.0 ₆	(1)
B ¹¹ ₄ H ₃	47	15.9 ₃ ± .5	15.5 ₂	(1)
B ¹¹ ₄ H ₂	46	17.9 ₉ ± .2	17.5 ₉	(1)
B ¹¹ ₄ H	45	19.9 ₇ ± 1.0	19.9 ₅	(1)

B¹¹₅D₉ APPEARANCE POTENTIAL DATA

B ¹¹ ₅ D ₉	73	9.7 ₇ ± 0.1	9.7 ₉	(10)
B ¹¹ ₅ D ₈ H (B ¹¹ ₄ B ¹⁰ D ₉)	72	9.3 ₈ ± .15	9.3 ₈	(10)
B ¹¹ ₅ D ₇	69	10.9 ₃ ± .2	11.1 ₄	(10)
B ¹¹ ₅ D ₆	65	12.9 ₂ ± .03	12.9 ₃	(10)

This method was then used to obtain the appearance potentials of some ions from pentaborane including: m/e 64, B¹¹₅H₉ (Fig. 2); m/e 62, B¹¹₅H₇ (Fig. 3); and m/e 65, B¹¹₅D₉ (Fig. 4). In each of these cases the log of the ion current was plotted against the uncorrected ionizing voltage.

When the curves for the internal standard gas and the ion of interest are not parallel, the first method cannot be used with any degree of accuracy. Another method used to find appear-

(1) (a) Presented in part before the Division of Inorganic Chemistry at the 140th National American Chemical Society Meeting, September, 1961. This research was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and in part by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government. (b) J. J. Kaufman, W. S. Koski, L. J. Kuhns and R. W. Law, *J. Am. Chem. Soc.*, **84**, 4198 (1962); presented at the 138th National American Chemical Society Meeting, New York, N. Y., September, 1960; also ONR Technical Report 2, March 19, 1962, Contract Nonr 3471(00).

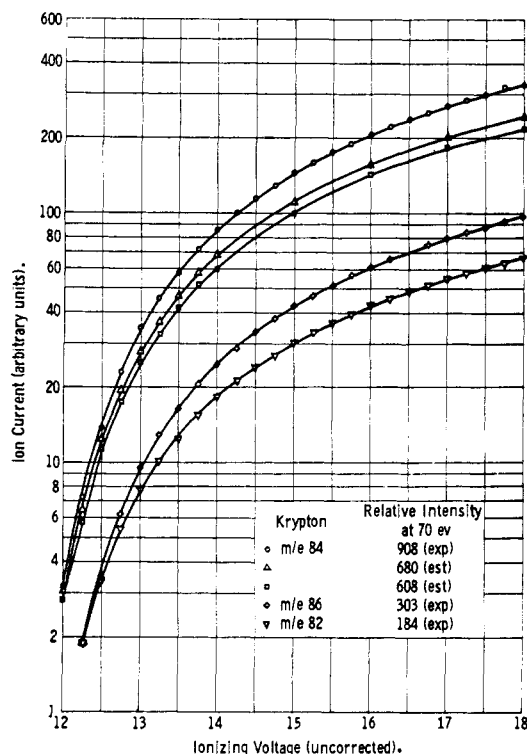


Fig. 1.—Calibration curve, krypton. Relative intensity versus ionizing voltage (experimental and estimated).

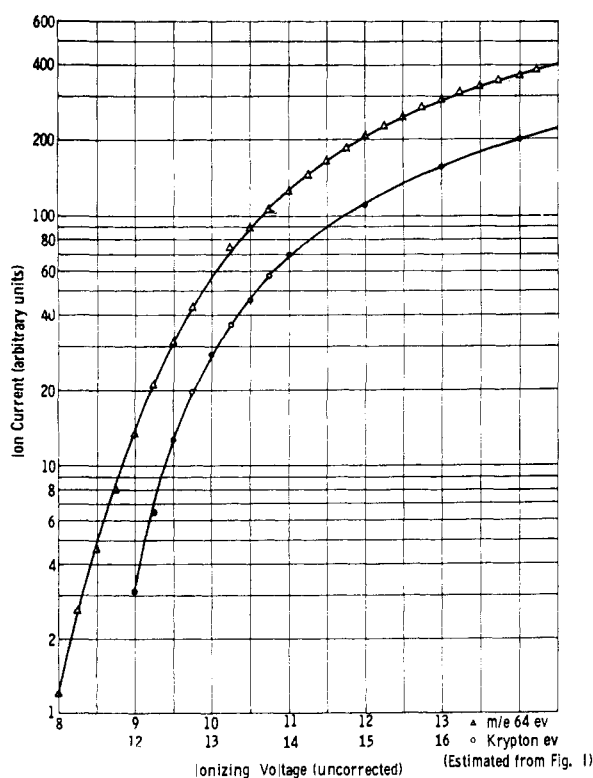


Fig. 2.—Ion efficiency curve m/e 64 ($B^{11}_5H_9$) and krypton.

ance potentials is to call the appearance potential of both the ion of interest and the calibrating gas the voltage at which the observed ion current is equal to some percentage of the ion current at 70 e.v. (usually about 1%).

This second method is just as valid as the first method for the ideal cases where both curves are parallel. It can be seen in Table I that the values of appearance potential obtained by the two methods for m/e 64 and m/e 62 are identical.

This second method has the advantage that it can be used for ions where the curves are not parallel. The accuracy is not as good in these cases but at least the method serves to give some indication of the appearance potential of the ion in question.

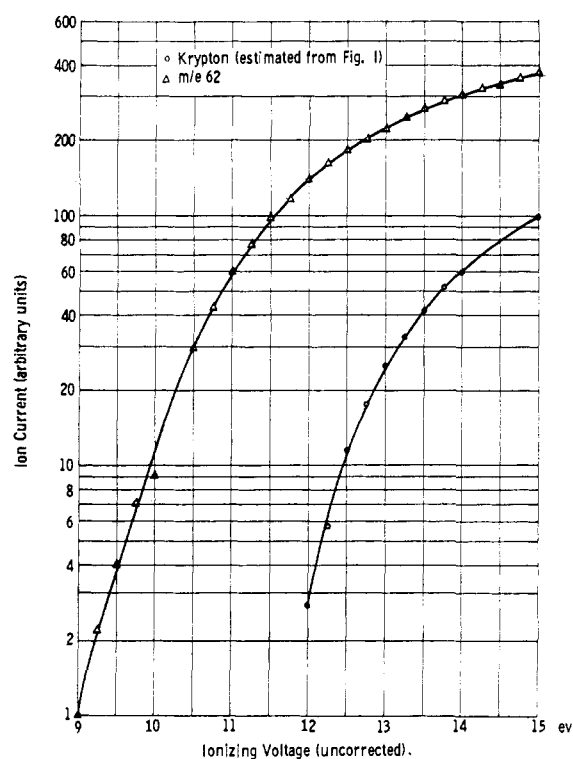


Fig. 3.—Ion efficiency curve m/e 62 ($B^{11}_5H_7$) and krypton.

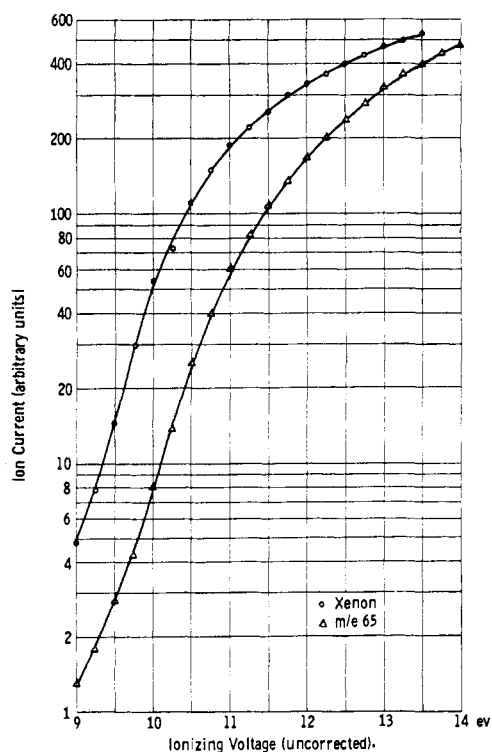


Fig. 4.—Ion efficiency curve m/e 65 ($B^{11}_5D_5$) and xenon

The differences between the appearance potential values are a bit more reliable for these ions than the absolute values may be. It is felt the limits of accuracy which have been assigned are realistic and cover the range of absolute value determination.

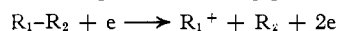
The pentaboranes were prepared by pyrolysis of diborane at 180° as previously published.² The methods of purification and criteria of purity are also described in the publication cited.

Calculations and Results

The method of obtaining ionization potentials and bond dissociation energies by ionization and dissociation

(2) W. S. Koski, P. C. Maybury and J. J. Kaufman, *Anal. Chem.*, **26**, 1992 (1954).

of molecules by electron impact has been used with considerable success in a number of types of compounds. If one represents the process taking place as



then by the equation

$$A(R_1^+) = I(R_1) + D(R_1-R_2)$$

either the ionization potential of R_1 or the dissociation energy of R_1-R_2 may be calculated directly from the measured $A(R_1^+)$, provided that one knows the value for the other unknown in the equation. A necessary (but not always sufficient) condition for the above equation to hold true is $I(R_1) < I(R_2)$.³ In order to interpret the appearance potentials of fragment ions correctly, it is necessary to know what neutral (or perhaps even charged) fragments are simultaneously formed and the states of excitation of the fragments and the molecule ion. However, it has been shown that in a number of cases the simplest set of assumptions suffices for the interpretation of the data.

Calculations of ionization potentials for the molecules and fragments of boron compounds have been previously carried out by the authors for B_2H_6 and various BY_3 compounds (where Y can be H, halogen, alkyl, or alkoxy substituents),^{4,5} as well as for $B_{10}H_{14}$.^{1b} The calculations on these boron compounds were performed following the same line of reasoning that was used in the early papers on appearance potentials of the hydrocarbons, before the ionization potentials of many of the fragments had been independently measured. The validity of this approach was demonstrated by the self-consistent set of ionization potentials calculated for the B compounds from which it became possible to derive a theory of the effect of substitution on ionization potentials in general.⁶ These values have been named the δ_K values and are valid for boron compounds, carbon compounds, and nitrogen compounds.

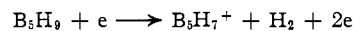
$B_5H_9^+$.—The appearance potentials of the parent ions may be associated with their vertical ionization potentials ("vertical" is taken to mean the transition favored by the Franck-Condon principle),⁷ therefore $I(B_5H_9) = 10.3_8$ e.v.

$B_5H_8^+$.— m/e 63 could correspond to either $B^{11}_5H_8$ or $B^{11}_4B^{10}H_8$. The ratio at 70 e.v. of m/e 63 to m/e 64 of 0.0667 would imply that if the initial B^{10} content of the B_5H_9 were 1.32% B^{10} , no $B^{11}_5H_8^+$ ions were present. From the B^{10}/B^{11} ratio measured at m/e 10 and m/e 11, there would appear to be only 1.17% B^{10} . However, it is known that the ratio estimated from the m/e 10 to m/e 11 values seems to give a slightly higher B^{10} ratio than that in the original parent molecule. Since the measured appearance potentials of m/e 64 and m/e 63 are close, it is possible that the appearance potential for m/e 63 is that of $B^{11}_4B^{10}H_9^+$. If the appearance potential really corresponded to $B^{11}_5H_8^+$, the calculated ionization potential of B_5H_8 would be 6.4₅ e.v., since a terminal hydrogen would be the one most likely to come off in this process.

$B_5H_7^+$.—In pentaborane as in diborane there are two completely different types of boron-hydrogen bonds. There are hydrogen atoms bonded to boron by normal covalent B-H bonds and there are the so-called bridge hydrogens which are bonded between two boron atoms with only two electrons total to be distributed between the two bonds. The assumption is made that the different B-H bond energies are constant for the boron

hydride series.⁸ Either terminal or bridge hydrogens could dissociate to form B_5H_7 ; however, since it takes less energy to break a terminal bond, 4.04 e.v., as compared to the energy necessary to withdraw a bridge H, 4.66 e.v., it is believed two terminal hydrogens come off in this step. The two hydrogens can exist as 2H or can form H_2 , but the $I(H)$ or the $I(H_2)$ are both higher than the calculated $I(B_5H_7)$ values, and so the relationship $I(R_1) < I(R_2)$ is satisfied.

It is presumed that the process taking place in this step is



Therefore

$$(a) \quad I(B_5H_7) = A(B_5H_7^+) - 2D(B-H) + D(H_2) \\ = 11.4_3 - 8.08 + 4.44 = 7.7_9 \text{ e.v.}$$

In addition to removal of two hydrogens, the formation of a B-B bond should logically be considered a part of the basic ionization and decomposition process. There is a question as to whether a 2-center B-B bond or a 3-center B-B-B bond will be formed. The corresponding energies would be

2-center

$$(b) \quad I(B_5H_7) = A(B_5H_7^+) - 2D(B-H) + D(H_2) + \\ D(B-B) \\ = 11.4_3 - 8.03 + 4.44 + 3.58 = 11.3_1 \text{ e.v.}$$

3-center

$$(c) \quad I(B_5H_7) = A(B_5H_7^+) - 2D(B-H) + D(H_2) + \\ D(B-B-B) \\ = 11.4_3 - 8.08 + 4.44 + 4.24 = 12.0_3 \text{ e.v.}$$

A 2-center B-B bond might be favored because it is felt that the electron deficiency of the skeleton is decreasing as H atoms are removed.

Besides this "basic process," it is important to consider the possibility of additional bond rupture, rearrangement, and bond formation. Since pentaborane itself contains five 3-center bonds, owing to its "electron deficiency," it is quite likely that some of these 3-center bonds will further rearrange to form normal covalent bonds once some of the electron deficiency is relieved. The following rearrangements may take place: (in each case the "basic process" is taken to be the one forming a 2-center B-B bond).

Rearranging one hydrogen bridge bond to form one normal B-H bond

$$(d) \quad I(B_5H_7) = \text{"basic process" energy} - D(B-H-B) + \\ D(B-H) \\ = 11.3_1 - 4.66 + 4.04 = 10.6_9 \text{ e.v.}$$

Rearranging one B-B-B 3-center bond to form one B-B normal bond

$$(e) \quad I(B_5H_7) = \text{"basic process" energy} - D(B-B-B) + \\ D(B-B) \\ = 11.3_1 - 4.24 + 3.58 = 10.6_3 \text{ e.v.}$$

Rearranging two B-H-B bridge bonds to form two B-H terminal bonds

$$(f) \quad I(B_5H_7) = \text{"basic process" energy} - 2D(B-H-B) + 2D(B-H) \\ = 11.3_1 - 9.32 + 8.08 = 10.0_7 \text{ e.v.}$$

Finally, rearranging one B-H-B bond and one B-B-B bond to form B-H and B-B

$$(g) \quad I(B_5H_7) = \text{"basic process" energy} - D(B-H-B) - \\ D(B-B-B) + D(B-H) + D(B-B) = \\ 11.3_1 - 4.66 - 4.24 + 4.04 + 3.58 \\ = 10.0_3 \text{ e.v.}$$

The best choice of these ionization potential values is felt to be 10.0₃ - 10.0₇ e.v. The values 10.6₃ - 12.0₃ e.v. are believed to be too high in that the ionization potential of B_5H_9 itself is only 10.3₈ e.v., and the ionization potentials of its lower fragments should be lower.

(8) E. J. Prosen, National Bureau of Standards, private communication.

(3) D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

(4) W. S. Koski, J. J. Kaufman, C. F. Pachucki and F. J. Shipko, *J. Am. Chem. Soc.*, **80**, 3202 (1958).

(5) W. S. Koski, J. J. Kaufman and C. F. Pachucki, *ibid.*, **81**, 1326 (1959).

(6) J. J. Kaufman and W. S. Koski, *ibid.*, **82**, 3262 (1960).

(7) D. P. Stevenson and J. A. Hipple, Jr., *ibid.*, **64**, 1585 (1942).

The ionization potential of a fragment lower than B_5H_9 itself should have a lower ionization potential because the electron removed from B_5H_9 upon ionization is almost certainly one from a boron skeletal orbital. To remove an electron from a terminal B—H bond would require about 11–12 e.v.⁹ and to remove an electron from a B—H—B bridge bond would require even more energy. The electron deficiency of the boron skeletal orbitals will be decreased in B_5H_7 because there are two more electrons donated to the skeleton.

This multiple of choices for possible rearrangements indicates some of the difficulties inherent in the calculations of ionization potentials from appearance potential measurements on boron hydrides.

The energy balances outlined in the text are formalized ones. No energy differentiation can be made between the process which would break off two terminal hydrogens and then rearrange two bridge hydrogens to form two terminal hydrogens and the process in which two bridge hydrogens come off directly. Clarification on this point could be obtained from dissociation of molecules in which the different positions are isotopically distinguished. A publication¹⁰ on dissociation from bridge deuterium-labeled decaborane states that "a preliminary examination of the mass spectrum for the bridge deuterated sample indicates that a high proportion of hydrogen pairs fragmented consist of one terminal proton and one bridge deuterium." However, there are no detailed calculations given and the mass spectra were run at 70 e.v., which is quite different from that at which appearance potentials are measured. Even if one terminal and one bridge proton come off of B_5H_9 in the original process to form $B_5H_7^+$, the energy difference is only 0.5 e.v. and to know the ionization potentials of fragments from boron hydrides correctly to within 0.5 e.v. is definitely worthwhile.

The two most probable processes are both so close in energy that either of these calculated values may be used for $I(B_5H_7)$.

In discussing the ionization potential of B_5H_7 , it is also of interest to compare the proposed resultant structures for B_5H_7 with those given by Lipscomb's topology for boron hydrides.¹¹ In his topological theory, values of s , t , y , and x are given for possible boron hydride structures, where s equals the number of hydrogen bridges (B—H—B), t equals the number of 3-center boron-boron bonds (B—B—B), y equals the number of boron-boron single bonds (B—B), and x equals the number of extra H atoms on B—H (*i.e.*, BH_2 groups), which are present in the molecule.

For B_5H_7 , Lipscomb gives two possible s , t , y , x combinations, namely, 2310 and 1401. Since, according to his terminology, the original structure in B_5H_9 corresponded to 4120, it is interesting to see what processes would have to take place upon ionization to give final s , t , y , x combinations of: (i) 2310, or (ii) 1401.

For case (i) (2310), two bridge hydrogen bonds and one single B—B bond would have to be broken, and two additional 3-center (B—B—B) bonds would have to be formed. The resulting ionization potential equation would be

$$\begin{aligned} \text{(i)} \quad I(B_5H_7) &= A(B_5H_7^+) - 2D(B-H-B) + \\ &\quad 2D(B-B-B) - D(B-B) + D(H_2) \\ &= 11.4_3 - 9.32 + 8.48 - 3.58 + 4.48 \\ &= 11.4_9 \text{ e.v.} \end{aligned}$$

(9) W. S. Koski, J. J. Kaufman, L. Friedman and A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).

(10) I. Shapiro, M. Lusty and R. E. Williams, *J. Am. Chem. Soc.*, **81**, 838 (1959).

(11) W. N. Lipscomb in "Advances in Organic Chemistry and Radiochemistry, Vol. I, Edited by H. J. Emeléus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1959, p. 129.

Similarly, for (ii) (1401), three bridge hydrogen bonds and two B—B single bonds would be broken, and three (B—B—B) 3-center bonds and one BH_2 group would have to be formed. Thus

$$\begin{aligned} \text{(ii)} \quad I(B_5H_7) &= A(B_5H_7^+) - 3D(B-H-B) + \\ &\quad 3D(B-B-B) - 2D(B-B) + \\ &\quad D(B-H) + D(H_2) \\ &= 11.4_3 - 13.98 + 12.72 - 7.16 + 4.04 + \\ &\quad 4.48 \\ &= 11.5_3 \text{ e.v.} \end{aligned}$$

As before, the processes outlined as necessary to give the resulting structures are formal, since energywise there is no way to distinguish intermediate rearrangements which may actually take place.

It is evident that the ionization potentials calculated for B_5H_7 corresponding to processes (i) and (ii) (11.4₉ — 11.5₃ e.v.) are higher than that measured for B_5H_9 itself (10.3₈ e.v.), and for the reasons stated previously, are therefore believed to be too high.

Similar ionization potential calculations can be carried out for the other B_xH_n fragments whose appearance potentials were measured in this study and a self-consistent set of ionization potentials can be derived.

The values of the calculated ionization potentials of the species B_xH_n down to B_4H_6 are given in Table II. For fragments below B_4H_6 , ionization potentials have been calculated for every possible reaction path leading to the respective ions. However, it is felt that until more conclusive evidence is available, it is impossible to determine which of the calculated ionization potentials is most likely to correspond to the true ionization process.

$B_4H_6^+$.—The B_4H_6 fragment formed from pentaborane is of interest because it is a hypothetical boron hydride "molecule" and can actually exist in the form of a stable Lewis base adduct, $B_4H_6 \cdot Z$ (where Z is an electron donor). The ionization potential of the B_4H_6 fragment would be a useful piece of knowledge in light of the relation of ionization potentials to the theory of charge transfer complexes. The ionization potential of B_4H_6 could be calculated from the measured appearance potential of $B_4H_6^+$ if one were able to postulate the correct mechanism for the formation and final structure of the B_4H_6 .

The process taking place upon electron impact of B_5H_9 to form $B_4H_6^+$ is presumed to be



In removing BH_3 from the pentaborane molecule, either a 2-center B—B bond or a 3-center (B—B—B) bond must be ruptured, in addition to the rupture of two adjacent bridge hydrogen bonds. As mentioned above, subsequent formation of a boron-boron bond is also considered a part of the basic ionization and decomposition process. Here again, the boron-boron bond formed may be either a 2-center or a 3-center bond.

If a 3-center (B—B—B) bond and two bridge (B—H—B) bonds are ruptured, and subsequently one 2-center B—B bond and two B—H bonds (in BH_3) are formed, the energy involved would be

$$\begin{aligned} \text{(a)} \quad I(B_4H_6) &= A(B_4H_6^+) - D(B-B-B) - 2D(B-H-B) + \\ &\quad D(B-B) + 2D(B-H) \\ &= 12.2_5 - 4.24 - 9.32 + 3.58 + 8.08 \\ &= 10.3_5 \text{ e.v.} \end{aligned}$$

If, however, a 3-center (B—B—B) bond is subsequently formed rather than a 2-center bond, the corresponding energy would be

$$\begin{aligned} \text{(b)} \quad I(B_4H_6) &= A(B_4H_6^+) - D(B-B-B) - 2D(B-H-B) \\ &\quad + D(B-B-B) + 2D(B-H) \\ &= 12.2_5 - 4.24 - 9.32 + 4.24 + 8.08 \\ &= 11.0_1 \text{ e.v.} \end{aligned}$$

TABLE II

Species	Process	Proposed structure				<i>I</i> (e.v.)	
		<i>s</i>	<i>t</i>	<i>y</i>	<i>z</i>		
B ₅ H ₉ ⁺	B ₅ H ₉ + e → B ₅ H ₉ ⁺ + 2e	4	1	2	0	10.3 ₈	
B ₅ H ₉ ⁺	B ₅ H ₉ + e → B ₅ H ₈ ⁺ + H + 2e	4	1	2	0	6.4 ₈	
B ₅ H ₇ ⁺	B ₅ H ₉ + e → B ₅ H ₇ ⁺ + H ₂ + 2e	(a)	2	1	3	0	10.1 ₁
		(b)	3	0	4	0	10.0 ₇
B ₅ H ₆ ⁺	B ₅ H ₉ + e → B ₅ H ₆ ⁺ + H ₂ + H + 2e	(a)	2	1	3	0	6.8 ₈
		(b)	3	0	4	0	6.7 ₉
B ₅ H ₅ ⁺	B ₅ H ₉ + e → B ₅ H ₅ ⁺ + 2H ₂ + 2e	(a)	0	1	4	0	10.1 ₅
		(b)	1	0	5	0	10.1 ₁
B ₅ H ₄ ⁺	B ₅ H ₉ + e → B ₅ H ₄ ⁺ + 2H ₂ + H + 2e	(a)	0	1	4	0	6.4 ₅
		(b)	1	0	5	0	6.4 ₁
B ₄ H ₆ ⁺	B ₅ H ₉ + e → B ₄ H ₆ ⁺ + BH ₃ + 2e		2	0	3	0	10.3 ₅
B ₅ D ₉ ⁺	B ₅ D ₉ + e → B ₅ D ₉ ⁺ + 2e		4	1	2	0	9.7 ₇
B ₅ D ₇ ⁺	B ₅ D ₉ + e → B ₅ D ₇ ⁺ + D ₂ + 2e	(a)	2	1	3	0	9.5 ₃
		(b)	3	0	4	0	9.5 ₆
B ₅ D ₅ ⁺	B ₅ D ₉ + e → B ₅ D ₅ ⁺ + 2D ₂ + 2e	(a)	0	1	4	0	10.1 ₂
		(b)	1	0	5	0	10.1 ₇

On the other hand, if a 2-center B—B bond and two B—H—B bonds are initially broken and either a 3-center B—B—B bond or a 2-center B—B bond is subsequently formed, the respective corresponding energies would be

$$\begin{aligned}
 \text{(c)} \quad I(\text{B}_4\text{H}_6) &= A(\text{B}_4\text{H}_6^+) - D(\text{B—B}) - 2D(\text{B—H—B}) + \\
 &\quad D(\text{B—B—B}) + 2D(\text{B—H}) \\
 &= 12.2_5 - 3.58 - 9.32 + 4.24 + 8.08 \\
 &= 11.6_7 \text{ e.v.}
 \end{aligned}$$

and

$$\begin{aligned}
 \text{(d)} \quad I(\text{B}_4\text{H}_6) &= A(\text{B}_4\text{H}_6^+) - D(\text{B—B}) - 2D(\text{B—H—B}) + \\
 &\quad D(\text{B—B}) + 2D(\text{B—H}) \\
 &= 12.2_5 - 3.58 - 9.32 + 3.58 + 8.08 \\
 &= 11.0_1 \text{ e.v.}
 \end{aligned}$$

Consideration of these four processes and their corresponding ionization potentials indicates that process (a), which requires the least total amount of energy, results in the most probable value for $I(\text{B}_4\text{H}_6)$, 10.3₅ e.v.

Lipscomb's topology gives *s*, *t*, *y*, *x* values of 2210 and 1301 for possible B₄H₆ structures. In order to arrive at these structures, the ionization processes and their resultant energies would formally be

$$\begin{aligned}
 \text{(i)} \quad 2210 \\
 I(\text{B}_4\text{H}_6) &= A(\text{B}_4\text{H}_6^+) - 2D(\text{B—H—B}) + D(\text{B—B—B}) - \\
 &\quad D(\text{B—B}) + 2D(\text{B—H}) \text{ (in BH}_3\text{)} \\
 &= 12.2_5 - 9.32 + 4.24 - 3.58 + 8.08 \\
 &= 11.6_7 \text{ e.v.}
 \end{aligned}$$

$$\begin{aligned}
 \text{(ii)} \quad 1301 \\
 I(\text{B}_4\text{H}_6) &= A(\text{B}_4\text{H}_6^+) - 3D(\text{B—H—B}) + 2D(\text{B—B—B}) - \\
 &\quad 2D(\text{B—B}) + 2D(\text{B—H}) \text{ (in BH}_3\text{)} \\
 &= 12.2_5 - 13.98 + 8.48 - 7.16 + 4.04 + 8.08 \\
 &= 11.7_1 \text{ e.v.}
 \end{aligned}$$

Just as in the case of B₅H₇, the resulting ionization potential values 11.6₇ – 11.7₁ e.v. appear to be too high to be compatible with the ionization potential of 10.3₈ e.v. for B₅H₉ itself.

B₅D₉. B₅D₉⁺.—The value $A(\text{B}_5\text{D}_9^+) = 9.7_7$ e.v. compared to the value $A(\text{B}_5\text{H}_9^+) = 10.3_8$ e.v. would imply that $I(\text{B}_5\text{H}_9) > I(\text{B}_5\text{D}_9)$ by 0.6₁ e.v. The internal standards for these two were different; xenon was used for B₅D₉ and krypton for B₅H₉. However, the measured difference for $A(\text{B}_5\text{H}_9)$ and $A(\text{B}_5\text{D}_9)$ is believed to be a real one and not to be accounted for by experimental errors.

This leads to some interesting speculation about the behavior of B—D compounds compared to B—H compounds in general. The appearance potentials and

ionization potentials of similar ions from B₂D₆ and B₂H₆ have been measured previously.⁴ $I(\text{B}_2\text{D}_6)$ was only ~0.1 e.v. higher than that of B₂H₆ and this was reasonable in view of the difference of 0.12 to 0.18 e.v. found between $I(\text{CD}_4)$ and $I(\text{CH}_4)$. Implicit in the comparison is the assumption that the electron ionized from diborane probably comes from a terminal B—H or B—D bond since it would take more energy to withdraw an electron from a bridge bond.

For pentaborane it is presumed that an electron is ionized from the boron skeleton rather than from either a terminal or bridge boron-hydrogen bond since the energy to remove a skeletal electron should be lower than that to remove either of the other types of electrons. This point is now being checked by a molecular orbital calculation which simultaneously considers the energy levels of all of the orbitals of pentaborane—B—H terminal, B—H—B bridge and skeletal boron orbitals.

A lower $I(\text{B}_5\text{D}_9)$ than $I(\text{B}_5\text{H}_9)$ might imply a difference in boron skeletal energy as a function of whether hydrogen or deuterium is present in the molecule, especially in bridge positions. This is not unlikely because there have been other indications that a compound with deuterium in the bridges does not necessarily behave like one with hydrogen bridges. Since negative charge is believed transferred from B atoms to a bridge hydrogen,¹¹ it is quite conceivable that a different amount of charge could be transferred to a bridge deuterium which would change the electron density of the boron skeleton. In this context it is of interest to note from the data in Table II on calculated ionization potentials of B₅D_{*n*} and B₅H_{*n*} compounds that while $I(\text{B}_5\text{D}_9) < I(\text{B}_5\text{H}_9)$ and $I(\text{B}_5\text{D}_7) < I(\text{B}_5\text{H}_7)$ each by about 0.6 e.v., the $I(\text{B}_5\text{D}_5) \cong I(\text{B}_5\text{H}_5)$. According to the processes chosen in this article as the ones corresponding to the measured appearance potentials of B₅D₅⁺ and B₅H₅⁺, the structures of the resultant B₅D₅ and B₅H₅ contain *no* bridge deuterium or bridge hydrogen bonds. The change in boron skeletal energy between regular or deuterated pentaborane (or their fragments) is believed to be dependent on whether hydrogen or deuterium are in the bridge positions. The equality of the values for $I(\text{B}_5\text{D}_5)$ and $I(\text{B}_5\text{H}_5)$, in which there were postulated to be *no* (B—D—B) or (B—H—B) bonds, seems to indicate some confirmation for this assumption.

Table II shows the calculated ionization potentials for B₅H_{*x*} and B₅D_{*x*} fragments, the ionization processes presumed to take place, and the *s*, *t*, *y*, *x* designations corresponding to the final structures proposed for the fragments ionized.

Fragmentation Pattern.—The monoisotopic fragmentation patterns for pentaboranes can be crudely approximated by the directly measured patterns from the B^{11} -labeled molecules. However, to obtain an accurate monoisotopic fragmentation pattern, the small contributions from the molecules containing B^{10} atoms were removed from the observed raw data peaks; for the deuteriated compounds both B^{10} and H contributions were removed. The calculated monoisotopic fragmentation patterns for B_5H_9 and B_5D_9 are shown in Table III. The calculations for B_5H_9 were performed using both 1.32% B^{10} (no $B^{11}_5H_8^+$ ions present at m/e 63) and 1.17% B^{10} (obtained from the m/e 10 to m/e 11 ratio, which is known to lead to an upper limit for % B^{10} in the parent molecule). The resulting calculated patterns are insensitive to these small changes in B^{10} percentage. The B_5D_9 monoisotopic fragmentation pattern was also calculated using both 1.32% B^{10} and 1.17% B^{10} . The B^{11} -labeled B_5H_9 and B_5D_9 were prepared from the same batch of B^{11} -labeled BF_3 by pyrolyzing the intermediate $B^{11}_2H_6$ or $B^{11}_2D_6$ in exactly the same manner, and thus each would be expected to contain almost exactly the same percentage of B^{10} . In Table IV, the monoisotopic fragmentation patterns calculated for B_5H_9 and B_5D_9 are compared. Prior calculations by other authors of the monoisotopic fragmentation patterns of B_5H_9 ¹² and B_5D_9 ¹³ were based on polyisotopic mass spectra of pentaboranes having a normal isotopic abundance of B^{10} and B^{11} .

There seems to be a small but regular isotope effect in the fragmentation of B_5D_9 as compared to that of B_5H_9 .

The method of treatment of the raw mass spectral data has been given in detail in an earlier publication by the authors.⁹ The calculations of monoisotopic fragmentation patterns for boron compounds, especially those labeled concurrently with both B^{10} - B^{11} and H-D, are extremely tedious. To remove the mass spectral raw data for deuterated pentaborane just down to mass 41 requires over 3000 separate calculations, each one dependent on the ones before it. For this reason, through the generous cooperation of the Martin Computing Center, a computer program for an IBM 7090 was written which calculates monoisotopic fragmentation patterns from mass spectral raw data. The program is completely general and can handle any X_nY_m compound where both X and Y are partially isotopically labeled. The program calculates all contributions to the lower masses, labels each contribution and optionally prints out either the entire calculated mass spectrum or just the monoisotopic fragmentation pattern.

There is known to be a great similarity among processes which take place upon mass spectral electron impact and those upon exposure to ionizing radiation.¹⁴ There should also be a close relationship to processes which occur as a result of an electric discharge through a vapor of the compound. The delineation of the most plausible modes of decomposition of pentaborane is of potential usefulness as an aid in determining the sequence of mechanisms involved in such reactions as that of the electric discharge method of preparation of $B_{10}H_{16}$ from B_5H_9 .¹⁵ The lowest energy process (4.04 e.v.), and therefore one of the most prevalent ones, should be the removal of a terminal H (undoubtedly the apex one) to leave the B_5H_8 free radical. B_5H_8 prefers to remain a free radical rather than become a

$B_5H_8^+$ ion, since it would take at least another 6.5 e.v. to ionize this radical. However, combination of two B_5H_8 radicals to form $B_{10}H_{16}$ would release approximately 3.6 e.v. which makes this a very attractive process energetically. In this method other reactions will undoubtedly take place simultaneously to form various products since the energy of the discharge is sufficient to cause fragmentation and ionization of the pentaborane in many different ways. An experiment in which conditions could be carefully regulated so as to permit only fragmentation of a B-H terminal bond should lead to a greater yield of $B_{10}H_{16}$.

TABLE III
Calculated monoisotopic fragmentation pattern normalized to m/e 62 (B_5H_7) = 100.00

m/e	Raw data	$B_xH_n^+$ species	(Using 1.32% B^{10})	(Using 1.17% B^{10})
64	74.60	B_5H_9	100.18	100.18
63	4.97	B_5H_8	-0.03	0.74
62	74.60	B_5H_7	100.00	100.00
61	9.55	B_5H_6	6.13	6.90
60	100.00	B_5H_5	133.70	133.75
59	24.90	B_5H_4	24.48	25.51
58	21.00	B_5H_3	26.32	26.50
57	21.90	B_5H_2	27.60	27.80
56	18.70	B_5H	23.22	23.43
55	23.70	B_5	30.22	30.40
54	1.65		0.15	0.38
53	0.37	B_4H_9	0.44	0.45
52	0.05	B_4H_8	0.04	0.04
51	0.05	B_4H_7	0.06	0.06
50	3.77	B_4H_6	4.99	5.00
49	8.53	B_4H_5	11.04	11.08
48	31.30	B_4H_4	40.88	41.01
47	22.50	B_4H_3	27.62	27.91
46	16.70	B_4H_2	20.61	20.81
45	11.00	B_4H	13.44	13.59
44	6.26	B_4	7.55	7.65
43	0.46		0.19	0.24
42	.13	B_3H_9	.16	.16
41	.06	B_3H_8	.07	.07
40	.05	B_3H_7	.06	.06
39	.67	B_3H_6	.87	.88
38	.72	B_3H_5	.91	.91
37	3.17	B_3H_4	4.11	4.13
36	5.90	B_3H_3	7.46	7.59
35	8.63	B_3H_2	10.98	11.05
34	3.13	B_3H	3.65	3.71
33	1.03	B_3	1.19	1.21

Calculated monoisotopic fragmentation pattern normalized to m/e 69 (B_5D_7) = 100.00

m/e	Raw data	$B_xD_n^+$ species	(Using 1.32% B^{10} and 1.529% H)	(Using 1.17% B^{10} and 1.529% H)
73	86.30	B_5D_9	99.40	99.90
71	2.14	B_5D_8	0.62	0.63
69	89.10	B_5D_7	100.00	100.00
67	4.92	B_5D_6	4.14	4.17
65	100.00	B_5D_5	108.97	108.80
63	15.90	B_5D_4	16.13	16.14
62	3.28	B_4D_9	1.55	1.63
61	16.50	B_5D_3	17.09	17.03
60	1.72	B_4D_8	-0.11	-0.01
59	18.20	B_5D_2	18.90	18.83
58	1.70	B_4D_7	-0.05	-0.07
57	14.80	B_5D	15.14	15.07
56	5.98	B_4D_6	5.21	5.33
55	18.20	B_5	17.71	17.62
54	10.30	B_4D_5	9.78	9.92

According to this theory very similar reactions should take place upon irradiation of pentaborane. A pre-

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liminary study¹⁶ indicated that proton irradiation of pentaborane-9 produced higher boron hydrides which consisted of smaller boron hydride polyhedra coupled together. In fact, in more recent work,¹⁷ it is found that deuteron irradiation of pentaborane produced decaborane-16 with no detectable amounts of decaborane-14 and irradiation of decaborane-14 resulted in the coupling of two of these units ($B_{10}H_{18}$) to produce icosaborane-26.

Carboranes, carbon-boron-hydrogen compounds with delocalized electron-deficient skeletons, have been prepared by electric discharge through mixtures of a boron hydride, such as pentaborane, and an unsaturated hydrocarbon, such as acetylene.¹⁸ The tracing of the mechanism of these reactions while more complex than that of $B_{10}H_{16}$ synthesis is closely related to it, since $B_{10}H_{16}$ is found among the products of these reactions.

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TABLE IV
COMPARISON OF B_5H_9 AND B_5D_9 MONOISOTOPIC
FRAGMENTATION PATTERNS

Species	$B^{11}_xH_n^+$ (calcd. using 1.17% B^{10})	Species	$B^{11}_xD_n^+$ (calcd. using 1.17% B^{10} and 1.529% H)
B_5H_9	100.18	B_5D_9	99.90
B_5H_8	0.74	B_5D_8	0.63
B_5H_7	100.00	B_5D_7	100.00
B_5H_6	6.90	B_5D_6	4.17
B_5H_5	133.75	B_5D_5	108.80
B_5H_4	25.51	B_5D_4	16.14
B_5H_3	26.50	B_5D_3	17.03
B_5H_2	27.80	B_5D_2	18.83
B_5H	23.43	B_5D	15.07
B_5	30.40	B_5	17.62
B_4H_9	0.45	B_4D_9	1.63
B_4H_8	0.04	B_4D_8	-0.01
B_4H_7	0.06	B_4D_7	0.07
B_4H_6	5.00	B_4D_6	5.33
B_4H_5	11.08	B_4D_5	9.92
B_4H_4	41.01		
B_4H_3	27.91		
B_4H_2	20.81		
B_4H	13.59		
B_4	7.65		

Hebel for the actual programming of the fragmentation pattern problem.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF ARGONNE NATIONAL LABORATORY, ARGONNE, ILL.]

Reaction Constants of the Hydrated Electron^{1a}

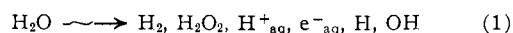
BY SHEFFIELD GORDON, EDWIN J. HART, MAX S. MATHESON, JOSEPH RABANI^{1b} AND J. K. THOMAS

RECEIVED FEBRUARY 14, 1963

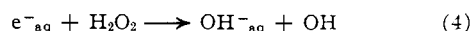
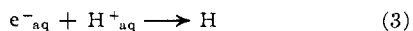
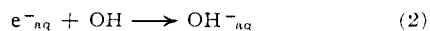
Intense pulses of energetic electrons produce an absorption in the visible in aqueous solutions which is attributed to the hydrated electron, e^-_{aq} . By following the decay of this absorption at 5780 Å., rate constants for a number of reactions of the hydrated electron have been measured. The effect of ionic strength on the rate constant for $e^-_{aq} + \text{ferricyanide ion}$, as well as the fact that some of the added reactants are known electron scavengers, confirms that the absorption is due to e^-_{aq} . Among the rate constants measured are: $e^-_{aq} + H^+_{aq}$, $2.36 \pm 0.24 \times 10^{10} M^{-1} \text{sec.}^{-1}$; $e^-_{aq} + H_2O_2$, $1.23 \pm 0.14 \times 10^{10} M^{-1} \text{sec.}^{-1}$; $e^-_{aq} + O_2$, $1.88 \pm 0.2 \times 10^{10} M^{-1} \text{sec.}^{-1}$; and $e^-_{aq} + e^-_{aq}$, $1 \times 10^{10} M^{-1} \text{sec.}^{-1}$; all rate constants being for $-d(e^-_{aq})/dt$.

The discovery² of the broad optical absorption band of the hydrated electron in irradiated water makes it possible to observe directly a primary radiation chemical species in water. We have now used the technique of pulsed radiolysis to measure rate constants for reactions of the hydrated electron. The apparatus used was developed by Matheson and Dorfman³ and has been described elsewhere.⁴ Generally, the decay of absorption at 5770–5790 Å. was followed, but a few experiments at 6850 Å. gave similar results.

The species formed by irradiation of water are given in eq. 1.



The hydrated electron is a very reactive species and possible reactions with other species in 1 are

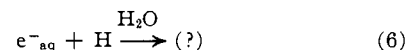
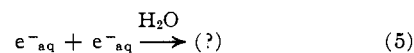


(1) (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission. (b) Post Doctoral Fellow from the Hebrew University, Jerusalem, Israel.

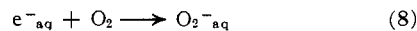
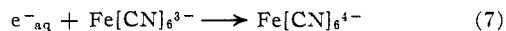
(2) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962); J. W. Boag and E. J. Hart, *Nature*, **197**, 45 (1963).

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The hydrated electron may also react with water in a first-order reaction, but Czapski and Schwarz⁵ set this rate constant as probably less than 10^4sec.^{-1} (our results show an upper limit of $4 \times 10^4 \text{sec.}^{-1}$) so that in our experiments with e^-_{aq} concentrations of 2 to 30 micromolar and second-order rate constants about $10^{10} M^{-1} \text{sec.}^{-1}$, second-order reactions predominate. The rate constants for 3 and 4 were measured by adding sufficient H_2SO_4 or H_2O_2 that the decay of e^-_{aq} absorption became pseudo-first order with first-order rate constants proportional to $[H^+_{aq}]$ or $[H_2O_2]$. These rate constants as well as those for reactions 7, 8 and 9 are given in Table I. The constants for 7, 8 and 9 were



measured in the presence of potassium ferricyanide, oxygen or cupric sulfate.

The reactions of Table I are consistent with the idea that the absorption decay followed is that of the hy-

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