# Mass Spectrum of Pentaborane (B₅H₉)

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The mass spectrum of B_5H_9 has been measured, and the monoisotopic spectrum has been computed using the isotope abundance $B^{10}=0.200$ and $B^{11}=0.800$. The mass spectrum shows that the molecule has a marked tendency for ionization with loss of either two or four hydrogen atoms, but little tendency to lose one or three. The high yield of ions containing five boron atoms and the tendency to give up either two or four hydrogen atoms suggests a five-membered ring structure with two pairs of loosely bound hydrogen atoms. Since the spectrum is quite different from that of C_5 ring compounds, however, no definite conclusion concerning the structure is drawn at present.

I. Introduction

The Mass Spectrometry Section has had an opportunity to run mass spectra of some very pure pentaborane, B_5H_9, prepared by the Naval Research Laboratory. This compound is considered by Pitzer[1] to be a five membered ring compound, B_5H_5, with two additional pairs of hydrogen atoms attached to two of the bonds to form protonated double bonds.

$$HB{=}BH{-}BH{=}BH{-}BH.$$
$$|\quad H \qquad\quad H \qquad\quad |$$
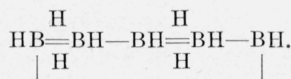
Bauer and Pauling had previously suggested a methylcyclobutane-like structure.[2]

An interpretation of hydroboron mass spectra is complicated by the fact that boron has two isotopes of masses 10 and 11 in the relative amounts 0.20 and 0.80. Consequently, in polyatomic ions many different combinations of boron isotopes and hydrogen atoms contribute to the spectrum. The monoisotopic spectrum of each isotopic configuration must first be evaluated and then all contributions with like numbers of hydrogen atoms summed to give the spectrum that one would obtain if there were only one isotope. To do this an accurate value of the isotope ratio must be found by trial that will give self-consistent results. Another paper on the mass spectrum of diborane has applied this method of analysis.[3]

[1] K. S. Pitzer, J. Am. Chem. Soc. **67**, 1126 (1945).
[2] S. H. Bauer, Chem. Rev. **31**, 43 (1942).
[3] V. H. Dibeler and F. L. Mohler, J. Am. Chem. Soc. **70**, 987 (1948).

II. Experimental Details

The mass spectra were obtained with a 180° Consolidated mass spectrometer using automatic emission control and thermostatic control of the ionization chamber temperature at 245° C. Mass spectra have been measured at 50 and 70 v ionizing voltage. Spectra were obtained with constant magnetic field for the mass range 10 to 64 and a lower field for 1 and 2.

The B_5H_9 was prepared under the direction of Roman R. Miller of the U. S. Naval Research Laboratory. A freezing point determination by J. T. Clarke and H. L. Johnston of Ohio State University indicates a purity of 99.97 percent (informal communication). The material was stored at −78° C until it was used. The sample was held at liquid nitrogen temperature, and any volatile gas pumped off before admitting to the mass spectrometer.

III. Results

Table 1 gives the mass spectrum of B_5H_9 at 50 and at 70v ionizing voltage. Ion intensities are relative to the maximum peak at mass 59 taken as 100. Four of the mass peaks come from doubly charged ions, and all the other peaks are due to singly charged ions. There are no metastable transition peaks.

From statistical considerations, the relative abundances of ions having various combinations of B^{10} and B^{11} atoms in radicals containing from 1 to 5 boron atoms are given by the separate

m/e	Relative intensities		m/e	Relative intensities	
	50 volts	70 volts		50 volts	70 volts
1	4.12	5.71	37	3.39	3.22
2	10.4	15.8	38	1.26	1.24
			39	0.83	0.78
10	6.12	8.24	40	.03	.05
11	23.4	32.3	41	.26	.29
12	7.17	9.26	42	1.45	1.72
13	16.2	18.6	43	5.56	6.03
			44	13.2	13.7
20	--------	0.08	45	22.0	21.5
21	0.20	.41	46	32.0	31.0
22	.86	1.47	47	39.7	39.0
23	2.98	3.56	48	32.6	32.3
24	3.79	4.10	49	8.56	8.58
25	2.28	2.25	50	3.26	3.33
26	1.14	1.14	51	0.31	0.44
27	1.75	1.80	52	2.31	2.52
a 27.5	0.05	0.08	53	9.92	9.85
28	.38	.47	54	25.1	24.1
a 28.5	.29	.31	55	37.0	34.9
a 29	.33	.39	56	38.9	35.7
a 29.5	.12	.17	57	47.1	44.1
30	.03	.13	58	68.6	66.7
31	.17	.24	59	100	100
32	.86	1.23	60	97.0	98.2
33	3.06	3.66	61	67.8	69.1
34	7.42	7.60	62	76.4	77.8
35	10.9	10.6	63	61.5	61.1
36	7.44	6.99	64	49.1	48.7

a Doubly charged ions.

terms in the binomial expansions of $(x+y)^n$, where "n" takes integral values from 1 to 5, and x and y are the fractions of B^{10} and B^{11}.[4] Table 2 lists the terms in the expansions for $n=1$ to 5, and for $x=0.20$ and $y=0.80$. The numbers 0.20 and 0.80 were found by trial to give the best fit. Ions containing the same number of boron

TABLE 2. *Statistical distribution for B^{10} and B^{11} atoms in ions containing one to five boron atoms* [a]

B11 \ B10	0	1	2	3	4	5
0	-----	20.00	4.00	0.80	0.16	0.032
1	80.00	32.00	9.60	2.56	.64	-----
2	64.00	38.40	15.36	5.12	-----	-----
3	51.20	40.96	20.48	-----	-----	-----
4	40.96	40.96	-----	-----	-----	-----
5	32.77	-----	-----	-----	-----	-----

a The first row gives the number of B^{10} atoms in a molecule, and the first column gives the number of B^{11} atoms. Diagonals from lower left to upper right give the distribution of B^{10} and B^{11} in molecules containing five, four, three, etc., boron atoms.

[4] The small correction due to hydrogen isotopes is omitted.

atoms will have the relative abundances given along the diagonals running from lower left to upper right. It is possible with the aid of table 2 to calculate the monoisotopic spectra from the mixture spectrum by starting at the heavy mass end and computing the contribution of each ion to each value of m/e.

Table 3 gives in the first and second columns the B_5 part of the 50-v mass spectrum of B_5H_9 and illustrates the computation of the monoisotopic spectrum. The peak at 64 comes entirely from the molecule ion $B_5^{11}H_9^+$. From the lower diagonal of table 2, the six B_5H_9 isotopes have the relative abundance 64=1.0, 63=1.25, 62=0.625, 61=0.156, 60=0.0195, 59=0.001. Multiplying 49.1 by these ratios gives the contribution of B_5H_9 to the mass peaks 64 to 59 shown on the lower diagonal of table 3. Subtracting the B_5H_9 contribution from the 63 peak gives the $B_5^{11}H_8$ contribution as 0.12, and multiplying this by the above ratio gives the B_5H_8 contributions to peaks from 63 to 58. Subtracting $B_2^{10}B_3^{11}H_9+B^{10}B_4^{11}H_8$ contributions from the 62 peak gives the value 45.56 for the ion $B_5^{11}H_7$, etc. When this computation is repeated for each peak down to 55, the complete B_5 spectrum should be accounted for and the residuals on peaks 51, 52, 53, and 54 afford a check on whether the correct isotope ratio has been used. These are all less than the experimental uncertainty. Contributions of all isotopes along each diagonal are then added to give the monoisotopic spectrum in the last column. A large residual, 3.25, on the mass 50 peak is assumed to be $B_4^{11}H_6$, and starting with this value the contributions of the various B_4 ions are computed in the same way as for B_5 ions using the values of table 2 along the second diagonal from the bottom for the relative isotopic abundances of ions containing four boron atoms. Similarly, the entire spectrum omitting doubly charged ions can be computed. Each group of ions with one, two, three, four, and five boron atoms affords one or more checks on the correctness of the analysis, and these check values are tabulated in table 4 for the mass spectrum at 50 volts ionizing voltage. An agreement within 0.2 percent of the maximum peak is entirely within experimental error, and it is only on the mass 10 peak that the discrepancy seems to be definitely greater than the experimental uncertainty. This is discussed in the following section.

TABLE 3. *The B_5 portion of the B_5H_9 spectrum at 50 volts illustrating computation of the monoisotopic spectrum*

m/e	Mixture spectrum	Monoisotopic spectra [a]						ΣB_5H_x
		$B_5^{11}H_x$	$B^{10}B_4^{11}H_x$	$B_2^{10}B_3^{11}H_x$	$B_3^{10}B_2^{11}H_x$	$B_4^{10}B^{11}H_x$	$B_5^{10}H_x$	
50	3.26	---------	---------	---------	---------	---------	0.012	38.7
51	0.31	---------	---------	---------	---------	0.25	.010	33.2
52	2.31	---------	---------	---------	1.98	.21	.013	40.8
53	9.92	---------	---------	7.93	1.70	.26	.013	40.5
54	25.1	---------	15.87	6.80	2.09	.26	.011	34.6
55	37.0	12.70	13.60	8.35	2.07	.22	.062	194.2
56	38.9	10.88	16.71	8.30	1.77	1.24	.003	9.5
57	47.1	13.37	16.61	7.08	9.94	0.06	.044	139.0
58	68.6	13.29	14.16	39.78	0.48	.89	---------	0.4
59	100..	11.33	79.57	1.93	7.12	.003	.048	149.9
60	97.0	63.66	3.87	28.49	0.02	.96	---------	---------
61	67.8	3.10	56.95	0.08	7.67	---------	---------	---------
62	76.4	45.56	0.15	30.69	---------	---------	---------	---------
63	61.5	0.12	61.38	---------	---------	---------	---------	---------
64	49.1	49.1	---------	---------	---------	---------	---------	---------

[a] "x" assumes integral values from zero to nine, reading down the column.

The four peaks of table 1 ascribed to doubly charged ions come from ions of masses 55, 57, 58, and 59. The small residual on the mass 30 peak (table 4) indicates that ions $B_5H_5^{++}$ are absent or very improbable and that the peak at 29.5 is largely $B_5^{11}H_4^{++}$. On this basis one can compute the monoisotopic doubly charged spectrum. The computations indicate that the 29 peak is entirely composed of doubly charged ions and the 28 peak is largely singly charged. The 27.5 peak can be either B_5^{11++} or $B_4^{11}B^{10}H^{++}$, but the absence of a 26.5 peak favors the latter possibility.

Table 5 gives the monoisotopic spectra of B_5H_9 computed as illustrated in table 3, on the basis of the B_5H_5 ion equal to 100 and includes the doubly charged ions. The B_5H_8 contribution is too small to be significant. If the ratio B^{10}/B^{11} were taken as 0.2505 instead of 0.2500, the computations would give $B_5H_8=0$ at 50 v with no significant change in the residuals used to check the computations. The $B_2H_6^+$ peak is not negligible but

TABLE 4. *Summary of check points for the mass spectrum of B_5H_9 at 50 volts ionizing voltage*

Group	Mixture peak		
	m/e	Observed	Calculated [a]
B_1	10	6.12	5.65
B_2	20	0	0.04
	21	0.20	.11
B_3	30	0.03	.01
	31	.17	.13
	32	.86	.64
B_4	40	.03	.01
	41	.26	.20
	42	1.45	1.48
	43	5.56	5.64
B_5	51	0.31	0.26
	52	2.31	2.20
	53	9.92	9.90
	54	25.1	25.0

[a] Calculated for the isotope abundances $B^{10}=0.20$, $B^{11}=0.80$.

TABLE 5. *Monoisotopic mass spectra of B_5H_9*

Ion	Relative intensities		Ion	Relative intensities	
	50 volts	70 volts		50 volts	70 volts
H	2.05	3.00	B_4	3.61	4.35
H_2	5.16	8.28	B_4H	6.96	7.37
			B_4H_2	13.2	12.8
B	14.8	20.7	B_4H_3	14.4	14.1
BH	2.01	3.03	B_4H_4	32.8	33.0
BH_2	10.5	12.2	B_4H_5	6.69	6.74
			B_4H_6	4.07	4.25
B_2	------	0.27			
B_2H	1.18	1.54	B_5	20.0	20.4
B_2H_2	2.22	2.54	B_5H	17.1	15.6
B_2H_3	1.62	1.64	B_5H_2	21.0	20.2
B_2H_4	0.27	0.27	B_5H_3	20.9	18.5
B_2H_5	1.26	1.28	B_5H_4	17.8	18.4
B_2H_6	0.31	0.39	B_5H_5	100.	100.
			B_5H_6	5.04	8.66
B_3	.61	.87	B_5H_7	71.4	71.7
B_3H	1.55	2.19	B_5H_8	0.25	0.36
B_3H_2	6.52	6.36	B_5H_9	77.2	78.0
B_3H_3	5.27	5.04			
B_3H_4	2.78	2.65	Doubly-charged ions		
B_3H_5	0.64	0.41			
B_3H_6	.83	.81	B_5H^{++}	0.03	0.06
			$B_5H_2^{++}$	0	0
			$B_5H_3^{++}$	0.28	0.28
			$B_5H_4^{++}$	.19	.26

could be ascribed to a trace of nitrogen in the pentaborane. In view of the precautions taken to pump out noncondensible gases, the evidence for $B_2H_6^+$ is considered probable but not certain. It is not diborane, as this would give a much larger $B_2H_5^+$ peak.

The H_2^+ ion is much more abundant than in hydrocarbons, but it definitely does not come from hydrogen in the sample. Thermal dissociation in the ionization chamber may account for a small part of this, but much less H_2^+ was found in the less stable compound, diborane.

IV. Discussion

The mass spectrum of B_5H_9 gives no definite information concerning the structure of the molecule. The high probability of ionization with loss of 2H or 4H is consistent with the view that four hydrogen atoms are loosely bound in "protonated double bonds", and the relative abundance of B_5 ions is suggestive of a stable 5-membered ring structure. However, there is no sound basis of comparison, as the spectrum is unlike that of C_5 ring compounds and also unlike that of diborane, the only other hydroboron that has been studied. In contrast to B_5H_9, diborane gives a very small molecule ion peak, and loss of H to give $B_2H_5^+$ is the most probable ionization product. The very small probability of losing one or three hydrogen atoms from B_5H_9 compared with loss of any other number from two to nine is an unusual feature. Also, the absence of a $B_5H_2^{++}$ ion is quite unlike all C_5 hydrocarbons. In

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most hydrocarbons ionization with loss of hydrogen atoms is more of a random process with certain processes favored but not to the extent of almost complete exclusion of a particular ion.

The analysis of the polyisotopic spectrum gives a value of the isotope ratio of $B^{10}/B^{11}=0.250\pm0.002$. This is in very satisfactory agreement with other values obtained in this laboratory. Samples of B_2H_6 from two different sources gave $B^{10}/B^{11}=0.251$ and 0.256, whereas the mass spectrum of BF_3 gave 0.250. These values are not in good agreement with the carefully measured values of Inghram [5] using the BF_3 spectrum and B^+ of $B(OCH_3)_3$, which both give $B^{10}/B^{11}=0.232$. The discrepancy is far beyond any experimental error and indicates a large difference in isotopic abundances in boron from different samples.

In the summary of check points, table 4, there is a significant discrepancy between the observed and calculated values for the mass 10 peak. This can be explained by the hypothesis that the probability of breaking a bond to B^{10} is slightly different from that for B^{11}. The heights of B, BH, and BH_2 peaks at 50 v give a value of $B^{10}/B^{11}=0.26$ as compared with 0.250 for the rest of the spectrum. This indicates that breaking a B^{10} bond is slightly more probable than breaking a B^{11} bond. A similar effect is well established in the case of C^{12} and C^{13} bonds in hydrocarbons.[6] In propane ionization, breaking a C^{12} bond is 20 percent more probable than breaking a C^{13} bond.

[5] M. G. Inghram, Phys. Rev. 70, 653 (1946).
[6] O. Beeck, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, J. Chem. Phys. 16, 255 (1948).