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B₉H₁₅ and B₈H₁₂: Synthesis, Equilibria, and Decomposition Kinetics

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Nonaborane-15 was prepared by reaction between liquid pentaborane-11 and gaseous diborane at 25 atm. pressure. Excepting yellow polymeric solids, nonaborane-15 was the only higher molecular weight species formed in more than trace amounts. In the inlet system of a mass spectrometer at about 50 μ pressure, the nonaborane-15 decomposed to octaborane-12, and the octaborane-12 in turn decayed to undetermined products, although one product almost certainly was hexaborane-10. Both decompositions occurred by first-order mechanisms. Mass spectra of these compounds are presented. Evidence also was obtained which indicated that reports of the existence of heptaboranes, at least five of which have been "observed" mass spectrally, are open to serious doubt. Certain alkylboranes, alkoxyboranes, and carboranes, which are readily generated by reactions between boranes and the common impurity, ethyl ether, have mass spectral characteristics similar to the anticipated heptaboranes. Reactions of boranes with ethane, an impurity frequently found with diborane, also could generate compounds in this spectral region.

In 1959 Parry and Edwards¹ systematized various aspects of borane chemistry based on observed properties and reactions, and they proposed the BH₃ group as a basic structural building block for boranes. Additionally, general tautomeric behavior by boranes had previously been postulated from n.m.r. by the fact that boranes display only one spatial configuration per empirical formula.² If one pictures a borane molecule as a (BH)_n framework (terminal hydrogens only), then normally it will additionally require either two or three BH₃ groups bridge-bonded to this framework. This arrangement completes the electronic occupation of four bonding orbitals per boron atom and provides the requisite stability. If the final assemblage contains two BH₃ groups, the species is a so-called "stable" borane, conforming to Stock's B_nH_{n+4} type; if it has three BH₃ groups it is an "unstable" borane of the B_nH_{n+6} type. If there is a deficiency of BH₃ groups, the bonding requirement is satisfied only by substitution of an electron-sharing ligand for the missing BH₃.

In order to depict this ostensibly functional role of the BH₃ group and also to facilitate "bookkeeping" in chemical reactions, we have found it useful to denote all boranes by one general expression, *viz.*, B_nH_n(BH₃)_x. According to this formula the more common boranes will have values of *n* ranging from 0 through 8. The so-called "stable" boranes correspond to *x* = 2, the "unstable" ones to *x* = 3, and transitions between opposite members in the two series (Table I) should in general occur with reasonable facility.

Table I includes all the known neutral-molecular polyboranes, up to and including *n* = 8, and it is conceivable that in this group only boranes conforming to the type formulas B_nH_n(BH₃)₂ and B_nH_n(BH₃)₃ may be stable enough to be isolated. Not all structures representable by these two formulas, however, will necessarily exist as isolable compounds, for some may simply represent a transient or very unstable species

TABLE I
ARRANGEMENT OF BORANES ACCORDING
TO THE FORMULA B_nH_n(BH₃)_x

<i>n</i>	<i>x</i> = 2 (stable)	<i>x</i> = 3 (unstable)
0	<i>B₂H₆</i> ^a	B ₃ H ₉
1	B ₃ H ₇	<i>B₄H₁₀</i>
2	B ₄ H ₈	<i>B₅H₁₁</i>
3	<i>B₅H₉</i>	B ₆ H ₁₂
4	<i>B₆H₁₀</i>	B ₇ H ₁₃
5	B ₇ H ₁₁	B ₈ H ₁₄
6	<i>B₈H₁₂</i>	<i>B₉H₁₅</i>
7	B ₉ H ₁₃	B ₁₀ H ₁₆ ^b
8	<i>B₁₀H₁₄</i>	B ₁₁ H ₁₇

^a Confirmed compounds are italicized, and for reasons to be given later heptaboranes are excluded from this category.
^b The dipentaboryl compound, B₁₀H₁₆, probably should be classified under *n* = 3; icosahedryl B₁₀H₁₆ as is yet unknown.

if a mechanistically easy addition or removal of BH₃ will produce a known polyborane. Prior to 1964 no more than one isolable borane had been substantiated for each of the values of *n*. The recent reporting of B₆H₁₂^{3,4} and B₈H₁₂,⁵ however, reveals that at least two members may be isolated from the *n* = 3 and *n* = 6 series. Other species such as B₃H₇ (from B₄H₁₀) and B₄H₈ (from B₅H₁₁) have been reported but only as reaction intermediates or as complexes in which the ligand, *e.g.*, Lewis base, H₂, H⁻, etc., substitutes for BH₃. These considerations suggest that very delicate (low-energy) methods might lead to the discovery of new unstable polyboranes, analogous to the recent discoveries of B₆H₁₂ and B₈H₁₂.

Lipscomb,⁶ from strictly geometrical considerations, has predicted that B₉H₁₃, B₇H₁₃ and B₇H₁₅, and possibly B₆H₁₄ and B₈H₁₄ should exist. Of these five species, B₆H₁₄ and B₇H₁₅ have *x* > 3 and hence are not included in Table I. Their respective generic formulas would be B₂H₂(BH₃)₄ and B₈H₈(BH₃)₄, and both com-

(3) D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, **3**, 438 (1964).

(4) C. A. Lutz, D. A. Phillips, and D. M. Ritter, *ibid.*, **3**, 1191 (1964).

(5) R. E. Enriore, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1451 (1964); *Inorg. Chem.*, **3**, 1659 (1964).

(6) W. N. Lipscomb, *ibid.*, **3**, 1683 (1964).

(1) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(2) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

pounds would have four bridge hydrogens and four BH₂ (terminal) groups.⁶ As such they would be very reactive and consequently highly unstable and difficult to isolate.

In the initial phases of our work we were attempting to generate boranes with $x > 3$, for example B₆H₁₄, by essentially forcing BH₃ to add to the already unstable compound B₅H₁₁. This would correspond to a transition from B₂H₂(BH₃)₃ to B₂H₂(BH₃)₄. The approach consisted simply of impressing high concentrations of gaseous diborane above liquid pentaborane-11, then observing spectral changes of the pressurized system by n.m.r. spectroscopy. The inherent instability of pentaborane-11 seemed to make this a good candidate reagent to add BH₃ from diborane. The result of the experiment, however, was the formation of B₉H₁₅, not B₆H₁₄, and the B₉H₁₅ furthermore appeared to be stabilized by the high concentration of diborane. The subsequent discussion includes a description of this mode of preparation of B₉H₁₅ and the kinetics of the subsequent decomposition of B₉H₁₅ to B₈H₁₂ and thence to unidentified products.

Experimental Section

Preparation of Nonaborane-15.—Pentaborane-11 was prepared and purified by methods previously described.^{7,8} In an initial experiment 0.319 mmole of pentaborane-11 and 1.20 mmoles of diborane were sealed in a 5-mm. tube, volume 1.16 ml., total pressure 25+ atm. Immediate observation of the mixture by B¹¹ n.m.r. showed simply diborane dissolved in pentaborane-11. After 2 days at room temperature, however, the resonant peak for apex boron atoms (in pentaborane-11) was barely discernible, thus revealing the diminution of pentaborane-11 and the absence of species such as pentaborane-9 and hexaborane-10. As was subsequently learned, however, some of these species had been formed but were below detectable limits (about 5%). Yellow coloration, indicating the formation of polymeric solids, also began to appear after about 2 days. The tube was allowed to remain at room temperature for several more days, but no further n.m.r. spectral changes were apparent.

After 1 week, the tube was opened and the contents were analyzed mass spectrometrically. Voluminous quantities of hydrogen, diborane (more diborane was recovered than was initially present), and tetraborane-10 were found. The remainder, however, consisted primarily of nonaborane-15 plus traces of the following: pentaboranes, hexaborane-10, an octaborane, and decaborane-14.⁹ Since nonaborane-15 is thermally unstable by itself,¹⁰ its presence after 1 week at room temperature in the initial experiment indicated that it was being stabilized (and perhaps formed initially) by some type of equilibrium reaction.

In two subsequent experiments, the products were fractionated in a high vacuum system and measured. The consumption of pentaborane-11 was greater for the first of these two experiments, but the total amount of nonaborane-15 formed was the same in both cases. The nonaborane-15 was subjected to simple distillation, but this did not entirely remove all impurities; fractionation of sample no. 2 (Table II) yielded a material having a

TABLE II

EXPERIMENTAL CONDITIONS FOR THE B ₂ H ₆ -B ₅ H ₁₁ REACTION		
Reactants (mmoles)	Expt. 2	Expt. 3
B ₂ H ₆	3.17	3.53
B ₅ H ₁₁	0.41	0.44
Final components (mmoles)		
B ₂ H ₆	3.24	3.58
B ₅ H ₁₁	0.20	0.315
B ₉ H ₁₅	0.04	0.04
B ₄ H ₁₀	0.06	0.02
H ₂	0.08	0.04
Reaction time, hr.	10.0	3.2
Tube volume, ml.	3.12	3.40

vapor pressure of 1 mm. at 28° and a melting point of -5°, compared with +2.7° obtained by Burg and Kratzer¹⁰ for nonaborane-15.

A series of experiments were then run in a stainless steel vessel attached directly to the mass spectrometer inlet system. The reaction temperature was maintained at 30°, the pressure at 27 atm. At 30-min. intervals, the reaction was quenched by immersing the vessel in liquid nitrogen. Any hydrogen that had formed was then pumped out, and the more volatile compounds (diborane, tetraborane, and the pentaboranes) were transferred out of the reactor into a second tank. The main transfer was carried out with the reactor at -30° to minimize further reaction, while the less volatile materials were removed after the reactor had been heated quickly to room temperature with a water bath. The last portion was admitted directly into the sample inlet system of the mass spectrometer (CEC Model 21-620) at pressures on the order of 50 μ. The inlet system was primarily of Pyrex glass construction; its volume was approximately 1400 cc.

Mass spectral scanning commenced within 1 min. after admission of the sample into the inlet system, primarily to see if the ostensibly metastable B₆H₁₄ could be detected. Generally, scanning required from 15 to 30 min., depending on the range of mass numbers, but we could arbitrarily select specific scanning areas—such as the B₆ range—if desired. After analysis was completed, the reactants were returned to the original stainless steel vessel and heated again for another 30-min. period. The process was repeated numerous times.

Nonaborane-15 and hexaborane-10 were detected in the initial experiments (as well as some pentaborane-11 that was not completely removed by fractionation), but in later runs hexaborane-10 was missing from the analyzed samples. (If B₆H₁₂ was present, it was masked by other boranes). It was not merely a matter of more efficient fractionation because the more volatile pentaborane was still present. We believe that the hexaborane-10 observed in the initial experiments probably formed during the 2- or 3-week storage period (at about -20°) prior to the first run and was not a product of the high pressure diborane-pentaborane-11 reaction.

Based on these experiments, then, nonaborane-15 and tetraborane-10 are the primary reaction products, and, under a high diborane pressure, the nonaborane-15 is stabilized by some type of equilibrium reaction. Compounds such as hexaborane-10, octaborane-12, and decaborane-14 are apparently formed by side reactions or by decomposition of nonaborane-15.

Results and Discussion

Improved Mass Spectrum of Nonaborane-15.—The mass spectrum of nonaborane-15 obtained in these experiments did not agree very well in the m/e 77 to 100 range with a sample we had previously handled and analyzed mass spectrometrically for Prof. A. Burg and Dr. R. Kratzer,¹⁰ indicating that it was decomposing to an eight-boron compound. With stable boranes, such as pentaborane-9 and decaborane-14, one can intro-

(7) A. B. Burg and F. G. A. Stone, *J. Am. Chem. Soc.*, **75**, 228 (1953).

(8) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).

(9) In the paper by Lutz, Phillips, and Ritter,⁴ B₆H₁₂ was observed to be one of the decomposition products of B₅H₁₁; this was unchanged even by the imposition of 10 atm. of B₂H₆. They did not report finding B₉H₁₅, but this perhaps was due to its decomposition in their chromatographic column. On the other hand, we did not observe hexaborane(s) in more than trace amounts. Furthermore, if B₆H₁₂ was present it occurred in such small amounts that it was masked by the spectrum of B₉H₁₅. The changes apparently effected by only a two- to threefold increase in diborane pressure are somewhat surprising.

(10) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

duce a sample into the inlet system and take successive spectra almost indefinitely without deterioration; unstable boranes such as pentaborane-11 and, to a lesser extent, tetraborane-10, can decompose appreciably in the finite time required for analysis. Thus, it is doubtful if anyone has ever obtained mass spectra of "pure" pentaborane-11 or tetraborane-10 because of the decay to other boranes. The same is true for nonaborane-15 and octaborane-12. Decomposition is particularly noticeable with a slow scanning spectrometer, such as the CEC-620 which we used. Our many attempts to approach the mass spectrum of "pure" nonaborane-15 have resulted in a spectrum which we intuitively feel contains less than 5% octaborane-12. Because the desirability of rapid analysis was unknown prior to these experiments, the spectrum obtained for Burg and Kratzer¹⁰ contains at least 25% octaborane-12, while a mass spectrum published by Lipscomb, *et al.*,¹¹ for nonaborane-15 appears to have about 60% octaborane-12 and only 40% nonaborane-15. We suspect the latter sample spent considerable time at room temperature between the time of its X-ray analysis and the subsequent mass spectral analysis. The mass spectrum of our best sample of nonaborane-15 is shown in Table III.

Kinetics of the Decomposition of Nonaborane-15.—Analysis of the sample of nonaborane-15 in the inlet system of the mass spectrometer over a period of several hours left no doubt that it was continuously decomposing to octaborane-12. Peaks in the m/e 90–100 range, in particular, were increasing while peaks in the m/e 102–112 region (nonaborane fragments) were decreasing. Complicating the analyses, of course, was the simultaneous decay of all ion intensities because of effusion of the molecules through the gold leak. Also, the initial sample of nonaborane-15 contained pentaborane-11 and tetraborane-10 impurities in addition to the small but unavoidable initial concentrations of octaborane-12.

Simultaneous with the B_8 and B_9 spectral changes, there were increases in ion intensities in the hexaborane-10 region (maximum at m/e 71 and cutoff at m/e 76) and in the hydrogen region (m/e 1 and 2). There was also a very slow increase in the concentration of decaborane-14, suggesting that it was probably being formed from some type of side reaction. Qualitative studies of the decomposition of tetraborane-10 and pentaborane-11 in the mass spectrometer inlet system indicated that they also produced hexaborane-10. For the present discussion, however, we are concerned only with the decomposition of nonaborane-15 to octaborane-12 and the subsequent decomposition of octaborane-12 to unspecified products.

The decay in intensity of mass number 105, which is the principal peak of nonaborane-15 and which is unencumbered by other borane species (except decaborane, which was present in negligible amounts) was found to follow a first-order rate law. Since the con-

TABLE III

POLYISOTOPIC MASS SPECTRUM OF NONABORANE-15					
m/e	Intensity	m/e	Intensity	m/e	Intensity
112	9.2	73	3.3	34	1.4
111	21.9	72	5.0	33	0.5
110	53.2	71	6.2	32	0.6
109	83.6	70	8.3	31	Tr.
108	94.7	69	10.4	30	0.0
107	85.3	68	10.5	29	1.1
106	90.1	67	10.1	28	2.2
105	100.0	66	7.1	27	9.5
104	86.7	65	3.7	26	8.2
103	57.5	64	1.4	25	5.2
102	34.8	63	0.4	24	6.9
101	25.9	62	0.1	23	3.4
100	24.3	61	0.4	22	0.9
99	25.1	60	1.4	21	Tr.
98	24.6	59	5.5	20	Tr.
97	22.9	58	7.7	19	...
96	22.0	57	7.7	18	...
95	20.7	56	5.8	17	...
94	28.2	55	4.4	16	...
93	37.3	54	3.5	15	0.5
92	38.5	53	5.5	14	3.3
91	35.5	52	8.1	13	34.5
90	29.7	51	5.3	12	14.1
89	16.6	50	2.2	11	24.8
88	20.2	49	2.0		
87	16.6	48	3.8		
86	9.8	47	6.4		Half-peaks
85	4.3	46	5.7		
84	2.1	45	3.8	53.5	2.2
83	2.8	44	1.7	52.5	7.1
82	6.1	43	1.3	51.5	6.8
81	9.3	42	0.4	50.5	3.6
80	13.0	41	0.5	49.5	1.1
79	15.7	40	0.2	48.5	0.4
78	14.5	39	1.5	47.5	1.7
77	12.7	38	1.5	46.5	1.7
76	10.4	37	2.2	45.5	1.4
75	6.8	36	2.5	44.5	0.6
74	4.3	35	2.4	43.5	Tr.

centration of nonaborane-15 is proportional to the intensity of m/e 105, we can write

$$-\frac{d[B_9H_{15}]}{dt} \propto -\frac{dI_{105}}{dt} = k_9 I_{105}$$

or

$$-\frac{d(\log I_{105})}{dt} = -\frac{k_9}{2.303}$$

If the reaction is first order, a plot of $\log I_{105}$ vs. time will produce a straight line with slope equal to $k_9/2.303$. Since, however, there is also a natural decay in all ion intensities due to effusion through the gold leak, the rate constant for this decay must be subtracted from the total rate constant, assuming that the pressure decay is also first order. The rate equation would then be broken down as follows

$$-\frac{dI_{105}}{dt} = (k_1 + k_{d_1})I_{105}$$

k_1 is the rate constant for leakage of B_9H_{15} through the gold leak and k_{d_1} is the rate constant for the chemical

(11) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).

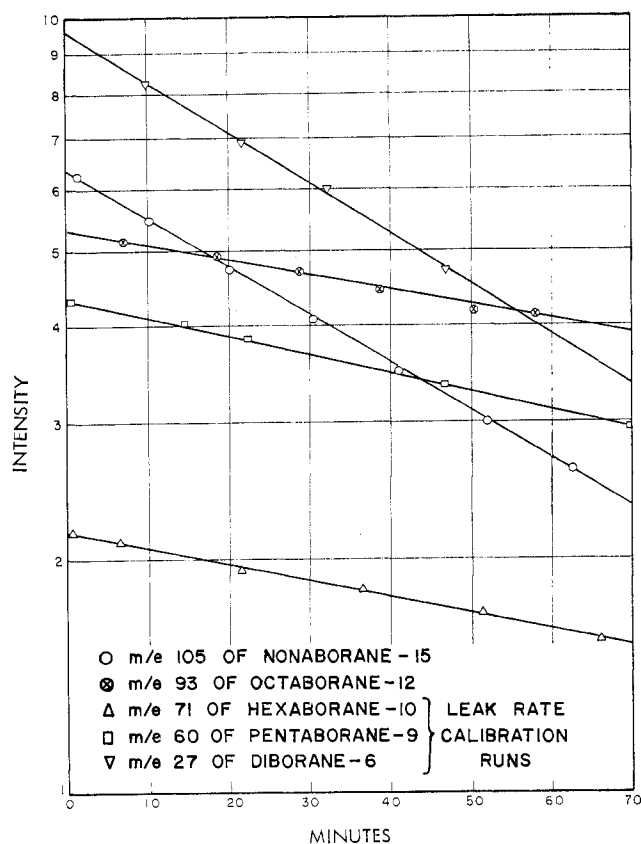


Figure 1.—Logarithmic plot of ion intensities vs. time for various boranes.

decomposition of B₉H₁₅. We were unable to analyze these two conditions separately with our experimental setup. Leak rate calibration runs were made with B₂H₆, B₅H₉, and B₆H₁₀ and were found to follow the expected first-order rate laws. The data are plotted in Figure 1; the experimental rate constants for the pressure decays of these three compounds are

$$k_{12} = 1.09 \times 10^{-4} \text{ sec.}^{-1} \quad (\text{B}_2\text{H}_6)$$

$$k_{15} = 9.65 \times 10^{-5} \text{ sec.}^{-1} \quad (\text{B}_5\text{H}_9)$$

$$k_{15} = 3.48 \times 10^{-5} \text{ sec.}^{-1} \quad (\text{B}_6\text{H}_{10})$$

According to molecular effusion equations, the volume rate of flow of an ideal gas through a small orifice is inversely proportional to the square root of its molecular weight. Hence, the leakage rate constants should be related as is shown in Table IV. The agreement between calculated and measured values is adequate. The measured value obtained for hexaborane-10 was used to calculate the values for octaborane-12 and nonaborane-15.

TABLE IV
LEAK RATE CONSTANTS OF BORANES
IN THE MASS SPECTROMETER INLET SYSTEM

		Calcd., sec. ⁻¹	Measd., sec. ⁻¹
B ₃ H ₉ :	$k_{15} = \sqrt{27.6/63.0}k_{12}$	7.2×10^{-5}	9.7×10^{-5}
B ₆ H ₁₀ :	$k_{15} = \sqrt{27.6/74.8}k_{12}$	6.6×10^{-5}	3.5×10^{-5}
B ₈ H ₁₀ :	$k_{15} = \sqrt{63.0/74.8}k_{15}$	8.9×10^{-5}	3.5×10^{-5}
B ₈ H ₁₂ :	$k_{15} = \sqrt{74.8/98.4}k_{15}$	3.0×10^{-5}	
B ₉ H ₁₅ :	$k_{15} = \sqrt{74.8/112}k_{15}$	2.8×10^{-5}	

From the slope of the time plot of *m/e* 105 in Figure 1, the rate constant for the *total* decay of mass number 105 is $k_{15} + k_{d_0} = 2.52 \times 10^{-4} \text{ sec.}^{-1}$. Substitution for k_{15} , then gives $k_{d_0} = 2.2 \times 10^{-4} \text{ sec.}^{-1}$.

Mass Spectrum of Octaborane-12.—In the decomposition studies of nonaborane-15, seventeen composite spectra were obtained over a period of 200 min., at which time the concentrations of nonaborane-15 and octaborane-12 were approximately equal. The spectrum of octaborane-12 was then obtained by subtracting the nonaborane-15 spectrum (Table III) from the final six composites for mass numbers in the range from 77 to 112. (The presence of trace amounts of octaborane-12 in the nonaborane-15 spectrum would reduce the total octaborane-12 intensity in the composite spectrum but would not affect the relative peak heights.) Therefore, the residual spectra (above *m/e* 77) were essentially pure octaborane-12. The six spectra were normalized by setting *m/e* 93 equal to 100, and the ion intensity for each peak was then taken as the average from the six normalized values. The mass cutoff occurred at *m/e* 100, corresponding to B₈H₁₂⁺. There were small residuals at *m/e* 101 and 102, but these were low enough to be attributable to experimental error.

The resultant spectrum of octaborane-12, shown in Table V, compares favorably, considering the different types of instruments, with the over-all spectral features reported previously.^{5,12,13} In fact, because of the close spectral similarities to the B₈H₁₂ compound characterized by Enrione, Boer, and Lipscomb,⁵ we assume that our compound is identical with theirs and is not B₈H₁₄.

TABLE V
POLYISOTOPIC MASS SPECTRUM
OF THE PRINCIPAL PEAKS OF OCTABORANE-12

<i>m/e</i>	Intensity	<i>m/e</i>	Intensity	<i>m/e</i>	Intensity
100	9.8	92	85.0	84	8.1
99	25.0	91	59.6	83	18.0
98	42.3	90	35.8	82 ^a	40.5
97	51.1	89	40.4	81	27.5
96	55.5	88	26.2	80 ^a	46.3
95	64.8	87	24.0	79	30.4
94	83.0	86	17.0	78	20.9
93	100.0	85	15.7	77	24.9

^a Mass numbers 80 and 82 contain HBr⁺ impurity from a previous analysis in the mass spectrometer.

Kinetics of the Decomposition of Octaborane-12.—As discussed in the previous section, the last six composite spectra were stripped of nonaborane-15 to give residual spectra due only to octaborane-12. These residual spectra then provided a time decay record of octaborane-12 in the experiment. Mass number 93, the highest peak, was selected to show this decay (Figure 1). Again the decay was observed to follow a first-order rate law. Since the rate in this case depends not only on the leak rate and the decomposition rate but also on

(12) I. Shapiro and B. Keilin, *J. Am. Chem. Soc.*, **76**, 3864 (1954).

(13) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, "Borax to Boranes," *Advances in Chemistry Series*, American Chemical Society, Washington, D. C., 1961, p. 127.

the rate of formation of B_8H_{12} from B_9H_{15} , we may write the rate equation as

$$-\frac{dI_{93}}{dt} = (k_{i_8} + k_{d_8} - k_{i_8})t$$

k_{i_8} has been estimated previously, and if we assume that one B_8H_{12} molecule is produced from the decomposition of each B_9H_{15} , then the rate constant for formation of octaborane-12, k_{i_8} , equals the rate constant for decomposition of nonaborane-15, k_{d_8} . From a plot of m/e 93 vs. time (Figure 1) we find that $k_{i_8} + k_{d_8} - k_{i_8} = 7.45 \times 10^{-5} \text{ sec.}^{-1}$. Substitution then gives $k_{d_8} = 2.6 \times 10^{-4} \text{ sec.}^{-1}$. Under the conditions of these experiments (room temperature, about 50 μ pressure), the decomposition rates of B_8H_{12} and B_9H_{15} are essentially equal and both reactions are first order.

Heptaboranes.—During the course of the mass spectral investigation, we were continuously looking for evidence of B_7 hydrides which have been reported numerous times in the literature. In previous work we had also observed peaks in this mass range and had attributed them to heptaborane. In this investigation, however, no B_7 compounds (and also no B_8 compounds other than hexaborane-10) were evident.

Among boranes of these types that have been reported are two heptaboranes, observed mass spectrometrically by Gibbins and Shapiro.¹⁴ These compounds were reported as superimposed on each other, one having a maximum at m/e 83 and the other at m/e 87. The high mass cutoff occurred at m/e 92, corresponding to $B_7H_{15}^+$. Fehlner and Koski¹⁵ have reported somewhat similar spectra except that the highest mass cutoff occurred at m/e 90 instead of m/e 92. The compound with a maximum at m/e 87 and cutoff at m/e 90 was reported as $B_7H_{13}^+$, while the one with a maximum at m/e 83 had a cutoff at m/e 88 and was reported as $B_7H_{11}^+$. Their composite spectrum had the same general profile as that observed—but not published in total—by Gibbins and Shapiro¹⁴ except that the cutoff occurred two mass numbers lower. Schaefer, Ludlum, and Wiberly¹⁶ have reported a $B_7H_{12}^+$ fragment, while Schaeffer¹⁷ observed $B_7H_{14}^+$. All in all, then, the heptaboranes that have been reported include B_7H_{11} , B_7H_{12} , B_7H_{13} , B_7H_{14} , and B_7H_{15} , or at least these are the parent ion fragments of the reported compounds. It is highly unlikely that all of them could exist.

To enable us to study this problem, Dr. Gibbins provided us with a sample of a higher boiling borane fraction (from electrical discharge reactions) which he had prepared in an identical manner with the fraction in which he had observed heptaborane compounds. The same critical mass spectral peaks in the B_7 ion region were also evident in this second sample.

Surprisingly, however, the compounds responsible for these ion fragments in the B_7 region survived 6–10

min. in a chromatographic column at 50° and, later, several months at room temperature. In fact, they increased in intensity relative to hexaborane-10, nonaborane-15, octaborane-12, etc., which were also present initially in various amounts. After several months at room temperature the mixture was heated for about 30 min. at 60°, then vacuum fractionated to concentrate the compounds of interest. Analysis then revealed that the "heptaborane" which had cut off at m/e 92 and which had a maximum at m/e 87 was in fact ethylpentaborane, identified by mass spectral comparison with a sample of 2-ethylpentaborane.¹⁸ Ethyl ether, with principal peaks at m/e 74, 59, and 31, and triethoxyborane, with a strong (rearrangement) peak at m/e 85 plus other higher mass peaks, were also positively identified in this mixture.

The compound which had a maximum at m/e 83 was not identified. Candidates include alkoxyboranes, various B_5 carboranes, and possibly methylhexaborane (not previously reported). Analogous to the relationship between pentaborane-9 and ethylpentaborane, which have maxima five mass numbers below their cutoff points, the maximum for methylhexaborane would occur at roughly the same relative position as that of hexaborane-10, *viz.*, seven mass numbers below the cutoff, which would put it in the vicinity of m/e 83.

With the spectra of the several species superimposed on one another, the profile of the composite spectrum changed with each successive fractionation step and one could "identify" practically any of the reported "heptaboranes" at one time or another during this treatment. Two small peaks above hexaborane-10, *viz.*, m/e 77 and 78, were also observed, and we presume these are due to methylpentaborane, not hexaborane-12.

As supporting evidence, we heated various mixtures of diborane and ethyl ether at 135° for periods up to 45 min., and in every sample we positively identified ethylpentaborane and triethyl borate; other undetermined peaks also were present. More vigorous treatment, such as electrical discharge, probably would have produced an even greater number of species. The relative intensities and mass spectral profiles could be modified as before by varying the fractionation procedures. Very small mass spectral peaks were again observed at m/e 77 and 78.

Another impurity frequently found in boranes, particularly in diborane, is ethane. Under mild conditions ethane would not react with boranes, but under more severe treatment, such as electrical discharge or shock tube reactions, the formation of alkylboranes or carboranes would be expected.

The above admittedly is negative evidence, but it certainly indicates at the very least that the identification of previously *unknown* compounds with nothing more than simple mass spectral evidence must be viewed very critically. Even if the unknown compound can be completely isolated, it cannot always be identified with certainty; the technique of reducing the polyisotopic

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

(15) T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 1012 (1964).

(16) R. W. Schaefer, K. H. Ludlum, and S. E. Wiberly, *ibid.*, **81**, 3157 (1959).

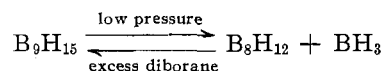
(17) R. Schaeffer, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959.

(18) Furnished by Prof. Thomas Onak, California State College, Los Angeles.

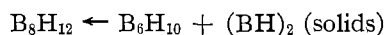
to a monoisotopic spectrum and then observing minimal residuals is unreliable when more than five or six borons are present in the molecule. Small errors can be greatly amplified during the process of reduction, least-squares methods notwithstanding, and the final result can be very misleading.

Dickerson and Lipscomb¹⁹ in their topological studies of borane structures in 1957 predicted that heptaboranes are not likely to exist. However, in a more recent paper⁶ based on geometrical considerations, as mentioned previously, Lipscomb has reanalyzed the situation and now nominates B₇H₁₃ and B₇H₁₅ as likely candidates awaiting discovery. Since the only experimental evidence for "heptaboranes" to date has been from simple mass spectral data, we feel their existence has not been demonstrated, and the evidence is open to serious doubt. More conclusive proof is needed before Lipscomb's predictions can be verified.

Discussion of Chemical Mechanisms.—In our experiments on the preparation of nonaborane-15, the exact role of diborane was undetermined. Once the nonaborane-15 was formed, however, the high pressure of diborane appeared to be the stabilizing effect that inhibited decomposition to octaborane-12. Subsequent experiments then showed that nonaborane-15 by itself decomposes by first-order kinetics to octaborane-12, almost certainly by simple loss of BH₃. The following equilibrium condition would explain these observations.



The octaborane-12 that was formed from the nonaborane-15 also decomposed by first-order reaction, and a primary product of this transition appeared to be hexaborane-10, presumably by a reaction such as



The general decay sequence, B₉H₁₅ → B₈H₁₂ → B₆H₁₀, appears feasible from a comparison of their structures, which have striking similarities. Drawings of the structures of nonaborane-15,²⁰ octaborane-12,⁵ and hexaborane-10²⁰ are shown in Figure 2.

(19) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

(20) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 7.

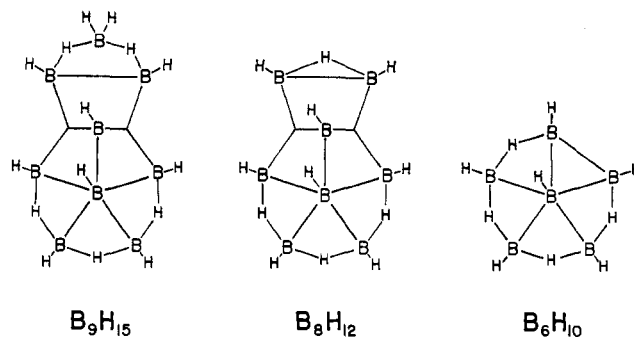


Figure 2.—Drawing showing structural similarities of nonaborane-15, octaborane-12, and hexaborane-10.

One can visualize two general routes by which nonaborane-15 might have been formed from pentaborane-11. The first route is that of successive stepwise additions of BH₃ to pentaborane-11, going through intermediates such as hexaborane-12, octaborane-12, etc., while the second is a more direct polymerization of pentaborane-11 and/or its decomposition product, tetraborane-10. There is no evidence to indicate which of these two routes is the preferred one.

Experimentally, the first observable reaction was the slow disappearance of pentaborane-11, which was essentially gone by the end of 2 days. The concentrations of diborane and tetraborane increased during this period, while hydrogen formation was essentially nil. The decomposition of pentaborane-11 to tetraborane and diborane is a well-known reaction,²¹ however, and, since it uses up hydrogen, it could explain the absence of hydrogen in the initial stages of the experiment.

At present we are constructing bench-scale equipment for preparation of fairly large quantities of pentaborane-11 and with this ample supply of raw materials we expect to be able to study the high pressure transition of pentaborane-11 to nonaborane-15 in considerably more detail than in the past.

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(21) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4009 (1933).