Molecular-Beam Mass Spectra of Hexaborane(12) and Octaborane(12)[1]

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Molecular-beam mass spectra and ionization potentials have been obtained for the easily decomposed boron hydrides hexaborane(12) and octaborane(12). Comparison of this type of spectrum with one which contains pyrolysis products formed on hot surfaces of the ion source and on the walls of the mass spectrometer suggests that another hexaborane and pentaborane(9) are formed pyrolytically from hexaborane(12). No pyrolytic decomposition of octaborane(12) is observable under similar conditions. Ionization potentials are measured to be 9.75 ± 0.2 eV (hexaborane(12)) and 9.52 ± 0.1 eV (octaborane(12)). Differences in fragmentation patterns of these two compounds, together with results from previous experimental work, are correlated with structure.

Introduction

Boron hydrides have been classified into two series called "stable" [B_nH_{n+4} or $B_nH_n(BH_3)_2$] and "unstable" [B_nH_{n+6} or $B_nH_n(BH_3)_3$].[3-6] This leads to the seemingly anomalous result that B_4H_8 and B_9H_{13}, hydrides which are not normally isolable in the free state, are classified as stable compounds; the unstable counterparts with the same number of borons, B_4H_{10} and B_9H_{15}, have, however, been isolated and characterized.

Relative stability of compounds is often reflected in mass spectra by the amount and type of fragmentation observed.[7] Carboranes, for instance, give rise to considerably fewer low molecular weight fragment ions than do the less stable boron hydrides.[8] Conventional-inlet[9] mass spectrometric work has indeed shown a correspondingly smaller contribution to lower molecular weight ions in the mass spectra of stable compounds such as B_5H_9[10,11] and B_6H_{10}[12,13] than in the spectra of the thermally unstable hydrides such as B_4H_{10}[13] and B_6H_{12}.[14] Recent molecular-beam mass spectrometric work,[15-20] however, shows that some of this supposed fragmentation of the unstable series may actually be due to spectra of pyrolysis products formed from the boron hydride in contact with the hot ion source.

Although conventional-inlet[9] mass spectra, which are comparable to the total-intensity[21] mass spectra in this work, have been published for both B_6H_{12}[14,22,23] and B_8H_{12},[4,13,24,25] molecular-beam mass spectra have not been reported for these two easily decomposed hydrides. The purpose of this paper, therefore, is to determine the fragmentation and pyrolysis behavior of these two boranes and to use them to help correlate the reactions and thermal stability of the boron hydrides.

Experimental Section

The reaction of tetramethylammonium triborohydride with polyphosphoric acid, as previously described in the literature, was used to prepare hexaborane(12).[22] Octaborane(12) was prepared by the decomposition of isononaborane(15).[26,27] A Nuclide Corp. (State College, Pa.) 12-in. radius, 60° magnetic

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(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1957.

(4) J. F. Ditter, J. R. Spielman, and R. E. Williams, *Inorg. Chem.*, **5**, 118, (1966).

(5) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(6) R. M. Adams, Ed., "Boron, Metallo-Boron Compounds and Boranes," Interscience, New York, N. Y., 1964.

(7) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966.

(8) J. F. Ditter, F. J. Gerhart, and R. E. Williams, *Advan. Chem. Ser.*, **No. 72**, 191 (1968).

(9) Our definition of "conventional" mass spectrometer inlet and source system is one in which the sample gases are held in a ballast volume, passed through a (gold) leak, and allowed to enter an ionizaion chamber. This chamber is usually designed to be as tightly closed as possible (to give high sensitivity). In addition it is heated by the ionizing electron filament and often is thermostated at about 250°. Consequently it can act as a flow reactor giving a reproducible and difficult to identify mixture of sample molecules, reactive intermediates, and/or pyrolysis products.

(10) A. Quayle, *J. Appl. Chem.*, **9**, 395 (1959).

(11) V. H. Dibeler, F. L. Mohler, L. Williamson, and R. M. Reese, *J. Res. Nat. Bur. Stand.*, **43**, 97 (1949).

(12) S. G. Gibbins and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

(13) J. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, *Advan. Chem. Ser.*, **No. 32**, 127 (1961).

(14) C. A. Lutz, D. A. Phillips, and D. M. Ritter, *Inorg. Chem.*, **3**, 1191 (1964).

(15) A. D. Norman, R. Schaeffer, A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 2151 (1966).

(16) S. J. Steck, G. A. Pressley, Jr., F. E. Stafford, J. Dobson, and R. Schaeffer, *Inorg. Chem.*, **8**, 930 (1969).

(17) F. E. Stafford, G. A. Pressley, Jr., and A. B. Baylis, *Advan. Chem. Ser.*, **No. 72**, 137 (1968).

(18) A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 2428 (1966).

(19) A. B. Baylis, G. A. Pressley, Jr., M. E. Gordon, and F. E. Stafford, *ibid.*, **88**, 929 (1966).

(20) R. E. Hollins, G. A. Pressley, Jr., A. B. Baylis, and F. E. Stafford, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; R. E. Hollins and F. E. Stafford, *Inorg. Chem.*, **9**, 877 (1970).

(21) The total-intensity mass spectrum is the molecular-beam mass spectrum of the compound plus the spectra of the pyrolysis products present in the ion source region. It is roughly equivalent to a spectrum from a conventional instrument (see ref 9).

(22) D. F. Gaines and R. Schaeffer, *Proc. Chem. Soc., London*, 267 (1963), *Inorg. Chem.*, **3**, 438 (1964).

(23) S. G. Gibbins and I. Shapiro, *J. Amer. Chem. Soc.*, **82**, 2968 (1960).

(24) I. Shapiro and B. Keilin, *ibid.*, **76**, 3864 (1954).

(25) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *ibid.*, **86**, 1451 (1964); *Inorg. Chem.*, **3**, 1659 (1964).

(26) J. Dobson, P. C. Keller, and R. Schaeffer, *ibid.*, **87**, 3522 (1965).

(27) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).

sector, Inghram-type mass spectrometer,[17,28] modified with a special gas inlet system,[17] was used to collect the data.

To minimize decomposition, the samples were distilled directly from a low-temperature slush bath through brass and stainless steel tubes and valves into the reactor assembly that served as the source of the molecular beam. (A figure is given in ref 17 and 18.) A toluene slush ($-95°$) was used for B_6H_{12}, and a chloroform slush ($-63°$), for B_8H_{12}. Before the actual experiment, however, the sample was placed in a slightly higher temperature bath while mass spectra were observed to ascertain removal of impurities more volatile than the sample.

A movable beam defining slit, located between the crucible assembly and the ion source region, permitted differentiation of species which originated from the crucible orifice from those which collided with the mass spectrometer walls or ion source assembly. Use of this "shutter" permitted any possible pyrolysis products to be excluded from the mass spectrum of the compound under study.[17,18,28]

In the ion source region, a beam of electrons ionized some of the molecules in the molecular beam. Normal operating conditions in this region were as follows: ionizing electron energy, 70 eV; total emission current, 1.2 mA which corresponds to about 10^{-5}-A trap current; and ion accelerating voltage, 4 kV. For appearance potential work, a graph of ion intensity *vs.* voltage was automatically plotted on an X-Y recorder.[29] The curves were calibrated against argon; the appearance potentials were evaluated using the vanishing-current method.

Mass separation of the ions was made with the instrument's $60°$ sector, 12-in. radius magnet. Both a 50% transmission grid collector and a 16-stage secondary electron multiplier were used to detect the ions. With 3.9 kV across the secondary electron multiplier, the multiplier gains for the various ion groups were as follows: $B_1H_x^+$, 3.0×10^4; $B_2H_x^+$, 7.5×10^4; $B_3H_x^+$, 1.5×10^5; $B_4H_x^+$, 1.7×10^5; $B_5H_x^+$, 1.8×10^5; $B_6H_x^+$ and $B_6H_x^+$, 1.9×10^5; $B_8H_x^+$, 2.0×10^5.

Results

Ions were identified on the basis of isotope ratios, mass defect, and "shutter per cent."[30] Ion intensities were corrected for secondary electron multiplier gain using the gain values given in the Experimental Section. Only the shutterable portion of each peak is considered in the molecular-beam mass spectra. The total-intensity mass spectra contain ion contributions from the species in the molecular beam and from the species that have diffused from the reactor compartment into the source compartment. Since the slit connecting the two compartments is only 1 mm $\times$ 10 mm, the latter species have suffered many surface collisions, including those with the hot plates of the ion source. Consequently these nonshutterable (background) species may include pyrolysis products. This total-intensity mass spectrum is therefore comparable to that obtained with a conventional-inlet system.[9]

Hexaborane(12).—The molecular-beam and total-intensity mass spectra of hexaborane(12) are given in Table I. Reproducibility of the data was verified by two separate measurements of approximately one-third of the peaks because approximately 10 hr was required for the measurement of a single molecular-beam mass spectrum. Half-mass peaks (relative intensity

(28) M. G. Inghram and J. Drowart in "High Temperature Technology," McGraw-Hill, New York, N. Y., 1960, p 219; W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

(29) F. E. Stafford and R. J. Loyd, *Advan. Chem. Ser.* **No. 72**, 127 (1968).

(30) "Shutter per cent" is the ratio of the molecular-beam intensity to the total ion intensity at a given mass peak.

TABLE I

POLYISOTOPIC MOLECULAR-BEAM AND TOTAL-INTENSITY MASS SPECTRA OF HEXABORANE(12)[a]

Mass	Molecular[b] beam	Total[c]	Shutter per cent[d]
78 P	3.39	2.13	51
77	13.9	9.77	37
76	41.6	36.4	30
75	50.6	46.2	29
74	72.3	65.8	29
73	76.3	70.0	28
72	100.0	97.2	27
71	98.7	100.0	26
70	67.9	69.9	25
69	41.1	43.2	25
68	29.2	30.1	25
67	26.3	27.3	25
66	22.9	24.1	25
65	13.7	14.7	24
64	5.5	28.6	5
63	3.14	33.9	2
62	11.5	51.4	6
61	15.0	51.1	8
60	25.7	72.7	9
59	35.3	84.6	11
58	32.9	66.2	13
57	27.6	48.5	15
56	22.0	39.7	14
55	16.2	34.5	12
54	10.3	22.3	12
53	4.36	9.47	12
52	1.05	2.33	12
51	0.44	0.67	17
50	9.83	12.9	20
49	14.7	20.7	19
48	22.6	40.9	14
47	25.4	46.4	14
46	17.4	32.7	14
45	9.81	19.6	13
43	1.82	5.75	8
42	0.46	2.40	5
41	0.18	2.27	2
40	0.03	0.28	3
39	7.44	9.43	21
38	8.26	10.4	21
37	7.63	10.7	19
36	8.54	11.6	19
35	6.82	11.1	16
34	3.62	6.58	14
33	1.20	2.27	14
32	0.23	0.69	9
29	0.21	5.31	1
28	0.37	2.73	4
27	7.65	15.2	13
26	4.43	9.69	12
25	2.71	6.05	12
24	2.92	7.66	10
23	0.12	0.37	8
22	0.01	5.13	0
14	0.14	3.88	1
13	12.4	26.0	13
12	3.86	8.51	12
11	18.4	36.3	13
10	4.67	9.03	13

[a] Taken at 70 eV and corrected for multiplier gain. P = parent. [b] Molecular-beam (shutterable) intensity relative to $I(72^+)$. [c] Total intensity (molecular beam plus background) relative to $I(71^+)$. [d] See ref 30.

<0.05%) and metastable transition peaks were not studied.

In the molecular-beam mass spectrum, a weak parent peak ($B_6H_{12}^+$) is observed at m/e 78. "Shutter per cent"[30] of this particular peak is considerably larger than that of any other peak in the spectrum. The principal peak is at m/e 72. Ion intensity of the $B_5H_x^+$ ion group is only about one-third that of the parent region; ion intensity of the $B_4H_x^+$ ion group is about one-fourth.

In the total-intensity mass spectrum, the relative intensity of the parent peak is even smaller than in the molecular-beam spectrum. The principal peak, moreover, is shifted down one mass unit to m/e 71. Ion intensity of the $B_5H_x^+$ ion group is approximately three-fourths that of the $B_6H_x^+$ ion group; intensity of the $B_4H_x^+$ ion group is approximately one-half.

The greater relative intensity of fragment peaks in the total-intensity spectrum is believed to result from ion contributions made by pyrolysis products. To identify these pyrolysis products, the molecular-beam and total-intensity mass spectra were first normalized using the intensity of $B_6H_{12}^+$ since the ion intensity at this peak comes from fragmentation of hexaborane(12). The molecular-beam mass spectrum is then subtracted from the total-intensity spectrum. The resulting difference spectrum for the $B_6H_x^+$ ion region, given in Table II, corresponds within experimental error to the

TABLE II

MASS SPECTRA OF PYROLYSIS PRODUCTS OBTAINED BY
SUBTRACTION OF THE MOLECULAR-BEAM MASS
SPECTRUM OF HEXABORANE(12) FROM THE TOTAL-INTENSITY
MASS SPECTRUM OF HEXABORANE(12)

	B$_6$H$_{10}$			B$_5$H$_9$	
m/e	Rel subtracted intens	Lit.[12] spectrum	m/e	Rel subtracted intens	Lit.[11] spectrum[a]
77	2.6		64	42	48.7
76	27	22.6	63	59	61.1
75	38	34.1	62	82	77.8
74	54	48.2	61	77	69.1
73	58	49.4	60	97	98.2
72	90	86.9	59	100	100.0
71	100	100.0	58	66	66.7
70	72	79.4	57	40	44.1
69	46	57.7	56	32	35.7
68	31	44.0	55	31	34.9
67	28	41.5	54	20	24.1
66	26	35.4			
65	16	20.7			

[a] Another spectrum for B_5H_9, which is slightly different, is available.[10]

published[12] mass spectrum of hexaborane(10). The change in shutter per cent between m/e 77 and 76 gives further evidence for the presence of hexaborane(10). We cannot exclude, however, the possibility that the spectrum is due to the isomeric hexaborane(10) reported by Shore[31] or indeed to another as yet unisolated isomer.

Formation of the thermally stable pentaborane(9) is

(31) R. A. Geanangel and S. G. Shore, *J. Amer. Chem. Soc.*, **89**, 6771 (1967).

indicated by the abrupt change in the shutter per cent between m/e 65 and 64. After ion contributions resulting from fragmentation of both B_6H_{12} and B_6H_{10} are subtracted out, the resulting spectrum for the $B_5H_9^+$ ion group (m/e 64–52) corresponds within experimental error to the spectra published for B_5H_9.[10,11] Ion intensity remaining for the lower mass regions after B_6H_{12}, B_6H_{10}, and B_5H_9 ion fragmentation contributions had been subtracted out could not be meaningfully interpreted. This difference intensity may represent tetraborane or other pyrolysis product contributions or may be due to instrumental differences. In addition, gradually decreasing shutter per cent with decreasing mass (increasing fragmentation) seems to be an artifact of the method. See the discussion below under octaborane(12).

The ionization potential of hexaborane(12) is determined to be 9.75 ± 0.20 eV. The uncertainty is the standard deviation of the measurements.

Octaborane(12).—Although the slush bath was frequently stirred, a temperature gradient caused a systematic, time-dependent variation of about 10% in the ion intensity of the principal peak of octaborane(12). Consequently, in order to obtain the mass spectrum given in Table III, it was necessary to normalize the ion intensity to several values of the principal peak, m/e 93 recorded periodically during the experiment.

Because of a relatively large exit slit setting used to improve the spectrometer sensitivity for these measurements, interference from an unresolved pentane impurity (from the synthesis) contributes to the comparatively large ion intensity at m/e 72. Other peaks that might have some pentane ion contributions are at m/e 57, 43, 42, 41, 39, 29, and 27.

The parent peak of octaborane(12) is observed at m/e 100 and is fairly intense (24%); the principal peak is at m/e 93. The intensity of the $B_7H_x^+$ ion group in the molecular-beam mass spectrum is only about 20% that of the parent ion group. Half-mass peaks of a few per cent relative intensity, as shown in Table III, were observed.

Starting with the parent peak, the shutter per cent decreases slowly with decreasing mass. It is believed that this decrease is due to a variation of the ion source collection efficiency for molecular-beam species relative to that for background as the degree of fragmentation increases. For instance, the shutter per cents for doubly charged ion peaks at half-masses between m/e 48.5 and 44.5 are comparable to those for the singly charged peaks between m/e 97 and 89. The shutter per cents for the peaks at integral masses between m/e 50 and 43, which contain contributions from both singly and doubly charged ions, are substantially lower. These doubly charged ions have undergone much less fragmentation than the singly charged species in the same mass range. Such a variation is believed due to the fact that the volume in which molecular-beam ions are formed, *i.e.*, the volume of intersection of the molecular beam with the ionizing electron beam, is smaller than the volume in which background ions are formed.

TABLE III
POLYISOTOPIC MOLECULAR-BEAM AND TOTAL-INTENSITY MASS SPECTRA[a] OF OCTABORANE(12)

Mass	Molecular beam[b]	Total[c]	Shutter per cent[d]	Mass	Molecular beam[b]	Total[c]	Shutter per cent[d]
100 P	24.0	17.0	44	58	3.23	4.11	25
99	48.6	35.9	42	57[e]	4.37	5.88	24
98	67.4	51.9	41	56	2.87	4.31	22
97	70.4	56.6	39	55	2.43	3.34	24
96	72.4	62.8	36	54	1.17	1.72	22
95	70.4	64.4	34	53	0.56	0.83	22
94	86.2	84.1	32	52	0.14	0.20	22
93	100.0	100.0	31	51	0.07	0.16	13
92	81.6	81.2	31	50	0.03	0.11	10
91	54.8	55.5	31	49	0.56	0.55	33
90	35.7	36.9	30	48.5	0.45	0.35	42
89	25.3	26.3	30	48	2.42	2.34	34
88	23.0	23.9	30	47.5	2.92	2.38	40
87	19.5	20.9	29	47	4.33	4.19	34
86	12.7	13.6	29	46.5	2.50	2.07	39
85	5.90	6.38	29	46	3.31	3.67	29
84	2.92	3.16	29	45.5	1.47	1.46	33
83	3.35	3.73	28	45	1.97	2.59	25
82	7.87	8.66	28	44.5	0.58	0.58	32
81	12.0	13.2	28	44	0.96	1.38	22
80	15.8	17.4	28	43[e]	6.28	8.74	23
79	19.3	20.9	29	42[e]	3.88	5.41	23
78	19.1	20.8	29	41[e]	2.09	4.05	17
77	17.3	19.0	28	40	0.15	0.30	17
76	13.3	14.6	28	39[e]	0.67	1.42	15
75	7.50	8.60	27	38	0.06	0.12	16
74	2.86	4.21	21	37	0.30	0.37	26
73	0.86	2.40	11	36	0.49	0.58	27
72[e]	3.62	5.64	21	35	0.59	0.77	25
71	1.61	4.69	11	34	0.41	0.47	28
70	3.59	6.33	18	33	0.13	0.18	22
69	6.60	9.05	24	29[e]	1.63	3.78	14
68	7.93	10.1	25	27[e]	2.18	6.02	12
67	8.01	10.3	25	26	0.44	0.53	27
66	6.27	8.10	25	25	0.33	0.49	22
65	3.64	4.69	25	24	0.46	0.59	25
64	1.27	1.71	24	23	0.23	0.29	26
63	0.27	0.43	20	13	5.57	7.03	26
62	0.09	0.22	14	12	1.80	2.01	29
61	0.11	0.27	13	11	5.99	7.87	25
60	0.45	0.98	15	10	1.55	1.98	25
59	1.96	3.06	21				

[a] Taken at 70 eV and corrected for multiplier gain. P = parent. [b] Molecular-beam (shutterable) intensity relative to $I(93^+)$. [c] Total intensity (molecular beam plus background) relative to $I(93^+)$. [d] See ref 30. [e] These peaks may have contributions from an unresolved pentane impurity.

Although a difference spectrum could be subtracted out of the total-intensity spectrum of Table III, it can be explained by the effect described above rather than by pyrolysis of the octaborane(12). The slow decrease in shutter per cent, which gives rise to the difference spectrum, is observed also for pentaborane(9), which does not give rise to pyrolysis products even when the reactor is heated above 500°.[20] In contrast to the data of Table III, the shutter per cents for hexaborane(12) (Table I) show an abrupt change between m/e 77 and 76 and again between m/e 65 and 64. It is this abrupt change that indicates pyrolytic formation, respectively, of hexaborane(10) and pentaborane(9).

The ionization potential of B_8H_{12} is determined to be 9.52 ± 0.10 eV.

Monoisotopic Mass Spectra.—Monoisotopic mass spectra for the parent ion groups of hexaborane(12) and octaborane(12) are given in Figure 1. These spectra were obtained by mathematically "stripping" the polyisotopic mass spectra ion intensities using an isotopic boron distribution of 20% ^{10}B and 80% ^{11}B.[8,13]

A salient feature of the monoisotopic spectra is the small relative intensity (8%) of the parent peak of B_6H_{12}. The monoisotopic spectra of both hexaborane-(12) and octaborane(12) show an alternation of intensity in the ion peaks; relative intensities of the ions in the two spectra, however, are significantly different. Principal peaks in both spectra show six hydrogens in the ion.

Discussion

The total-intensity[21] mass spectrum of hexaborane-(12) reported in Table I corresponds within estimated experimental error to the published conventional-inlet[9] spectrum of Lutz, Phillips, and Ritter[14] and the partial spectra of Gaines and Schaeffer[22] and of Gibbons and
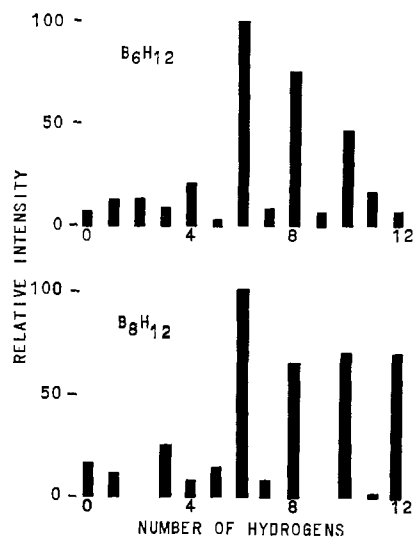
Figure 1.—Calculated monoisotopic mass spectra of the parent peak regions of hexaborane(12) (top) and octaborane(12) (bottom). The original spectra were for the naturally occurring boron isotopic distribution, 20% ^{10}B and 80% ^{11}B. For B_6H_{12}, the gradual increase of ion intensity starting with the parent peak is called a "linear buildup" profile and is characteristic of the unstable[3,4,8] series of boranes. The profile for B_8H_{12}, because the intensities of the peaks with 12, 10, 8, and 6 hydrogens are nearly equal, is called "square" and is characteristic of the stable series.

Shapiro.[23] All of these spectra show a relatively small parent peak, a gradual buildup of intensity, and a principal peak at m/e 71. Large contributions to low molecular weight ions are observed in the present total-intensity spectrum and in that of Lutz, *et al.*

The total-intensity mass spectrum of octaborane(12), Table III, agrees reasonably well with the spectrum published by Shapiro, *et al.*,[13] and with the partial spectrum published by Ditter, *et al.*[4] All three spectra show a relatively large parent peak and a principal

peak at m/e 93. Smaller contributions to the $B_6H_x{}^+$ ion group than found by Shapiro, however, were observed in this work.

Molecular-beam spectra for these compounds have not been reported previously. This spectrum of hexaborane(12) shows less fragmentation than either the conventional-inlet[9] spectra[14,22,23] or the total-intensity spectrum. Previous work with boron hydrides has shown that this difference in fragmentation pattern is due to contributions of pyrolysis products formed on hot surfaces or walls of the spectrometer. Any correlation work with the fragmentation patterns of the boranes, particularly the thermally unstable ones, therefore should be made using molecular-beam mass spectra.

Classification of the Boron Hydrides.—Ditter, *et al.*,[4,8] have shown that various aspects of borane mass spectra can be correlated with whether the borane fits the "stable" or "unstable" classification. (See Table IV.) This is now reexamined using the newly available molecular-beam mass spectra for B_4H_8,[20] B_4H_{10},[15,19] B_5H_9,[20] B_5H_{11}, B_6H_{12}, and B_8H_{12}.

TABLE IV
CLASSIFICATION OF THE BORANES INTO STABLE AND UNSTABLE SERIES ACCORDING TO STOCK[3] AND TO DITTER, SPIELMAN, AND WILLIAMS[4]

No. of borons	Stable	Unstable	No. of borons	Stable	Unstable
2	B_2H_6		7	B_7H_{11}	B_7H_{13}
3	B_3H_7	B_3H_9	8	B_8H_{12}	B_8H_{14}
4	B_4H_8	B_4H_{10}	9	B_9H_{13}	B_9H_{15}
5	B_5H_9	B_5H_{11}	10	$B_{10}H_{14}$	$B_{10}H_{16}$
6	B_6H_{10}	B_6H_{12}			

There is a large difference in importance of the parent peaks of the two series. Table V, which contains all the available data, shows that relative intensities of

TABLE V
COMPARISON OF RELATIVE INTENSITIES OF PARENT PEAKS AND OF IONIZATION POTENTIALS OF KNOWN "STABLE" AND "UNSTABLE" BORON HYDRIDES

Boron hydride	Stable Rel intens of parent peak	IP, eV	Boron hydride	Unstable Rel intens of parent peak	IP, eV
B_2H_6	1.5^a	11.9 ± 0.1^d			
	$6.8^{b,c}$	12.1 ± 0.2^e			
		$<11.84 > 11.21^f$			
B_4H_8	$\sim 30^g$	10.2 ± 0.5^g	B_4H_{10}	$0.2^{p,q}$	$10.4^{r,i}$
B_5H_9	74.9^h	10.38 ± 0.05^h	B_5H_{11}	0.2^j	$10.3^{r,i}$
	78.0^i	10.5 ± 0.1^i			
		10.8 ± 0.5^k			
B_6H_{10}	41.0^j	9.3 ± 0.1^j	B_6H_{12}	$3.39^{p,n}$	9.75 ± 0.2^n
	$39.2^{l,m}$				
B_8H_{12}	24.1^n	9.52 ± 0.1^n	B_8H_{14}		
			B_9H_{15}	Not reported[s,t]	Not reported
$B_{10}H_{14}$	17.80^o	10.26 ± 0.5^o			
		11.0 ± 0.5^k			

[a] F. J. Norton, *J. Amer. Chem. Soc.*, **71**, 3488 (1949). [b] Parent of 96% ^{10}B compound. [c] A. B. Bayliss, *et al.*[18] [d] W. S. Koski, J. J. Kaufman, C. F. Pachuki, and F. J. Shipko, *J. Amer. Chem. Soc.*, **80**, 3202 (1958). [e] J. L. Margrave, *J. Phys. Chem.*, **61**, 38 (1957). [f] J. H. Wilson and H. A. McGee, Jr., *J. Chem. Phys.*, **46**, 1444 (1967). [g] R. E. Hollins, *et al.*[20] [h] J. J. Kaufman, W. S. Koski, L. J. Kuhns, and S. S. Wright, *J. Amer. Chem. Soc.*, **85**, 1369 (1963). [i] V. H. Dibeler, *et al.*[11] [j] T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, **86**, 581 (1964). [k] J. L. Margrave, *J. Chem. Phys.*, **32**, 1889 (1960). [l] Our calculation of the monoisotopic spectrum from the literature data.[m] [m] S. G. Gibbins and I. Shapiro.[12] [n] This work. [o] J. J. Kaufman, W. S. Koski, L. J. Kuhns, and R. W. Law, *J. Amer. Chem. Soc.*, **84**, 4198 (1962). [p] Molecular-beam mass spectral data. [q] A. Norman, *et al.*[15] [r] Ionization potential is estimated from appearance potentials of other ions in the spectrum. [s] J. F. Ditter, *et al.*[4] [t] A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

TABLE VI

COMPARISON OF THE AMOUNT OF FRAGMENTATION TO LOWER, MOLECULAR WEIGHT IONS FOR OCTABORANE(12) AND HEXABORANE(12)[a,b]

	Octaborane(12)		Hexaborane(12)	
	$\Sigma B_y H_x^+$ (rel intens)	$\Sigma B_y H_x^+ / \Sigma B_8 H_x^+$	$\Sigma B_y H_x^+$ (rel intens)	$\Sigma B_y H_x^+ / \Sigma B_6 H_x^+$
$B_8 H_x^+$	798			
$B_7 H_x^+$	121	0.15		
$B_6 H_x^+$	43.7	0.055	663	
$B_5 H_x^+$	17.4	0.022	205	0.31
$B_4 H_x^+$	33.9	0.042[c]	102	0.16
$B_3 H_x^+$	3.06	0.004	43.7	0.066
$B_2 H_x^+$	5.27	0.006	18.4	0.028
BH_x^+	14.91	0.019	39.5	0.060

[a] By $\Sigma B_y H_x^+$ is meant the sum of the relative intensities of all the peaks with a given number of borons; thus $\Sigma I(B_7 H_x^+)$ includes intensities from m/e 84 to 74. [b] Net fragmentation relative to parent group: $\Sigma\Sigma B_y H_x^+ / \Sigma B_8 H_x^+ = 0.30$; $\Sigma\Sigma B_y H_x^+ / \Sigma B_6 H_x^+ = 0.62$. By $\Sigma\Sigma B_y H_x^+$ is meant the sum of relative intensities for all peaks except those in the parent group. [c] Some ion intensity contributions from pentane impurities.

parent peaks of the $B_n H_{n+4}$ boranes range from 18 to 77% (with the exception of diborane), while the three reported values for $B_n H_{n+6}$ boranes are 0.2, 0.6, and 3.4%.

Consequently, the envelope of ions containing the parent number of borons tends to be "square" for the stable series and to build up linearly for the unstable series. This is shown by the monoisotopic spectra for $B_8 H_{12}$ and $B_6 H_{12}$, respectively, shown in Figure 1.

A third difference between the two series is the amount of fragmentation to lower molecular weight ion groups. Since most previous borane spectra may contain spectra of pyrolysis products, the comparison of fragmentation observed in the molecular beam mass spectra of $B_6 H_{12}$ and $B_8 H_{12}$ is particularly enlightening. On a statistical basis, octaborane(12) would be expected to show more fragmentation to lower molecular weight ions, but Table VI shows that hexaborane(12) fragments approximately twice as much.

These three comparisons suggest that fragmentation patterns of the boron hydrides can be divided into two series.

As shown in Table V, however, the ionization potentials do not distinguish between the two series but rather seem to follow more nearly the apparent stability on transfer in a vacuum system. The dip in the ionization potentials at the hexa- and octaboranes, moreover, was not predicted by a set of molecular orbital calculations.[32]

Correlation of mass spectral fragmentation patterns and low-pressure pyrolysis behavior of the boron hydrides with the stability classifications outlined by Stock[3] suggest how mass spectra can be valuable in identifying the yet unknown boron hydrides. The postulated reactive intermediates, $B_3 H_7$ and $B_7 H_{11}$, and $B_9 H_{13}$ belong to the stable series and should exhibit moderately intense parent peaks and relatively little fragmentation; the corresponding unstable species $B_3 H_9$, $B_7 H_{13}$, and the unknown icosahedral isomer of $B_{10} H_{16}$, however, should exhibit weak parents and considerable fragmentation and pyrolysis. In fact, although it is of lower molecular weight, a stable boron hydride is likely to make a larger contribution to the ion intensity at its parent peak than does its unstable counterpart which has two more hydrogens.

Conclusions

The molecular-beam mass spectra observed for hexaborane(12) and octaborane(12), together with other newly observed molecular-beam spectra, provide a means of distinguishing between the stable and unstable series[3,4,8] (Table IV) of boranes. Three criteria can be used: the relative size of the parent peak (Table V), the profile of the monoisotopic spectrum in the parent region (Figure 1), and the extent of boron fragmentation (Table VI).

(32) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).