

Each tetrahedral unit 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,²⁶ 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 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 SO_4^{2-} is almost as weak a base as $\text{P}_3\text{O}_9^{3-}$ or $\text{P}_4\text{O}_{12}^{4-}$,²⁷ and much weaker than 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.²⁸

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

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 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.¹⁵ Examples of rather small salt effects in reactions between anions have already been studied, usually when large ions are involved.³⁰ 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,³¹ but there are instances in which the reverse is true.^{30a,32}

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

(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.

(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).

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(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)¹

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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 B_4H_{10} was ca. $10^{-5.2}$ atm. B_4H_8 was identified as an intermediate produced in the pyrolysis. Diborane as well as a combination of pentaboranes (B_5H_9 and B_5H_{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 B_4H_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).²⁻⁴ The copyrolysis of

B_4H_{10} and B_2H_6 was studied by Pearson and Edwards⁵ who suggested that B_4H_{10} decomposes by two simultaneous first-order reactions which yield B_3H_7 and B_4H_8 , respectively. The triborane(7) was postulated to react with hydrogen to give diborane.

Dupont and Schaeffer⁶ 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).

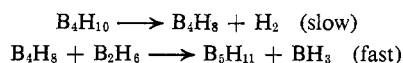
(1) This work was supported in part by the Advanced Research Projects Administration through the Northwestern University Materials Research Center and by the United States Atomic Energy Commission, Document COO-1147-5.

(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.

from tetraborane(10)



A kinetic study of the thermal decomposition of B_4H_{10} in the presence of CO by Brennan and Schaeffer⁷ confirms this mechanism. Schaeffer⁸ suggested also that cleavage to B_3H_7 in reactions of B_4H_{10} such as



seems improbable since B_3H_7 in the presence of B_2H_6 rapidly forms B_4H_{10} . Any products other than tetraborane would therefore be minor.

Fehlner and Koski⁹ include higher boranes in their mechanism for the pyrolysis of diborane in a shock tube. They have hypothesized both B_3H_7 and B_4H_8 as intermediates for the decomposition of tetraborane(10). Two hexaboranes, B_6H_{10} and B_6H_{12} , and two heptaboranes, B_7H_{11} and B_7H_{13} , also are mentioned. Gibbins and Shapiro¹⁰ found both B_6H_{10} and B_6H_{12} (or B_6H_{14}) in their mass spectrometric studies of hexaborane. Clapper, *et al.*,⁴ suggest that the formation of B_8H_{14} , B_8H_{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 B_6H_{10} and B_6H_{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.¹¹

Ditter, Landesman, and Williams¹² have followed the decomposition of nonaborane (B_9H_{15}) and have found that



However, in the later report by Williams, Spielman, and Ditter,¹¹ the resultant octaborane is believed to be B_8H_{12} . Quayle¹³ observed B_6H_{10} , B_7H_{11} , B_8H_{12} , B_9H_{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 organic¹⁴ systems and on the thermal decomposition of boranes¹⁵⁻¹⁸ 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).

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(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 B_4H_{10} (meaning 80.2% ^{11}B and 19.8% ^{10}B) and to detect the presence of higher boranes produced.

Experimental Section

The samples of B_4H_{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^{16, 17, 19, 20} built by Nuclide Corporation was used to study the pyrolysis of B_4H_{10} .

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

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^{17, 22} 0.75-in. stainless steel crucible²³ 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 profile²⁰ (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^{24, 25} could be measured.

Data and Results

The pressure in the crucible was calculated from B_4H_{10} vapor pressure measurements of Stock and Kuss²⁶ 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°) 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.

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

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(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).

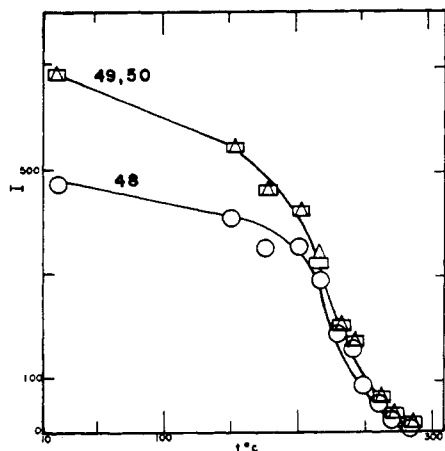


Figure 1. "Shutterable" ion intensity in mv due to mass peaks 48⁺, 49⁺, and 50⁺ vs. temperature. The "shutterable" or molecular beam intensity is the intensity for molecules with zero source contact. Run 650607 symbols: peak 48⁺, O; peak 49⁺, Δ; and peak 50⁺, □.

With a constant flow of B₄H₁₀ 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 ¹⁰B₄H₁₀ at 10° (Table I) obtained in this experiment differs from that obtained by other experimenters.^{27,28} For example, in the literature spectrum the relative intensity of peak 48⁺ (¹¹B₄H₄⁺, ¹¹B₃¹⁰BH₅⁺, ...) is 100, but the relative intensity of 48⁺ presented here is 64.3. While the relative intensities of peaks 49⁺ (¹¹B₄H₅⁺, ¹¹B₃¹⁰BH₆⁺, ¹¹B₂¹⁰B₂H₇⁺, ...) 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 B₃⁺, B₂⁺, 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 B₁H₉⁺ relative to B₄H₉⁺ 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.²⁹

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 B₄H₁₀ 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

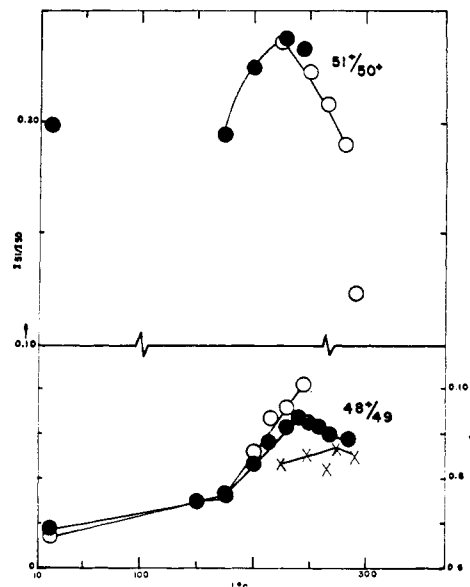


Figure 2. Ratio of $I(51^+)/I(50^+)$ vs. temperature for the runs 650601 (●) and 650603 (○) (top). Ratio of $I(48^+)/I(49^+)$ vs. temperature for runs 650601 (○), 650603 (●), and 650607 (×) (bottom). Notice the discontinuity and change in the scale for the ratios.

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°, the literature spectra taken with conventional source mass spectrometers are believed to be caused in part by pyrolysis products.

Change of Tetraborane Spectrum (B₄ Region) with Increased Temperature. B₄H₈. 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 pattern²³ in the B₄ 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⁺ ≡ 100%) changes from 64.3% at 10° to a maximum of 93.5% at 240° 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°. The relative intensity of 52⁺, however, increases in this same temperature region. Consequently, the ratio $I(52^+)/I(53^+)$ increases with temperature until 215°, as shown in Figure 3. At 230°, the ratio of intensities starts to decrease. The ions occurring at 53⁺ can correspond only to the species ¹¹B₄H₉⁺ as the contribution from the parent ion ¹¹B₃¹⁰BH₁₀⁺ has been measured to be negligible.²³ The ions corresponding to 52 are ¹¹B₄H₈⁺ and ¹¹B₃¹⁰BH₉⁺.

With the spectrometer focused on the B₄H₈⁺ peak (arising presumably from B₄H₁₀) 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

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(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.

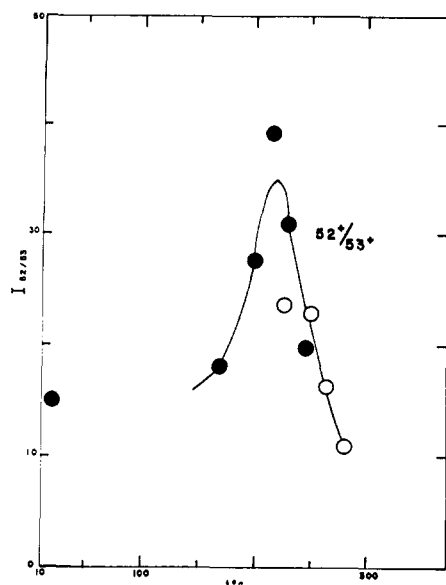


Figure 3. Ratio of $I(52+)/I(53+)$ vs. temperature for runs 650601 (●) and 650603 (○).

“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 spectrum²³ of the B_4 ions at 240° to that obtained by Brennan^{7,23} 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 Schaeffer⁶ 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_5H_9 , often give parent ion peaks; those with $-BH_2$ groups often do not.

Triborane. The ratio $[I(36-38+)/I(47-49+)]$ changed²³ 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} .

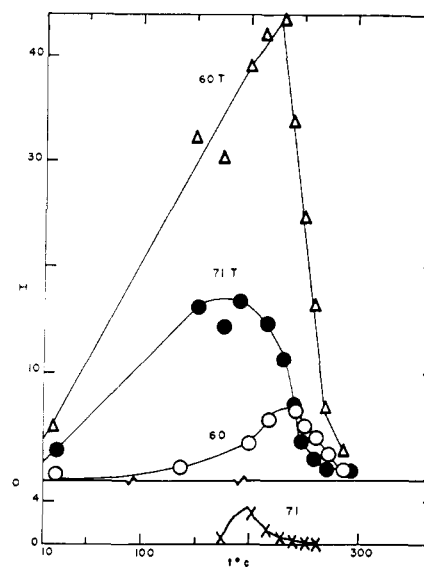


Figure 4. “Shutterable” intensity for mass peaks 60^+ and 71^+ vs. temperature for run 650607. Total intensity of high mass peaks at 60^+ and 71^+ vs. temperature for run 650607 (marked 60 T and 71 T).

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 ratio²³ $I(26-27+)/I(48-50+)$ 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^+ and 27^+ (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^+ with the contributions due to B_2H_6 and B_4H_{10} subtracted out) increases²³ 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} ²⁸ might be appreciable and might therefore cause the increase in the ratio with temperature.

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

Although other experimenters¹⁵ have suggested the formation of a monoborane in the pyrolysis of tetra-

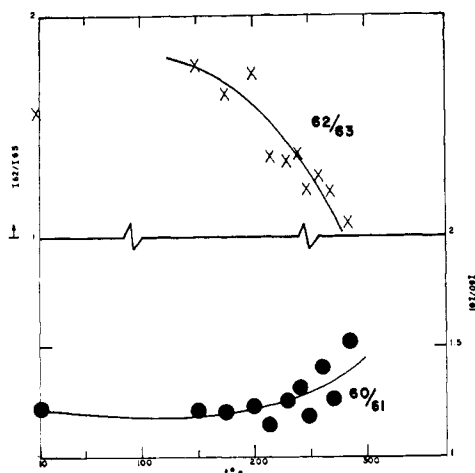


Figure 5. Ratio of $I(62^+)/I(63^+)$ vs. temperature for run 650607 (top). Ratio of $I(60^+)/I(61^+)$ vs. temperature for run 650607 (bottom). In both cases I is the total intensity of the high mass peak of the doublets at these masses. Notice the discontinuity in the ratio scale.

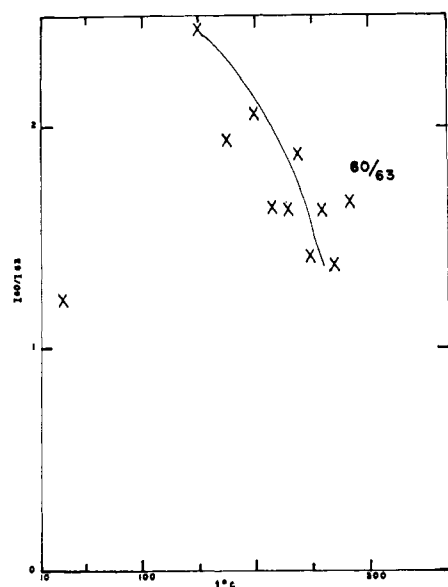


Figure 6. Ratio of $I(60^+)/I(63^+)$ vs. temperature for run 650607. I is the total intensity of the high mass peak of the doublets at these masses.

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 observed²³ 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.

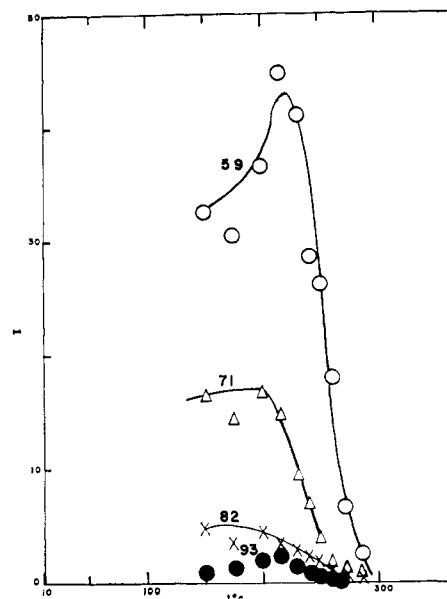


Figure 7. Total intensity for high mass side peaks at 59^+ , 71^+ , 82^+ , and 93^+ vs. temperature for run 650607. Symbols: peak 59^+ , \circ ; 71^+ , Δ ; 82^+ , \times ; 93^+ , \bullet .

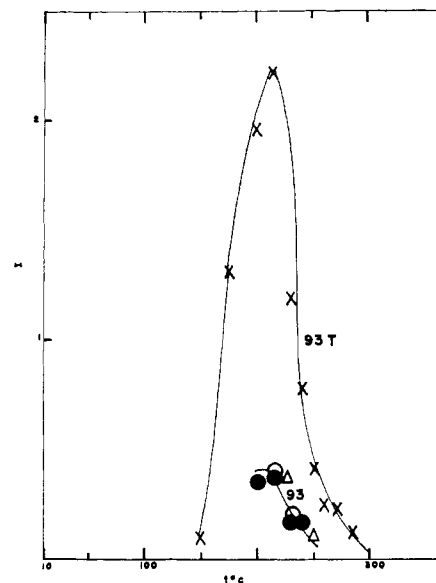


Figure 8. Shutterable and total (T) intensity of mass peak 93^+ vs. temperature for runs 650601, 650603, and 650607.

The spectrum of B_5^{23} when compared with the literature spectrum of pentaborane²⁸ 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° .

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

The spectra²³ 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-

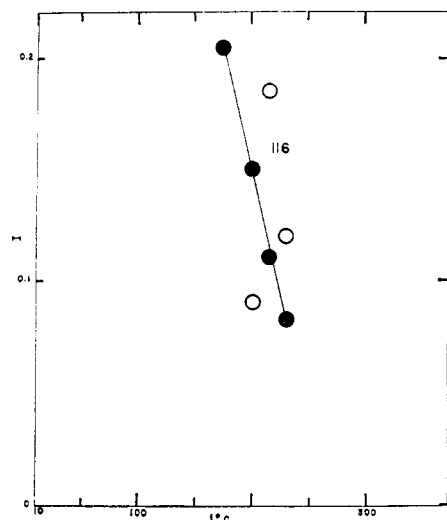


Figure 9. Shutterable intensity for mass peak 116⁺ vs. temperature for runs 650601 (O) and 650607 (●).

ane, respectively.^{5,9-12,28,30} The spectrum of B₆ seems to correspond to that given for B₆H₁₂ more closely than to the spectrum of B₆H₁₀.^{10,30} The spectrum of B₇ corresponds to the literature spectrum for a combination of B₇H₁₁ and B₇H₁₃.⁹ In view of the differences in mass spectra obtained with different instruments, and particularly that presently observed for B₄H₁₀ 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 B₆H₁₀ and B₆H₁₂ (with no B₆H₁₂⁺ peak in the mass spectrum) might be attributed to alkylboranes, carboranes, and/or alkoxyboranes.¹¹ This problem has not been resolved in this experiment, except that no ether was present (<0.01 %).

Although the intensity of B₁₀ is greater than that for B₉, the B₉ peaks do not seem to be due solely to fragmentation of decaborane since their intensity is too great, according to the literature spectrum,²⁸ for this to be true.

The maximum intensities²³ of B₆ and B₇ are reached at 215° while the maximum intensities of B₅ and B₈ are reached at 230° (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_n⁺ ions, especially the increase in the ratio of I(52⁺)/I(53⁺) with increasing temperature, provides good evidence for the previously unobserved tetraborane, B₄H₈. This was confirmed by observation of B₄H₈⁺ 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 B₂ ions with the spectrum of B₂H₆, 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).

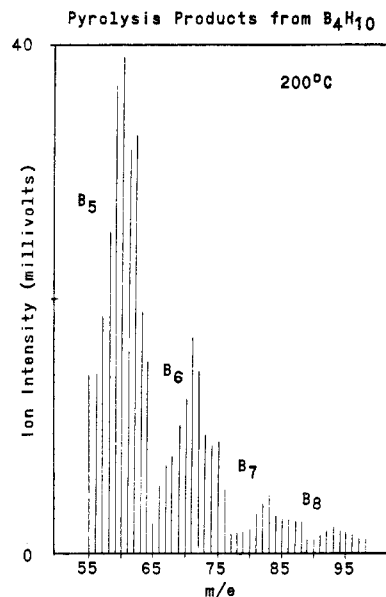


Figure 10. Mass spectrum and relative intensity of the B₅, B₆, B₇, and B₈ hydrides formed at 200° during ¹⁰B₄H₁₀ pyrolysis. At this temperature, peak 60 (B₅) is only 2.8% as intense as peak 50 (B₄).

There was no evidence for the formation of triborane or monoborane. Their formation in amounts small compared to B₄H₈ was not eliminated. If the contributions to the B_nH_n⁺ peaks due to B₂H₆, B₄H₁₀, and B₄H₈ could be subtracted out, it would be possible to determine the formation of monoborane. Although it was possible to estimate the contribution due to B₂H₆ and B₄H₁₀, the contribution of B₄H₈ was uncertain and probably accounts for the otherwise unaccounted increase of ion intensity in the B₁ 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 B₄H₁₀) at 150°. As the temperature increased, the amount of B₅H₉ relative to B₅H₁₁ 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 B₄H₈, 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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