

Each tetrahedral unit  $\text{PO}_4$ , therefore, has the tendency to have only one negative charge in aqueous solution, each additional charge being easily neutralized by a proton. During reaction 12 the iodide ion must lose two electrons, and in the activated complex, which is about in the middle of the reaction path,<sup>26</sup> about one electron must have been transferred to the peroxydiphosphate ion. The two negative charges of the complex  $\text{H}_3\text{P}_2\text{O}_8\text{I}^{2-}$  will belong almost entirely to the two  $\text{PO}_4$  units, conferring to the activated complex a relative stability, which corresponds to a high reaction rate.

In the case of peroxydisulfate, on the contrary, the tendency to have only one negative charge for each sulfur atom is not remarkable. In fact  $\text{SO}_4^{2-}$  is almost as weak a base as  $\text{P}_3\text{O}_9^{3-}$  or  $\text{P}_4\text{O}_{12}^{4-}$ ,<sup>27</sup> and much weaker than  $\text{HPO}_4^{2-}$ . Accordingly, the effect of the hydrogen ions in the reaction peroxydisulfate-iodide is merely a salt effect, and is even smaller than the effect of the alkali metal ions.<sup>28</sup>

On the other hand, acid catalysis is operating in many reactions of the peroxides, which Edwards considers as nucleophilic substitutions.<sup>29</sup> Edwards attributes the effect of the protonation to the lesser basicity of the leaving group, and this also is a non-

(26) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 10.

(27) C. W. Davies, H. W. Jones, and C. B. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952); C. W. Davies and C. B. Monk, *J. Chem. Soc.*, 413 (1949); A. Indelli and G. Mantovani, *Trans. Faraday Soc.*, **61**, 909 (1965).

(28) W. J. Howells, *J. Chem. Soc.*, 463 (1939).

(29) J. O. Edwards, see ref 13, p 67.

electrostatic effect. The reasons given by Edwards are difficult to compare directly with the ones presented above, because of the difference in the ways to look at the mechanism of the reactions of the peroxides, but they do not seem to be totally different.

The salt effects on reaction 13 are remarkably small. Despite the fact that under the conditions of run 30 over 60% of the reaction takes place through reaction 13, no decrease in rate is observed when the same run is performed in the absence of  $\text{KClO}_4$  (run 38). Apparently the negative salt effect on equilibrium 11 is sufficient to compensate for the positive salt effect on reaction 13. According to the Brønsted-Debye limiting law it should not be. Only in the presence of calcium and barium ions is the positive salt effect clearly visible, although it is not as great as in other cases reported in the literature.<sup>15</sup> Examples of rather small salt effects in reactions between anions have already been studied, usually when large ions are involved.<sup>30</sup> The accelerating effect of the barium ions is slightly superior to that of the calcium ions. Barium ions are often more effective than calcium ion,<sup>31</sup> but there are instances in which the reverse is true.<sup>30a,32</sup>

**Acknowledgment.** This work was supported by the Consiglio Nazionale delle Ricerche (Rome).

(30) (a) J. I. Hoppé and J. E. Prue, *J. Chem. Soc.*, 1775 (1957); (b) A. Indelli and G. Saglietto, *Trans. Faraday Soc.*, **58**, 1033 (1962); (c) A. Indelli, *ibid.*, **59**, 1827 (1963).

(31) See, for instance, V. Carassiti and C. Dejak, *Boll. Sci. Fac. Chim. Ind. Bologna*, **15**, 63 (1957).

(32) B. Holmberg, *Z. Physik. Chem.*, **79**, 147 (1912); A. Indelli and A. Giacomelli, *Ann. Chim. (Rome)*, **55**, 170 (1965).

## Mass Spectrometric Investigation of the Pyrolysis of Boranes. Tetraborane(10)<sup>1</sup>

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*Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received September 13, 1965*

**Abstract:** The intermediates produced in the pyrolysis of  $^{10}\text{B}_4\text{H}_{10}$  were studied with an "integral furnace" mass spectrometer with reactor temperatures between 10 and 285°. The reactor pressure of  $\text{B}_4\text{H}_{10}$  was ca.  $10^{-5.2}$  atm.  $\text{B}_4\text{H}_8$  was identified as an intermediate produced in the pyrolysis. Diborane as well as a combination of pentaboranes ( $\text{B}_5\text{H}_9$  and  $\text{B}_5\text{H}_{11}$ ), hexaborane, a combination of heptaboranes, octaborane, decaborane, and possibly nonaborane also were observed. Monoborane and triborane were not observed, but quantities small compared to  $\text{B}_4\text{H}_8$  could not be excluded.

There have been many studies to elucidate the pyrolysis mechanism of diborane and, in particular, the steps involving tetraborane(10).<sup>2-4</sup> The copyrolysis of

(1) This work was supported in part by the Advanced Research Projects Administration through the Northwestern University Materials Research Center and by the United States Atomic Energy Commission, Document COO-1147-5.

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

(3) R. M. Adams, in "Boron, Metallo-Boron Compounds and Boranes," Interscience Publishers, Inc., New York, N. Y., 1964, p 507 ff.

(4) Reference 3, p 576, in reference to an article by T. W. Clapper, AFN, Inc., Los Angeles, Calif., Technical Report NR ASD-TDR-62-1025, Vol. II, June 1962.

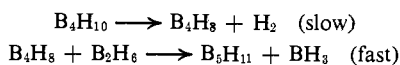
$\text{B}_4\text{H}_{10}$  and  $\text{B}_2\text{H}_6$  was studied by Pearson and Edwards<sup>5</sup> who suggested that  $\text{B}_4\text{H}_{10}$  decomposes by two simultaneous first-order reactions which yield  $\text{B}_3\text{H}_7$  and  $\text{B}_4\text{H}_8$ , respectively. The triborane(7) was postulated to react with hydrogen to give diborane.

Dupont and Schaeffer<sup>6</sup> proposed the following two-step reaction for the formation of pentaborane(11)

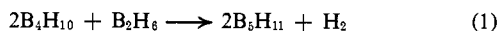
(5) R. K. Pearson and L. J. Edwards, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., 1957, p 15N.

(6) J. A. Dupont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).

from tetraborane(10)



A kinetic study of the thermal decomposition of  $\text{B}_4\text{H}_{10}$  in the presence of CO by Brennan and Schaeffer<sup>7</sup> confirms this mechanism. Schaeffer<sup>8</sup> suggested also that cleavage to  $\text{B}_3\text{H}_7$  in reactions of  $\text{B}_4\text{H}_{10}$  such as

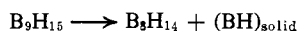


seems improbable since  $\text{B}_3\text{H}_7$  in the presence of  $\text{B}_2\text{H}_6$  rapidly forms  $\text{B}_4\text{H}_{10}$ . Any products other than tetraborane would therefore be minor.

Fehlner and Koski<sup>9</sup> include higher boranes in their mechanism for the pyrolysis of diborane in a shock tube. They have hypothesized both  $\text{B}_3\text{H}_7$  and  $\text{B}_4\text{H}_8$  as intermediates for the decomposition of tetraborane(10). Two hexaboranes,  $\text{B}_6\text{H}_{10}$  and  $\text{B}_6\text{H}_{12}$ , and two heptaboranes,  $\text{B}_7\text{H}_{11}$  and  $\text{B}_7\text{H}_{13}$ , also are mentioned. Gibbins and Shapiro<sup>10</sup> found both  $\text{B}_6\text{H}_{10}$  and  $\text{B}_6\text{H}_{12}$  (or  $\text{B}_6\text{H}_{14}$ ) in their mass spectrometric studies of hexaborane. Clapper, *et al.*,<sup>4</sup> suggest that the formation of  $\text{B}_8\text{H}_{14}$ ,  $\text{B}_8\text{H}_{12}$ ,  $\text{B}_{10}\text{H}_{16}$ ,  $\text{B}_{10}\text{H}_{14}$ ,  $\text{B}_{11}\text{H}_{15}$ , and  $\text{B}_{12}\text{H}_{12}$  precede the formation of the polymer.

Recently, there has been discussion concerning the existence of heptaboranes and hexaboranes other than  $\text{B}_6\text{H}_{10}$  and  $\text{B}_6\text{H}_{12}$  (with no  $\text{B}_6\text{H}_{12}^+$  peak in the mass spectrum). It has been suggested that the spectra attributed to these other boranes actually may be due to alkylboranes, carboranes, and/or alkoxyboranes formed by reaction of pure boranes with ether.<sup>11</sup>

Ditter, Landesman, and Williams<sup>12</sup> have followed the decomposition of nonaborane ( $\text{B}_9\text{H}_{15}$ ) and have found that



However, in the later report by Williams, Spielman, and Ditter,<sup>11</sup> the resultant octaborane is believed to be  $\text{B}_8\text{H}_{12}$ . Quayle<sup>13</sup> observed  $\text{B}_6\text{H}_{10}$ ,  $\text{B}_7\text{H}_{11}$ ,  $\text{B}_8\text{H}_{12}$ ,  $\text{B}_9\text{H}_{13}$ , and  $\text{B}_{20}\text{H}_{24}$  when taking the mass spectra of diborane, pentaborane, and decaborane.

As can be seen from this discussion, the pyrolysis of tetraborane is at best very complicated. It would be advantageous to detect directly the species formed during pyrolysis under controlled conditions. Previous work on organic<sup>14</sup> systems and on the thermal decomposition of boranes<sup>15-18</sup> has shown that reactive intermediates often can be identified through use of a mass spectrometer.

(7) G. L. Brennan and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **20**, 205 (1961); G. L. Brennan, Dissertation, Iowa State University, 1960; University Microfilms No. Mic 60-2860.

(8) R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 190 (1960).

(9) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 1012 (1964).

(10) S. G. Gibbins and I. Shapiro, *ibid.*, **82**, 2968 (1960).

(11) R. E. Williams, J. Spielman, and J. F. Ditter, private communication and paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(12) J. F. Ditter, H. E. Landesman, and R. E. Williams, National Engineering Science Company Report, Contract No. AF 04 (611)-5156, Oct 1962.

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

(14) F. P. Lossing in "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 442.

(15) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 2733, (1964).

(16) E. J. Sinke, G. A. Pressley, Jr., A. B. Baylis, and F. E. Stafford, *J. Chem. Phys.*, **41**, 2207 (1964).

(17) A. B. Baylis, G. A. Pressley, Jr., E. J. Sinke, and F. E. Stafford, *J. Am. Chem. Soc.*, **86**, 5358 (1964).

(18) T. P. Fehlner and W. S. Koski, *ibid.*, **87**, 409 (1965).

The purpose of this mass spectrometric study was to determine the intermediate(s) formed during the pyrolysis of  $^{10}\text{B}_4\text{H}_{10}$  (meaning 80.2%  $^{11}\text{B}$  and 19.8%  $^{10}\text{B}$ ) and to detect the presence of higher boranes produced.

## Experimental Section

The samples of  $\text{B}_4\text{H}_{10}$  used in this experiment were supplied by Professor R. Schaeffer and Dr. A. Norman of Indiana University. The samples were stored in liquid nitrogen.

An Inghram-type integral furnace mass spectrometer<sup>16, 17, 19, 20</sup> built by Nuclide Corporation was used to study the pyrolysis of  $\text{B}_4\text{H}_{10}$ .

During this pyrolysis, the sample was introduced into the inlet system of the mass spectrometer through a Delmar<sup>21a</sup> Teflon-on-glass seal needle valve sealed to the sample tube, and metered using a needle valve.<sup>21b</sup>

In order to achieve the low background pressures at which this experiment was run, the spectrometer had a three-stage differential pumping system. The furnace was pumped with a 6-in. mercury diffusion pump. The pumping speed in this chamber is estimated to be 250 l./sec. Two 2-in., three-stage mercury diffusion pumps provided a pumping speed of 20 l./sec each in the ion source and analyzer chambers.

The tetraborane entered a baffled<sup>17, 22</sup> 0.75-in. stainless steel crucible<sup>23</sup> whose orifice size was 1 mm. The crucible was heated by radiation from the tungsten filaments surrounding it. The temperature was measured by one platinum-platinum-10% rhodium and two chromel-alumel thermocouples which were spot welded to the walls and the cover of the crucible.

Molecules effusing from the orifice pass through a series of collimating and ion-deflecting slits which define a molecular beam. An ion-intensity profile<sup>20</sup> (a plot of intensity vs. the position of a movable beam defining slit, "shutter") makes it possible to differentiate between molecules emerging from the orifice and those originating from residual gases. Such species emerging from the orifice have zero contact with the source or other surfaces outside the reactor.

The molecular beam is then ionized with nominal 70-ev electrons except where noted.

The mass analyzer used was a single-focusing, 12-in. radius, 60° sector magnetic deflector. The mass-analyzed ions could then be detected simultaneously by a 50% transmission grid and an electron multiplier so that multiplier gain<sup>24, 25</sup> could be measured.

## Data and Results

The pressure in the crucible was calculated from  $\text{B}_4\text{H}_{10}$  vapor pressure measurements of Stock and Kuss<sup>26</sup> and from a conductance value for the distance from the sample tube to the crucible orifice. The crucible pressure was *ca.*  $10^{-5.2}$  atm at 10° using a methylcyclohexane slush bath ( $-127^\circ$ ) on the sample reservoir.

Ions and their neutral progenitors were identified by mass spectrum, mass defect, dependence on inlet valve setting, temperature dependence, and "shutter" profile.

(19) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

(20) M. G. Inghram and J. Drowart, "Proceedings of an International Symposium on High Temperature Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 219.

(21) (a) Delmar Scientific Laboratories, Inc., Catalog No. 60-D-3, Maywood, Ill.; (b) Hoke, Inc., Catalog No. HRB280, Cresskill, N. J.

(22) J. Berkowitz, *J. Chem. Phys.*, **36**, 2533 (1962).

(23) Material supplementary to this article has been deposited as Document No. 8669 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$5.00 for photoprints, or \$2.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(24) M. G. Inghram, R. J. Hayden, and D. C. Hess in "Mass Spectroscopy in Physics Research," National Bureau of Standards Circular 522, U. S. Government Printing Office, Washington, D. C., p 257.

(25) H. E. Stanton, W. A. Chupka, and M. G. Inghram, *Rev. Sci. Instr.*, **27**, 109 (1956).

(26) A. Stock and E. Kuss, *Ber.*, **56**, 789 (1923).

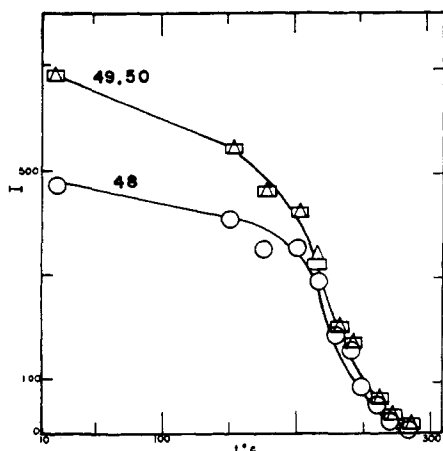


Figure 1. "Shutterable" ion intensity in mv due to mass peaks  $48^+$ ,  $49^+$ , and  $50^+$  vs. temperature. The "shutterable" or molecular beam intensity is the intensity for molecules with zero source contact. Run 650607 symbols: peak  $48^+$ , O; peak  $49^+$ ,  $\Delta$ ; and peak  $50^+$ ,  $\square$ .

With a constant flow of  $B_4H_{10}$  into the crucible, the intensities of the ion peaks and the ratio of peak heights were studied as a function of temperature. All mass peaks up to mass 120 were studied.

**Spectrum of Tetraborane at Room Temperature.** The mass spectrum of  $^{10}B_4H_{10}$  at  $10^\circ$  (Table I) obtained in this experiment differs from that obtained by other experimenters.<sup>27,28</sup> For example, in the literature spectrum the relative intensity of peak  $48^+$  ( $^{11}B_4H_4^+$ ,  $^{11}B_3^{10}BH_5^+$ , ...) is 100, but the relative intensity of  $48^+$  presented here is 64.3. While the relative intensities of peaks  $49^+$  ( $^{11}B_4H_5^+$ ,  $^{11}B_3^{10}BH_6^+$ ,  $^{11}B_2^{10}B_2H_7^+$ , ...) through  $52^+$  are slightly lower in the literature spectrum, the relative intensity for peaks  $43^+$ – $49^+$  are up to twice as great as those presented here. In the literature spectra, the contribution of mass peaks for  $B_3^+$ ,  $B_2^+$ ,  $B^+$  also are much greater and for some peaks exceeds the presented spectrum by more than a factor of 2. This is not due completely to secondary electron multiplier discrimination as the measured decrease of gain for  $B_1H_x^+$  relative to  $B_4H_y^+$  is at most a factor of 2.

While pentaborane has been observed in a mass spectrum of tetraborane taken on a conventional (cycloidal) spectrometer, no "shutterable" pentaborane was observed in a spectrum of the same sample taken on the mass spectrometer used in this experiment.<sup>29</sup>

A related phenomenon was observed in this experiment. Before the furnace heating filaments were turned on, only trace amounts of boranes other than tetraborane were observed. When the heating filaments were turned on, however, pentaborane was observed prior to the pyrolysis of  $B_4H_{10}$  in the crucible. An immediate response to the turning on or off of the heating filaments was observed, which, because of the large heat capacity of the crucible, would not occur if the pentaborane were formed in the crucible. The "shutter" profile for the pentaborane observed at that

(27) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 1905 (1963).

(28) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, *Advances in Chemistry Series*, No. 32, American Chemical Society, Washington, D. C., 1961, p 127.

(29) A. Norman, R. Schaeffer, A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, submitted.

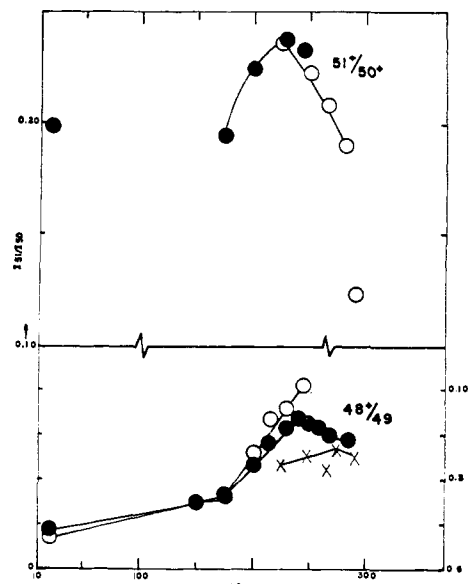


Figure 2. Ratio of  $I(51^+)/I(50^+)$  vs. temperature for the runs 650601 (●) and 650603 (○) (top). Ratio of  $I(48^+)/I(49^+)$  vs. temperature for runs 650601 (○), 650603 (●), and 650607 (×) (bottom). Notice the discontinuity and change in the scale for the ratios.

time was very broad and indicative of pentaborane being formed outside the crucible. The appearance of this pentaborane must be due to formation on the heating filaments.

Because of these observations as well as those given under "Diborane" below, and because the literature spectra are similar to those obtained with reactor temperatures of  $250^\circ$ , the literature spectra taken with conventional source mass spectrometers are believed to be caused in part by pyrolysis products.

**Change of Tetraborane Spectrum ( $B_4$  Region) with Increased Temperature.  $B_4H_8$ .** Figure 1 shows that the intensity of tetraborane peaks  $48^+$  through  $50^+$  decreases with an increase in temperature owing to the loss of sample at elevated temperatures.

The change in fragmentation pattern<sup>23</sup> in the  $B_4$  region of the spectrum with increase in temperature can be studied by looking at the change in the ratios of peak heights as a function of temperature.

The relative intensity of peak  $48^+$  (relative to peak  $49^+$  or  $50^+ \equiv 100\%$ ) changes from 64.3% at  $10^\circ$  to a maximum of 93.5% at  $240^\circ$  when a decrease in the ratio can first be seen (Figure 2). This same trend can be observed for the ratio  $I(51^+)/I(50^+)$  (Figure 2).

There is a large decrease in the relative intensity of  $53^+$  from 20 through  $215^\circ$ . The relative intensity of  $52^+$ , however, increases in this same temperature region. Consequently, the ratio  $I(52^+)/I(53^+)$  increases with temperature until  $215^\circ$ , as shown in Figure 3. At  $230^\circ$ , the ratio of intensities starts to decrease. The ions occurring at  $53^+$  can correspond only to the species  $^{11}B_4H_9^+$  as the contribution from the parent ion  $^{11}B_3^{10}BH_{10}^+$  has been measured to be negligible.<sup>23</sup> The ions corresponding to  $52$  are  $^{11}B_4H_8^+$  and  $^{11}B_3^{10}BH_9^+$ .

With the spectrometer focused on the  $B_4H_8^+$  peak (arising presumably from  $B_4H_{10}$ ) and the reactor at room temperature, the ionizing electron energy was lowered to the ion's appearance potential. The reactor temperature was then raised. Ion intensity

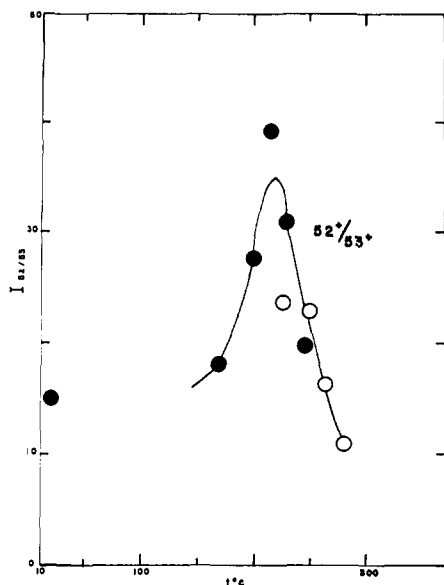


Figure 3. Ratio of  $I(52^+)/I(53^+)$  vs. temperature for runs 650601 (●) and 650603 (○).

“grew in” and was clearly observable at temperatures above 200° which correspond to the range expected for  $B_4H_8$  from Figures 2 and 3. The fraction of total ion intensity due to molecular beam molecules was close to 100%. The ion current available, *ca.*  $10^{-17.5}$  amp, was not sufficient for an appearance potential measurement nor was there enough ion intensity at mass peak  $B_4H_9^+$  for a similar experiment.

Because of the change with temperature in the ratios  $I(48^+)/I(49^+)$ ,  $I(51^+)/I(50^+)$ , and especially in  $I(52^+)/I(53^+)$ , as well as the  $B_4H_8^+$  ion growing in at low electron energies, it is concluded that a new tetraborane was observed:  $B_4H_8$ .

Since the maximum for the ratio  $I(52^+)/I(53^+)$  (Figure 3) was reached at a temperature of 240°, it is reasonable to conclude that the maximum amount of  $B_4H_8$  present also occurs at 240°. The similarity of the mass spectrum<sup>23</sup> of the  $B_4$  ions at 240° to that obtained by Brennan<sup>7,23</sup> for  $B_4H_8CO$  suggests that the  $B_4H_8CO$  is pyrolyzed in the conventional spectrometer ion source and that the  $B_4H_8$  spectrum is in fact observed.

Dupont and Schaeffer<sup>6</sup> have proposed structures for  $B_4H_8$ . Also, a symmetrical tetrahedral structure formed through replacement of H on the apex positions with a B(2)-B(4) bond also might be considered. Similar structures with no  $-BH_2$  groups, such as  $B_3H_9$ , often give parent ion peaks; those with  $-BH_2$  groups often do not.

**Triborane.** The ratio  $[I(36-38^+)/I(47-49^+)]$  changed<sup>23</sup> by only 6.1% from 215 through 285°. The same ratio increased by only 13.8% in the temperature range of 10 to 250°. This change can be attributed to the change in fragmentation of  $B_4H_8$  with respect to  $B_4H_{10}$ .

The per cent “shutter” effects (fraction of ion intensity due to molecular beam species) for mass peaks in the 30’s and those in the 40’s were of the same order of magnitude. If a triborane were present and formed ions to the same extent as  $B_3$  ions are present owing to the fragmentation of tetraborane, the per cent shutter effect for  $B_3$  should be different from that for  $B_4H_{10}$ .

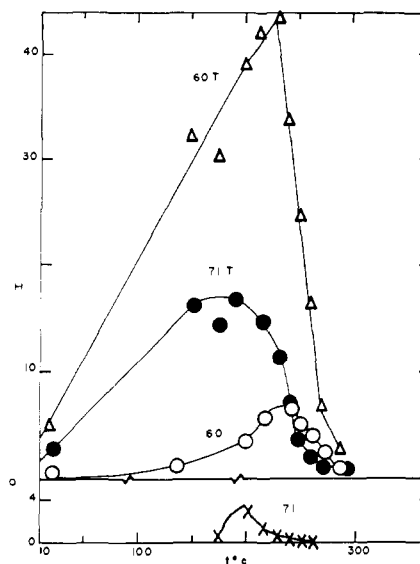


Figure 4. “Shutterable” intensity for mass peaks 60<sup>+</sup> and 71<sup>+</sup> vs. temperature for run 650607. Total intensity of high mass peaks at 60<sup>+</sup> and 71<sup>+</sup> vs. temperature for run 650607 (marked 60 T and 71 T).

This is due to the expected differences in the ability of the two boranes to form stable background. Therefore, there is no evidence in this study for the formation of a triborane intermediate in any quantity. Small amounts could not be excluded.

**Diborane.** The ratio<sup>23</sup>  $I(26-27^+)/I(48-50^+)$  increases with increasing temperature. It changed by 35% for the temperature range 20 through 200°, but by 34% for the small temperature range of 200 to 215°.

The spectrum of  $B_2$  ions obtained in this experiment in the temperature range 260 through 285° is similar to the spectrum of  $B_2H_6$  previously obtained on the same mass spectrometer.

The per cent shutter effect is much lower for 26<sup>+</sup> and 27<sup>+</sup> (by a factor of 1/2) than for the mass peaks in the 30’s and 40’s. Diborane has been observed to have a lower per cent shutter effect than tetraborane (because it is less efficiently pumped). This difference in the per cent shutter was first observed at 215°.

Because of the correspondence of the spectrum of  $B_2$  ions with that of  $B_2H_6$ , the relatively high change in the ratio  $I(26-27^+)/I(48-50^+)$  for the temperature range 200 to 215°, and the change in per cent shutter effect at 215°, it is concluded that diborane is formed in this pyrolysis and is most evident at temperatures above 215°.

**Monoborane.** The ratio  $I^+(13^+)/I(49^+)$  (where  $I^+(13^+)$  is the intensity of mass peak 13<sup>+</sup> with the contributions due to  $B_2H_6$  and  $B_4H_{10}$  subtracted out) increases<sup>23</sup> by a factor of 2 from 150 to 270°. It was not possible to subtract out the contribution due to  $B_4H_8$  which by analogy to the spectrum of  $B_5H_9$  as compared to the spectrum of  $B_5H_{11}$ <sup>28</sup> might be appreciable and might therefore cause the increase in the ratio with temperature.

The per cent shutter effect for mass peaks 11<sup>+</sup> through 13<sup>+</sup> is of the same order of magnitude as that for peaks in the 30’s and 40’s.

Although other experimenters<sup>15</sup> have suggested the formation of a monoborane in the pyrolysis of tetra-

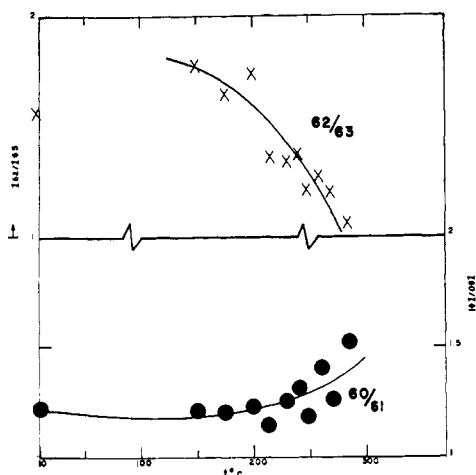


Figure 5. Ratio of  $I(62^+)/I(63^+)$  vs. temperature for run 650607 (top). Ratio of  $I(60^+)/I(61^+)$  vs. temperature for run 650607 (bottom). In both cases  $I$  is the total intensity of the high mass peak of the doublets at these masses. Notice the discontinuity in the ratio scale.

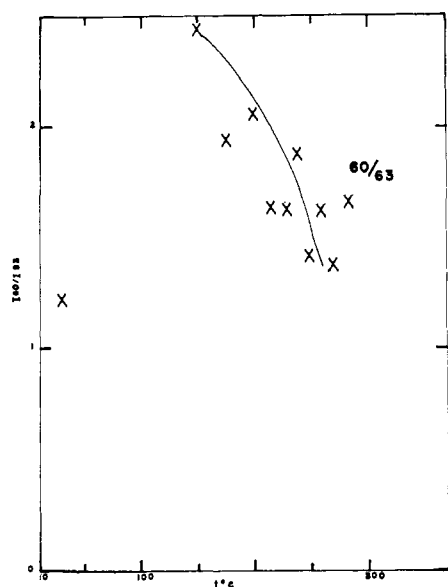


Figure 6. Ratio of  $I(60^+)/I(63^+)$  vs. temperature for run 650607.  $I$  is the total intensity of the high mass peak of the doublets at these masses.

borane, we could not confirm it under these conditions. Since it is not possible to determine the contribution of  $B_4H_8$  to peaks  $11^+$  through  $13^+$ , other experiments will have to be done before it is possible to determine to what extent monoborane is a product of the thermal decomposition of tetraborane.

**Higher Boranes.** As shown in Figures 4–10, pentaborane, hexaborane, heptaborane, octaborane, nonaborane, and decaborane were observed<sup>23</sup> during the pyrolysis. The intensity of each higher borane was lower than the intensity of the preceding borane except for decaborane which had a greater intensity than nonaborane [ $I(B_5^+) > I(B_6^+) > I(B_7^+) > I(B_8^+) > I(B_{10}^+) > I(B_9^+)$ ]. The appearance of these higher boranes cannot be causing the change in the  $B_4$  spectrum discussed above because the total intensity of pentaborane (the most intense of the higher boranes) is only 8% of the intensity of tetraborane.

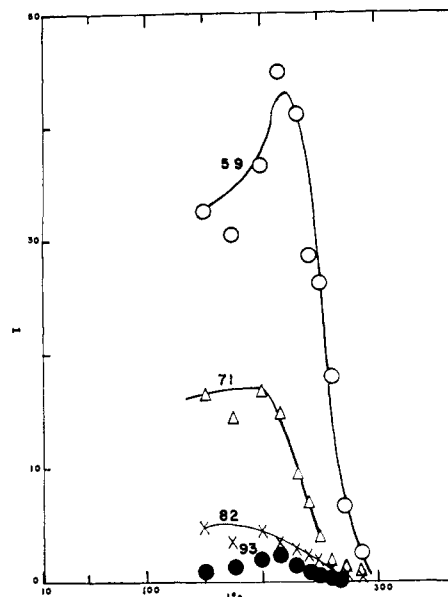


Figure 7. Total intensity for high mass side peaks at  $59^+$ ,  $71^+$ ,  $82^+$ , and  $93^+$  vs. temperature for run 650607. Symbols: peak  $59^+$ ,  $\circ$ ;  $71^+$ ,  $\Delta$ ;  $82^+$ ,  $\times$ ;  $93^+$ ,  $\bullet$ .

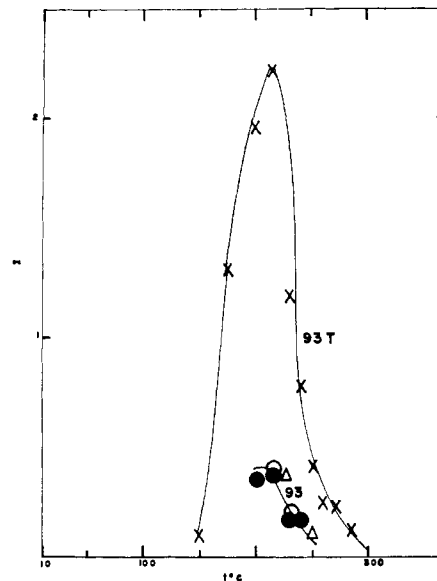


Figure 8. Shutterable and total (T) intensity of mass peak  $93^+$  vs. temperature for runs 650601, 650603, and 650607.

The spectrum of  $B_5^{23}$  when compared with the literature spectrum of pentaborane<sup>28</sup> seems to be that of a mixture of  $B_5H_9$  and  $B_5H_{11}$ . As can be seen from Figure 4, the maximum intensity (both shutterable intensity and total intensity of the "high mass side" of the peak) for mass 60 occurs at a temperature of  $230^\circ$ .

Since  $63^+$  is more intense and  $61^+$  less intense for  $B_5H_9$  than for  $B_5H_{11}$ ,<sup>28</sup> the decrease in the ratio  $I(62^+)/I(63^+)$ , the increase in the ratio  $I(60^+)/I(63^+)$ , and the decrease in the ratio  $I(60^+)/I(63^+)$  indicate that the pentaborane spectrum presented seems to be approaching that of  $B_5H_9$  as the temperature increases (Figures 5 and 6).

The spectra<sup>23</sup> of  $B_6$ ,  $B_7$ ,  $B_8$ ,  $B_9$ , and  $B_{10}$  correspond approximately to the literature spectra of hexaborane, heptaborane, octaborane, nonaborane, and decabor-

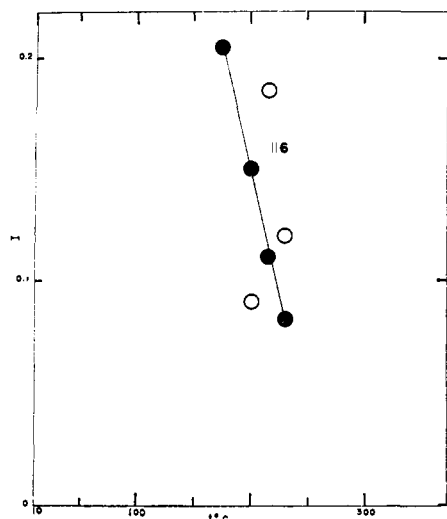


Figure 9. Shutterable intensity for mass peak  $116^+$  vs. temperature for runs 650601 (O) and 650607 (●).

ane, respectively.<sup>5,9-12,28,30</sup> The spectrum of  $B_6$  seems to correspond to that given for  $B_6H_{12}$  more closely than to the spectrum of  $B_6H_{10}$ .<sup>10,30</sup> The spectrum of  $B_7$  corresponds to the literature spectrum for a combination of  $B_7H_{11}$  and  $B_7H_{13}$ .<sup>9</sup> In view of the differences in mass spectra obtained with different instruments, and particularly that presently observed for  $B_4H_{10}$  which is more stable than some of the higher boranes, these comparisons are tentative pending our own measurement of spectra from authentic compounds.

The existence of heptaboranes and hexaboranes other than  $B_6H_{10}$  and  $B_6H_{12}$  (with no  $B_6H_{12}^+$  peak in the mass spectrum) might be attributed to alkylboranes, carboranes, and/or alkoxyboranes.<sup>11</sup> This problem has not been resolved in this experiment, except that no ether was present ( $<0.01\%$ ).

Although the intensity of  $B_{10}$  is greater than that for  $B_9$ , the  $B_9$  peaks do not seem to be due solely to fragmentation of decaborane since their intensity is too great, according to the literature spectrum,<sup>28</sup> for this to be true.

The maximum intensities<sup>23</sup> of  $B_6$  and  $B_7$  are reached at  $215^\circ$  while the maximum intensities of  $B_5$  and  $B_8$  are reached at  $230^\circ$  (Figures 4, 6, 7, and 8), probably reflecting greater thermal stability of the latter two.

## Conclusion

The change in the mass spectrum of the  $B_nH_x^+$  ions, especially the increase in the ratio of  $I(52^+)/I(53^+)$  with increasing temperature, provides good evidence for the previously unobserved tetraborane,  $B_4H_8$ . This was confirmed by observation of  $B_4H_8^+$  ion peak with low appearance potential. This peak "grew in" at the expected reactor temperature and exhibited nearly 100% shutter effect.

Because of the change in the ratio  $I(26-27^+)/I(48-50^+)$ , the change in the per cent shutter effect, and the correspondence of the  $B_2$  ions with the spectrum of  $B_2H_6$ , it was concluded that diborane was formed during the pyrolysis.

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

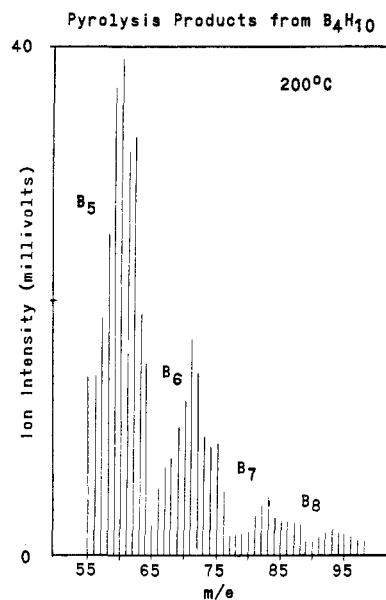


Figure 10. Mass spectrum and relative intensity of the  $B_5$ ,  $B_6$ ,  $B_7$ , and  $B_8$  hydrides formed at  $200^\circ$  during  $B_4H_{10}$  pyrolysis. At this temperature, peak 60 ( $B_5$ ) is only 2.8% as intense as peak 50 ( $B_4$ ).

There was no evidence for the formation of triborane or monoborane. Their formation in amounts small compared to  $B_4H_8$  was not eliminated. If the contributions to the  $B_nH_x^+$  peaks due to  $B_3H_6$ ,  $B_4H_{10}$ , and  $B_4H_8$  could be subtracted out, it would be possible to determine the formation of monoborane. Although it was possible to estimate the contribution due to  $B_2H_6$  and  $B_4H_{10}$ , the contribution of  $B_4H_8$  was uncertain and probably accounts for the otherwise unaccounted increase of ion intensity in the  $B_1$  region.

Pentaborane(9) and pentaborane(11), hexaborane, heptaborane, octaborane, nonaborane, and decaborane were produced under the present experimental conditions. Pentaboranes were first observed to an appreciable extent (0.2% of the  $B_4H_{10}$ ) at  $150^\circ$ . As the temperature increased, the amount of  $B_5H_9$  relative to  $B_5H_{11}$  increased. Because of the large amounts of tetraborane present, it was not possible, because of the sensitivity limits of this experiment, to determine a time sequence for the formation of  $B_4H_8$ , diborane, and pentaborane. The higher boranes, however, were clearly evident even with the low pressure of reactant, presenting the possibility of a detailed, step-by-step elucidation of the pyrolysis polymerization.

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