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Appearance and Ionization Potentials of Selected Fragments from Decaborane, $B^{11}{}_{10}H_{14}$[1]

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The appearance potentials of selected ions from decaborane $B^{11}{}_{10}H_{14}$ (99.68% B^{11}) were measured by mass spectroscopy. A set of apparently self-consistent ionization potentials for decaborane and various $B_{10}H_n$ fragments were 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. An IBM 7090 computer program to calculate monoisotopic fragmentation patterns from mass spectral raw data was written. From the mass spectrum of $B^{11}{}_{10}H_{14}$ at 70 ev. the monoisotopic fragmentation pattern of decaborane was calculated. For comparison, from mass spectral raw data at 70 ev. of decaborane containing normal isotopic abundances of B^{10} and B^{11}, several different monoisotopic fragmentation patterns of decaborane were calculated which varied depending upon the method of choice of the original % B^{10} in the molecule.

The progress on the electron impact induced dissociations and ionizations of boron compounds is at about the same stage now as the work on electron impact studies of the hydrocarbons was twenty years ago, with two great added disadvantages. First, naturally occurring boron contains ~20% B^{10} and ~80% B^{11}. This means that the boron skeletons of every natural boron compound contain all possible combinations of B^{10} and B^{11} atoms as governed by binomial distribution probabilities. For certain simple compounds such as the boron trihalides, this boron distribution presents no problem. However, for all hydrogen-containing boron compounds, it is virtually impossible to realize any meaningful results from appearance potential data unless one makes the completely B^{10} or B^{11} labeled compound starting from the BF_3 compound, which is the only usable source of labeled boron.

Second, there are almost no available independent thermochemical data from which to calculate the energies of the possible states of combination in which the boron and other atoms may exist.

The appearance potentials of selected ions from decaborane, $B^{11}{}_{10}H_{14}$ (99.68% B^{11}), were measured mass spectroscopically. A set of apparently self-consistent ionization potentials for decaborane and various $B_{10}H_n$ fragments were calculated from these appearance potentials using what few thermochemical bond energy data are available, combined with the authors' interpretation of the processes taking place on ionization and fragmentation.

An IBM 7090 computer program to calculate monoisotopic fragmentation patterns from mass spectral raw data was written. From the mass spectrum of $B^{11}{}_{10}H_{14}$ at 70 ev. the monoisotopic fragmentation pattern of decaborane was calculated. For comparison, from mass spectral raw data at 70 ev. of decaborane containing normal isotopic abundances of B^{10} and B^{11}, several different monoisotopic fragmentation patterns of decaborane were calculated which varied depending upon the method of choice of the original % B^{10} in the molecule.

Experimental

The instrument used to measure the appearance potentials of the decaborane and its fragments was a Consolidated 21-103B mass spectrograph modified for appearance potential work by use of a 150,000 ohm Helipot and a 200 ohm resistor inserted into the ionizing voltage circuit so that the ionizing voltage could be varied from about 6 to 100 v. and measured accurately with the Leeds and Northrup Model 7665 potentiometer. Scanning was done over a small range of ion accelerating voltage with the magnet current adjusted to bring the ion of interest on the collector at 500 ± 10 v. The voltage on the metastable suppressor slit was zero. A sample of the gas to be studied was admitted to the expansion bulb and then an internal standard (argon) was admitted until the signal from the calibrating gas was equal to that for the ion of interest. The data were treated in two ways: by means of a semilog plot of ion current *versus* apparent ionizing voltage[2] and by using the appearance potential as equal to the voltage when the ion current was 1% of the current at 70 ev.[3] Using known spectroscopic values for the internal standard, a correction was determined and applied to the unknown, giving its appearance potential. The accuracy of the first method was verified by measuring the appearance potential of $C_2H_6^+$ from C_2H_6 which checked to within 0.4 ev. higher than the spectroscopic value (the appearance potentials of ions are usually 0.2–0.3 ev. higher than spectroscopic ionization potentials).

The $B^{11}{}_{10}H_{14}$ was prepared by pyrolysis of diborane at 125° as previously described.[4a]

Calculations and Results

A. Ionization Potentials.—The appearance potentials of decaborane and its fragment ions were carried out on the $B^{11}{}_{10}H_{14}$ compound (containing 99.68% B^{11}). The % B^{10} in the molecule was calculated from the ratio of *m/e* 10 to *m/e* 11, which leads to an upper limit for % B^{10}. The use of the completely B^{11} labeled compound was a necessity because it would have been impossible to untangle the appearance potentials due to ions of the same mass (containing either one less hydrogen atom or else one B^{10} atom instead of one B^{11} atom in the boron skeleton of decaborane). Even for appearance potentials of ions from diborane containing normal isotopic abundance of B^{10} and B^{11},[4b] it was not possible to determine to which ion an observed appearance potential corresponded at any *m/e* value lower than the one corresponding

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[2] V. H. Dibeler, R. M. Reese and F. L. Mohler, *J. Res. Natl. Bur. Standards*, **57**, 113 (1956).

[3] J. B. Farmer, F. P. Lossing, D. G. H. Marsden and C. A. McDowell, *J. Chem. Phys.*, **24**, 52 (1956).

[4] (a) Joyce J. Kaufman and W. S. Koski, *J. Am. Chem. Soc.*, **78**, 5774 (1956). (b) W. S. Koski, Joyce J. Kaufman, C. F. Pachucki and F. J. Shipko, *ibid.*, **80**, 3202 (1958).

to the highest mass. Only after measuring the appearance potentials of ions from $B^{10}{}_2H_6$, and assigning the corresponding ions, was it possible to go back and then assign certain ions to the observed appearance potentials from the normal diborane. This was difficult even for diborane and would have been completely out of the question for decaborane.

The appearance potentials of the ions from decaborane were measured mass spectroscopically and were calculated by two different methods.

One method for obtaining appearance potentials from the observed ion current at different voltages is to construct a semilog plot of ion current *versus* ionizing voltage.[2] The correct appearance potential for an ion is determined by measuring the voltage interval between two parallel straight lines plotted on the same normalized scale, one of which corresponds to the ion of unknown critical potential and the other corresponding to an ion of known ionization potential such as argon. Normalization of the two curves is accomplished by adjusting partial pressures of the gases so as to give approximately equal ion current for the two ions at electron energies of 70 ev.

As a check on the accuracy and reproducibility of this method, the appearance potential of $C_2H_6^+$ from ethane was measured and found to be 11.89 and 12.01 ev. (relative to argon 15.76 ev.) in two successive determinations. The ionization potential of ethane by photoionization is 11.65 ev.,[5] and the mass spectroscopically measured appearance potential is expected to be several tenths of an ev. higher than the photoionization value.

This method was then used to obtain the appearance potentials of the following ions from decaborane: *m/e* 122, $B^{11}{}_{10}H_{12}$, Fig. 1, and *m/e* 120, $B^{11}{}_{10}H_{10}$. In both of these cases the argon and the ion of interest gave parallel straight lines when the log of the ion current was plotted against the uncorrected ionizing voltage.

When the curves for the argon and the ion of interest are not parallel, the first method cannot be used with any degree of accuracy. Another method used to find appearance potentials is to call the appearance potential of both the ion of interest and the argon the voltage at which the observed ion current is equal to some percentage of the ion current at 70 ev. (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* 122 and *m/e* 120 are identical.

TABLE I

APPEARANCE POTENTIALS OF IONS FROM $B^{11}{}_{10}H_{14}$

Species	*A* (method 1) ev.	*A* (method 2) ev.
$B_{10}H_{14}^+$		10.26 ± 0.5
$B_{10}H_{12}^+$	10.90 ± 0.2	10.87 ± .2
$B_{10}H_{11}^+$		10.81 ± .5
$B_{10}H_{10}^+$	11.62 ± .2	11.62 ± .2
$B_{10}H_8^+$	12.66 ± .3	12.67 ± .3
$B_{10}H_7^+$		12.51 ± .5
$B_{10}H_6^+$	13.56 ± .3	13.14 ± .3

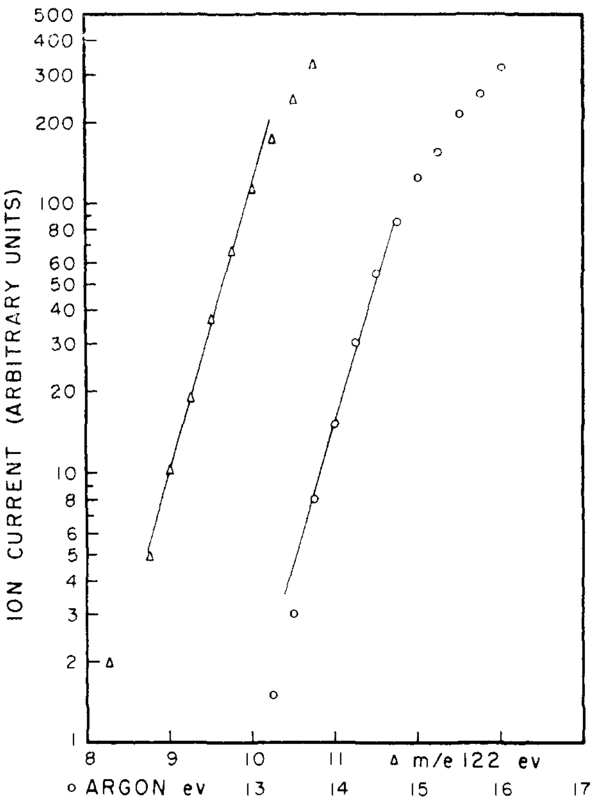

Fig. 1.—Ion efficiency curve *m/e* 122 and argon.

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.

The values of appearance potential for *m/e* 124, 121 and 117 were calibrated against the same standard argon since these peaks were approximately equal in intensity. 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 method of obtaining ionization potentials and bond dissociation energies by ionization and dissociation 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

$$R_1 - R_2 + e \longrightarrow R_1^+ + R_2 + 2e$$

then by the equation

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

(where $A(R_1^+)$ is the mass spectroscopically measured appearance potential of R_1^+, $I(R_1)$ is the ionization potential of R_1 and $D(R_1 - R_2)$ is the dissociation energy of $R_1 - R_2$, either the ionization potential of R_1 or the bond dissociation energy $R_1 - R_2$ may be calculated directly from the measured $A(R_1^+)$, *provided* that one knows the value for the other unknown in the equation.

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(5) K. Watanabe, *J. Chem. Phys.*, **26**, 543 (1957).

TABLE II

PROCESSES, CONFIGURATIONS AND CALCULATED IONIZATION POTENTIALS FOR VARIOUS DECABORANE FRAGMENTS

Species	Process $B_{10}H_{14} + e \rightarrow$	Bonds ruptured	Bonds formed	Bonds ruptured (rearrangement)	Bonds formed (rearrangement)	I (calcd.) ev.
$B_{10}H_{14}^+$	$B_{10}H_{14}^+ + 2e$					10.26
$B_{10}H_{12}^+$	$B_{10}H_{12}^+ + H_2 + 2e$	2 B–H	1 B–B	2 B—H—B or	2 B–H	9.61
				2 B—B—B	2 B–B	9.54
$B_{10}H_{11}^+$	$B_{10}H_{11}^+ + H_2 + H + 2e$	3 B–H	1 B–B	2 B—H—B or	2 B–H	5.51
				2 B—B—B	2 B–B	5.43
$B_{10}H_{10}^+$	$B_{10}H_{10}^+ + 2H_2 + 2e$	4 B–H	2 B–B	4 B—H—B or	4 B–H	9.10
				4 B—B—B or	4 B–B	8.94
				2 B—H—B 2 B—B—B	2 B–H 2 B–B	9.02
$B_{10}H_8^+$	$B_{10}H_8^+ + 3H_2 + 2e$	6 B–H	3 B–B	4 B—H—B 2 B—B—B or	4 B–H 2 B–B	8.81
				2 B—H—B 4 B—B—B or	2 B–H 4 B–B	8.73
				6 B—B—B	6 B–B	8.65
$B_{10}H_7^+$	$B_{10}H_7^+ + 3H_2 + H + 2e$	6 B–H	3 B–B	Same as $B_{10}H_8$		4.45–4.61
$B_{10}H_6^+$	$B_{10}H_6^+ + 4H_2 + 2e$	8 B–H	4 B–B	4 B—H—B 4 B—B—B or	4 B–H 4 B–B	A (method 1) 8.36 A (method 2) 7.94
				2 B—H—B 6 B—B—B	2 B–H 6 B–B	A (method 1) 8.28 A (method 2) 7.86

A condition for hydrocarbons formulated by Stevenson[6] that the appearance potential of R_1^+ from $R_1 - R_2$ will involve no excess energy when $I(R_1) < I(R_2)$ has often been found to be valid. If $I(R_1) > I(R_2)$ then $A(R_2^+) > I(R_1) + D(R_1 - R_2)$. In order to interpret correctly the appearance potentials of fragment ions, it would also be necessary to know what neutral (or perhaps even charged) fragments are simultaneously formed and the states of electronic excitation of the fragments and the molecule ion. However, it has been shown that in a number of cases the simplest set of assumptions suffice for the interpretation of the data. Accordingly, for the calculations in this article it has been tacitly assumed that no activation energies are involved in rearrangements and that no excess energies, kinetic or otherwise, are involved in the various processes. This latter assumption is probably reasonable for the principal ions; it may be less valid for ions of relatively small intensity.

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).[4b,7] 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 boron compounds from which it became possible to derive a theory of the effect of substitution on ionization potentials in general.[8] These values have been named the δ_K values and are valid for boron compounds, carbon compounds and nitrogen compounds.

In Table I are presented the appearance potentials of the ions; in Table II are presented processes, bonds ruptured, formed and rearranged and the resulting calculated ionization potentials.

$B_{10}H_{14}^+$.—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[9]), therefore

$$I(B_{10}H_{14}) = 10.26 \text{ ev.}$$

This value is a little lower but in the same range as the values reported by other authors for the ionization potential for decaborane: 11.0 ± 0.5 ev.,[10] 10.7 ev.[11] The other determinations of the ionization potential of decaborane were measured on decaborane containing normal isotopic abundance of boron where only about 11% of the molecules have a boron skeleton corresponding to $B^{11}{}_{10}H_{14}$ which corresponded to the ion observed. In this research in which almost completely B^{11} labeled decaborane was used, about 97% of the molecules had a boron skeleton corresponding to $B^{11}{}_{10}H_{14}$. It is to be expected that this preponderance of $B^{11}{}_{10}H_{14}$ molecules should make it possible to observe the initial appearance potential of the

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[6] D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

[7] W. S. Koski, J. J. Kaufman and C. F. Pachucki, *J. Am. Chem. Soc.*, **81**, 1326 (1959).

[8] J. J. Kaufman and W. S. Koski, *ibid.*, **82**, 3262 (1960).

[9] D. P. Stevenson and J. A. Hipple, Jr., *ibid.*, **64**, 1588 (1942).

[10] J. L. Margrave, *J. Chem. Phys.*, **32**, 1889 (1960).

[11] V. H. Dibeler, private communication quoted in 10.

ion more easily and at a lower voltage than for the normal decaborane where the fragment $B^{11}{}_{10}H_{14}^+$ is in small abundance.

$B_{10}H_{12}^+$.—In decaborane 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.

It was proposed by Prosen[12] that, for calculational purposes, one assume that the different B–H bond energies are constant for the boron hydride series. His suggestion has been followed for the calculations reported in this article. Either terminal or bridge hydrogens could dissociate to form $B_{10}H_{12}$; however, since it takes less energy to break a terminal B–H bond, 4.04 ev., as compared to the energy necessary to withdraw a bridge H, 4.66 ev., 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 $I(B_{10}H_{12})$ 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

$$B_{10}H_{14} + e \longrightarrow B_{10}H_{12} + H_2 + 2e$$

After the process is assigned, and a choice is made for which bonds rupture initially, there are still several possible energy values which may be calculated for $I(B_{10}H_{12})$ depending upon the choice of final structure of the molecule ion.

The first choice of structure for a molecule ion is simply the one in which two terminal B–H bonds are broken. For this structure

$$\begin{aligned} I(B_{10}H_{12}) &= A(B_{10}H_{12}^+) - 2D(\text{B–H}) + D(H_2) \\ &= 10.87 - 8.08 + 4.48 = 7.27 \text{ ev.} \end{aligned}$$

In addition to formation of H_2 in this process, it is also possible (and very probable) to form a B–B bond after the two terminal hydrogens are removed from the decaborane. For the value of a single B–B bond in these compounds, the value D(B–B) = 3.58 ev. is used.[12] This would give

$$\begin{aligned} I(B_{10}H_{12}) &= A(B_{10}H_{12}^+) - 2D(\text{B–H}) + D(H_2) + D(\text{B–B}) \\ &= 10.87 - 8.08 + 4.48 + 3.58 = 10.85 \text{ ev.} \end{aligned}$$

The possible rearrangements which might take place in $B_{10}H_{12}^+$ as formed would be for two B—H—B bridge bonds then to rearrange to two B–H terminal bonds, or for two B—B—B 3-center bonds to rearrange to two 2-center B–B bonds. The energies involved in these rearrangements are very close and yield

$$\begin{aligned} I(B_{10}H_{12}) &= A(B_{10}H_{12}^+) - 2D(\text{B—H—B}) + D(H_2) + D(\text{B–B}) \\ &= 10.87 - 9.32 + 4.48 + 3.58 = 9.61 \text{ ev.} \end{aligned}$$

or

$$\begin{aligned} I(B_{10}H_{12}) &= A(B_{10}H_{12}^+) - 2D(\text{B–H}) + D(H_2) + 3D(\text{B–B}) - 2D(\text{B—B—B}) \\ &= 10.87 - 8.08 + 4.48 + 10.74 - 8.48 = 9.53 \text{ ev.} \end{aligned}$$

The problem is now to choose a correct configuration for the fragment ion and to justify the choice if possible.

Of the possibilities listed above, $I(B_{10}H_{12}) = 7.27$ ev. is ruled out for two reasons. First, the value of $I(B_{10}H_{12}) = 7.27$ ev. is too low to be compatible with an ionization potential to be expected for this type of compound. Secondly, this would leave $B_{10}H_{12}^+$ as a tri-radical which seems unreasonable.

$I(B_{10}H_{12}) = 10.85$ ev. might not be too bad a choice. However, the value $I(B_{10}H_{12}) = 10.85$ ev. is too high as compared to the measured $I(B_{10}H_{14}) = 10.26$ ev. Even slightly higher values up to $I(B_{10}H_{14}) \approx 11$ ev. would in no way alter these conclusions. It is to be expected that the ionization potential of $B_{10}H_{12}$ should be about 1 ev. less than that of $B_{10}H_{14}$, not equal to it or higher.

The last value $I(B_{10}H_{12}) = 9.53 - 9.61$ ev. seems to be the best choice. In diborane, for the formation of $B_2H_4^+$ from $B_2H_6^+$ was postulated initial rupture of two B–H bonds, formation of H_2, formation of a B–B bond and then rearrangement of two B—H—B bonds to form two B–H bonds. This is essentially the same process as postulated for formation of $B_{10}H_{12}^+$ from $B_{10}H_{14}^+$ —the final step being rearrangement of two 3-center bonds to form two normal 2-center bonds.

Here, a pause to generalize that it is quite probable that this type of behavior may well be followed for the formation of $B_nH_{n+2}^+$ from B_nH_{n+4} (also possibly for the formation of $B_nH_{n+4}^+$ from B_nH_{n+6}).

It is interesting to note that the rearrangement of two B—H—B bonds to form two terminal B–H bonds would leave $B_{10}H_{12}$ in the same configuration as is reported in molecules of the type $ZB_{10}H_{12}Z$ where Z is an electron-donor molecule. The first of these $ZB_{10}H_{12}Z$ molecules noted was bis-acetonitrile decaborane[13] whose structure was determined by Lipscomb[14] by X-ray analysis. The $ZB_{10}H_{12}Z$ is presumed to be formed by attack of two electron-donor molecules (each capable of donating an electron pair) on the 6,9-positions of the decaborane rupturing the four bridge hydrogen bonds and forming two B–Z bonds and reforming two new bridge hydrogen bonds. The over-all result is a $B_{10}H_{12}$ unit with ten B–H bonds, two B—H—B bonds and the remaining electrons assigned to the boron skeleton. These addition compounds have been regarded as derivatives of $B_{10}H_{14}^{-2}$, but this does not alter the implication that the $B_{10}H_{12}$ unit is basically the same.

$B_{10}H_{10}^+$.—Process

$$B_{10}H_{14} + e \longrightarrow B_{10}H_{11}^+ + H_2 + H + 2e$$

Three B–H bonds are presumed ruptured in the initial step and a B–B bond is formed giving $I(B_{10}H_{11}) = 6.75$ ev.

Then if two B—H—B bonds rearrange to two B–H bonds

$$I(B_{10}H_{11}) = 5.51 \text{ ev.}$$

or two 3-center B—B—B bonds rearrange to form two 2-center B–B bonds

$$I(B_{10}H_{11}) = 5.43 \text{ ev.}$$

The values of $I(B_{10}H_{11}) = 6.75$ or $5.43 - 5.51$ ev. are both reasonable. Since $I(B_{10}H_{12}) = 9.53$ ev.

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

(13) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957).

(14) J. V. D. M. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

has been chosen corresponding to a process of the last type, it is almost obligatory to choose $I(B_{10}H_{11}) = 5.51$ ev. because the same process should hold for the molecule ion or the next lower radical ion. The ionization potential is low, but it is an experimental fact in simpler compounds that ionization potentials of the radicals often run 3–4 ev. lower than those of the corresponding molecule.

$B_{10}H_8^+$.—It is interesting to note that the ionization potential of naphthalene ($C_{10}H_8$) is 8.26 ev.[15] (e impact) or 8.12 ev. (photoionization).[5] This compared to $I(B_{10}H_8)$ follows the correlation observed for diborane that the ionization potentials of the boron compounds are approximately 0.3 ev. higher than those of the corresponding carbon compounds.

$B_{10}H_7^+$.—The same relationship noted for

$$I(B_{10}H_{12}) - I(B_{10}H_{11}) = 4.10 \text{ ev.}$$

holds true for

$$I(B_{10}H_8) - I(B_{10}H_7) = 4.20 \text{ ev.}$$

$B_{10}H_6^+$.—The appearance potentials measured for $B_{10}H_6^+$ by methods 1 and 2 differ by 0.4 ev.

Either measurement is sufficiently acceptable to show that $I(B_{10}H_6) < I(B_{10}H_8)$ as would be expected.

An ultimate goal of appearance potential values for fragments formed from the parent molecules is to enable one to derive some idea of processes taking place upon fragmentation and the energies involved in these processes. It is hoped that these calculations on decaborane and the fragments formed from it may serve as an indication of the most probable structures of the resulting species. Many of these species while not stable by themselves do exist as entities in addition compounds and very little is known about their properties.

There seems to have been virtually no work published on appearance potentials of fragment ions from complicated molecules. A rather recent publication[15] presents the appearance potentials of parent ions and doubly charged ions from several fused ring aromatic hydrocarbons, but appearance potentials for fragment ions are only promised for a later publication. It will be very interesting to compare the $I(C_{10}H_7)$ and $I(C_{10}H_6)$ with the calculated $I(B_{10}H_7)$ and $I(B_{10}H_6)$. From the fragmentation patterns of these aromatic compounds, it can be seen that almost all the ionization is due to the molecule ion, multiply charged molecule ions or simple loss of hydrogen atoms and hydrogen molecules from the molecular ion. Ions arising from the rupture of a ring and subsequent loss of a neutral fragment are almost nonexistent. This can be attributed to the well known resonance stabilization of fused ring aromatic compounds.

The situation is quite different for decaborane. The geometrical structure has been determined by X-ray diffraction.[16] Decaborane has four B—H—B bridge bonds and ten normal B–H terminal bonds. The boron skeleton is presumed to be held together by two B–B single bonds and six 3-center B—B—B bonds.

B. **Monoisotopic Fragmentation Patterns. 1. Decaborane.**—The monoisotopic fragmentation pattern for decaborane can be approximated directly from the measured intensity values for each fragment ion formed by electron impact of $B^{11}{}_{10}H_{14}$ since this compound is 99.68% B^{11} labeled. To calculate the monoisotopic fragmentation pattern of decaborane is a laborious task—for this reason a computer program to calculate exact monoisotopic fragmentation patterns has been written with the generous coöperation of the Martin Computing Center. The calculated monoisotopic fragmention pattern of the B^{11} labeled decaborane is presented in Table III. From the data it can be seen that, contrary to fused ring hydrocarbons, there are appreciable contributions from lower ions.

There is a substantial contribution from ions in the B_9 range, and this is to be expected since a BH_3 group is the fragment which is the one most apt to be withdrawn on rupture of the boron skeleton. There is a moderate contribution from ions in the B_8 range which undoubtedly corresponds to withdrawal of 2 BH_3 groups from the boron skeleton followed then by rearrangement and a possible further loss of hydrogen. Contributions in the lower mass ranges show that it seems possible to get every conceivable fragment ion from electron impact induced dissociation of decaborane, as well as some multiply charged ions.

The monoisotopic fragmentation pattern for $B_{10}H_n$ fragments obtained from $B^{11}{}_{10}H_{14}$, normalized to 100.00 for m/e 122, Table III, may be compared with monoisotopic fragmentation patterns calculated from electron impact of normal decaborane run under the same conditions on the same spectrometer, calculated using 18.83% B^{10}, 20.00% B^{10}, 20.52% B^{10} or 29.34% B^{10} to obtain binomial distribution probabilities for different B^{10}–B^{11} contents of the boron skeleton, Table IV. 18.83% B^{10} and 20.00% B^{10} correspond to the percentages of B^{10} usually assigned as "normal" isotopic distribution, 20.52% B^{10} is the percentage of B^{10} which would be calculated from the contribution of $B^{11}{}_9B^{10}H_{14}$ to mass 123 computed by using the fragmentation pattern derived from B^{11} labeled decaborane and 29.34% B^{10} is the percentage one would estimate from the ratios of m/e 10 to m/e 11 (corrected at m/e 11 for $B^{10}H$). Obviously this last procedure, although widely used in calculation of monoisotopic fragmentation patterns of "normal" boron compounds, is not a valid procedure for "normal" boron compounds because it leads to a large negative residue even at m/e 123.

It is quite apparent that the fragmentation pattern of decaborane calculated from the B^{11} labeled decaborane must be the most nearly correct one. The percentage of B^{10} estimated from the ratio m/e 10 to m/e 11 is always an upper limit to the actual % B^{10} in the molecule; in practice the % B^{10} will be less than the amount estimated in this fashion. Therefore, the value of 0.32% B^{10} is an upper limit to the % B^{10} in the B^{11} labeled decaborane. Several of the other fragmentation patterns calculated from normal decaborane show apparently large negative contributions at some of the lower $B_{10}H_n$ masses, especially those computed

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(15) M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).

(16) J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

TABLE III: MONOISOTOPIC MASS SPECTRUM OF DECABORANE—FROM ELECTRON IMPACT OF $B^{11}{}_{10}H_{14}$

m/e	$B^{11}{}_xH_n{}^+$ Species	Raw data	Calculated monoisotopic fragmentation pattern[a] (normalized to *m/e* 122 = 100.00)
124	$B_{10}H_{14}$	17.77	17.80
123	$B_{10}H_{13}$	3.80	3.24
122	$B_{10}H_{12}$	100.00	100.00
121	$B_{10}H_{11}$	16.27	13.14
120	$B_{10}H_{10}$	73.73	73.35
119	$B_{10}H_9$	13.97	11.67
118	$B_{10}H_8$	109.82	109.54
117	$B_{10}H_7$	21.28	17.85
116	$B_{10}H_6$	59.33	58.78
115	$B_{10}H_5$	22.94	21.11
114	$B_{10}H_4$	18.18	17.51
113	$B_{10}H_3$ (B_9H_{14})	14.78	14.24
112	$B_{10}H_2$ (B_9H_{13})	13.90	13.46
111	$B_{10}H$ (B_9H_{12})	17.00	16.59
110	B_{10} (B_9H_{11})	18.87	18.36
109	B_9H_{10}	4.18	3.59
108	B_9H_9	1.40	1.29
107	B_9H_8	4.94	4.89
106	B_9H_7	7.37	7.22
105	B_9H_6	8.77	8.55
104	B_9H_5	11.46	11.19
103	B_9H_4	17.34	16.98
102	B_9H_3 (B_8H_{14})	22.02	21.49
101	B_9H_2 (B_8H_{13})	22.50	21.84
100	B_9H (B_8H_{12})	12.01	11.36
99	B_9 (B_8H_{11})	17.27	16.91
98	B_8H_{10}	3.55	3.05
97	B_8H_9	1.25	1.16
96	B_8H_8	0.92	0.88
95	B_8H_7	0.34	0.32
94	B_8H_6	2.39	2.37
93	B_8H_5	3.78	3.70
92	B_8H_4	9.11	8.97
91	B_8H_3 (B_7H_{14})	11.25	10.97
90	B_8H_2 (B_7H_{13})	7.96	7.64
89	B_8H (B_7H_{12})	9.11	8.87
88	B_8 (B_7H_{11})	9.24	8.97
87	B_7H_{10}	1.62	1.38
86	B_7H_9	0.40	0.36
85	B_7H_8	.18	.17
84	B_7H_7	.23	.22
83	B_7H_6	.92	.91
82	B_7H_5	1.60	1.57
81	B_7H_4	2.52	2.46
80	B_7H_3 (B_6H_{14})	4.86	4.57
79	B_7H_2 (B_6H_{13})	4.78	4.64
78	B_7H (B_6H_{12})	3.03	2.90
77	B_7 (B_6H_{11})	4.23	4.13
76	B_6H_{10}	0.67	0.57
75	B_6H_9	.21	.20
74	B_6H_8	.15	.14
73	B_6H_7	.04	.04
72	B_6H_6	.56	.55
71	B_6H_5	.85	.83
70	B_6H_4	.21	.19
69	B_6H_3 (B_5H_{14})	3.61	3.57
68	B_6H_2 (B_5H_{13})	2.35	2.26
67	B_6H (B_5H_{12})	3.06	2.98
66	B_6 (B_5H_{11})	0.73	0.67
65	B_5H_{10}	.13	.12
64	B_5H_9	.06	.06
63	B_5H_8	.02	.02
62	B_5H_7	.07	.07
61	B_5H_6	.14	.14

m/e	Species $B_xH_n{}^+$	$B_yH_m{}^{++}$	Raw data
60	B_5H_5	$B_{10}H_{10}$	2.28
59.5		$B_{10}H_9$	1.09
59	B_5H_4	$B_{10}H_8$	9.06
58.5		$B_{10}H_7$	1.67
58	B_5H_3	$B_{10}H_6$	4.82
57.5		$B_{10}H_5$	2.26
57	B_5H_2	$B_{10}H_4$	8.52
56.5		$B_{10}H_3$	2.67
56	B_5H	$B_{10}H_2$	3.18
55.5		$B_{10}H$	0.49
55	B_5	B_{10}, B_9H_{11}	1.42
54	B_4H_{10}	B_9H_9	0.32
53	B_4H_9	B_9H_7	.06
52.5		B_9H_6	.63
52	B_4H_8	B_9H_5	.25
51.5		B_9H_4	.49
51	B_4H_7	B_9H_3	.60
50.5		B_9H_2	.46
50	B_4H_6	B_9H	.21
49.5		B_9	.11
49	B_4H_5		1.13
48	B_4H_4		1.19
47	B_4H_3		2.14
46	B_4H_2		1.39
45	B_4H		0.73
44	B_4		.32
43	B_3H_{10}		.13
	Probably slight contribution $B^{11}{}_3B^{10}$		
42	B_3H_9		.05
41	B_3H_8		.12
40	B_3H_7		.04
39	B_3H_6		1.14
38	B_3H_5		0.98
37	B_3H_4		1.43
36	B_3H_3		2.43
35	B_3H_2		2.05
34	B_3H		0.37
33	B_3		.09
32			.76
31	Background		.06
30			.06
29			.42
28	B_2H_6		2.82
27	B_2H_5		2.36
26	B_2H_4		0.58
25	B_2H_3		2.85
24	B_2H_2		2.00
23	B_2H		0.30
22	B_2		0.06
21			..
20	...		..
19	...		..
18	H_2O		7.54
17	Background		2.15
16			0.42
15	BH_4		.15
14	BH_3		.48
13	BH_2		57.20
12	BH		3.09
11	B^{11}		57.24
10	B^{10}		0.18

[a] Corrected for the small residual amount of B^{10}.

TABLE IV

MONOISOTOPIC MASS SPECTRA OF DECABORANE FROM ELECTRON IMPACT OF "NORMAL" $B_{10}H_{14}$

m/e	$B_x{}^{11}H_n{}^+$	Raw data	Monoisotopic fragmentation patterns calculated using the different percentages of B^{10} (normalized to *m/e* 122 = 100.00)			
			18.83% B^{10}	20.00% B^{10}	20.52% B^{10}	29.34% B^{10}
124	$B_{10}H_{14}$	3.28	14.67	14.64	14.61	47.87
123	$B_{10}H_{13}$	8.47	3.85	1.21	0.01	−75.16
122	$B_{10}H_{12}$	32.30	100.00	100.00	100.00	100.00
121	$B_{10}H_{11}$	64.10	23.40	5.32	−2.93	109.05
120	$B_{10}H_{10}$	82.70	58.73	60.39	54.66	−320.50
119	$B_{10}H_9$	82.50	21.43	10.30	15.50	−649.98
118	$B_{10}H_8$	87.50	102.39	102.00	91.44	−335.55
117	$B_{10}H_7$	99.00	34.01	15.63	16.35	440.87
116	$B_{10}H_6$	100.00	45.30	45.16	39.56	−819.88
115	$B_{10}H_5$	87.50	26.30	18.18	18.43	−2286.62
114	$B_{10}H_4$	68.10	14.92	12.83	9.94	−2825.45
113	$B_{10}H_3$	48.90	13.52	11.52	11.94	−2043.22
112	$B_{10}H_2$	33.60	6.58	4.79	3.39	−881.38
111	$B_{10}H$	26.70	23.82	23.18	23.29	−84.85
110	B_{10}	25.10	5.62	1.53	−0.48	253.74
109	B_9H_{10}	24.10	12.49	12.56	11.86	−508.33
108	B_9H_9	18.10	−5.99	−7.90	−7.64	−1205.56
107	B_9H_8	10.90	−4.55	−8.34	−8.61	−1427.94
106	B_9H_7	7.50	7.85	4.46	3.78	−1041.91
105	B_9H_6	8.30	7.75	12.14	12.76	−472.10
104	B_9H_5	12.50	12.70	5.55	3.63	−640.67
103	B_9H_4	16.20	8.86	11.93	12.51	121.28
102	B_9H_3	23.00	29.38	24.67	23.04	−223.16
101	B_9H_2	29.70	12.49	9.93	8.64	−447.14
100	B_9H	32.20	19.20	17.19	16.57	−397.29

with the higher B^{10} percentages. Obviously, it is physically just not possible to have a negative contribution to an observed *m/e* intensity. It is suggested that the most valid procedure to obtain monoisotopic fragmentation patterns for boron compounds would be to run the mass spectrum of a monoisotopically B labeled compound and then correct for the small amount of isotopic impurity. Alternatively, if the exact B^{10} content of a sample is known by an independent technique, such as neutron absorption, then the computer program can be used to calculate a monoisotopic fragmentation pattern.

Quite often the observed ratio of *m/e* 10 to *m/e* 11 (corrected or uncorrected for $B^{10}H$) is used as a measure of the % B^{10} present in the original molecule. It is well known that this leads to a value which is somewhat too high for the apparent B^{10} percentage of the original molecule, but as the results of the calculations in this article show, the error can be appreciably greater than one might expect. In the example calculated in Table IV, the overestimation of the total amount of B^{10} in "normal" decaborane was about 43% too high. This overestimation of the B^{10} content of the sample can have serious consequences especially in the cases where one is using a "normal" boron compound for neutron shielding purposes. The cross section for neutron capture by B^{10} to give an α particle and Li^7 is quite high—many orders of magnitude greater than that of B^{11}. Shielding by "normal" boron compounds relies on the absolute amount of B^{10} present to serve as the shielding agent. It is not valid to use the mass spectroscopically observed ratio of *m/e* 10 to *m/e* 11 to obtain the % B^{10} in the original molecule.

There are two valid methods to calculate the B^{10} content in the original molecule from mass spectral data. One way is to use a previously obtained monoisotopic fragmentation pattern and strip the lower masses for all contributions other than that of a parent species and then sum up the relative amounts of each parent labeled with different numbers of B^{10} and B^{11} atoms times the number of each kind of atom. The number of B^{10} atoms obtained in this way divided by the total number of boron atoms is a true measure of the amount of B^{10} in the sample. Previous calculations show that this method is accurate to at least 1% even if the isotopes are preferentially rather than binomially distributed (such as in samples resulting from isotopic exchange reactions).

A second method can be used on "normal" boron compounds. Because the distribution of B^{10} and B^{11} atoms should be completely governed by the laws of binomial probability distribution, it is only necessary to strip the first two or three peaks to obtain the amounts of the parent species labeled with one, two or three B^{10} atoms instead of B^{11} atoms. The magnitudes of these peaks relative to that of the completely B^{11} labeled species exactly follow binomial distribution laws for the percentage of B^{10} in the original molecule. The first several members of a binomial distribution series are quite sufficient to determine accurately the per cent. B^{10} in the molecule.

2. Computer Program to Calculate Monoisotopic Fragmentation Patterns.—The computer program as written is completely general and capable of handling any molecule X_nY_m 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 and labeled mass spectrum or just the monoisotopic fragmentation pattern.

Conclusion.—One most important feature of the method in which the appearance potential data on fragments from the boron hydrides are treated in order to calculate ionization potentials is that it is quite independent of the correct bond structure of the original parent boron hydride. All that is postulated is what particular types of bonds rupture on electron impact and what other types of bonds are formed or rearranged. If the original structure of a parent boron hydride should prove to be different from the one accepted now, this would in no way alter the calculations performed. Also, if the principle of the constancy of the bond energies of B–H terminal or B—H—B bridge bonds or B–B or B—B—B bonds should prove to be only an approximately valid assumption, the calculations for the potentials are set up in such a way that it will be a simple matter to insert the modified bond energy.

When more independent data become available on heats of formation of the boron hydrides themselves and then heats of formation of some of the fragments, it will become possible to check the validity of some of the assumptions in the calculations of their ionization potentials.

The method employed does seem to have given quite self-consistent results for the boron hydrides and BY_3 compounds and should prove generally applicable to any other types of compounds, most particularly aluminum, silicon and phosphorus compounds in which there is a great deal of interest and a great scarcity of thermochemical data.

It is postulated that there is a similarity between processes which take place in ionization and fragmentation mass spectroscopically and those which may take place in radiation studies. Calculations performed on the boron hydrides where there are so few independent thermochemical data available necessitated development of general procedures for interpretation of such processes, and these may aid in interpreting the mass spectra and radiation studies of compounds for which there are so few other data.[17]

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(17) W. F. Libby, *J. Chem. Phys.*, **35**, 1714 (1961).

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On the Nature of Some Higher Boron Hydrides Produced in Radiation-Induced Reactions in Penta- and Decaborane[1]

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The mass spectra of the solid products produced by deuteron irradiation of mixtures of various known boron hydrides reveal several groups of peaks attributed to some new higher hydrides of boron. Small amounts of these hydrides were obtained by separation in a vapor-phase chromatograph. The mass spectra of the isolated materials yield molecular weights which suggest that these new higher hydrides are produced by the coupling of smaller polyhedral units. The irradiation of pure pentaborane-9 and decaborane-14 is shown to produce two new hydrides identifiable from their mass spectra as decaborane-16 and icosaborane-26.

Introduction

Three years ago, Schmied and Koski[3] reported some results on products obtained from proton radiation-induced reactions in pentaborane-9. Indication was obtained that at least some of the higher hydrides of boron were produced by the coupling of two simpler polyhedral boron hydride molecules. For example, evidence was obtained that two pentaborane-9 units could couple across the apical borons to produce a decaborane different in structure from decaborane-14. Mass spectroscopic measurements which were made at a variety of laboratories were used for the analyses. Unfortunately, only small amounts of materials were available and since the compounds were not separated and also contained small amounts of organic impurities, the results obtained were not completely unambiguous. Recently, with the acquisition of appropriate instrumental facilities in our laboratories, we have resumed our activities in this field. This paper is a brief summary of our exploratory results to date on the products obtained by deuteron irradiation of mixtures of several volatile hydrides, of pentaborane-9, and of decaborane-14. In this study many of the earlier results are confirmed and extended.

Experimental

The mass spectra were made on a Consolidated Electrodynamics Mass Spectrometer Model 21–103C supplied with a heated inlet system. The mass ranges scanned are as indicated in Figs. 1 and 2 using a slit on the collector of 7 mil width. The temperature of both the inlet system and gold leak were maintained at 100°. The hydride vapors were admitted to the expansion volume by heating the solids to 95° in the external sample outlet with a small tubular

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(2) Lever Brothers Company Foundation Fellow.

(3) H. Schmied and W. S. Koski, Abstracts of Papers, 135th Meeting of ACS, 1959, p. 38-M.