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Fragmentation of Tetraborane by Electron Impact[1]

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The fragmentation of the isotopically labeled tetraboranes, $B^{11}_4H_{10}$, $B^{11}_4D_{10}$ and $B_4H_8D_2$ by electron impact has been studied. A preferred path of decomposition and structures of the fragment ions are proposed from the observed fragmentation patterns and the numerous metastable transitions. Using these structures and the measured appearance potentials of selected fragments, ionization potentials are calculated. Metastable transitions involving the loss of 3H or 3D, not found in hydrocarbon mass spectra, are observed.

Introduction

Ionization and dissociation of complex molecules by electron impact give rise to "fragmentation patterns" or mass spectra characteristic of each molecule. Attempts have been made in previous years to develop a theory of mass spectra,[2,3] using the concept that the fragment ions result from a series of competing consecutive unimolecular decompositions of excited parent ions.[4]

As there is a time lag between ion formation and collection, decompositions with the proper rate constant (about 10^6 sec.$^{-1}$)[5] may occur outside the ionization region, after acceleration but before collection. Decompositions occurring in this manner are observed as small diffuse peaks, generally at non-integral mass numbers, whose intensity varies linearly with the sample pressure. The apparent mass of these so-called metastable transitions is given by $m^* = m_2^2/m_1$, where m_2 is the final mass of the charged fragment and m_1 the initial mass.[6] As some of these ions decompose in the ionizing region, some after acceleration and some not at all, peaks corresponding to the initial and final fragments will also be observed.

On the basis of the theory above, one can show that the appearance of metastable transitions indicates an energetically preferred route of decomposition of the various ions.[3] However, as an ionizing voltage of 70 v. is generally used in obtaining mass spectra, the ions may be sufficiently excited for decompositions to occur by other routes.

Appearance potential studies of isotopically substituted diborane, pentaborane-9 and decaborane have been made.[7-9] The monoisotopic fragmentation patterns were given, but no metastable transitions were reported. Dibeler reported the presence of two metastable transitions in B_2D_6 and one in B_2H_6 in the mass spectra of these compounds.[10] Therefore it was thought that a more general study of the fragmentation of the boron hydrides, including an examination of metastable transitions, would be useful in gaining insight into the structures and properties of the ions produced by electron impact. The following is the result of work on tetraborane.

Experimental

A standard Consolidated 21-103C mass spectrometer was used to obtain the data presented.

(1) This work was done under the auspices of the United States Atomic Energy Commission.

(2) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Natl. Acad. Sci.*, **38**, 667 (1952).

(3) H. M. Rosenstock, *J. Chem. Phys.*, **23**, 2200 (1955).

(4) M. B. Wallenstein, Doctoral Thesis, University of Utah, 1951.

(5) J. A. Hipple, *Phys. Rev.*, **71**, 594 (1947).

(6) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960.

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

(8) J. J. Kaufman, W. S. Koski, L. J. Kuhns and S. S. Wright, Division of Inorganic Chemistry, 140th National Meeting of the American Chemical Society, September, 1961.

(9) J. J. Kaufman, W. S. Koski, L. J. Kuhns and R. W. Law, *J. Am. Chem. Soc.*, **84**, 4198 (1962).

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

The isotopically labeled tetraboranes were obtained by pyrolysis of labeled diboranes, previously prepared in this Laboratory.[11] However, a different manner of purification was employed. A co-distillation–fractionation apparatus, similar to one described by Cady and Seigwarth, was constructed.[12] With this apparatus, small amounts of the desired boron hydride could be obtained in an exceptionally pure state. Mass spectral analysis showed the total impurities to be less than 0.2%.

The dideuteriotetraborane was prepared using information obtained by Todd and Koski on the exchange reaction between tetraborane and deuterated diborane.[13] In their work, they found that the exchange reaction was occurring along two paths with differing rates. The path with the faster rate involved two protons and the other involved eight protons. It was then possible to choose conditions that maximized the ratio of the two rates in favor of the exchange involving two protons. In a typical experiment in which the temperature was 45°, the pressure of the B_2D_6 was 9 mm. and that of the B_4H_{10} was 3 mm. The products were immediately separated on the fractionation apparatus and the diborane and tetraborane trapped for analysis on the spectrometer.

Results

The spectra of $B^{11}_4H_{10}$, $B^{11}_4D_{10}$ and $B_4H_8D_2$ are presented in Table I. From these data the true monoisotopic spectrum for the B_4 fragments in the case of $B^{11}_4H_{10}$ and $B^{11}_4D_{10}$ was calculated by stripping 1.34% B^{10} from the protonated sample and 1.34% B^{10} and 1.88%H from the deuterated sample in the customary manner.[10,14] The maximum B^{10} content was determined from the m/e 10 and 11 peaks.[9] The H content was taken as the maximum value possible, using a B^{10} content of 1.34%, without obtaining negative residues. The results are given in Table II.

It is to be noted that no peak corresponding to the parent ion of relative intensity greater than 0.05% was observed from an ionizing voltage of 70 to 10 v., either in the protonated or deuterated samples. A peak of relative intensity 0.02 to 0.04% was observed, but could not be definitely assigned to the parent ion. However, small $B_4H_9^+$ and $B_4D_9^+$ peaks of relative intensities, 0.4% and 0.5%, respectively, were observed. The relative rates of decay of the m/e 53 and m/e 52 peaks were determined as a function of time for $B^{11}_4H_{10}$. The rates were found to be equal, which indicates both peaks result from the same compound. This species was previously unobserved.

The spectrum of tetraborane that had been allowed to react with B_2D_6 was analyzed in the following manner. The amount of D that had exchanged was calculated from the spectrum of the B_2D_6 after the exchange had taken place. From this, the amount of unreacted B_4H_{10} could be calculated and its contribution to the spectrum removed. The contribution from the B^{10} isotope was then stripped from the remainder, thus leaving the monoisotopic fragmentation pattern of $B^{11}_4H_8D_2$. The result is also given in Table II.

The metastable transitions observed are listed in Table III. They were identified both by their diffuse appearance at non-integral mass numbers and by the change in relative intensity with differing collector slit

(11) J. J. Kaufman and W. S. Koski, *J. Chem. Phys.*, **24**, 403 (1956).

(12) G. H. Cady and D. P. Seigwarth, *Anal. Chem.*, **31**, 620 (1959).

(13) J. E. Todd and W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2319 (1959).

(14) V. H. Dibeler, F. L. Mohler, L. Williamson and R. M. Reese, *J. Research Natl. Bur. Standards*, **43**, 97 (1949).
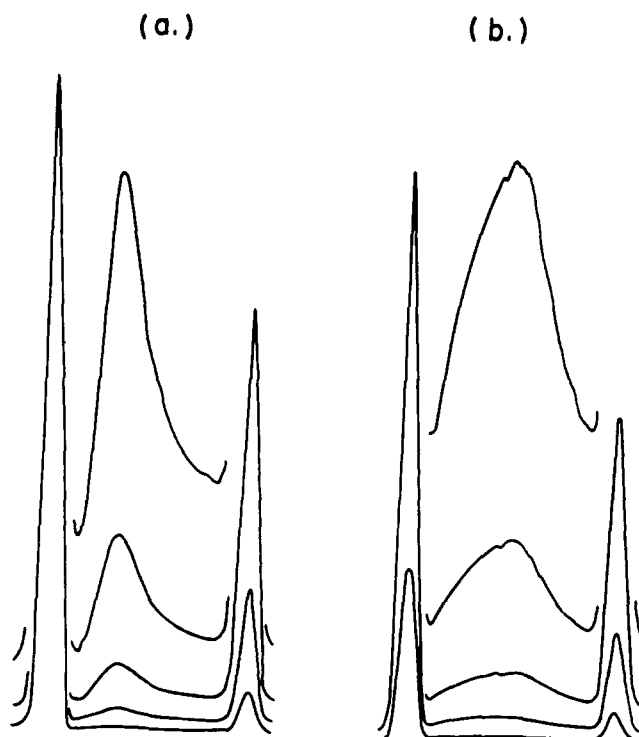
(a.)   (b.)

Fig. 1.—Part of the $B^{11}_4D_{10}$ spectrum showing the m/e 52.3 (a) and the m/e 48.3 and 48.6 (b) metastable transition peaks.

TABLE I

SPECTRA OF $B^{11}_4H_{10}$, $B^{11}_4D_{10}$ AND $B_4H_8D_2$

$B^{11}_4H_{10}$ (1.34% B^{10})		$B^{11}_4D_{10}$ (1.34% B^{10}, 1.88% H)				$B_4H_8D_2$ (20% B^{10})	
m/e	Rel. intens.	m/e	Rel. intens.	m/e	Rel. intens.	m/e	Rel. intens.
53	0.4	62	0.4	35	3.9	54	22.9
52	8.2	61	0.1	34	0.2	53	20.5
51	13.4	60	8.7	33	1.7	52	25.1
50	100	59	1.8	32	4.6	51	37.1
49	18.7	58	13.2	31	0.5	50	100
48	58.9	57	2.3	30	1.5	49	96.2
47	21.6	56	100	29	0.3	48	82.3
46	16.4	55	15.5	28	11.1	47	66.8
45	11.3	54	12.3	27	0.5	46	47.2
44	5.8	53	1.9	26	6.8	45	34.1
43	0.4	52	52.7	25	0.4	44	23.6
		51	6.4	24	1.8	43	10.9
41	0.2	50	13.9	23	0.1	42	4.0
		49	1.9	22	0.7		
39	2.3	48	12.5	17	0.1	40	12.0
38	14.0	47	1.1	16	0.3	39	20.5
37	6.9	46	8.2	15	18.2	38	28.5
36	11.9	45	3.0	14	1.6	37	32.3
35	10.9	44	4.0	13	5.3	36	33.0
34	2.9	43	24.7	12	0.2	35	33.4
33	1.4	42	3.2	11	17.1	34	20.0
		41	9.3	10	0.2	33	9.6
29	0.1	40	1.0				
28	0.3	39	18.6				
27	2.3	38	1.6				
26	0.8	37	17.4				
25	2.0	36	1.2				
24	3.1						
23	0.4						
14	0.6						
13	7.0						
12	1.8						
11	9.1						
10	0.1						

TABLE II

MONOISOTOPIC SPECTRA OF $B^{11}_4H_{10}$, $B^{11}_4D_{10}$ AND $B^{11}_4H_8D_2$

$B^{11}_4H_{10}$ (0% B^{10})		$B^{11}_4D_{10}$ (0% B^{10})		$B^{11}_4H_8D_2$ (0% B^{10})	
Ion	Rel. intens.	Ion	Rel. intens.	m/e	Rel. intens.ᵃ
$B_4H_9^+$	0.4	$B_4D_9^+$	0.5	54	19.4
$B_4H_8^+$	8.2	$B_4H_8^+$	9.1	53	0
$B_4H_7^+$	13.1	$B_4D_7^+$	13.5	52	15.0
$B_4H_6^+$	100	$B_4D_6^+$	100	51	16.6
$B_4H_5^+$	13.6	$B_4D_5^+$	11.0	50	64.4
$B_4H_4^+$	58.3	$B_4D_4^+$	56.6	49	15.9
$B_4H_3^+$	18.5	$B_4D_3^+$	13.7	48	34.4
$B_4H_2^+$	15.4	$B_4D_2^+$	11.6	47	17.4
$B_4H_1^+$	10.6	$B_4D_1^+$	7.4	46	11.9
B_4^+	5.2	B_4^+	3.6	45	10.4
				44	5.6

ᵃ Normalized to m/e 45 = 10.4.

TABLE IIIa

METASTABLE TRANSITIONS OBSERVED IN $B^{11}_4H_{10}$

Transition	Rel. intens.	m^* exptl.
$BH_2^+ \rightarrow B^+ + H_2$	0.002	9.3
$BH^+ \rightarrow B^+ + H$	.007	10.1
$B_3H_2^+ \rightarrow B_3^+ + H_2$	.002	31.1
$B_3H_4^+ \rightarrow B_3H_2^+ + H_2$	.08	33.1
$B_3H_5^+ \rightarrow B_3H_3^+ + H_2$	.25	34.1
$B_3H_6^+ \rightarrow B_3H_4^+ + H_2$	.08	35.1
$B_4H_2^+ \rightarrow B_4^+ + H_2$	.10	42.1
$B_4H_3^+ \rightarrow B_4H^+ + H_2$	.16	43.1
$B_4H_4^+ \rightarrow B_4H_2^+ + H_2$	.19	44.1
$B_4H_5^+ \rightarrow B_4H_3^+ + H_2$	.23	45.1
$B_4H_7^+ \rightarrow B_4H_4^+ + H_2 + H$	.23	45.2
$B_4H_8^+ \rightarrow B_4H_5^+ + H_2 + H$	1.37	46.2
$B_4H_7^+ \rightarrow B_4H_5^+ + H_2$	0.61	47.1
$B_4H_8^+ \rightarrow B_4H_6^+ + H_2$	1.03	48.1

size. The ratio of the intensity with the 30-mil slit to the intensity with the 7-mil slit is 1.8 for a normal peak. For the metastable peaks it is 3 to 4 on the spectrometer used. The difference in relative intensity occurs because metastable ions are spread over a greater width in the plane of the collector slit than are normal ions. In the instrument used, the repeller voltage is a certain fraction of the accelerating voltage and, as metastable peaks are sensitive to this voltage, the intensity of the metastable peaks will be some function of the accelerating voltage.

The apparent mass of each transition was determined using the 7-mil slit for greater resolution. Figure 1a shows a reproduction of the peak 52.3 in $B^{11}_4D_{10}$. In three cases there were two metastable peaks between two mass numbers. These occurrences were easily seen, at least in the deuterated case, by comparison. Figure 1b shows the 48.6 and 48.3 transitions while Fig. 1a shows the single 52.3 transition in $B^{11}_4D_{10}$. The fragments involved in a metastable transition were determined from the equation $m^* = m_2^2/m_1$ and it was found m^* (experimental) $= m^*$ (calculated) $\pm$ 0.05. The appearance potentials were measured for the strongest transitions and, as the appearance potential of the metastable transition peak equals the appearance potential of the daughter ion peak involved in the transition, the transition could be identified exactly.[15]

The appearance potentials of selected fragments and metastable transitions are given for the protonated and deuterated cases in Table IV. The values were determined both by the vanishing current method and log ion current $vs.$ voltage plots. The curves were run with a calibrating gas, either xenon or krypton, and by using the spectroscopic ionization potentials of the rare gases (12.06 and 13.96 v., respectively) the appearance potential for the ion in question was calcu-

(15) R. E. Fox and A. Langer, J. Chem. Phys., 18, 460 (1950).

TABLE IIIb
METASTABLE TRANSITIONS OBSERVED IN $B^{11}{}_4D_{10}$

Transition			Rel. intens.	m^* exptl.
$BD_2{}^+$	$\rightarrow B^+$	$+ D_2$	0.002	8.0
BD^+	$\rightarrow B^+$	$+ D$	.006	9.3
$B_2D_4{}^+$	$\rightarrow B_2D_2{}^+$	$+ D_2$	.002	22.5
$B_2D_5{}^+$	$\rightarrow B_2D_3{}^+$	$+ D_2$	.006	24.5
$B_4D_2{}^+$	$\rightarrow B_3D_2{}^+$	$+ B$	.004	28.5
$B_3D_2{}^+$	$\rightarrow B_3{}^+$	$+ D_2$	.004	29.5
$B_3D_3{}^+$	$\rightarrow B_3D^+$	$+ D_2$	.006	31.5
$B_3D_4{}^+$	$\rightarrow B_3D_2{}^+$	$+ D_2$	.11	33.4
$\lbrace B_3D_4H^+$	$\rightarrow B_3D_2H^+$	$+ D_2$	.06	34.4
$\lbrace B^{11}{}_2B^{10}D_5{}^+$	$\rightarrow B^{11}{}_2B^{10}D_3{}^+$	$+ D_2$		
$B_3D_5{}^+$	$\rightarrow B_3D_3{}^+$	$+ D_2$	.34	35.4
$B_3D_6{}^+$	$\rightarrow B_3D_4{}^+$	$+ D_2$	.11	37.4
$B_4D_2{}^+$	$\rightarrow B_4{}^+$	$+ D_2$	.14	40.3
$B_3D_8{}^+$	$\rightarrow B_3D_5{}^+$	$+ D_2$	.07	41.3
$B_4D_3{}^+$	$\rightarrow B_4D^+$	$+ D_2$	.20	42.3
$B_4D_4{}^+$	$\rightarrow B_4D_2{}^+$	$+ D_2$	.20	44.3
$B_4D_5{}^+$	$\rightarrow B_4D_3{}^+$	$+ D_2$	.16	46.3
$B_4D_7{}^+$	$\rightarrow B_4D_4{}^+$	$+ D_2 \; + D$	.16	46.6
$\lbrace B_4D_6H^+$	$\rightarrow B_4D_3H^+$	$+ D_2 \; + D$	.16	47.5
$\lbrace B^{11}{}_3B^{10}D_7{}^+$	$\rightarrow B^{11}{}_3B^{10}D_4{}^+$	$+ D_2 \; + D$		
$B_4D_6{}^+$	$\rightarrow B_4D_4{}^+$	$+ D_2$	$\sim.9$	48.3
$B_4D_8{}^+$	$\rightarrow B_4D_5{}^+$	$+ D_2 \; + D$	1.62	48.6
$B_4D_6H^+$	$\rightarrow B_4D_4{}^+$	$+ HD + D$	0.74	49.3
$B_4D_7{}^+$	$\rightarrow B_4D_5{}^+$	$+ D_2$	.53	50.3
$\lbrace B_4D_7H^+$	$\rightarrow B_4D_5H^+$	$+ D_2$	.69	51.3
$\lbrace B^{11}{}_3B^{10}D_8{}^+$	$\rightarrow B^{11}{}_3B^{10}D_6{}^+$	$+ D_2$		
$B_4D_8{}^+$	$\rightarrow B_4D_6{}^+$	$+ D_2$	1.49	52.3
$B_4D_7H^+$	$\rightarrow B_4D_6{}^+$	$+ HD$	0.59	53.2
$B_4D_9{}^+$	$\rightarrow B_4D_7{}^+$	$+ D_2$	0.50	54.3

TABLE IV
APPEARANCE AND IONIZATION POTENTIALS

Ion	A (e.v.) from $B^{11}{}_4H_{10}$	I (e.v.) from $B^{11}{}_4H_{10}$	A (e.v.) from $B^{11}{}_4D_{10}$
$B_4X_9{}^+$	12.2 ± 0.2	8.2	11.9 ± 0.2
$B_4X_8{}^+$	$10.4 \pm .1$	9.8	$9.9 \pm .1$
$B_4X_7{}^+$	$12.5 \pm .2$	7.9	$12.2 \pm .1$
$B_4X_6{}^+$	$11.2 \pm .1$	10.0	$11.1 \pm .1$
$B_4X_5{}^+$	$12.5 \pm .3$	7.3	$12.5 \pm .2$
$B_4X_4{}^+$	$12.4 \pm .2$	10.6	$12.5 \pm .2$
$B_4X_3{}^+$	$14.0 \pm .4$	8.3	$14.8 \pm .4$
$B_3X_5{}^+$	$12.1 \pm .2$		$12.8 \pm .3$
$B_3X_3{}^+$	$14.2 \pm .3$		$13.8 \pm .3$
$B_3X_2{}^+$	$17.8 \pm .8$		
B_3X^+	$16.5 \pm .8$		

Metastable peaks

$B^{11}{}_4H_{10}$	$B^{11}{}_4D_{10}$
$A(48.1) = 11.0 \pm 1.0$	$A(52.3) = 11.1 \pm 0.5$
$A(47.1) = 12.3 \pm 1.0$	$A(48.6) = 12.4 \pm 0.5$
$A(46.2) = 12.5 \pm 0.2$	
$A(45.2) = 13.6 \pm 1.0$	

lated. The appearance potentials of C_6H_6 and $B^{11}{}_5H_9$ were determined as a check on the calculations. A value of 10.5 v. was obtained for $B^{11}{}_5H_9$ as compared to 10.4 obtained previously.[8] A value of 9.5 v. was obtained for C_6H_6 compared to 9.56 and 9.52 obtained previously.[16,17]

Conclusions

Metastable transitions involving masses of 2, 4, 6 and 11 in the deuterated compound and 1, 2 and 3 in the protonated compound were observed. The loss of 2D and 2H were by far the most common, which is not surprising in light of work done on hydrocarbons.[18]

(16) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

(17) K. Higasi, I. Omura and H. Baba, *J. Chem. Phys.*, **24**, 623 (1956).

(18) E. G. Bloom, F. L. Mohler, C. E. Wise and E. J. Wells, *J. Research Natl. Bur. Standards*, **43**, 65 (1949).

The observed transitions are shown in Table III. Presumably $B_4H_9{}^+$ and $B_4H_8{}^+$ are formed very rapidly (compared to 10^{-6} sec.) from the parent ion, although transitions corresponding to these decompositions were not observed.

As mentioned above, metastable transitions correspond to highly probable decompositions and thus this table represents the energetically favored path of decomposition with respect to H and D. Because of the numerous transitions found, the path is nearly complete.

Several important conclusions can be drawn from this table. First of all there is only one transition (in the deuterated compound) that involves the loss of a boron. This means that the loss of boron-containing fragments is either very slow with respect to 10^{-6} sec. or very fast. If it were very fast, one would expect the fragmentation pattern to exhibit much larger peaks in the region corresponding to the lower fragments. However, the monoisotopic spectra show that this is not the case and thus the loss of boron-containing fragments must be slow, the rate being enhanced by D. This enhancement is confirmed by comparison of the monoisotopic spectra of $B^{11}{}_4H_{10}$ and $B^{11}{}_4D_{10}$. It is seen that the relative intensities of the lower fragments in $B^{11}{}_4D_{10}$ are much larger than with $B^{11}{}_4D_{10}$. For example, $I(B_3H_5{}^+) = 14.0$, $I(B_3D_5{}^+) = 24.7$, $I(B_2H_5{}^+) = 2.3$, $I(B_2D_5{}^+) = 4.6$.

Secondly, there are many more transitions involving D than H. Comparing the relative intensities of the monoisotopic spectra of $B^{11}{}_4H_{10}$ and $B^{11}{}_4D_{10}$ (Table II), it is seen that $B^{11}{}_4H_{10}$ loses H more readily than $B^{11}{}_4D_{10}$, which might be expected from comparison of B–D and B–H bond energies. As D retards these decompositions and as there are many more transitions involving D, then $k_H > k_D \cong 10^6$ sec.$^{-1}$.

It is to be noted that strong transitions in both compounds involve the loss of 3X (X = H,D). Presumably the mass lost is $X_2 + X$ as 3X and X_3 would not be energetically favored. However, nothing definite can be said about the state of aggregation of the neutral fragments. This type of transition involving 3X has not been observed in hydrocarbon spectra.[18] It would be of great interest to know what structural features would permit or enhance this transition.

For this reason an attempt was made to explain structurally the decompositions occurring in the fragments containing four borons. This can be done consistently if it is assumed that closest adjacent hydrogens come off easiest, and 2H's from one boron do not come off. As 2H's leave as H_2, it is logical that closest adjacent hydrogens would be favored. In Table II of reference 19 the various H–H distances are given. It has been suggested that the formation of a "normal" two-center B–B bond is a part of the process,[8] and if 2H's from one boron came off it would be difficult to form a B–B bond without extensive rearrangement. The resulting structures are shown in Fig. 2. Lipscomb's nomenclature is used to denote the structures.[20] The additional number in parentheses gives the number of borons without hydrogens.

All the transitions shown, except those from the parent ion, are observed in $B^{11}{}_4D_{10}$ and all except three are observed in $B^{11}{}_4H_{10}$. The structures of $B_4H_8{}^+$ and $B_4H_7{}^+$ were deduced from the fragmentation of $B_4H_8D_2$. In the deuterium exchange reaction between diborane and tetraborane, it has been found that two of the protons in tetraborane exchange at a faster rate than the other eight. It is therefore logical to assume

(19) C. E. Nordman and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 1856 (1956).

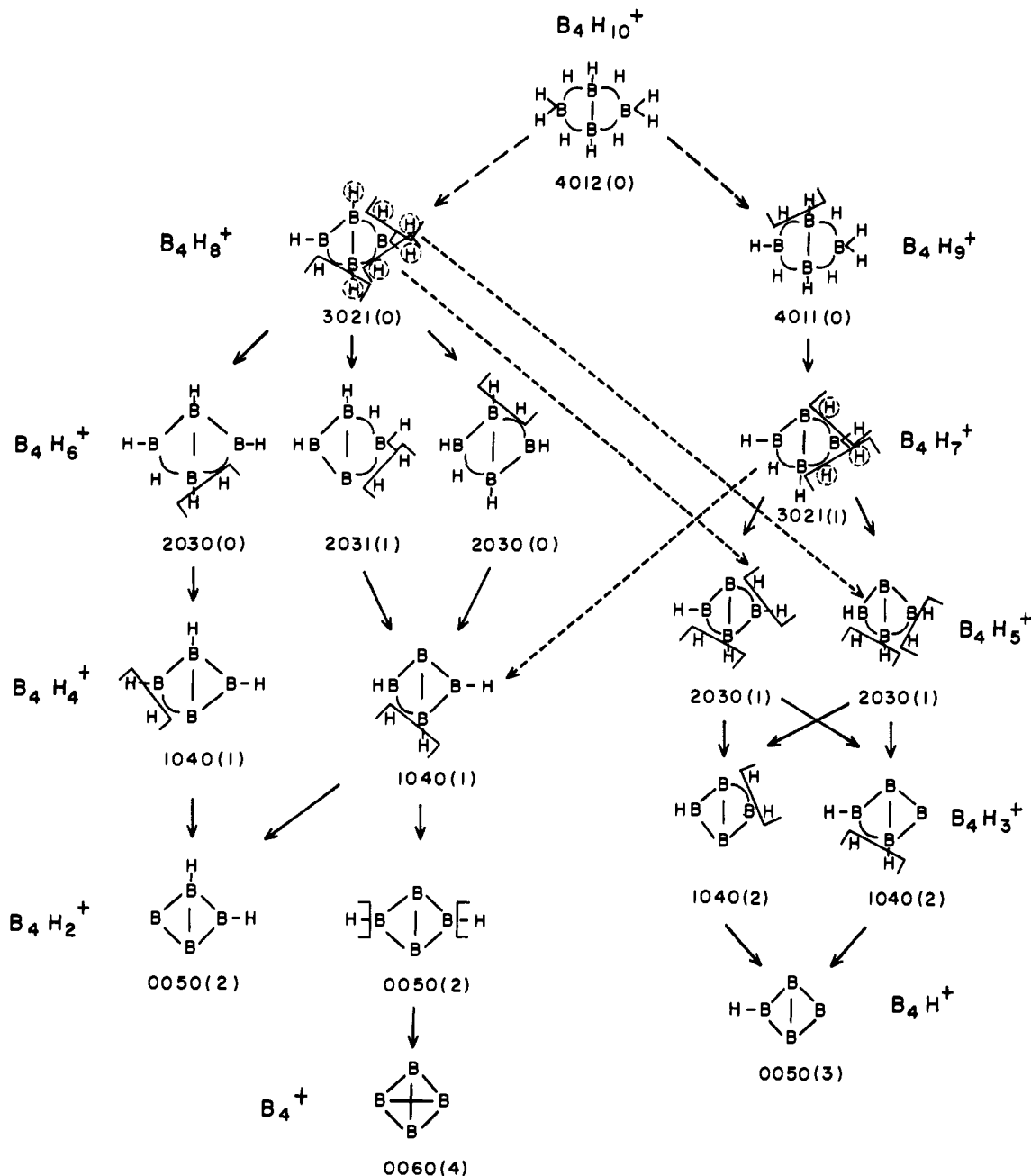(20) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

Fig. 2.—The decomposition scheme of the B_4 fragment ions from tetraborane. The transitions involving 3H are shown with dotted circles and arrows and the transitions involving 2H are shown with brackets and solid arrows.

that the 1- and 3-positions become deuterated. Since $B_4H_8^+$ and $B_4H_7^+$ appear in the spectrum of B_4H_{10} and since there is no m/e 53 peak in the spectrum of $B_4H_8D_2$, $B_4H_5D_2^+$ and $B_4H_7D^+$ must be absent. In view of the assumptions made, $B_4X_8^+$ (X = H,D) must be $B_4H_6D_2^+$ and $B_4X_7^+$ is $B_4H_6D^+$ for the dideuterio compound. The remaining transitions are filled in using the two assumptions above. In several cases, more than one equivalent route is shown. Others routes equivalent by symmetry are not shown. As the electron deficiency decreases, three-center bonds are replaced by two-center bonds. The structure for B_4^+ has one electron less than the number required for the six covalent bonds shown. The more intense transition involving 3H's does not involve breaking two bridge bonds, which are stronger than "normal" B–H bonds, but both involve an H from a B–H$_2$ group. According to this scheme, one should observe a transition $B_4D_9^+ \rightarrow B_4D_6^+ + 3D$. However, the $B_4D_9^+$ intensity is small, so the relative intensity would probably be weak and

would be hidden by the $B_4D_7^+ \rightarrow B_4D_5^+ + 2D$ transition.

This scheme cannot be considered unique, however, at the ionizing voltage used. As mentioned above, non-energetically favored paths may contribute to the fragmentation pattern. This would result in a certain amount of nearly random withdrawal of H and would account for the similarity in the B_4H_{10} and $B_4H_8D_2$ spectra. Both in the random fragmentation and in the energetically favored fragmentation scheme, the substitution of 2D should make little difference in the intensities of m/e 44 and 45. If these peaks in the spectra of B_4H_{10} and $B_4H_8D_2$ are normalized such that they are equal, then the effect of the energetically favored decompositions can be easily seen. The relative intensities of m/e 46, 47, 48 and 50 are down, and m/e 49, 51 and 52 are up. This agrees very well with the proposed scheme.

There is other evidence for a scheme of this type. Shapiro and co-workers made a preliminary examina-

tion of the mass spectra of decaborane in which the bridge positions were deuterated.[21] The monoisotopic spectra indicate the loss of H in pairs, and they found in the deuterated case that a high percentage of these pairs consisted of one terminal proton and one bridge deuterium. Nearly all the transitions postulated here involve a bridge and terminal proton. Finally the structure for $B_4H_6^+$ is the same as that postulated from appearance potential measurements of the fragments from $B^{11}{}_5H_9$.[8]

From the appearance potential data, it can be seen that the activation energies for the transition states involved in the decomposition reactions are approximately 2 e.v. or less. This is comparable to those determined for butane.[22]

In the usual manner,[8,23] one can also calculate the ionization potentials of the fragment ions from their appearance potentials, if it is assumed the structure of the product is given by the above diagram and 2H leaves as H_2 molecules when possible. For example,

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

(22) H. M. Rosenstock and C. E. Melton, *J. Chem. Phys.*, **26**, 314 (1957).

(23) W. J. Dunning, *Quart. Rev.*, **9**, 23 (1955).

consider $B_4H_6^+$. One can write the strictly formal process for the formation of this ion from B_4H_{10} as

$$B_4H_{10} + e = B_4H_6^+ + 2H_2 + 2e$$
$$(4012) \qquad (2030)$$
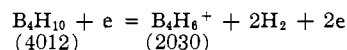
$$I(B_4H_6) = A(B_4H_6^+) + 2D(H_2) - 2D(B-H) - 2D(B-H-B) + 2D(B-B)$$

taking[24]

$$D(H_2) = 4.5$$
$$D(B-H) = 4.0$$
$$D(B-H-B) = 4.7$$
$$D(B-B) = 3.6$$

one obtains

$$I(B_4H_6) = 11.2 + 9.0 - 8.0 - 9.4 + 7.2 = 10.0 \pm 0.1$$

which agrees rather well with $I(B_4H_6) = 10.2 \pm 0.2$ obtained from the appearance potential of $B_4H_6^+$ from B_5H_9.[8] The calculated ionization potentials for the protonated compound are given in Table IV.

(24) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).
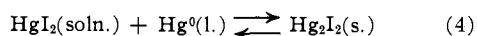

The Reactions of Iodine in Solution with Elementary Mercury
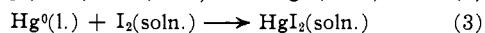
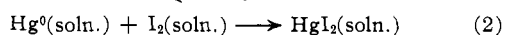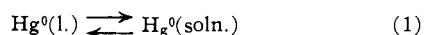By Percy Warrick, Jr., Eugene M. Wewerka and Maurice M. Kreevoy[1]

Iodine in a stirred solution in isoöctane in contact with a sizable, unbroken, droplet of mercury reacts *via* a number of paths. (1) The mercury dissolves in the isoöctane and once in solution reacts with the iodine at a rapid rate, producing mercuric iodide. (2) Iodine reacts with the metallic surface, producing mercuric iodide; the rate of this process can be controlled either by transport or chemical considerations, depending on the stirring rate. (3) Mercuric iodide, produced in processes 1 and 2, reacts with the metallic surface giving (solid) mercurous iodide. As long as excess iodine remains each mole of mercurous iodide is rapidly converted to two moles of mercuric iodide, but after the iodine is entirely consumed mercurous iodide accumulates as the ultimate product. Suitable rate laws are derived and observed rates are shown to obey them. Process 2 has a small, negative $\Delta H^{\ddagger}$ and a large negative apparent $\Delta S^{\ddagger}$ under conditions where it is not transport limited. This is rationalized on the basis of a one-electron transfer rate-determining step.

A large number of important reactions seem to proceed at metal–solution interfaces, but for the most part the detailed mechanism of these reactions is not known. Reactions taking place at the surface of metallic mercury seem to be particularly amenable to mechanistic study because the surface area is reproducible and roughly calculable. The present report primarily concerns the reaction of iodine in solution with metallic mercury. "Isoöctane" (2,2,4-trimethylpentane) was the solvent used for most of this work, but some work was also done in water as a solvent. The problems attacked are: (1) the identification of the actual reacting species and the first products of each reaction; (2) distinguishing between transport-controlled and chemically-controlled reactions; (3) deduction of mechanism for chemically-controlled reactions.

The following reactions were found to be significant

$$Hg^0(l.) \rightleftharpoons Hg_s^0(soln.) \qquad (1)$$

$$Hg^0(soln.) + I_2(soln.) \longrightarrow HgI_2(soln.) \qquad (2)$$

$$Hg^0(l.) + I_2(soln.) \longrightarrow HgI_2(soln.) \qquad (3)$$

$$HgI_2(soln.) + Hg^0(l.) \rightleftharpoons Hg_2I_2(s.) \qquad (4)$$

$$Hg_2I_2(s.) + I_2(soln.) \longrightarrow 2HgI_2(soln.) \qquad (5)$$
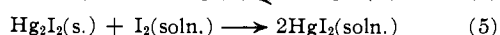
The rates of all these processes have been examined, but attention is focused on the reaction shown in eq. 3.

The rate constants for reactions taking place at the surface of the liquid mercury sample are indicated as

$k_n{}^x$ where x is the substance being consumed from solution and n is the apparent order with respect to that substance. In most cases a 17.6-g. mercury sample with an exposed area of 11.2 cm.^{2} was used. Exceptions are individually noted.

Results

In all of the work with metallic mercury described below, the mercury was an unbroken drop of known mass remaining relatively stationary at the bottom of a round-bottom flask. The solution above it was stirred mechanically. Samples were withdrawn periodically, analyzed spectrophotometrically, and then returned to the flask.

Mercury in Solution.—In order to evaluate the role played by the homogeneous solution reaction, eq. 2, in the presence of liquid mercury, the rate of the reaction between mercury atoms and iodine molecules in homogeneous solution in isoöctane was estimated by following the disappearance of the characteristic mercury peak at 257 mμ. Both reagents were initially present at about 5×10^{-6} M concentration. The rate was too fast to measure. If the reaction was first order with respect to each reagent it had a rate constant, k_2, $>10^4$ l. mole^{-1} sec.$^{-1}$ at 25°. The product was shown to be mercuric iodide by its ultraviolet spectrum.

A plausible rate law for the solution of elementary mercury from a drop of fixed size is shown in eq. 6 in which k_0 is the rate of solution and the second term is the rate of precipitation.