*e.g.*, for $OF_2$ and $AsF_5$ (1:1) at 200 atm and 200° the cylinder would be charged with $\sim$0.064 mol of $OF_2$ and $\sim$0.064 mol of $AsF_5$. The reactor was then placed in an oven. After the reaction period the remaining gases were pumped off through traps in $N_2$(l) followed by a scrubber containing a NaOH–CaO mixture to protect the pump. The white solid products were removed and handled in a drybox. Yields (based on $AsF_5$) varied from 40% in the 1:1 case to 81% in the 2:1 case at 200° for 6 days.

(b) **With Oxygen and Fluorine.**—Reactants were charged to the cylinder as above in the Lewis acid:$O_2$:$F_2$ ratio of 1:1:$^1/_2$. After 1 week at temperatures in the range of 130–200°, a yield of 97–98% of the salt was realized.

*Anal.* Calcd for $O_2AsF_6$: As, 33.91; F, 51.6. Found: As, 33.56; F, 51.8. Calcd for $O_2SbF_6$: Sb, 45.47; F, 42.59. Found: Sb, 45.8; F, 41.3.

**Analytical Methods.** (1) **Fluoride.**—This was steam distilled from sulfuric acid at 155°. The distillate was buffered to pH 3.1 and titrated with $Th(NO_3)_4$ using alizarin red S as the indicator. The procedure used was a modification of that of Willard and Winter.[17–20]

(2) **Antimony and Arsenic.**—These elements were reduced to the +3 oxidation state with sulfur and then determined by titration with $KBrO_3$.[21, 22]

(3) **Infrared Spectra.**—A Perkin-Elmer 337 spectrophotometer was used to record ir spectra in the range 2.5–25 $\mu$. Spectra of solids were made by using mulls of Kel-F oil between AgCl disks or by using KCl pellets. Spectra of gases were made using a 5-cm length cell made from 1-in. nickel pipe fitted with a valve. Windows were 25-mm diameter rolled AgCl and were sealed to the cell with Kel-F 200 wax.

(4) **X-Ray Powder Patterns.**—Samples were transferred to Pyrex capillary tubes and sealed. These operations were made in a drybox. The photographs were made using a GE 143.2-mm camera and Cu $K\alpha$ irradiation through a nickel filter.

**Acknowledgment.**—We acknowledge the help of Mr. Karl Schmidt in the experimental work and Dr. V. G. Meadors for consultation and suggestions. Also, we thank Dr. C. Maddin and Mr. R. Van Nordstrand for their help with the X-ray powder patterns.

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[20] R. J. Rowley and H. V. Churchill, *Ind. Eng. Chem., Anal. Ed.*, **9**, 551 (1937).

[21] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, Ed., "Applied Inorganic Analysis," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1953, pp 273–276.

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# Molecular Beam Mass Spectrum, Pyrolysis, and Structure of Octaborane(18)[1]

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The molecular beam mass spectrum of octaborane(18) and the appearance potential of the ion $B_4H_9^+$ were measured. These measurements support a proposed structure for the compound in which two tetraborane fragments are joined by a single B–B bond. In addition, a pyrolysis study was made to determine the nature of the thermal decomposition of this unusual boron hydride; both tetraborane(8) and tetraborane(10) appear to be formed in the initial steps of the decomposition.

## Introduction

Reaction of the unstable boron hydride octaborane(18) with hydrogen and with carbon monoxide results in cleavage to tetraborane(10) and tetraborane carbonyl, respectively.[3] Formation of these compounds is suggestive that octaborane(18) is comprised of two tetraborane(9) units connected by a B–B bond. This structure is one of two which are compatible with observed nmr data for the compound. The second structure is a belt-line icosahedral fragment.[3]

Neither a crystal structure nor a mass spectrum for octaborane(18) has been published. Since the ion fragmentation patterns of the two diverse structures that have been proposed for this boron hydride should be distinctly different,[4,5,6] the mass spectrum of octaborane(18) is expected to give evidence for its structure.

Because of the thermal instability of the boron hydrides, pyrolysis of a compound in the room-temperature inlet or on the hot-ion source of a conven-

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[2] Recipient of Public Health Service Fellowship 1-F1-GM-29, 815-01A1 from the National Institute of General Medical Sciences, 1966–1968.

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TABLE I

POLYISOTOPIC MOLECULAR BEAM[a] AND TOTAL INTENSITY[b] MASS SPECTRA OF OCTABORANE(18)

| m/e | Molecular beam[a] | Total[b] | Shutter %[c] | m/e | Molecular beam[a] | Total[b] | Shutter %[c] |
|---|---|---|---|---|---|---|---|
| 106 P[d] | 0.05 | 0.06 | 33 | 66 | 4.08 | 4.90 | 23 |
| 105 | 0.05 | 0.08 | 26 | 65 | 2.49 | 2.80 | 25 |
| 104 | 0.05 | 0.06 | 31 | 64 | 3.50 | 7.86 | 12 |
| 103 | 0.05 | 0.07 | 30 | 63 | 4.98 | 10.6 | 13 |
| 102 | 0.04 | 0.07 | 23 | 62 | 8.44 | 18.2 | 13 |
| 101 | 0.03 | 0.14 | 7 | 61 | 10.2 | 19.2 | 15 |
| 100 | 1.06 | 0.77 | 38 | 60 | 10.3 | 21.7 | 13 |
| 99 | 2.11 | 1.59 | 37 | 59 | 11.1 | 22.5 | 14 |
| 98 | 3.83 | 2.96 | 36 | 58 | 10.7 | 17.9 | 17 |
| 97 | 5.56 | 4.18 | 37 | 57 | 8.00 | 12.6 | 18 |
| 96 | 6.14 | 5.03 | 34 | 56 | 5.84 | 10.2 | 16 |
| 95 | 6.03 | 5.26 | 32 | 55 | 3.80 | 8.08 | 13 |
| 94 | 6.16 | 5.53 | 31 | 54 | 2.37 | 4.90 | 13 |
| 93 | 6.24 | 6.01 | 29 | 53 | 20.7 | 15.3 | 38 |
| 92 | 5.04 | 4.83 | 29 | 52 | 76.8 | 56.8 | 38 |
| 91 | 3.15 | 3.37 | 26 | 51 | 100.00 | 79.5 | 35 |
| 90 | 2.00 | 2.06 | 27 | 50 | 96.4 | 100.00 | 27 |
| 89 | 1.69 | 1.62 | 29 | 49 | 63.8 | 79.7 | 22 |
| 88 | 2.15 | 2.09 | 29 | 48 | 35.0 | 57.1 | 17 |
| 87 | 2.33 | 2.23 | 29 | 47 | 22.7 | 42.8 | 15 |
| 86 | 2.23 | 2.19 | 28 | 46 | 14.6 | 27.5 | 15 |
| 85 | 1.96 | 2.16 | 25 | 45 | 7.15 | 15.7 | 13 |
| 84 | 2.91 | 2.80 | 29 | 44 | 2.55 | 8.41 | 8 |
| 83 | 3.51 | 3.78 | 26 | 43 | 0.53 | 4.74 | 3 |
| 82 | 3.69 | 3.73 | 28 | 39 | 11.9 | 11.6 | 29 |
| 81 | 4.10 | 3.60 | 32 | 38 | 12.9 | 22.8 | 16 |
| 80 | 3.80 | 3.52 | 30 | 37 | 12.9 | 20.8 | 17 |
| 79 | 3.80 | 3.44 | 31 | 36 | 9.60 | 17.5 | 15 |
| 78 | 3.50 | 3.26 | 30 | 35 | 6.27 | 13.7 | 13 |
| 77 | 3.28 | 3.04 | 30 | 34 | 2.63 | 6.67 | 11 |
| 76 | 5.59 | 5.55 | 28 | 33 | 0.76 | 2.13 | 10 |
| 75 | 6.38 | 6.78 | 26 | 27 | 5.82 | 19.5 | 8 |
| 74 | 8.37 | 9.36 | 25 | 26 | 3.40 | 14.7 | 6 |
| 73 | 8.52 | 9.66 | 25 | 25 | 2.76 | 8.82 | 9 |
| 72 | 10.3 | 13.0 | 22 | 24 | 2.09 | 11.2 | 5 |
| 71 | 9.92 | 13.9 | 20 | 14 | 0.17 | 2.99 | 2 |
| 70 | 8.53 | 11.3 | 21 | 13 | 6.77 | 21.6 | 9 |
| 69 | 7.35 | 8.87 | 23 | 12 | 1.94 | 8.01 | 7 |
| 68 | 6.75 | 7.48 | 25 | 11 | 5.63 | 20.3 | 8 |
| 67 | 5.92 | 6.76 | 24 | 10 | 1.68 | 5.24 | 9 |

[a] Intensity of the shutterable (molecular beam) portion of the peak relative to the most intense peak at *m/e* 51. [b] Total intensity spectrum: background plus molecular beam (shutterable) species relative to *m/e* 50. [c] Ratio of shutterable to total intensity, *i.e.*, column 2/column 3. See also footnote 17. [d] P = parent.

tional[7] instrument may interfere with the determination of its fragmentation pattern. Molecular beam mass spectra,[8–13] however, do not include spectra of these pyrolysis products and can be used to determine borane fragmentation patterns and to study their low-pressure pyrolysis behavior.

The purpose of this work is to investigate the molecular beam mass spectrum of octaborane(18) and to use it to draw conclusions about the structure of this compound. In addition, pyrolysis behavior of the compound is studied.

## Experimental Section

Octaborane(18) was prepared as a trace product in the reaction of tetramethylammonium triborohydride with polyphosphoric acid.[3, 14] Data were collected with a Nuclide Analysis Associ-

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(7) 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 ionization 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.

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

(9) S. J. Steck, G. A. Pressley, Jr., F. E. Stafford, J. Dobson, and R. Schaeffer, unpublished work.

(10) F. E. Stafford, G. A. Pressley, Jr., and A. B. Baylis, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968, p 137.

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

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

(13) 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, No. V4.

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

ates Model 12-60 HT Inghram-type mass spectrometer[15] with a gas-inlet system that permitted the sample to be distilled from a low-temperature bath directly to the molecular beam source.[8-13]

The sample tube was placed in a chlorobenzene slush bath until impurities more volatile than the octaborane(18) were no longer detected with the mass spectrometer. For the measurement of the mass spectrum, a Dry Ice–acetone slush bath was used to obtain a suitably low vapor pressure of the boron hydride. Sample vapor entered the spectrometer through a brass and stainless steel inlet line leading to a 0.75-in. i.d. baffled stainless steel reactor with a $9.1 \times 10^{-3}$ cm$^2$ orifice in its cap. This orifice served as the source of the molecular beam. For study of the pyrolysis reaction of octaborane(18), the reactor was heated by radiation from tungsten filaments; the temperature was measured using thermocouples spot-welded to the reactor. Drawings of this inlet system are given elsewhere.[10,11]

Molecular beam species originating from the reactor orifice were differentiated from those present in the ion source region as background by use of a movable beam defining slit ("shutter").[8,10] This device permitted exclusion of pyrolysis products of octaborane(18) from the molecular beam spectrum.

Normal operating conditions for the ion source were: ionizing voltage, 70 eV; total emission current, 1.2 mA; trap current, $\sim 10^{-6}$ A; and ion-accelerating voltage, 4 kV. Appearance potential curves of ion intensity *vs.* voltage were automatically plotted by an X-Y recorder.[16] Curves were evaluated by the vanishing current method and were calibrated against argon.

After being mass analyzed in a 60°, 12-in. radius of curvature magnetic sector, the ions were detected by a 50% transmission grid that served as a Faraday collector and a 16-stage secondary electron multiplier. Total energy of the ions striking the first dynode was 7900 eV. Typical multiplier gains at this energy were: $B_1H_x^+$ ion group, $3.0 \times 10^4$; $B_2H_x^+$, $7.5 \times 10^4$; $B_3H_x^+$, $1.5 \times 10^5$; $B_4H_x^+$, $1.7 \times 10^5$; $B_5H_x^+$, $1.8 \times 10^5$; $B_6H_x^+$ and $B_7H_x^+$, $1.9 \times 10^5$; and $B_8H_x$, $2.0 \times 10^5$.

## Results

**Mass Spectra.**—Ions and their neutral progenitors are identified by means of mass defect, isotope ratio, and percentage shutter effect.[17]

Two mass spectra, observed when octaborane(18) is admitted to the spectrometer, are given in Table I. The first is the molecular beam spectrum, *i.e.*, that due to species in the molecular beam as determined by using the shutter. These species are believed to have had no chance to strike the walls of the vacuum chamber nor the various hot surfaces of the ion source. The second spectrum is the total intensity spectrum and is due to molecular beam species plus those molecules that have escaped from the reactor orifice and have entered the ion source after collisions with the various metal surfaces. This spectrum can include products of the decomposition of the octaborane(18) on such surfaces as the hot plates of the ion source.

The data had a small, systematic time dependence because the slush bath warmed up slowly during the 12–15 hr required to measure a mass spectrum. Both spectra in Table I have been corrected for this effect on the basis of mass scans in opposite directions. The remaining error in the relative intensities is believed to be small.

Small ion intensities (*ca.* 0.02%) were observed in the molecular beam mass spectrum at masses higher than *m/e* 106, the parent peak of octaborane(18). The intensity distribution of these peaks and of those at *m/e* 106–101 indicate that the latter result from impurities, probably nona- and decaboranes. *m/e* 100 ($^{11}B_8H_{12}^+$), with a relative intensity of 1.06%, is the first peak attributable to octaborane(18) and corresponds to the loss of six hydrogens from the parent ion; this loss is unusual for a boron hydride.

The molecular beam mass spectrum of octaborane(18), depicted in Figure 1, markedly differs from any others so far observed for boron hydrides.[5,6,9,10,18] In previously determined spectra,[5,6,9,10,18] the most intense ions are those containing the parent number of borons. In the present case, the most intense ions contain four borons; the most intense peak is at *m/e* 51 ($^{11}B_2{}^{10}B_2H_9^+$, $^{11}B_3{}^{10}BH_8^+$, and $^{11}B_4H_7^+$). This anomalous ion distribution does not result from any known tetraborane present as an impurity. Both pentaborane and hexaborane impurities, which are less volatile than tetraborane(10), were observed to distil away while the sample tube was in a chlorobenzene slush preliminary to the measurement of the mass spectrum.

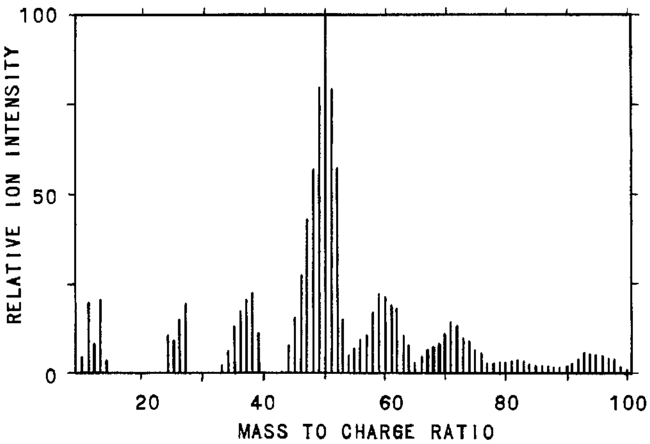

Figure 1.—Molecular beam mass spectrum of octaborane(18).

The total intensity mass spectrum of octaborane(18), given in column 3 of Table I, differs from the molecular beam spectrum because of the contributions from pyrolysis products. In the $B_6H_x^+$ ion group (*m/e* 77–65), the most intense peak in the molecular beam mass spectrum is at *m/e* 72; that of the total intensity spectrum is at *m/e* 71. Together with the somewhat

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

(16) R. J. Loyd and F. E. Stafford, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968, p 127.

(17) "Shutter per cent" is the ratio of the molecular beam intensity to the total ion intensity at a given mass peak. Ions formed from a stable molecule, such as CO and C from CO, would have about a 10% shutter effect at these temperatures. Ions from a reactive species, one that is rapidly pumped by collisions with the vacuum chamber walls, would have a 100% shutter effect. The higher the per cent shutter effect, therefore, the less stable the progenitor molecule is likely to be.

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

different relative intensities for this ion region in the two spectra, this change in the principal peak indicates pyrolytic formation of a hexaborane which is observed only in the total intensity spectrum.

Formation of a stable pentaborane is suggested by the larger relative intensity of the $B_5H_x^+$ ion group (*m/e* 64–54) and the abrupt change in the shutter per cent[17] (Table I) between masses 65 and 64. Pyrolytic formation of tetraborane is indicated by a change of the principal peak at *m/e* 51 in the molecular beam mass spectrum to a principal peak at *m/e* 50 in the total intensity spectrum and by the small shutter per cents[17] at the lower molecular weight $B_4H_x^+$ ions (*m/e* 53–43). Formation of diborane is suggested by the different relative intensities in the two spectra for the $B_2H_x^+$ ion group (*m/e* 27–23) and by the small shutter per cents[17] observed for these ions. Because of these pyrolysis contributions to the low mass peaks, particularly the principal peaks at *m/e* 50, relative intensities of many high-mass ions in the total intensity spectrum are not so large as those in the molecular beam mass spectrum.

A careful search for metastable ion peaks was made with the sample in a chloroform slush. Slow sweeps at high sensitivity were carried out to seek, in particular, evidence for the reaction $B_8H_x^+ \rightarrow B_4H_y^+ + B_4H_z$. Because of the presence of two boron isotopes (80% $^{11}B$, 20% $^{10}B$), these metastable peaks would be seen at every quarter-mass. Since they were not observed, an upper limit of 0.01% (probably 0.003%) can be set for their relative intensity under our conditions of repeller and accelerating voltages. Metastable transitions involving neither loss of hydrogen, *e.g.*, $B_4H_x^+ \rightarrow B_4H_{x-2}^+ + H_2$, nor loss of boron species, *e.g.*, $B_4H_x^+ \rightarrow B_3H_y^+ + BH_z$, were found; the upper limit for the relative intensity of these transitions was about 0.1%.

Peaks at half-masses were too small to be measured during the mass spectral measurements, but a number of them were visible under the conditions of the metastable search. A considerably different intensity distribution from that of the singly charged ions was observed for the total intensities of these doubly charged ions. The $B_8H_x^{2+}$ ions were about 4 times as intense as the $B_4H_y^{2+}$ ions and about 20 times as intense as the $B_6H_u^{2+}$ ions. Molecular beam intensities were not measured.

The ionization potential for $B_8H_{18}^+$ could not be determined experimentally because the parent peak was not observed. The appearance potential for mass $53^+$, $B_4H_9^+$, however, is equally interesting since this peak has the highest mass in the unusually intense tetraborane ion region. Relative ion intensity of this particular peak is much greater than that observed for tetraborane(10);[8] this mass peak does not occur for tetraborane(8). The appearance potential for the ion $B_4H_9^+$ is determined to be 11.2 ± 0.1 eV; the uncertainty is the standard deviation. This value indicates the $B_4H_9^+$ results from fragmentation rather than direct ionization of the free radical $\cdot B_4H_9$ since appearance potentials of free radicals are normally lower (~9 eV).

**Pyrolysis.**—A complete pyrolysis study of octaborane(18) could not be undertaken because of the limited amount of compound available; therefore, only selected peaks were monitored so that an idea of the pyrolysis trends could be obtained. Peaks monitored were: $96^+$, one of the more intense, higher molecular weight ions in the octaborane region; $76^+$, a high molecular weight ion in the hexaborane region; $64^+$ and $60^+$, ions which considered together should indicate grossly the relative amounts of pentaborane(9) and -(11); $53^+$, $52^+$, $50^+$, and $48^+$, ions which represent, respectively, two unusually intense peaks in the tetraborane region, the principal peak for tetraborane(10), and the principal peak for tetraborane(8); $37^+$, the ion to represent $B_3H_x^+$ ion intensity; and $27^+$, one of the most intense diborane(6) peaks.

The absolute ion intensities at *m/e* 96 and 52 are plotted as a function of temperature in Figure 2. Most of the ion intensity at *m/e* 52 is believed to result from fragmentation of octaborane(18) since ion contributions to this peak from such boron hydrides as $B_5H_9$, $B_4H_{10}$, and $B_4H_8$ will be small until their concentrations are large compared to that of $B_8H_{18}$. There are several possible explanations of why $I(52^+)$ does not show the same change in slope that $I(96^+)$ does at about 120°. These are a change in the fragmentation pattern of octaborane(18) with temperature, formation of and consequent fragmentation of nona- or decaborane, and influence of time-dependent temperature gradients in slush-bath temperature on the absolute intensities of both peaks. Thermal decomposition during the 40-msec contact time with the reactor, however, is indicated by the appearance of various boron hydride pyrolysis products at about 140° as well as by the change in the slope of $I(96^+)$ at about 120°. Since $I(96^+)$ was small and difficult to follow, $I(52^+)$, which could be more reproducibly measured, is used as a measure of the $B_8H_{18}$ concentration in the reactor effluent.

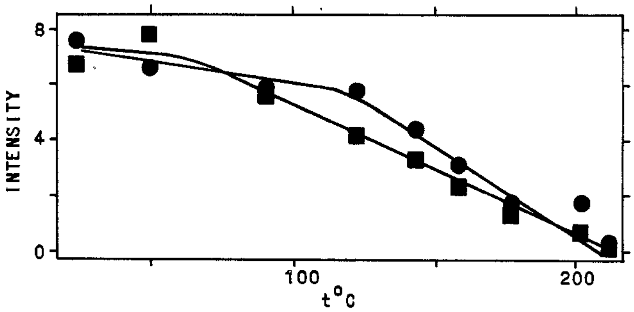

Figure 2.—Absolute "shutterable" intensity of mass peaks $96^+$ and $52^+$ as a function of reactor temperature. The "shutterable" or molecular beam intensity is the intensity from molecules that come directly from the reactor and that have not had contact with the hot-ion source. Both mass peaks are thought to represent the concentration of octaborane(18) in the reactor. The decrease in intensity starting at about 120° is ascribed to pyrolysis of the octaborane(18) in the reactor. Run 661118 symbols: ●, peak $96^+$, ion current is in units of $10^{-12}$ A; ■, peak $52^+$, ion current is in units of $10^{-11}$ A.

An increase with reactor temperature in the absolute intensity of a fragment ion is an indication that there is a new source for this ion, *i.e.*, from a pyrolysis product. Even if a pyrolysis product is formed, however, the absolute intensity of a given peak due to both parent and daughter need not increase, depending on the relative contributions of each. Another indicator for pyrolytic formation of new species is the ratio of ion intensity at a sensitive peak for the suspected daughter to that at a peak, such as *m/e* 52 or 96, which arises only from the parent. If, with the reactor cold, the effluent vapor consists of only one species, then an increase in the intensity ratio indicates formation of one or more new species.

Ions from the parent, *m/e* 106, up to *m/e* 130 were checked several times during the pyrolysis experiment. Any change in the relative intensity of these high molecular weight ions was small, especially compared to changes in the lower molecular weight ions. High molecular weight species do not, therefore, contribute to the changes discussed below.

Because the most intense peaks of the spectrum are found in the $B_4H_x^+$ ion group, the pyrolysis behavior of these ions is discussed first. Figure 3 gives the intensities of mass peaks $53^+$, $50^+$, and $48^+$ all relative to mass peak $52^+$. Of these, the ratios $I(50^+)/I(52^+)$ and $I(48^+)/I(52^+)$ increase with increasing temperature. The ratio $I(53^+)/I(52^+)$ first decreases and then increases at the highest temperatures. The absolute intensity of *m/e* 50 decreases whereas that of *m/e* 48 remains constant.

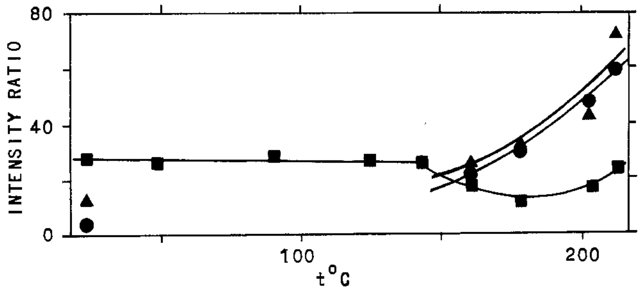

Figure 3.—Ratios of ion intensities of mass peaks $53^+$, $50^+$, and $48^+$ of the $B_4H_x^+$ ion group to ion intensity of mass peak $52^+$ as a function of reactor temperature. Run 661118 symbols: ■, $I(53^+)/I(52^+)$; ▲, $I(50^+)/I(52^+)$, this ratio is 10 times that given on the scale; ●, $I(48^+)/I(52^+)$, this ratio is 10 times that given on the scale.

Figure 4 shows that the ratio $I(76^+)/I(52^+)$ increases at high temperatures; absolute intensity of $76^+$, however, is decreasing at these temperatures.

The large increase in the ratios $I(64^+)/I(52^+)$ and $I(60^+)/I(52^+)$ is illustrated in Figure 5; the absolute intensities of *m/e* 64 and 60 increase up to temperatures above 200°. Intensities of these peaks increase even relative to *m/e* $48^+$.

Figure 6 shows a marked increase in the ratios $I(37^+)/I(52^+)$ and $I(27^+)/(52^+)$ at approximately 120°. The absolute shutterable intensities of *m/e* 37 and 27 start to increase between 120 and 140° and then decrease above 170°.

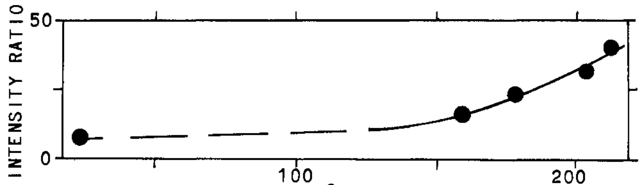

Figure 4.—Ratio of $I(76^+)/I(52^+)$ as a function of reactor temperature for run 661118.

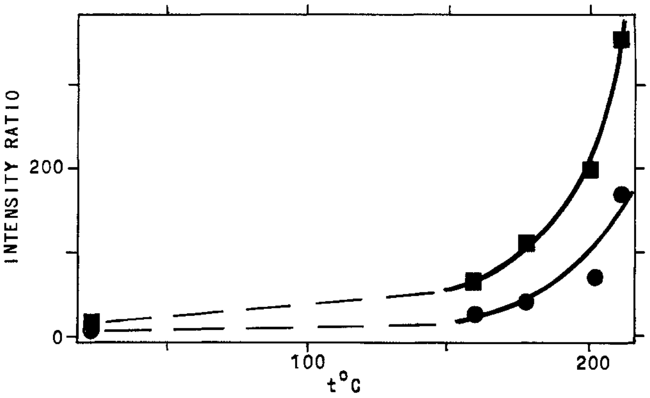

Figure 5.—Ratios of ion intensity of mass peaks $64^+$ and $60^+$ to ion intensity of mass peak $52^+$ as a function of reactor temperature. Run 661118 symbols: ●, $I(64^+)/I(52^+)$, this ratio is one-tenth that given on the scale: ■, $I(60^+)/I(52^+)$.

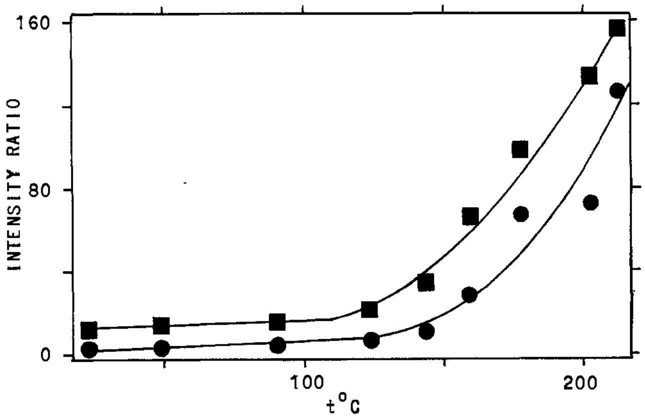

Figure 6.—Ratios of ion intensity of mass peaks $37^+$ and $27^+$ to ion intensity of mass peak $52^+$ as a function of reactor temperature. Run 661118 symbols: ●, $I(37^+)/I(52^+)$; ■, $I(27^+)/I(52^+)$.

## Discussion

**Mass Spectra.**—The unique shape of the molecular beam mass spectrum of octaborane(18) (Figure 1), notably the maximum of ion intensity in the $B_4H_x^+$ region, does not result from thermal decomposition of the compound during inlet into the mass spectrometer. This is indicated by three pieces of evidence. First, distinct differences are observed between the molecular beam spectrum and the total intensity mass spectrum which contains also the pyrolysis products formed when the compound comes in contact with the hot walls of the spectrometer. Second, no known boron hydride shows such large relative intensities at *m/e* 53 and 52. Third, the ratio $I(96^+)/I(52^+)$ stays relatively constant (Figure 2); these two ion peaks disappear together indicating that they have a common progenitor. The probable explanation for this unusual mass spectrum is the structure of the molecule and the related ion decomposition mechanism of octaborane(18).

Principal fragment ion peaks in a mass spectrum correspond to the most stable ions formed in favored reaction pathways.[4] Favorable ion decomposition schemes, in turn, appear to follow condensed-phase chemistry of the compound. Of the two structures given by Dobson, Gaines, and Schaeffer[3] the belt-line icosahedral fragment structure (II) contains no unusual structural element that would be expected to show preferential fragmentation of $B_8H_{18}$ to $B_4H_x^+$ ions. Structure I, however, has an unusual B–B single bond connecting two $B_4H_9$ units.

The only other known borane with a B–B single bond connecting two icosahedral fragments is decaborane(16), $(B_5H_8)_2$. The crystal structure determination of decaborane(16)[19] indicates that this molecule has a B–B single bond connecting two $B_5H_8$ units formed by removing the apical hydrogens of pentaborane(9). Decaborane(16) like the ordinary boron hydrides exhibits the greatest ion intensity in its parent ion group; unlike other boron hydrides, it does show a noticeably large pentaborane ion group.[20] That the $(B_5H_8)_2$ mass spectrum does not show the extensive cleavage seen in the octaborane(18) spectrum can be explained in the following manner. Pentaborane(9) gives rise to an intense (~75%) parent. The apical B–H bond cannot, therefore, be extensively cleaved. By analogy, it is reasonable that the B–B single bond in $(B_5H_8)_2$ also not be cleaved. Tetraborane(10), on the other hand, contains a $BH_2$ group. This structural unit is associated with absence of the parent peak in a mass spectrum. This implies, in particular, that the B–H bonds of the $BH_2$ group (*i.e.*, the 2 position in tetraborane(10)) are extensively cleaved. By analogy, the B–B bond in $(B_4H_9)_2$, which is at the 2 position also should be cleaved extensively. It is therefore a difference in the geometries around the B–B single bonds that accounts for the difference in mass spectra of these two molecules. The presently obtained mass spectrum is that expected from structure I, $(B_4H_9)_2$, and constitutes strong evidence for it.

The correlation of the presence of a $BH_2$ group with the absence of a parent ion can be extended to decaborane(16) and octaborane(18) themselves. The former has no $BH_2$ structural unit and indeed gives rise to a parent ion. The latter has two $BH_2$ units, not counting these involved in the B–B single bond, and gives no parent peak. Octaborane(18), in fact, loses six hydrogen atoms before an observable ion is formed. This is unusual: tetraborane(10), for instance, gives rise to a measurable $B_4H_8^+$ peak. For its molecular weight, octaborane(18) is uniquely rich in hydrogen. Condensation of the ion with loss of hydrogen is therefore likely.

Further evidence for the $(B_4H_9)_2$ structure is the similarity of appearance potentials of $B_4H_9^+$ from octaborane(18) (11.2 ± 0.1 eV) and of $B_5H_8^+$ from decaborane(16) (11.6 ± 0.2 eV).[20] These relatively low, analogous appearance potentials suggest formation of these two ions by similar mechanistic paths, *i.e.*, by cleavage of a B–B single bond and not by fragmentation of an icosahedral unit such as that in structure II.

**Pyrolysis.**—The temperature dependence study of octaborane(18) shows the formation of a number of lower molecular weight pyrolysis products. Unfortunately, because of the limited amount of sample, the study is not complete enough to identify unambiguously all of the products and the sequence of their formation. Valuable information could nonetheless be obtained and will be discussed in the order of decreasing molecular weight of the ions in question.

Small relative and absolute intensities of the $B_8H_x^+$ ion group and the higher molecular weight $B_9H_y^+$ to $B_{10}H_z^+$ do not permit ready distinction between formation of pyrolysis products and change in fragmentation patterns of the $B_8H_{18}$ and the higher molecular weight impurities.

Although the absolute intensity of *m/e* 76 does not increase with increasing temperature, the ratio $I(76^+)/I(52^+)$ does. The increase in the ratio suggests formation of a hexaborane, possibly from the pyrolytically formed lower molecular weight boron hydrides to be discussed below.

Increases in the absolute intensities at *m/e* 60 and 64 indicate pyrolytic formation of a pentaborane. Ratios of $I(60^+)/I(64^+)$, as well as the small shutter per cents observed for these peaks, suggest the predominant formation of pentaborane(9). Formation of pentaborane(11), however, cannot be precluded. Pyrolysis of $B_4H_{10}$ may be responsible for the formation of the pentaborane; previous work with $B_4H_{10}$ in this mass spectrometer shows that such a reaction takes place at these temperatures[12] in a reactor identical with that presently used.

Although there is no increase in the absolute intensities of *m/e* $50^+$ (the principal peak of $B_4H_{10}$) and of *m/e* $48^+$ (the principal peak of $B_4H_8^+$ [13]), the increases in the ratios $I(50^+)/I(52^+)$ and $I(48^+)/I(52^+)$ with increasing temperature suggest the formation of tetraborane(s). Gains in the absolute intensities of these peaks probably are not observed because of their initially large relative intensities in the $B_8H_{18}$ mass spectrum. The increase in intensity of *m/e* 48 and 50 relative to *m/e* 52 is expected because *m/e* 52 has a much larger relative ion intensity arising from $B_8H_{18}$ than from $B_4H_8$,[13] $B_4H_{10}$, or $B_5H_9$; the relative ion intensities of *m/e* 48 and 50

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[19] R. Grimes, F. E. Wang, R. Levin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 996 (1961).

[20] L. H. Hall, V. V. Subbanna, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 3969 (1964).

are more nearly equivalent in the mass spectra of $B_8H_{18}$ and the tetraboranes. Formation of $B_4H_8$ as well as $B_4H_{10}$ is suggested by the fact that the absolute intensity of m/e 48 remained constant while that of m/e 50 decreased. The behavior of $I(53^+)$ relative to $I(52^+)$ (Figure 3) can be explained by the formation of tetraborane(8) and tetraborane(10) both of which would contribute more ion intensity to m/e 52 than to m/e 53 and cause a relative decrease of $I(53^+)$. At high temperatures, pentaborane is formed and would contribute more ion intensity to m/e 53 than to m/e 52 causing the observed increase in the ratio $I(53^+)/I(52^+)$.

Although the ratios $I(37^+)/I(52^+)$ and $I(27^+)/I(52^+)$ increase with increasing temperature, formation of di- or triboranes is not necessarily indicated. Even though the absolute intensities of these peaks increase between approximately 130 and 170°, relative intensity changes for these two peaks are considerably less than that for the tetraboranes. Fragmentation of the $B_4H_8$, $B_4H_{10}$, $B_5H_9$, and the hexaborane, all of which are believed to be formed, could account for the observed increases.

## Conclusions

The unusual fragmentation pattern in the molecular beam mass spectrum of octaborane(18) is strong evidence for a structure in which two $B_4H_9$ groups are joined by a single B–B bond. An appearance potential of 11.2 ± 0.1 eV determined for $B_4H_9^+$ also supports this structure.

Pyrolysis of octaborane(18) appears to lead to tetraborane(8) and tetraborane(10). Formation of pentaborane(9), possibly pentaborane(11), and hexaborane(s) is indicated; however, their formation may result from the pyrolysis of the tetraboranes. Increase with temperature of diborane and triborane ion intensities is observed but can be due to fragmentation of other pyrolysis products.

This work shows also that comparison of the molecular beam and total intensity mass spectra can help identify the pyrolysis products of a boron hydride. The conclusions drawn from such a comparison and the pyrolysis study are in agreement for octaborane(18).

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# The Crystal and Molecular Structure of Phosphorus Trifluoride–Tris(difluoroboryl)borane, $B_4F_6 \cdot PF_3$[1]

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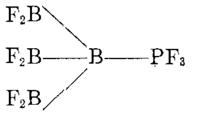
The crystal structure of phosphorus trifluoride–tris(difluoroboryl)borane, $B_4F_6 \cdot PF_3$, has been determined by an X-ray diffraction study of single-crystal specimens. The orthorhombic unit cell, space group Pnma, with $a = 13.893 \pm 0.005$ Å, $b = 10.578 \pm 0.005$ Å, and $c = 6.075 \pm 0.005$ Å, contains four formula units. The calculated density is 1.82 g/cm³. The structure was solved by statistical methods and refined by full-matrix least squares to a conventional R of 9.3% for 703 data collected by counter methods (6.7% for the 603 nonzero data). The molecule consists of a central boron atom, tetrahedrally bonded to three $BF_2$ groups and the $PF_3$ group in such a way that the molecule has approximately 3m ($C_{3v}$) point symmetry, one mirror of which is required by the crystal symmetry. Distances found (uncorrected for thermal motion) are: B–F, 1.305 Å; B–B, 1.68 Å; B–P, 1.825 Å; P–F, 1.51 Å (all ±0.015 Å).

## Introduction

Timms has recently reported[3] the synthesis of a number of novel boron fluoride compounds by reactions of the high-temperature species, boron monofluoride, on cold surfaces. Cocondensation of BF and $PF_3$ produces $B_4F_6 \cdot PF_3$, a pyrophoric and water-sensitive substance which readily sublimes (mp 55°, bp 74°) to form well-developed, colorless crystals which are stable at room temperature. The present X-ray diffraction investigation was undertaken to verify the proposed structure



and to determine the bond distances and angles in this molecule.

## Experimental Section

Samples of the compound, sealed into thin-walled glass capillaries, were provided by Professor Timms. Crystals formed quite readily as the compound was sublimed back and forth in the

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[1] Work done under the auspices of the U.S. Atomic Energy Commission.

[2] National Science Foundation graduate fellow, 1964–1967.

[3] P. L. Timms, *J. Am. Chem. Soc.*, **89**, 1629 (1967).