line hydrolysis.[13] The acidified solution gave no hydrogen; whether the B–H bonds remained in a protected situation or had served to reduce half of the CF_3 groups was not determined. A phosphorus analysis[8] gave 17.7% P; calcd., 17.0%.

A final analysis for all components of the trimer was done by a reaction with HCl and methanol—far easier to complete than the acid hydrolysis. The 58.0 mg. sample was heated with 1.112 mmole of HCl and 0.2 ml. of CH_3OH in a soda-lime glass tube for 15 hr. at 86°. The resulting H_2 was measured as 0.643 mmole (calcd., 0.638). The boric acid titration gave 0.318 mmole (calcd., 0.319). All of the HCl had been converted to CH_3Cl, so that the excess gas volume of the CH_3Cl–$(CF_3)_2PH$ fraction could be ascribed to $(CF_3)_2PH$: 0.326 mmole (calcd., 0.319). In a parallel experiment, 83.5 mg. of the trimer had been heated with aqueous methanol–HCl (8 days at 85°), and the $(CF_3)_2PH$ was isolated and fully identified: 0.459 mmole (calcd., 0.459). In this case the H_2 amounted to 0.916 mmole (calcd., 0.918).

Physical Properties of the Tetramer.—The less volatile phosphinoborine material, from the $(CF_3)_2PH$-B_2H_6 reaction with $(CH_3)_2O$, had a mol. wt. of 742 (calcd. for bis-trifluoromethyl-phosphinoborine tetramer, 727). The crystals, which melted sharply at 116°, were observed under a microscope and seemed to be orthorhombic. The vapor tensions of the solid, shown in Table IX, determined the equation $\log_{10} p_{mm} = 12.683 - 4489.2/T$.

Table IX

Vapor Tensions of Solid $[(CF_3)_2PBH_2]_4$

t (°C.)	45.5	54.4	75.7	82.0	89.9	98.4	104.9
p_{mm}(obsd.)	0.04	0.10	0.66	1.10	2.11	4.00	6.44
p_{mm}(calcd.)	0.04	0.10	0.66	1.11	2.09	4.00	6.46

Analysis of the Tetramer.—A sample of the tetramer, roughly estimated as 23 mg., was sublimed into a soda-lime glass seal-off tube, into which 0.609 mmole of HCl and 0.3 ml. of methanol were condensed. The sealed tube was heated for 7 days at 93° and then yielded 0.268 mmole of H_2, 0.131 mmole of $(CF_3)_2PH$ (fully identified by its 6.5 mm. vapor tension at −78°) and methyl borate titrating as 0.136 mmole. These results would correspond to 24.3 mg. of $[(CF_3)_2PBH_2]_4$; calcd. values, 0.267, 0.134 and 0.134, respectively.

Los Angeles 7, California

(13) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 3899 (1954).

[Contribution from the Department of Chemistry, The Johns Hopkins University* and the Knolls Atomic Power Laboratory, General Electric Company†]

A Mass Spectrometric Appearance Potential Study of Isotopically Labeled Diboranes[1]

By W. S. Koski,* Joyce J. Kaufman,* C. F. Pachucki† and F. J. Shipko†

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The appearance potentials of the molecule ions formed by electron impact from B_2H_6, $B^{10}{}_2H_6$, B_2D_6 and $B^{10}{}_2D_6$ have been measured mass spectrometrically. A set of apparently self-consistent ionization potentials for these molecule ions has been estimated from the appearance potentials of the B^{10} enriched compounds. The resulting calculated ionization potentials for the fragments from $B^{10}{}_2H_6$ are compared with the ionization potentials the authors estimate for fragments from $B^{10}{}_2D_6$ and are also compared with the results obtained from C_2H_6. The mass spectra of B_2H_6, $B^{10}{}_2H_6$, B_2D_6 and $B^{10}{}_2D_6$ were also run at 70 e.v. ionizing voltage in order to obtain a set of fragmentation patterns of the isotopically labeled diboranes under identical conditions; from these the monoisotopic spectrum of each type of diborane was calculated.

The method of obtaining 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 spectrometrically 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. A necessary condition for the above equation to hold true is $I(R_1) < I(R_2)$.[2] If $I(R_1) > I(R_2)$, then $A(R_1^+) > I(R_1) + D(R_1 - R_2)$. In order to interpret correctly the appearance potentials of fragment ions, it is necessary to know what neutral fragments are simultaneously formed and the states of electronic excitation of the neutral 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.

There have been two recent papers[3] in which the investigators have reported the appearance potentials of some boron compounds, but with the exception of assigning 10.9 e.v. as the $I(BH_3)$ by employing the relation

$$A(BH_3^+) = I(BH_3) + D(BH_3 - BH_3)$$

and using $D(BH_3 - BH_3)$ the dissociation energy of a B_2H_6 into two BH_3 fragments (28.4 ± 2 kcal./mole),[4] no calculations have been published in this field.

We have measured mass spectrometrically the appearance potentials of the molecule ions formed by electron impact from B_2H_6, $B^{10}{}_2H_6$, B_2D_6 and $B^{10}{}_2D_6$. Unfortunately, no ionization potentials had ever been reported for any of the ions except B and an estimate for BH_3. We have attempted to calculate a self-consistent set of ionization potentials for these molecule ions formed from diborane using what thermochemical data were available, and have compared these results for fragments from B_2H_6 with those from C_2H_6 and B_2D_6.

The progress on the electron impact induced dis-

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

(3) (a) R. W. Law and J. L. Margrave, *J. Chem. Phys.*, **25**, 1086 (1956); (b) J. L. Margrave, *J. Phys. Chem.*, **61**, 38 (1957).

(4) R. E. McCoy and S. H. Bauer, This Journal, **78**, 2061 (1956).

sociations 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 the great added disadvantage that 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 hydrogen atoms may exist.

We have done our calculations on the boron compounds 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.

Experimental

The instrument used to measure the appearance potentials was a General Electric Analytical Mass Spectrometer. Our instrument normally employs 70 volt ionizing electrons; its accelerating potential is 2000 volts; magnetic scanning is used while the accelerating voltage is held constant. The mass spectrometer was modified to allow us to read the appearance potentials using a Leeds and Northrup Precision Potentiometer. A gold-plated ion source was used.

The diborane sample was admitted into the expansion volume and scanned through its entire mass range, the source being adjusted to give maximum peak heights for each of the fragments. This scan was used to determine the cracking pattern of the sample. A second scan was then run holding the source constant for all the ion fragments of the diborane. An internal standard (argon) was then admitted to coincide with each of the diborane peak heights from the lowest to the highest. The appearance potential of the argon and of a diborane peak was determined under exactly the same conditions. The point at which current flow was first detectable was used as the basis for these determinations. Using known spectroscopic values for the internal standard, a correction was determined. This correction was then applied to the unknown, giving its appearance potential. In samples where a mass 20 peak was present, it was impossible to use argon as an internal standard due to the presence of doubly ionized argon at mass 20. Under these circumstances a separate sample was taken using krypton as an internal standard.

The diborane and deuterated diborane were prepared by reaction of $LiAlH_4$ or $LiAlD_4$ with boron trifluoride–ethyl ether and purified as described previously.[5] The B^{10} enriched compounds were made by the same procedure using $B^{10}F_3$ obtained by heating $CaF_2 \cdot B^{10}F_3$.

Calculations and Results

Table I presents the appearance potentials of the fragments formed by electron impact from normal diborane and B^{10} enriched diborane.

For this first series of calculations we have used the values of the appearance potentials of molecule ions from $B^{10}{}_2H_6$ ($\sim$ 96% B^{10}) to lessen the chances of ambiguity which could arise from using the appearance potentials of molecule ions from B_2H_6 with normal isotopic abundance of boron.

$B^{10}{}_2H_6$

$B_2H_6^+$.—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),[6] therefore we assign $I(B_2H_6) = 11.9$ e.v.

$B_2H_5^+$.—There are two completely different types of boron–hydrogen bonds in the boron hydrides. There are hydrogen atoms bonded to boron by normal covalent B–H bonds called terminal hydrogens, 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. Either a terminal or a bridge hydrogen could dissociate to form B_2H_5; however, since it takes less energy to break a terminal B–H bond, 4.04 e.v., as compared to the energy necessary to withdraw a bridge H, 4.66 e.v.,[7] we believe a terminal hydrogen is the one which comes off. This is in analogy to hydrocarbon dissociation by electron impact where a tertiary hydrogen comes off before a secondary hydrogen, and a secondary hydrogen comes off in preference to a primary hydrogen in just the reverse order of the bond strengths.

TABLE I

APPEARANCE POTENTIALS OF THE FRAGMENTS FORMED BY ELECTRON IMPACT FROM NORMAL DIBORANE AND B^{10} ENRICHED DIBORANE

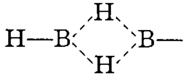
m/e	Appearance potential, e.v. B_2H_6	$B_2{}^{10}H_6$	Ion from $B_2{}^{10}H_6$
28	12.9 ± 0.5		
27	11.9 ± .2		
26	12.2 ± .2	11.9 ± 0.1	$B_2H_6^+$
25	12.6 ± .2	11.9 ± .1	$B_2H_5^+$
24	13.4 ± .2	12.3 ± .1	$B_2H_4^+$
23	14.0 ± .2	14.2 ± .1	$B_2H_3^+$
22	14.4 ± .2	13.8 ± .1	$B_2H_2^+$
21	22.3 ± .5	20.1 ± .1	B_2H^+
20		21.1 ± .2	B_2^+
13	13.2 ± .2	13.1 ± .2	BH_3^+
12	13.4 ± .2	13.4 ± .1	BH_2^+
11	18.0 ± .2	14.9 ± .1	BH^+
10	18.9 ± .2	18.7 ± .1	B^+

The I(H), 13.6 e.v.,[8] is greater than any value which would be calculated for $I(B_2H_5)$ and as a result the following relation should hold true

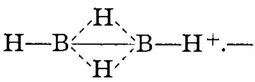
$$I(B_2H_5) = A(B_2H_5^+) - D(B_2H_5\text{–}H) = 7.8_6 \text{ e.v.}$$

(We shall take the liberty of carrying the extra decimal place throughout our calculations.)

$B_2H_4^+$.—There are several possible energy values which can be calculated for $I(B_2H_4)$ depending upon the choice of structure of the molecule ion and what fragments are presumed to be formed in the dissociation. Either 2H or H_2 can be formed in this step, but the I(H) or the $I(H_2)$ (15.4 e.v.) are both higher than the calculated $I(B_2H_4)$ values.


$H\text{—}B(H)_2B\text{—}H^+$.—The first choice of structure for a molecule ion is one in which two terminal B–H bonds have been broken. We have no way of distinguishing the difference in energy between $D(B_2H_5\text{–}H)$ and $D(B_2H_4\text{–}H)$ and for the dissociation of all terminal B–H bonds we have simply used the average dissociation energy, 4.04 e.v. For this structure

$$I(B_2H_4) = A(B_2H_4^+) - 2D(\text{B–H}) + D(H_2) = 8.7_0 \text{ e.v.}$$


$H\text{—}B(H)_2B\text{—}H^+$.—In addition to the formation

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[5] Joyce J. Kaufman and W. S. Koski, *J. Chem. Phys.*, **24**, 403 (1956).

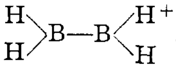
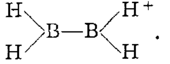
[6] D. P. Stevenson and J. A. Hipple, Jr., THIS JOURNAL, **64**, 1588 (1942).

[7] M. B. Wallenstein and E. J. Prosen, "Bond Energies and Heats of Formation of Some Boron Compounds," National Bureau of Standards Report 3455 (corrected) June 30, 1954.

[8] Charlotte E. Moore, "Atomic Energy Levels Vol. I," National Bureau of Standards Circular 467, June 15, 1949.

of H_2 in the above step, it is also possible to form a B–B bond after the two terminal hydrogens are removed from the diborane molecule. For the value of a single B–B bond in these compounds, we shall use the value $D(B\text{–}B) = 3.47$ e.v.[7] This would give

$$I(B_2H_4) = A(B_2H_4^+) - 2D(B\text{–}H) + D(H_2) + D(B\text{–}B) = 12.1_7 \text{ e.v.}$$

However, still another possibility exists if the molecule ion looks like  .—This would arise from the dissociation of two B–H bonds (we still feel that the terminal B–H bonds may dissociate first, since in the hydrocarbons the C–H bonds which dissociate first are the ones with the lowest bond energy). The dissociation of two B–H bonds would then be followed by a rapid intramolecular rearrangement to  . The bonding of this molecule ion would be simliar to that of B_2Cl_4. This arrangement would involve the formation of one B–B bond, the breaking of two B- -H- -B bridge bonds and the reformation of two B–H terminal bonds. The net result would be the same as if two bridge bonds were broken and a B–B bond formed.

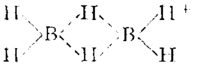
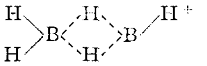
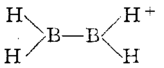
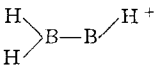
$$I(B_2H_4) = A(B_2H_4^+) + D(H_2) - 2D(B\text{- -}H\text{- -}B) + D(B\text{–}B) = 10.9_3 \text{ e.v.}$$

$I(B_2H_4)$ could equal 8.7_0, 12.1_7 or 10.9_3 e.v. Our choice for the most likely value is $I(B_2H_4) = 10.9_3$ e.v. because we have the feeling that the correct structure for the molecule ion may well be the last one.

There are a number of possible choices for the processes taking place and for various structures of the lower fragment ions which in turn lead to a number of choices for the calculated ionization potentials. In Table II we have listed the processes we assume to be taking place in each case and the calculated ionization potentials for the configurations indicated.

Table II

Processes, Configurations and Calculated Ionization Potentials for Various Diborane Fragments

Ion	Process	Configuration	I.P., e.v.
$B_2H_6^+$	$B_2H_6 + e \rightarrow B_2H_6^+ + 2e$		11.9
$B_2H_5^+$	$B_2H_6 + e \rightarrow B_2H_5^+ + H + 2e$		7.8_6
$B_2H_4^+$	$B_2H_6 + e \rightarrow B_2H_4^+ + H_2 + 2e$		10.9_3
$B_2H_3^+$	$B_2H_6 + e \rightarrow B_2H_3^+ + H_2 + H + 2e$		8.7_9
$B_2H_2^+$	$B_2H_6 + e \rightarrow B_2H_2^+ + 2H_2 + 2e$	H- - -B=B- - -H$^+$	11.3_6
B_2H^+	$B_2H_6 + e \rightarrow B_2H^+ + 2H_2 + H + 2e$	H—B—B$^+$	10.6_2
B_2^+	$B_2H_6 + e \rightarrow B_2^+ + 3H_2 + 2e$	B—B$^+$	12.0_6

$B_2H_2^+$.—In the formation of the $B_2H_2^+$ from diborane the terminal hydrogens may break off first, followed by a rearrangement to the structure H–B=B—H$^+$. If we could label diborane with deuterium in any one specified position and the deuterium would stay put, we might be able to resolve the dilemma of which hydrogen bonds break first. But even if we could place the deuterium in a specified position, the self-exchange of B_2H_6 and B_2D_6 is so rapid even at room temperature[9] that the deuterium would just be statistically distributed. (In this case we have used the lower value of 3.00 e.v. for $D(B\text{–}B)$).

B_2^+.—The $D(B\text{–}B)$ in the B_2 molecule has been found to be either 3.48[10] or 3.00 e.v.[11] The latter value appears to be more acceptable for the B_2 molecule itself.[7]

Up to the $C_2H_2^+$ or the $B_2H_2^+$ ions we have made the same assumptions for the final state of the hydrogen extracted from the diborane molecule as other investigators have postulated for the hydrogen extracted from the ethane molecule.[6,12]

There seem to be some regularities in this series of our calculated ionization potentials for the molecule ions formed from diborane when compared to the molecule ions from ethane.[13]

The values for which there can be little ambiguity are certainly $I(B_2H_6)$ and probably $I(B_2H_5)$. Comparing these values to those of ethane, the $I(B_2H_6)$ and $I(C_2H_6)$ are quite close with $I(B_2H_6)$ being a little higher. The $I(B_2H_5)$ is on the order of one electron volt lower than $I(C_2H_5)$.

The other ionization potentials for the molecule ions from diborane listed in Table III are the values calculated by us which we feel may correspond to the most nearly correct mechanism for the formation of each molecule ion. For the ionization potentials of diborane molecule ions containing even numbers of hydrogens we get values close to and just a little higher than the values for corresponding hydrocarbon molecule ions containing the same even numbers of hydrogen atoms. For the ionization potentials of molecule ions from diborane containing odd numbers of hydrogen atoms we get values about 1 e.v. lower than the corresponding values for the carbon compounds.

The same types of calculations were performed for the ionization potentials of the molecule ions from $B_2{}^{10}D_6$. Listed in Table IV are the appearance potentials of the fragments formed by electron impact from deuterated diborane and B^{10} enriched deuterated diborane.

In Table III a comparison is made of the appearance potentials of the corresponding ions from $B^{10}{}_2H_6$ and $B^{10}{}_2D_6$ with their ionization potentials calculated by the same mechanism for each pair of molecule ions. In most cases the appearance potentials and calculated ionization potentials of

[9] P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

[10] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950.

[11] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman-Hall, London, 1947.

[12] J. A. Hipple, *Phys. Rev.*, **53**, 530 (1938).

[13] G. C. Ellenton, *J. Chem. Phys.*, **15**, 455 (1947).

TABLE III

COMPARISON OF SIMILAR FRAGMENTS FORMED BY ELECTRON IMPACT FROM DIBORANE AND DEUTERATED DIBORANE WITH THOSE FORMED FROM ETHANE

E.v.			E.v.			E.v.		
Ion	*I*	*A* from $B^{10}_2H_6$	Ion	*I*	*A* from $B^{10}_2D_6$	Ion	*I*	*A* from C_2H_6
$B_2H_6^+$	11.9	11.9 ± 0.1	$B_2D_6^+$	12.0	12.0 ± 0.1	$C_2H_6^+$	11.6	11.6 ± 0.1
$B_2H_5^+$	7.8_6	11.9 ± .1	$B_2D_5^+$	8.0_1	12.1 ± .1	$C_2H_5^+$	8.7	12.9 ± .2
			$B_2D_4H^+$	7.9_1	12.0 ± .1			
$B_2H_4^+$	10.9_3	12.3 ± .1	$B_2D_4^+$	10.9_0	12.3 ± .1	$C_2H_4^+$	10.8	12.1 ± .1
			$B_2D_3H^+$	10.9_0	12.3 ± .1			
$B_2H_3^+$	8.7_9	14.2 ± .1	$B_2D_3^+$	8.8_1	14.3 ± .1	$C_2H_3^+$	9.9	15.2 ± .3
			$B_2D_2H^+$	8.7_1	14.2 ± .1			
$B_2H_2^+$	11.3_6	13.8 ± .1	$B_2D_2^+$	11.5_0	14.0 ± .1	$C_2H_2^+$	11.2	15.0 ± .3
			B_2DH^+	11.5_0	14.0 ± .1			
B_2H^+	10.6_2	20.1 ± .1	B_2D^+	11.7_1 8.7_1	18.3 ± .1	C_2H^+	11.3	27.0 ± 1.0
B_2^+	12.0_6	21.1 ± .1	B_2^+	12.6_7	21.8 ± .2	C_2^+	12	31.5 ± 1.0

TABLE IV

APPEARANCE POTENTIALS OF THE FRAGMENTS FORMED BY ELECTRON IMPACT FROM DEUTERATED DIBORANE AND B^{10} ENRICHED DEUTERATED DIBORANE

	Appearance potential, e.v.		
m/e	B_2D_6	$B^{10}_2D_6$	Ion from $B^{10}_2D_6$
32	12.1 ± 0.1	12.0 ± 0.1	$B_2D_6^+$
31	12.0 ± .1		
30	12.2 ± .1	12.1 ± .1	$B_2D_5^+$
29	12.4 ± .1	12.0 ± .1	$B_2D_4H^+$
28	12.9 ± .1	12.3 ± .1	$B_2D_4^+$
27	13.7 ± .1	12.3 ± .1	$B_2D_3H^+$
26	13.9 ± .1	14.3 ± .1	$B_2D_3^+$
25	13.9 ± .1	14.2 ± .1	$B_2D_2H^+$
24	14.2 ± .1	14.0 ± .1	$B_2D_2^+$
23	14.9 ± .2	14.0 ± .1	B_2DH^+
22	20.0 ± .2	18.3 ± .1	B_2D^+
21	23.3 ± .2		
20		21.8 ± .2	B_2^+
17	12.6 ± .2		
16		12.7 ± .2	BD_3^+
15	13.5 ± .1	13.6 ± .2	
14	13.5 ± .1	13.6 ± .1	BD_2^+
13	14.7 ± .1	14.2 ± .2	
12	15.2 ± .2	14.8 ± .1	BD^+
11	18.6 ± .1	19.0 ± .2	
10	18.7 ± .2	18.6 ± .1	B^+

corresponding ions are very close. There is a tendency for the potentials of the deuterated compounds to be just slightly higher than those for the protiated compounds. This difference of ~0.1 e.v. is something which might be expected in view of the difference of 0.12 to 0.18 e.v. found between $I(CD_4)$ and $I(CH_4)$.[14,15] However there is a discrepancy, the appearance potential of B_2H^+ is 1.8 e.v. higher than that of B_2D^+. At present we have no satisfactory explanation for this. There could be a subtle difference in the process taking place in the formation or ionization of B_2D^+ as compared to B_2H^+. This difference, if real, is still only apparent in the appearance potential of B_2D^+ from $B^{10}_2D_6$ and not in the appearance potential of B_2^+ from $B^{10}_2D_6$ which agrees to within experimental error with the appearance potential of B_2^+ from $B^{10}_2H_6$.

Now we should like to calculate ionization potentials for the BH_x ions. This is difficult because we do not know exactly what fragments are formed in these dissociations and we know nothing about the amounts of extra energy—electronic, vibrational or otherwise—possessed by these fragments.

The best interpretation that can be made of the $A(BH_3^+)$ is to set an approximate upper limit of $I(BH_3)$ in the neighborhood of 11–12 e.v.

It is not significant to carry the detailed analysis for BH_x^+ ions beyond this point because of the number of possible combinations involved. We are carrying out these further calculations merely as a matter of academic interest.

The electronic configurations for the lowest states of B, BH, BH_2 and BH_3 have been assigned. While no unambiguous order can be inferred from the electronic configurations, we feel the following order for the ionization potentials should be reasonable.

$$I(BH_3) > I(BH) > I(B) \cong I(BH_2)$$

$I(B)$ is known with great accuracy[8] and $I(BH_3)$ can be estimated using the known heat of dissociation of diborane. These values should at least serve to bracket $I(BH)$ and perhaps give an estimate of $I(BH_2)$.

Our calculations lead to

$$I(BH_3) \leqq 11\text{–}12 \text{ e.v.}$$
$$I(BH_2) \leqq 8.1_2 \text{ e.v.}$$
$$I(BH) \leqq 10.0_6 \text{ e.v.}$$

While these values are upper limits since we have no assumptions regarding excess energy, the order of the magnitudes of the ionization potentials is as expected.

We later checked this order by calculating the ionization potentials for the molecule ions produced by bombardment of BCl_3 where there is less chance for ambiguity in the fragments formed.

It can be seen in Table V that our calculated values for the ionization potentials of the boron–chlorine fragments have not only the same order as those for the boron–hydrogen fragments but to within experimental error have approximately the same values.[16]

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(14) F. P. Lossing, A. W. Tickner and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

(15) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *ibid.*, **22**, 621 (1954).

(16) The values of the ionization potentials of the BCl_x molecule ions were calculated from the quoted literature values. Very recent experimental studies indicate that these values may be altered somewhat.

TABLE V

COMPARISON OF THE CALCULATED IONIZATION POTENTIALS OF SIMILAR FRAGMENTS CONTAINING ONE B ATOM FORMED FROM DIBORANE AND FROM BORON TRICHLORIDE

From diborane	From boron trichloride
$I(BH_3) \leqq$ 11–12 e.v.	$I(BCl_3) \leqq$ 12.0 e.v.
$I(BH_2) \leqq 8.1_2$ e.v.	$I(BCl_2) \leqq$ 8.5 e.v.
$I(BH) \leqq 10.0_6$ e.v.	$I(BCl) \leqq$ 9.8 e.v.
$I(B) \equiv$ 8.296 e.v.	$I(B) \leqq$ 8.4 e.v.

The values for the appearance potentials for BD_x molecule ions are quite close to those of the BH_x ions in most cases. Again there is a discrepancy, this time just within the limits of our experimental error, of 0.4 e.v. between $A(BH_3^+)$ and $A(BD_3^+)$. While the error may be experimental, this discrepancy is worth noting because there may well be a fundamental difference in the nature of bridging of completely protiated and completely deuterated boron hydrides. Deuterated diborane is known to have a vapor pressure of 238 mm. at −112° compared to 225 mm. for diborane at this temperature, which is in line with the fact that the $A(BD_3^+)$ is lower than the $A(BH_3^+)$.

The ionization potentials of the fragments formed in the dissociation of diborane by electron impact were calculated from the appearance potentials of the B^{10} enriched compounds (containing 96% B^{10}) to avoid the complications in using diboranes with normal isotopic abundance of boron.

We have studied the lowest appearance potentials of the fragments from the diboranes containing the normal isotopic abundance for comparison purposes. Assignment of the molecule ions corresponding to each observed appearance potential of the B^{10} compounds has enabled us to correlate many of the observed appearance potentials resulting from the fragmentation of the normal diboranes with the appropriate molecule ion.

TABLE VII

MONOISOTOPIC MASS SPECTRA OF DIBORANES AND DEUTERATED DIBORANES

Relative abundance

Species	$B^{11}{}_2H_x$ (calcd. from normal diborane)	$B^{10}{}_2H_x$ (calcd. from B^{10} enriched diborane)	Species	$B^{11}{}_2D_x$ (calcd. from normal deuterated diborane)	$B^{11}{}_2D_xH$ (calcd. from normal deuterated diborane)	$B^{10}{}_2D_x$ (calcd. from B^{10} enriched deuterated diborane)	$B^{10}{}_2D_xH$ (calcd. from B^{10} enriched deuterated diborane)
B_2H_5	100.00	100.00	B_2D_5	100.00		100.00	
			B_2D_4H		12.67		8.34
B_2H_4	54.01	52.08	B_2D_4	49.20		46.96	
			B_2D_3H		5.14		3.10
B_2H_3	25.21	26.25	B_2D_3	25.42		24.71	
			B_2D_2H		1.91		0.89
B_2H_2	76.92	72.32	B_2D_2	72.36		67.63	
			B_2DH		2.48		2.21
B_2H	6.04	6.33	B_2D	4.98		4.15	
			B_2H		−0.02		0.04
B_2	2.75	2.47	B_2	1.59		1.24	

The second portion of this research was a comparison of the fragmentation patterns and monoisotopic spectrum calculations obtained from the mass spectra of B_2H_6, $B^{10}{}_2H_6$, B_2D_6 and $B^{10}{}_2D_6$. There is good agreement between our observed values for normal diborane and diborane containing 96% B^{10} and those obtained by Norton[17] and Margrave.[3b] The agreement between our observed values for deuterated diborane and the values reported by Dibeler, Mohler and Williamson[18] is quite good, in view of the fact these fragmentation patterns are very sensitive to a slight difference in total deuterium content. In Table VI is presented the cracking pattern of $B^{10}{}_2D_6$ throughout the entire mass range, since there are no previously reported values for this mass spectrum of this compound.

TABLE VI

FRAGMENTATION PATTERN OF $B^{10}{}_2D_6$ USING 70 VOLT ELECTRONS

Mass *m/e*	Relative abundance $B^{10}{}_2D_6$ (96% B^{10}) ~98% D
33	0.24
32	7.67
31	
30	100.00
29	12.17
28	46.90
27	5.12
26	24.71
25	6.47
24	67.30
23	2.53
22	4.12
21	0.14
20	1.23
17	0.13
16	1.46
15	1.34
14	21.80
13	1.17
12	9.45
11.5	
11	0.73
10	13.98
4	18.51
3	3.30
2	1.69

Table VII contains the monoisotopic spectra of the protiated diboranes calculated from normal diborane ($B^{11}{}_2H_x$) and from B^{10} enriched diborane ($B^{10}{}_2H_x$). These two spectra are quite similar and the ionization probabilities for $B^{11}{}_2$, $B^{11}B^{10}$ and

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(17) F. J. Norton, THIS JOURNAL, **71**, 3488 (1949).

(18) V. H. Dibeler, F. L. Mohler and Laura Williamson, *J. Re Natl. Bur. Standards*, **44**, 489 (1950).

$B^{10}{}_2$ molecules must be very nearly the same for each type of molecule.

Table VII also contains the monoisotopic spectra of the deuterated diboranes calculated from B_2D_6 ($B^{11}{}_2D_x$ and $B^{11}{}_2D_xH$) and from $B^{10}{}_2D_6$ ($B^{10}{}_2D_x$ and $B^{10}{}_2D_xH$). These samples contained 97–98% D and as a result there were some molecules of B_2D_5H originally present. There is no way to distinguish between ions from B_2D_6 and from B_2D_5H once the H atom has been removed and the contributions to B_2D_4, B_2D_3, B_2D_2, etc., are the sums of the fragments from the B_2D_6 and B_2D_5H molecules.

The agreement between the monoisotopic spectra of deuterated diborane calculated from B_2D_6 and $B^{10}{}_2D_6$ is quite good, especially in view of the fact that there were slightly different total percentages of deuterium in the two compounds.

A comparison of the values obtained for the monoisotopic spectra of the diboranes and the deuterated diboranes confirms the observation made previously on normal deuterated diboranes[17] that there is an isotope effect in the fragmentation of deuterated diborane. Due to the scarcity of parent ions $B_2X_6^+$ in the diborane mass spectra, no attempt has been made to calculate the weighing factors for the rupture of B–H or B–D bonds.

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Some Further Comments on the Properties of Bolaform Electrolytes

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The equilibrium and transport properties of bolaform electrolytes are considered with emphasis on the necessity for self-consistency of molecular parameters. It is shown that the application of the hydrodynamic theory of short chains leads to results in agreement with secondary dissociation constants and with the distribution of end to end distances. The diffusion coefficient of a bolaform electrolyte is calculated and the role of ion atmosphere asymmetry discussed, the result being: $\mathfrak{D} = \mathfrak{D}_0[1 + q_2q_1\kappa/2DkT + q_2q_1\kappa^2h/4DkT]$.

I. Introduction

From the structural point of view bolaform electrolytes partially bridge the gap between ordinary electrolytes and polymeric electrolytes. It is therefore to be anticipated that the properties of solutions of bolaform electrolytes will likewise be intermediate between the properties of solutions of small electrolytes and of polyions. For example, the very precise conductance measurements of Fuoss, *et al.*,[1–4] have demonstrated the existence of ion pair formation between the bolaform ion (bolion) and its counterions even in solvents such as water. The magnitude of the dissociation constant for the reaction

$$ {}^{+}\mathrm{BRB}^{+}\mathrm{C}^{-} \overset{K_2}{\rightleftarrows} {}^{+}\mathrm{BRB}^{+} + \mathrm{C}^{-} $$

varies with the dielectric constant in the expected manner,[1] and charge separations computed from the Bjerrum relation[5] for the ratio of the dissociation constants of a dibasic acid are consistent with the known structures of the bolions. It has been proposed that the phenomena of ion pair formation in bolaform electrolytes[6] is closely related to a similar phenomenon observed in solutions of polyelectrolytes.[7–9] A study of the equilibrium and transport properties of bolaform electrolytes therefore has relevance for the analogous but much more difficult problems arising in the consideration of these same properties of polyelectrolytes. In this communication we shall extend our previous discussion[6] to an examination of the magnitude of the ion pair dissociation constant, of the limiting conductance and of the concentration dependence of the frictional coefficient in dilute solution. Throughout our emphasis will be on the necessity for internal consistency between molecular parameters deduced from equilibrium and non-equilibrium properties in a manner rather different from the classical analysis of Fuoss.[1,3]

II. The Secondary Dissociation Constant as a Function of Chain Length

We consider first the ion pair dissociation constants and the intercharge separations required to fit the experimental data. The dissociation equilibrium discussed in section I may be characterized by the mass action expression

$$ K_2 = c_{\mathrm{c}^-}\frac{K_{\mathrm{s}}{}^0(2\alpha - 1) + \alpha c_{\mathrm{c}^-}}{2K_{\mathrm{s}}{}^0(1 - \alpha)} \qquad (1) $$

where $K_{\mathrm{s}}{}^0$ is the intrinsic dissociation constant for the group in question ($K_1 = 2K_{\mathrm{s}}{}^0$), α is the degree of dissociation and c_{c^-} is the concentration of the counterions to the bolion. The relationship between the degree of dissociation α and the electrostatic energy of interaction, χ, readily can be shown to be[6]

$$ \alpha = \frac{\lambda + \lambda^2 e^{-\chi/kT}}{1 + 2\lambda + \lambda^2 e^{-\chi/kT}} \qquad (2) $$

where λ plays the role of an absolute activity. In general, the relation required for closure of the set of equations is

$$ \ln a_{\mathrm{c}^-} + \ln \lambda - \ln K_{\mathrm{s}}{}^0 = 0 \qquad (3) $$

where a_{c^-} is the activity of the counterions. Equations 2 and 3 suffice for the calculation of the counterion activity or, if this is known, of

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(2) R. M. Fuoss and V. H. Chu, *ibid.*, **73**, 949 (1951).
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(4) O. V. Brody and R. M. Fuoss, *J. Phys. Chem.*, **60**, 156 (1956).
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