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INTERMEDIATES IN THE
DECOMPOSITION OF DIBORANE-6

by

Gerald Lee Brennan

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Dean of Graduate College

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INTRODUCTION

For about 50 years chemists have been studying the preparation and reactions of the binary compounds of boron and hydrogen. These compounds have proven to be somewhat difficult to work with experimentally since most are inflammable in air. Stock (71) and co-workers developed the high vacuum technique for handling such reactive compounds as these and eventually discovered and studied reactions of six of the seven hydrides known today. The electron deficiency of these compounds became a very intriguing theoretical problem since the classical valence bond theory failed to explain the bonding in the molecules. The structures of these compounds have only been determined experimentally during the last 13 years; a good review of the structures and theoretical explanation of the bonding in the molecules has been written by Lipscomb (35).

The decomposition of diborane-6 has been found to be very complex with many reactions taking place simultaneously. The initial decomposition has, however, a weight of evidence to show that it is a three-halves order reaction. The initial reaction of diborane-6 to form two borane groups is widely accepted, but most of the proposed reactions after the initial one have been suggested as taking place based on a limited amount of experimental evidence.

The conversion of tetraborane-10 to pentaborane-11 has been studied by two groups (19, 51) and was shown to be dependent only on the concentration of tetraborane-10. Dupont (19) measured the first order rate constants and calculated the heat of activation for the interconversion whereas Pearson and Edwards (51) showed the first order dependence of tetraborane-10. In addition, the latter measured the rate and calculated the heat of activation of the thermal decomposition of tetraborane-10. The values for the heat of activation were identical for the two reactions whereas the rate of decomposition was an order of magnitude slower. Pearson and Edwards suggested that either of two intermediate molecules, triborane-7 or tetraborane-8, were produced in the decomposition and Dupont predicted tetraborane-8 as the reactive intermediate in the interconversion reaction.

The possibility that the triborane-7 molecule is the intermediate in conversion of tetraborane-10 to pentaborane-11 appears at first glance attractive, since tetraborane-10 is known to be cleaved at low temperatures with various Lewis bases (25) to form base adducts of triborane-7 and borane-3. It must be recognized, however, that these conditions are far from those prevailing in the thermal interconversion reaction. A better analysis of the nature of the intermediate in the conversion of tetraborane-10 to pentaborane-11 might be made by considering the evidence for the importance of triborane-7 in the pyrolysis of diborane-6 to form higher hydrides. Thus a recent investigation of the kinetic isotope effect on the rate of decomposition of diborane-6 by Enrione and Schaeffer (22), supports the suggestion that formation of the triborane-7 molecule is the rate limiting step in the mechanism of conversion of diborane-6 to higher hydrides. Evidence concerning the fate of this reactive intermediate must at present be obtained by indirect means. The problem can be resolved only by providing evidence for the immediate fate of the triborane-7 molecule by establishing which of the higher boranes is formed first from it.

Klein et al. (30) studied the decomposition of diborane-6 in a reactor with narrow annular space separating a hot wall from a cold wall. Under the conditions of that investigation both tetraborane-10 and pentaborane-11 are relatively efficiently removed from the gas phase and further reactions of these substances quenched. These authors observed that tetraborane-10 exceeded pentaborane-11 in the reaction products by a factor of five to 20 depending upon reaction conditions and the reactor used. Thus it may be concluded that tetraborane-10 is the first stable pyrolysis of diborane-6 or that the pentaborane-11 first formed is rapidly converted by the reaction

$$2B_5H_{11} + 2H_2 \rightleftharpoons 2B_4H_{10} + B_2H_6$$

and that the equilibrium constant for that reaction is substantially greater than one. However, Stewart and Adler (70) have estimated the equilibrium constant for the above reaction from data obtained during a kinetic study of the decomposition of diborane-6 to be about 10^{-3} mm^{-1}. The combination of data from these three sources provide strong support for the postulate that triborane-7 in the presence of diborane-6 is rapidly converted to tetraborane-10 and thus is an unlikely intermediate in the conversion of tetraborane-10 to pentaborane-11.

The purpose of this study was to obtain new evidence concerning the nature of the intermediate in the tetraborane-10 to pentaborane-11 conversion. The classical technique of obtaining a derivative of the reactive intermediate by introduction of a suitable trapping agent was used. Carbon monoxide was shown to be suitable for this purpose and the chemical and physical properties as well as the structure of the tetraborane carbonyl were studied.

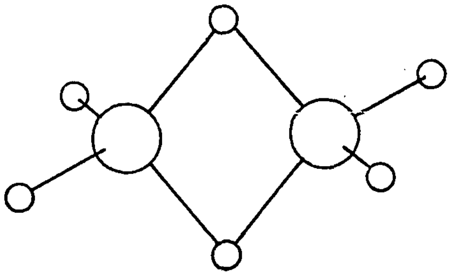
LITERATURE REVIEW

Before the turn of the last century chemists knew that a metal boride treated with mineral acid liberated gases which burned with a green flame, reduced silver salts, had a nauseating odor and produced boron when heated. Jones and Taylor's (27, 28) experiments suggested that the formula for the liberated gas was BH_3 as did later work by Sabatier (60).

Ten years later Ramsay and Hatfield (57) undertook a more "rigorous" study of "boron hydrides" and at this time thought that the formula of the compound was B_3H_3. However, they admitted that attempts to reproduce the work failed, but they were able to separate hydrides from hydrogen gas by diffusion of the hydrogen through clay tubes.

In 1912 the now classic work of Alfred Stock (71) began. He and his associates developed a high vacuum method to handle the unstable, volatile hydrides in the absence of air, moisture and lubricants. By this technique they isolated and identified six binary compounds of boron and hydrogen. These compounds were prepared by the pyrolysis of tetraborane-10 which had been produced by the hydrolysis of magnesium boride with hydrochloric or phosphoric acids. Those six compounds were diborane-6 (B_2H_6), tetraborane-10 (B_4H_{10}), pentaborane-9 (B_5H_9), pentaborane-11 (B_5H_{11}), hexaborane-10 (B_6H_{10}) and decaborane-14 ($B_{10}H_{14}$).

Inasmuch as the boron hydrides were thermally unstable, very reactive and electron deficient, they became a challenging branch of chemistry. By the older valence bond theory, the simplest hydride would be borane-3, but it was always found as the dimer (diborane-6). The structure of this eight atom molecule has been discussed both theoretically and experimentally in many publications. One of the first significant papers on the structure of diborane-6 was published in 1921 by Core (13, 14) who advanced the hydrogen bridge structure for the molecule. Six years later Dilthey (18) advanced the same idea. This structure is shown below:



Sidgwick (69) in 1927 suggested an ethane-like structure for diborane-6. One-electron bonds were postulated to account for the electron deficiency in the molecule. Pauling (49) in 1931 concurred with this since boron and hydrogen were nearly equal in electronegativity. He further predicted the molecule to be stabilized by resonance energy of the two one-electron bonds among the six positions. Lewis (34) in 1933 proposed that the molecule contained six electron pair bonds resonating among seven positions to stabilize the molecule. In 1939 Pauling (50) stated that both these viewpoints could be correct since the two electrons involved in the one-electron bond could have spins either opposed or parallel. With spins opposed, the electrons were formally paired and those structures proposed by Lewis were correct whereas with spins parallel the one-electron bond model of Sidgwick was possible.

Longuet-Higgins and Bell (36) in 1943 suggested a resonance hybrid between structures containing only normal electron-pair bonds. Later (37), they made detailed calculations of the normal vibrations of a diborane-6 molecule containing a symmetrical bridge structure and obtained excellent quantitative agreement with the observed infrared and Raman spectra. They concluded that this agreement made it unlikely that the central hydrogen atoms were unsymmetrically placed.

Pitzer (53) in 1945 suggested the "protonated double bond" structure. He proposed that the two boron atoms were connected via a double bond and two protons were implanted in the pi-electron cloud, one above and one below the plane formed by the two boron atoms and terminal protons. In a review article, Mulliken (42) discussed the respective molecular orbital electron configurations required by the ethane-like and the bridge model of diborane-6. He concluded that all previous evidence favored the bridge model.

Rundle (58, 59) agreed with the bridge model, but explained it in terms of tetrahedral orbitals of boron, two of which are connected to protons by normal two electron bonds while the remaining two form the bridge. The bridge itself required three orbitals (the two sp^3 orbitals of boron and the 1s orbital of hydrogen) and only two electrons. He predicted that the B-H-B bond energy was of the magnitude of 30% greater than a B-H bond.

In 1954, Eberhardt et al. (21) advanced the concept of a three-center bond to explain the boron hydride structures. In this concept orbitals from three atoms interacted to form one bonding and two antibonding orbitals; two electrons then filled the bonding orbital to form a three-center bond. The idea was applicable to both hydrogen bridge bonds and bonds between three boron atoms. In addition, equations of electron, orbital and hydrogen balance were employed in a systematic study of the number of three-centered and normal bonds in the hydride structures. All the possible bonding combinations based on three-centered and normal bonds could be calculated for a proposed hydride. Later (16), topological arguments were advanced to further limit the number of possible structures.

In applying these ideas to the diborane-6 molecule, it was assumed that the orbitals of each boron atom are hybridized to sp^3. Two of the orbitals of a boron atom form normal bonds with two hydrogen atoms while the remaining orbitals lie in a plane normal to the plane of the external B-H bonds. One hybrid from each boron is directed toward each hydrogen atom with the formation of two, three-center bridge bonds.

One of the first attempts to determine the structure of diborane-6 was made in a low temperature X-ray study by Mark and Pohland (39) in 1925. These authors were able to show only that the structure was similar to ethane. Stock (71) reported, on the other hand, that the ultraviolet spectrum was very similar to that of the ethylene molecule rather than to ethane.

A chemical investigation of the structure was conducted by Schlesinger and Walker (65) in 1935. They studied the methyl derivatives of diborane-6 formed by the reaction of boron trimethyl with diborane-6. This study revealed that the mono-, di-, tri- and tetramethyl substituted compounds were the only ones formed. At no time did they find evidence for the formation of penta- or hexamethyl substituted products. They inferred from this that two of the hydrogen atoms in diborane-6 were held by a type of bond different from that which held the other four hydrogen atoms.

In 1937 Bauer and Pauling (2) observed the electron diffraction pattern of diborane-6. They also suggested an ethane-like structure for the diborane-6 molecule. However, interpretation of electron diffraction data obtained by Nekrasov (43, 44) in 1948 and by Hedberg and Schomaker (24) in 1951 led these investigators to conclude that the bridge structure was correct.

A reinvestigation of the ultraviolet spectrum by Price (54) in 1947 agreed well with the hydrogen bridge structure as did the infrared (1, 37, 38, 55, 56) and Raman (37, 74, 75, 76) absorption spectra. The Raman (67) and infrared (38, 75, 76) absorption spectra of deuterodiborane-6 also supported the hydrogen bridge structure.

The nuclear-magnetic resonance spectrum (29, 46, 52, 68) disclosed the presence of two types of hydrogen atoms in the molecule. The resonance of the bridge hydrogens occurred at higher magnetic fields than the terminal hydrogens, signifying a greater diamagnetic shielding of the bridge protons and implied that these bridge hydrogens were in a field of greater negative charge than the terminal hydrogens.

In the early studies of boron hydrides the investigators were hampered by lack of a suitable reaction for the preparation of the hydrides and a method for handling the volatile compounds once they were formed. Stock solved the latter problem when he developed the high vacuum system. The preparatory problem, however, was not solved until relatively recently. All early work was done on small quantities (about three percent yield) of boranes (predominantly tetraborane-10) obtained by reaction of large quantities of magnesium or beryllium boride with either hydrochloric or phosphoric acid. Even with this method quantities of silicon hydrides were always found as impurities and were difficult to separate from boron hydrides. This method was so slow that a month of work was required for the production of a few grams of a mixture of the hydrides.

The thermal decomposition of tetraborane-10 produced three additional hydrides: diborane-6, pentaborane-9 and small amounts of decaborane-14. From diborane-6 the remaining hydride pentaborane-11 and all the other hydrides that Stock discovered can be prepared by pyrolysis.

The hydrolysis of a metal boride remained the only source of the hydrides until 1931 when Schlesinger and Burg (64) prepared diborane-6 directly by subjecting a gaseous mixture of hydrogen and boron trichloride at low pressure to a high voltage discharge. This produced monochlorodiborane (60% yield) which on warming dissociated into diborane-6 and boron trichloride. This technique allowed the preparation of five to ten grams of pure diborane-6 per week and was a decided improvement over Stock's method.

In 1944 Schlesinger *et al.* (66) showed that diborane-6 could be prepared in very good yields by the reduction of boron halides with metal hydrides or borohydrides. Lithium and sodium compounds were used with boron trifluoride or boron trichloride. Diethyl ether was used as solvent for the reactions involving lithium compounds. Diethyleneglycol dimethylether (diglyme) has subsequently proved superior for reactions involving sodium compounds. This proved to be a very useful method for preparing large quantities of diborane-6 in a short time.

Only hexaborane-10 and enneaborane-15 proved to be difficult to prepare from dibornae-6. However, several investigators (31, 45, 71, 72) have described the preparation of hexaborane-10 in small yield by pyrolysis of diborane-6. It was not until 1957 that larger amounts were made available (32) by the decomposition of diborane-6 in a silent discharge. This procedure also produced the new hydride enneaborane-15.

More recently, still more convenient preparation of hexaborane-10 was accomplished in 1958 by Boone and Burg (4) who prepared tetraborane-10, pentaborane-9 and hexaborane-10 from pentaborane-11 and pentaborane-9 from tetraborane-10 by reacting these two hydrides with certain basic reagents such as water, bis-dimethylamineborane, diethyl ether and diethyleneglycol dimethylether (diglyme). The yields of hexaborane-10 were as high as 27% based upon boron in the consumed pentaborane-11.

In order to find the best method of preparation of pentaborane-11, Burg and Schlesinger (8) in 1933 studied the pyrolysis of diborane-6 and pentaborane-11. Their pyrolysis was conducted by both static and flow techniques. Of the two, the flow system proved to be faster and more efficient. The following reaction

$$2\ B_5H_{11} + 2H_2 \rightleftharpoons 2\ B_4H_{10} + B_2H_6$$

seemed to be taking place when pentaborane-11 was heated to 100°C. because small quantities of hydrogen, diborane-6 and tetraborane-10 were formed. Traces of a slightly volatile substance which they suggested might be an octaborane, were also observed. Nonvolatile solids appeared soon after the reaction started but their formation seemed to be inhibited by the accumulation of hydrogen. After an hour at 100°C. pentaborane-9, decaborane-14 and nonvolatile solids began to form. To show that pentaborane-11 and hydrogen would produce diborane-6 and tetraborane-10, a large excess of hydrogen was heated with pentaborane-11. Within a very short time diborane-6 and tetraborane-10 appeared in approximate accord with the stoichiometry of the postulated equation. When the reaction time was lengthened, the quantities of pentaborane-11 and tetraborane-10 were much lower than the equation above predicted. To account for this abnormality, a slower secondary reaction

$$B_4H_{10} + H_2 \longrightarrow 2B_2H_6$$

was suggested as taking place. With proper adjustment of experimental conditions, any of the three boron hydrides were easily prepared.

In 1936 when larger quantities of diborane-6 were easily produced by the reduction of boron trichloride with hydrogen using the technique of Burg and Schlesinger, Stock and Mathing (72) also tried to find proper conditions for formation of the higher hydrides by pyrolysis. A gas circulating pump caused diborane-6 to go through a hot zone and into cold traps in which all the products were condensed out except diborane-6 and hydrogen which were allowed to recirculate. They found that pentaborane-11 and pentaborane-9 were the products when the initial pressure of diborane-6 was about 15 mm. and the hot zone between 190° and 250°C. Some yellow polymer was found but no tetraborane-10 could be isolated. As the temperature was increased the yield of pentaborane-9 went up while that of pentaborane-11 went down.

When hydrogen was introduced into the system initially, the quantity of pentaborane-11 formed was higher than pentaborane-9 and less nonvolatile polymeric material was produced. Upon increasing the initial pressure of diborane-6 to 144 mm. at 180°C. but without hydrogen present, only pentaborane-11, tetraborane-10 and very small quantities of nonvolatile polymeric materials were formed. Upon increasing the pressure of diborane-6 to 440 mm. the percentage of tetraborane-10 had increased at the expense of the pentaborane-11. When the temperature was increased to 300°C. with the initial pressure of diborane-6 at 120 mm., pentaborane-9 was the principal product with only very small amounts of pentaborane-11 and tetraborane-10 being produced.

In addition to the investigation of diborane-6 decomposition, Stock and co-workers also studied the decomposition of pentaborane-11. They observed that pentaborane-11 heated to 100°C. for ten minutes in a large excess of hydrogen reacted according to the following equation:

$$2B_5H_{11} + 1.55\ H_2 \longrightarrow 1.45\ B_4H_{10} + 1.15\ B_2H_6 + .09\ B_5H_9$$

This was approximately what Burg and Schlesinger had observed. Stock and co-workers were then led to believe that the first step in the decomposition of diborane-6 was the formation of tetraborane-10 which in turn decomposed to give pentaborane-11. To confirm this, tetraborane-10 was introduced into the flow system and circulated from a -80°C. trap (vapor pressure of tetraborane-10 was 2.5 mm.) through a zone heated to 180°C. and the products frozen out at -80°C. Separation of the condensable products revealed that pentaborane-11 was the principal product, with nearly equal quantities of pentaborane-9 and hexaborane-10 but in smaller yields. Also formed in this reaction were nonvolatile products, hydrogen and a trace of diborane-6. Stock concluded from this that pentaborane-11 was formed from tetraborane-10 during the pyrolysis of diborane-6.

Dillard (17) in 1949 further studied the reactions

$$2\ B_2H_6 \rightleftharpoons B_4H_{10} + H_2$$
$$B_2H_6 + 2\ B_4H_{10} \rightleftharpoons 2B_5H_{11} + 2H_2$$

and his inconclusive data indicated that the initial disappearance of diborane-6 was second order. He found that tetraborane-10 was the principal product when diborane-6 was stored at room temperature between 35 and 50 atmospheres of pressure for several days. Under similar conditions, except that the pressure was less than one atmosphere, pentaborane-11 was the main product. The decomposition of diborane-6 at 100°C. was found to be inhibited by the presence of hydrogen. Pentaborane-11 heated with an excess of hydrogen produced tetraborane-10 and diborane-6, but not in the ratio expected from the following equation:

$$B_2H_6 + 2B_4H_{10} \rightleftharpoons 2B_5H_{11} + 2H_2$$

The equilibrium below was suggested to explain the discrepancy:

$$2B_2H_6 \rightleftharpoons B_4H_{10} + H_2$$

The reaction of a large excess of diborane-6 with tetraborane-10 at 100°C. for short periods of time (five minutes) produced stoichiometric quantities of pentaborane-11 and hydrogen. Dillard postulated the irreversible equation

$$B_2H_6 + 2B_4H_{10} \longrightarrow 2B_5H_9 + 4H_2$$

to be important because of the following results: (a) pyrolysis of diborane-6 with tetraborane-10 at high temperature produced significant quantities of pentaborane-9, (b) pentaborane-9 heated with hydrogen from 25-100°C. for long periods decomposed very little and (c) when pentaborane-9 was decomposed with diborane-6 at 100°C., the percentage of pentaborane-9 which reacted with a given portion of diborane-6 was always less when no hydrogen was initially present.

Simultaneously with Dillard's investigation, the kinetic study of diborane-6 pyrolysis was being carried out by Clarke and Pease (12). They followed the pyrolysis by total pressure rise and by analysis of products (i.e. hydrogen, diborane-6 and products condensable at -130°C.). During the decomposition of the first 25% of diborane-6, the rate controlling step was three-halves order when the runs were conducted at the same temperature. The observed activation energy was 22,600 ± 100 calories. They also found that hydrogen did not act only as a diluent, since it slowed down the disappearance of diborane-6 whereas the presence of nitrogen had no such effect. There was no rate increase upon increasing the surface area, or introducing quantities of potassium chloride, quartz or running the reaction in a vessel in which diborane-6 had been decomposed to form a nonvolatile hydride surface coating.

Clark and Pease postulated the following sequence of reactions as the mechanism of diborane-6 thermal decomposition:

$$\begin{aligned} B_2H_6 &\overset{K}{\rightleftharpoons} 2BH_3 \\ BH_3 + B_2H_6 &\xrightarrow{k} B_3H_7 + H_2 \\ B_3H_7 + H_2 &\xrightarrow{k_3} B_2H_6 + BH_3 \\ B_3H_7 + B_2H_6 &\xrightarrow{k_4} B_4H_{10} + BH_3 \end{aligned}$$

The system was much more complicated than these equations indicated because the amount of tetraborane-10 recovered was but a small fraction of that required by this mechanism. They suggested that the over-all process resembled a radical-type addition polymerization complicated by a quasireversible dehydrogenation.

An independent study was being conducted at the same time by Bragg et al. (6) who followed the reaction kinetics by three methods: (1) the rate of increase of total pressure as a function of temperature and initial pressure, (2) the rate of formation of hydrogen, and (3) the concentrations of the products measured at various time intervals by a mass spectrometer. The data collected from the first method led them to conclude that the rate controlling step was three-halves order, the reaction was homogeneous in glass, and the activation energy of the rate controlling step was 27,400 ± 700 calories. The second method also gave three-halves order for the rate controlling step, but the activation energy was only 25,500 ± 500 calories. They proposed that this difference was due to the temperature effect upon secondary reactions. The mass spectrometric method revealed a three-halves order rate and pentaborane-11 was shown to be an intermediate in the formation of most other boranes from diborane-6. The reaction scheme was postulated as:

$$B_2H_6 \rightleftharpoons 2\ BH_3$$

$$B_2H_6 + BH_3 \longrightarrow \text{intermediate products}$$

$$\text{intermediate products} + B_2H_6 \longrightarrow B_5H_{11} + H_2$$

$$B_5H_{11} \longrightarrow B_5H_9 + H_2$$

$$B_5H_{11} \longrightarrow B_2H_6 + \text{higher hydrides}$$

Experiments by McCarty and DiGiorgio (40) definitely established that the presence of hydrogen in the decomposition of diborane-6 gave larger yields of pentaborane-9, although the rate of disappearance of diborane-6 was decreased. Also, the reaction producing pentaborane-9 was found to be irreversible.

Morrey and Hill (41) in 1958 studied diborane-6 pyrolysis using the infrared spectrum to quantitatively identify the hydrides. They found that the rate of disappearance of diborane-6 in a brass infrared cell corroborated those obtained by Clarke (11) in Pyrex cells. However, the results were high with respect to those reported by Bragg et al.(6) Pentaborane-11 was found as the major condensable product of decomposition in a Pyrex cell at low pressures and low temperatures whereas at high temperatures pentaborane-9 was the product. The high temperature decomposition of diborane-6 was also found to produce pentaborane-11 which then decomposed rapidly to form pentaborane-9. Further heating caused pentaborane-9 to decompose to solid polymeric compounds. When tetraborane-10 was subjected to a high temperature, pentaborane-9 was the first product to be formed. It further reacted to produce solid polymeric hydrides.

The pyrolysis of pentaborane-11 produced diborane-6 and pentaborane-9 along with decreasing amounts of tetraborane-10 and an increasing quantity of hydrogen. The order of the reaction depended upon the reaction conditions. The order was three-halves at high temperatures and pressures, first order at low pressures and higher temperatures and second order at lower temperatures. Morrey and Hill proposed the following mechanism to account for their data as well as the data of Clarke and Pease, and of Pearson and Edwards (51):

$$B_2H_6 \rightleftharpoons 2BH_3$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_7 + H_2$$

$$B_3H_7 + B_2H_6 \rightleftharpoons B_5H_{11} + H_2$$

$$B_3H_7 + B_2H_6 \rightleftharpoons B_4H_{10} + BH_3$$

$$B_4H_{10} \rightleftharpoons B_4H_8 + H_2$$

$$B_4H_{10} \rightleftharpoons B_3H_7 + BH_3$$

$$B_4H_8 \longrightarrow \text{Polymer} + H_2$$

$$B_5H_{11} \xrightarrow{\text{surface}} B_5H_9 + H_2$$

$$B_5H_9 + \text{Active Species} \longrightarrow \text{Polymer} + xH_2$$

Morrey and Hill found it impossible to choose satisfactory equations that would precisely account for their observed kinetic data. Because of the complexity of the pyrolysis reaction, these equations are modifications of mechanisms postulated by Clarke and Pease and of Pearson and Edwards.

These authors made some observations on catalytic properties of their equipment. For example, sodium chloride and silicone rubber had a pronounced increase on the rate of decomposition of diborane-6. Such materials as brass, Apiezon grease, mercury and Teflon, however, had no such catalytic properties.

Their over-all results seemed to indicate that the pyrolysis of diborane-6 was entirely dependent upon the reaction conditions and no one mechanism would be applicable to each condition.

Dupont (19) studied the rate of thermal decomposition of tetraborane-10 in the presence of diborane-6 with the formation of pentaborane-11 and hydrogen. The reaction

$$2B_4H_{10} + B_2H_6 \rightleftharpoons 2B_5H_{10} + 2H_2$$

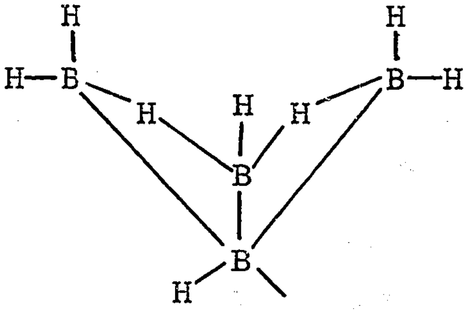
was found to be first order in tetraborane-10 and zero order in diborane-6 since the reaction was independent of the initial diborane-6 concentration. The rate constants were 0.248, 0.123, 0.0370 and 0.0124 minutes^{-1} at temperatures of 92.5°, 85.4°, 72.5° and 62.5°C respectively. Least mean squares treatment of the data gave an activation energy of 23,400 calories, identical to that reported by Pearson and Edwards for the decomposition in the absence of diborane-6. A B_4H_8 molecule was postulated as being formed in the rate determining step. The following reactions were postulated for the mechanism:

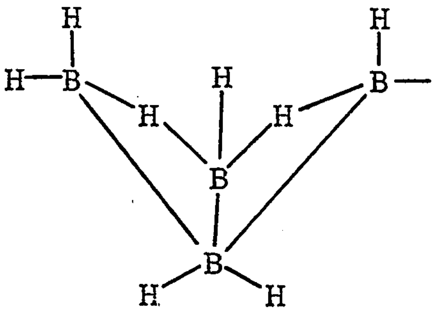
$$B_4H_{10} \rightleftharpoons [B_4H_8] + H_2$$

$$[B_4H_8] + B_2H_6 \rightleftharpoons B_5H_{11} + BH_3$$

$$2B_4H_{10} + B_2H_6 \rightleftharpoons 2B_5H_{11} + 2H_2 \text{(overall reaction)}$$

In the published article (20) by Dupont and Schaeffer, they viewed the tetraborane-8 structure in terms of Dickerson and Lipscomb's (16) topological approach. The treatment was modified so that structures of molecules with a vacant orbital could be considered. One pair of structures based upon an icosahedral fragment was found for the tetraborane-8 molecule. These structures are shown below:





Dupont also found from his kinetic study that pentaborane-11 was always contaminated with a very small amount of pentaborane-9 as noted by vapor pressure measurements. Effective fractionation of the reaction products eliminated any other hydrides which would have been presented. Schaeffer (62) proposed that the following reaction

$$B_4H_{10} + B_5H_{11} \longrightarrow B_5H_9 + 2B_2H_6$$

was responsible for pentaborane-9 contamination observed by Dupont. The stoichiometry of the reaction below 100°C. was found by Dupont to produce the required amount of pentaborane-11 in accordance with the reaction of tetraborane-10 with diborane-6. However, at temperatures above 100°C., the amount of pentaborane-11 was less then the amount required and the quantity of diborane-6 recovered was more. This tended to substantiate the reaction proposed by Schaeffer for pentaborane-9 formation.

Pearson and Edwards (51) in 1957 reported the results of the pyrolysis of tetraborane-10 at 60°, 80° and 100°C. The kinetic order of unity was established. The estimated first order rate constants for the respective temperatures were 1.8×10^{-5}, 1.1×10^{-4}, 7.9×10^{-4} seconds^{-1}. These data gave a value for the activation energy of 23,400 calories. The gas phase reaction produced diborane-6, pentaborane-11, hydrogen and yellow, nonvolatile solids with traces of pentaborane-9, hexaborane-10 and decaborane-14. The reaction of tetraborane-10 with diborane-6 gave pentaborane-11 and the reaction was independent of either the diborane-6 or pentaborane-11 concentrations.

Two simultaneous reaction paths for the decomposition were suggested:

$$\begin{aligned} B_4H_{10} &\rightleftharpoons B_4H_8 + H_2 \\ B_4H_{10} &\rightleftharpoons B_3H_7 + BH_3 \\ B_3H_7 + H_2 &\longrightarrow B_2H_6 + BH_3 \\ B_2H_6 + B_3H_7 &\longrightarrow B_5H_{11} + H_2 \\ B_3H_7 &\longrightarrow (BH)_x \end{aligned}$$

The intermediates proposed by this scheme, B_3H_7 and B_4H_8, were assumed to be unstable and could decompose to form solid hydride polymers. The authors favored the B_3H_7 intermediate.

Harrison et al. (23) recently reported the preparation, structure and properties of dimethylenetetraborane ($C_2H_4B_4H_8$). The compound was prepared in 70% yields by the reaction of ethylene with tetraborane-10 in a "hot-cold" reactor. The structure was determined by infrared and chemical analysis, chemical degradation, reaction stoichiometry and nuclear magnetic resonance. The compound was found to be a cyclic-bridged structure, with the two carbon atoms connected to the "top" boron atoms of tetraborane-10. The model was consistent with the required bond distances and angles. The two terminal protons in close proximity to each other at the top of the molecule appeared to be the ones displaced.

A second adduct of the tetraborane-8 molecule was prepared by Burg and Spielman (9) by the reaction

$$B_5H_{11} + 2CO \longrightarrow B_4H_8CO + BH_3CO$$

This suggests that pentaborane-11 was cleaved into B_4H_8 and BH_3 fragments. The reaction was carried out at a high pressure of carbon monoxide (i.e. 20 atmospheres) with a quantitative conversion to the two products. The chemical analysis of tetraborane carbonyl was difficult, requiring several successive methods before the formula was established. The compound was found to react with water and trimethylamine, but without liberation of carbon monoxide. It had been previously (63) suggested that this compound might be triborane carbonyl but further examination of the compound and knowledge of the stoichiometry of the reaction proved the compound to be tetraborane carbonyl.

Larson (33) in 1956 found from a kinetic study of B^{10}-B^{11} and H-D exchange reactions between diborane-6 and pentaborane-11 that the rate of each exchange reaction was the same. He noted that each reaction was first order in diborane-6 and one-half order with respect to pentaborane-11. The following steps were postulated for the mechanism:

$$B_5H_{11} \rightleftharpoons B_4H_8 + BH_3$$
$$B_2D_6 + BH_3 \longrightarrow B_2H_3D_3 + BD_3$$
$$B_2D_6 + B_4H_8 \longrightarrow B_5H_5D_6 + BH_3$$
$$BH_3 + BD_3 \longrightarrow B_2H_3D_3$$

He found that all the boron and hydrogen atoms would exchange in pentaborane-11. This suggested that all atoms in the reacting fragment were chemically equivalent since all atoms in the original pentaborane-11 exchanged nonpreferentially. Since the total molecular concentrations of diborane-6 and pentaborane-11 remained unchanged during the course of the reaction, the original molecule was reformed, differing only in isotopic content.

A kinetic study of the exchange of deuterium between diborane-6 and tetraborane-10 was recently reported by Todd and Koski (73). Exchange studies between 25° and 45°C. proved to be quite complex. A plot of ln (1-F) versus time (F is the fraction exchange) would have given a straight line for a simple homogeneous exchange reaction, but a curved line was indicated. This was interpreted as being due to two different exchange rates and hence two different types of hydrogen atoms in the molecule. The analyzed data showed that two hydrogens were exchanged faster than the remaining eight. They considered both B_4H_8 and B_3H_7 as possible intermediates but eliminated both in favor of an activated tetraborane-10 molecule. They gave the mechanism of exchange of two hydrogen atoms as:

$$B_4H_{10} + B_4H_{10} \rightleftharpoons B_4H_{10}^{*} + B_4H_{10}$$
$$B_4H_{10} + B_2D_6 \rightleftharpoons B_4H_{10}^{*} + B_2D_6$$
$$B_4H_{10}^{*} + B_2D_6 \rightleftharpoons B_4H_8D_2 + B_2D_4H_2$$

and the exchange of the remaining protons as:

$$B_2^{10}D_6 \rightleftharpoons 2B^{10}D_3$$
$$B^{10}D_3 + B_4H_{10} \longrightarrow B^{10}D_3B_3H_7 + BH_3$$
$$BH_3 + B^{10}D_3 \longrightarrow BH_3B^{10}D_3$$

This last list of equations was very speculative because the B^{10} exchange experiments were only preliminary.

The tetraborane-10 order for the exchange was 1.15 for reaction I and 1.04 for reaction II while the order of deuterodiborane-6 was 0.25 and 0.6 for reactions I and II respectively. The activation energies were estimated to be 25,500 and 14,100 calories for reactions I and II. The exchange reaction involving two tetraborane-10 hydrogen positions was denoted as reaction I and the other, involving eight positions, as reaction II.

A very recent study by Enrione and Schaeffer (22) of the deuterium isotope effect in the decomposition of diborane-6, showed that diborane-6 decomposed five times faster than deuterodiborane-6. The authors considered three reactions which might be rate limiting in this pyrolysis:

$$B_2H_6 + BH_3 \longrightarrow B_3H_7 + H_2$$
$$B_2H_6 + BH_3 \longrightarrow B_3H_9$$
$$B_3H_9 \longrightarrow B_3H_7 + H_2$$

Detailed calculations were made which showed deuterodiborane-6 to be dissociated to a greater extent than diborane-6. At the same temperature, the BD_3 concentration was twice as large as the BH_3 concentration, but the rate of decomposition of deuterodiborane-6 was observed to be only one-fifth as large as for diborane-6.

The third reaction above was postulated as the rate limiting step to best fit the observed isotope effect and the sequence of reactions for the decomposition of diborane-6 as:

$$B_2H_6 \rightleftharpoons 2BH_3$$
$$B_2H_6 + BH_3 \rightleftharpoons B_3H_9$$
$$B_3H_9 \longrightarrow B_3H_7 + H_2$$

EXPERIMENTAL

Vacuum System and Equipment

The usual type of high vacuum system was employed as described by Sanderson (61). A mechanical Welch Duo-Seal pump in series with a mercury diffusion pump gave a pressure of 10^{-5} to 10^{-6} millimeters of mercury. Vacuum stopcocks lubricated with Apiezon T or Silicone high vacuum grease and mercury valves were used throughout the system. An automatic Toepler pump supplemented a fractionating system, storage vessels and an inlet system. A gas circulating pump similar to that described by Brunfeldt and Holm (7) was used to move gaseous mixtures through a heated zone in the kinetic study.

Volumes of gases were measured at ambient temperatures in the fractionating system previously calibrated with a known amount of carbon dioxide. Unless otherwise stated, volumes of gases are given in cubic centimeters of gas at 0°C. and 760 mm. pressure. Pressures between one millimeter and one atmosphere were measured with a mercury manometer.

The temperature control of the heated decomposing zone for the kinetic study was achieved by a Thermistemp Temperature Controller Model 71 purchased from Yellow Springs Instrument Company, Yellow Springs, Ohio.

A Perkin-Elmer Infrachard Spectrophotometer Model 137, a Consolidated Engineering Corporation Mass Spectrometer Model 21-620 equipped with a micromanometer, and a Varian Associates Nuclear Magnetic Resonance Spectrometer were used to obtain the various spectra.

Preparation and Purification of Chemicals

Diborane-6 used in this study was supplied by Olin Mathieson Chemical Company in a high pressure gas cylinder. After standing at room temperature for several months, sizeable quantities of tetraborane-10 and pentaborane-11 were present, providing a convenient source of these two hydrides. The preparation of additional tetraborane-10 was accomplished by the slow decomposition of diborane-6 at 40 atmospheres of pressure in a stainless steel cylinder which had been heated to 70°C. for six hours prior to opening.

The purification of diborane-6 was accomplished by first pumping the hydrogen away while the hydrides were cooled to -196°C. Separation from other hydrides was accomplished by passing the gaseous mixture into a trap cooled to either -135° or -157°C. (ether-ethanol and isopentane slush-baths respectively). The diborane-6 went through this trap and stopped in one cooled to -196°C. while the higher hydrides remained behind. The process was repeated until the vapor pressure was 225 millimeters (literature gave 225 mm.) at -112°C.

Diborane-6 and pentaborane-11 were the major impurities in tetraborane-10. This mixture was pumped through traps cooled to -95°, -112° and -196°C. respectively. The pentaborane-11 fraction remained in the -95°C. trap, whereas tetraborane-10 stopped in the -112°C. trap, and a trace of diborane-6 went through to the -196°C. trap. This procedure was continued until the tetraborane-10 had a vapor pressure of 387 mm. (literature gave 386.8 mm.) at 0°C.

The pentaborane-11 remaining in the -95°C. trap was passed two times through a -63°C. trap and the mixture of pentaboranes which came through was pumped through a -80°C. trap until the vapor pressure remained constant at 53 mm. (literature, 52.8 mm.) at 0°C. These hydrides were then stored at -196°C. until they were used.

The deuterodiborane-6 was prepared several years ago by Schlesinger et al. at the University of Chicago from the reaction of lithium deuteride with boron trifluoride etherate, and since then had been stored at room temperature sealed in liter Pyrex bulbs. Purification of this material was accomplished by the method used for diborane-6. The pure material had a vapor pressure of 238 mm. at -112°C.

The carbon monoxide was purchased from the Matheson Company and the cylinder was attached to the vacuum system via copper tubing and a Kovar seal to glass so that the system could be evacuated to 10^{-5} or 10^{-6} mm. of mercury. The carbon monoxide was passed through a trap filled with Pyrex wool and cooled to -196°C. before using.

The phosphorus trifluoride was prepared by the following reaction:

$$PCl_3 + ZnF_2 \longrightarrow PF_3 + ZnCl_2$$

Zinc fluoride (10 grams) (Amend Drug and Chemical Company) powder was put into a 250 ml. three-necked flask equipped with a dry ice condenser and dropping funnel containing 13 grams of phosphorus trichloride (Merck). The powder was stirred magnetically while the system was evacuated. As the phosphorus trichloride was slowly added, the liberated gases passed through the dry ice condenser into the lower manifold of the vacuum line. They were periodically removed by opening a stopcock leading to a U-tube where they were condensed at -196°C. The reaction produced several gaseous products and the phosphorus trifluoride was separated out by quickly passing the gaseous mixture through a trap cooled to -157°C. The phosphorus trifluoride came through this trap and stopped in a -196°C. trap. This compound was distilled through a column of solid potassium hydroxide, to remove trace amounts of hydrogen chloride. Then two more quick passes through a

-157°C. trap gave phosphorus trifluoride with a vapor pressure of 376 mm. at -112°C. (literature gave 388 mm.) (5). Further fractionation failed to give a higher vapor pressure. The mass spectrum Table 1 showed the presence of no impurities. The material was stored at -196°C. until it was used.

Table 1. Mass spectrum of phosphorus trifluoride

Mass-charge ratio (m/e)	Ion	Relative intensity
88	PF_3^+	78
69	PF_2^+	100
50	PF^+	8.8
44	PF_3^{++}	4.3
34.5	PF_2^{++}	6.4
31	P^+	7.1
25	PF^{++}	22.1
19	F^+	7.9
15.5	P^+	5.2

The trimethylamine was liberated from the hydrochloride with a concentrated solution of potassium hydroxide. The gas was pumped through -80° and -95°C. traps and stopped in one at -196°C. The vapor pressure was 7.1 mm. (literature gave 6.6 mm.) at -80°C. It was kept at -196°C. until used.

Description of Kinetic Procedure

The reaction between tetraborane-10 and carbon monoxide was conducted in a vacuum system consisting of three U-tubes and a gas circulating pump. This system was separated from the conventional vacuum system by a mercury valve and the first U-tube had a mercury valve on either side in order to isolate it completely. A known quantity of tetraborane-10 was condensed into this U-tube and kept frozen to -196°C. An oil bath around the second U-tube was brought to the appropriate temperature. Next, the required amount of carbon monoxide was introduced into the entire system including the pump. With a -196°C. bath on the third U-tube, the first U-tube containing tetraborane-10 was allowed to warm to the predetermined low temperature. The pumping and timing were immediately started. Thus the mixture of tetraborane-10 and carbon monoxide was forced through the heated U-tube and immediately cooled in the next allowing only the carbon monoxide and hydrogen formed to recirculate. After a predetermined time, the mercury valves on either side of the first U-tube were closed and pumping stopped.

Carbon monoxide and the tetraborane-10 which did not circulate was transferred to the fractionating system where tetraborane-10 stopped in a -196°C. trap and carbon monoxide was pumped out. The quantity of tetraborane-10 recovered subtracted from the original quantity gave the amount which went through the hot U-tube. After the decomposition zone cooled to below 40°C., the carbon monoxide was pumped from the remaining two U-tubes and circulating pump. The products of the reaction and unreacted tetraborane-10 were transferred to the fractionating system and separated. This was accomplished by passing the mixture into -95° and -196°C. traps. The tetraborane carbonyl remained in the -95°C. trap while the excess tetraborane-10, trace amounts of diborane-6 and borane carbonyl were condensed in the -196°C. trap. The tetraborane-10 was considered completely removed from tetraborane carbonyl when the latter had a vapor pressure of five to six millimeters at -45°C. The tetraborane-10 was purified from trace amounts of diborane-6 and borane carbonyl by passing the mixture through a -135°C. trap twice. Pure tetraborane-10 was found in this trap while impurities were found in the -196°C. trap. The quantity of tetraborane-10 recovered subtracted from the amount which went through gave the amount of tetraborane-10 either reacted with the carbon monoxide or decomposed to form other hydrides. Since the rate of decomposition of tetraborane-10 was known to be much slower than the observed rate of reaction (51) and since only traces of contaminants could be isolated, a fairly accurate measure of the tetraborane-10 converted to the carbonyl was obtained. Direct quantitative recovery of the carbonyl could not be carried out reliably owing to its instability.

To calculate the residence time the following variables were needed: the length of time for passing a known amount of tetraborane-10 through the hot zone, the partial pressure of the tetraborane-10 and the volume and temperature of the heated zone. The following equation was derived for calculation of residence time:

$$t_i = \frac{V_h T}{V_g}$$

Where: V_h = volume of the heated zone
V_g = total volume of the gas passed
T = time for the gas to pass through the heated zone.

The volume of the heated zone was determined by marking the depth to which the U-tube was immersed in the hot oil and weighing the water required to fill it to the mark. The volume was determined to the nearest tenth of a milliliter. The volume of the gas which went through the heated zone was calculated by using the ideal gas equation $PV = nRT$. The pressure term used in this calculation was the partial pressure of tetraborane-10 which was equivalent to the vapor pressure at the low temperature used in the particular run. The temperature in the equation corresponded to the temperature of the hot zone and n was the number of millimoles of tetraborane-

10 which went through the hot zone determined by difference as previously described.

Kinetic Data

The thermal decomposition of tetraborane-10 in the presence of carbon monoxide was investigated at four different temperatures, a variety of carbon monoxide pressures and three different partial pressures of tetraborane-10. The values of the rate constant calculated from the first order rate equation

$$2.3 \log C_i/C_f = kt_i$$

for each of these variations are found in Table 2. The variation of rate constants for a given temperature was an indication of the difficulties encountered in the experiment.

Several factors involved in the experimental method and the method of calculation should be specifically noted. Thus, it was assumed that as tetraborane-10 was pumped through the hot U-tube each molecule was heated to the appropriate temperature even though the pumping speed was quite fast or consequently the residence time low. (The short residence time was necessary to prevent the formation of both volatile and nonvolatile higher hydrides and side reactions leading to such products took place when the temperature of the heated zone was 120°C. or higher). The residence time was changed by

Table 2. Kinetic data for the decomposition of tetraborane-10 in the presence of carbon monoxide

Reaction no.	Temp. (°C.)	Init. B4 (mmoles)	Final B4 (mmoles)	B4 lost (mmoles)	Time (min.)	Low temp. (°C.)	CO press. (mm.)	Heated vol. (ml.)	t. (min.)	k (min.$^{-1}$)
72	80	12.567	12.002	.565	60	-45	204	82.9	.7011	.0668
73	80	5.246	4.843	.403	45	-45	402	82.9	1.260	.0642
75	80	8.168	7.535	.633	45	-45	203	82.9	.8091	.099
76	80	7.556	7.076	.480	45	-45	201	82.9	.8748	.0757
77	80	5.946	5.540	.400	45	-45	404	82.9	1.111	.0644
40b	98	8.760	7.638	1.122	57	-45	402	36.0	.3908	.351
40c	98	7.638	6.720	.918	44	-45	402	36.0	.3450	.371
46	100	14.529	10.765	3.764	180	-45	422	36.0	.7370	.405
74	100	6.537	3.975	2.562	45	-45	204	83.5	.9510	.523
78	100	4.146	2.402	1.744	30	-45	200	83.5	.9999	.544
79	100	3.062	1.986	1.076	20	-45	402	83.5	.9024	.479
52	110	4.023	2.643	1.380	30	-45	410	36.0	.4362	.9696
53	110	2.185	1.331	.854	20	-45	406	36.0	.5188	.933
54	110	2.594	1.342	1.252	70	-63	400	36.0	.4880	1.350
55	110	.934	.211	.723	70	-63	408	36.0	1.355	1.099
59	110	4.457	3.470	.987	90	-63	402	28.3	.2864	.873
60	110	3.152	2.529	.623	60	-63	400	28.3	.2700	.815
61	110	3.576	2.707	.869	60	-63	200	28.3	.2380	1.168
62	110	3.621	2.725	.896	60	-63	197	28.3	.2351	1.121
63	110	4.625	3.362	1.263	30	-45	200	28.3	.2953	1.076
64	110	3.134	2.170	.964	30	-45	200	28.3	.4357	.842
65	110	4.298	3.078	1.220	30	-45	200	28.3	.3177	1.050

varying the volume of the heated zone and to a small extent by changing the partial pressure of tetraborane-10. It was necessary to assume that the partial pressure of tetraborane-10 remained constant. The slow transfer of tetraborane-10 from the U-tube cooled with a constant temperature bath would probably introduce very little deviation from the calculated value of the partial pressure. There was no attempt to measure any deviation therefore the amount of error introduced here was unknown. The total pumping time was probably known to ±5 seconds. The only assumption was that tetraborane-10 did not diffuse into and through the hot zone before the pump was turned on. The high pressure of carbon monoxide present made this assumption seem valid. The timing was started the instant the pump was turned on and stopped exactly at a predetermined time by closing the mercury valves on either side of the first U-tube containing the reservoir of tetraborane-10. The quantity of diborane-6 and borane carbonyl formed during the reaction was always very small and entirely neglected in all the calculations.

The approximate zero order dependence of carbon monoxide was established by changing the pressure from 200 to 400 mm. of mercury and noting that the first order rate constant was nearly unchanged except for experimental error as found in Table 2. Had carbon monoxide entered the rate equation, the values of the rate constant would have differed by approximately a factor of two for the two different pressures of the carbon monoxide. This large difference was not observed and it was concluded that the rate of the reaction was approximately independent of carbon monoxide concentration.

The least mean squares treatment of the data given in Table 3 gives the best values for rate constants at different temperatures.

Table 3. Calculated first order rate constants with respect to tetraborane-10

Temp. (°C.)	k (min.$^{-1}$)
80	0.070
98	0.360
100	0.500
110	1.071

The heat of activation of the reaction was calculated from the Arrhenius equation:

$$k = Ae^{-E_{act.}/RT}$$

A plot of the ln k *versus* 1/T is found in Figure 1. The least mean squares treatment of this slope gave a value of 24,560 calories for the heat of activation and 1.119×10^{14} for the frequency factor. Thus the temperature dependent equation may be written as:

$$k = 1.119 \times 10^{14}\ e^{\frac{-24,560}{RT}}$$

The rate constants calculated from this equation are compared to values obtained from the least mean squares treatment in Table 4.

Table 4. Observed and calculated rate constants

Temp. (^{o}C.)	$k_{obs.}$	$k_{calc.}$
80	0.070	0.070
98	0.360	0.380
100	0.500	0.455
110	1.071	1.130

To check the kinetic procedure used in this study, a single first order rate constant for the reaction studied by Dupont (19)

$$B_2H_6 + 2B_4H_{10} \rightleftharpoons 2B_5H_{11} + 2H_2$$

was determined as 1.09 min.$^{-1}$ at 110^{o}C. This value compared very well with the value 1.10 min.$^{-1}$, extrapolated from the data given by Dupont who studied the interconversion reaction at lower temperatures by the more commonly used static technique. The values are in better agreement than anticipated because of the inherent errors of this experiment.

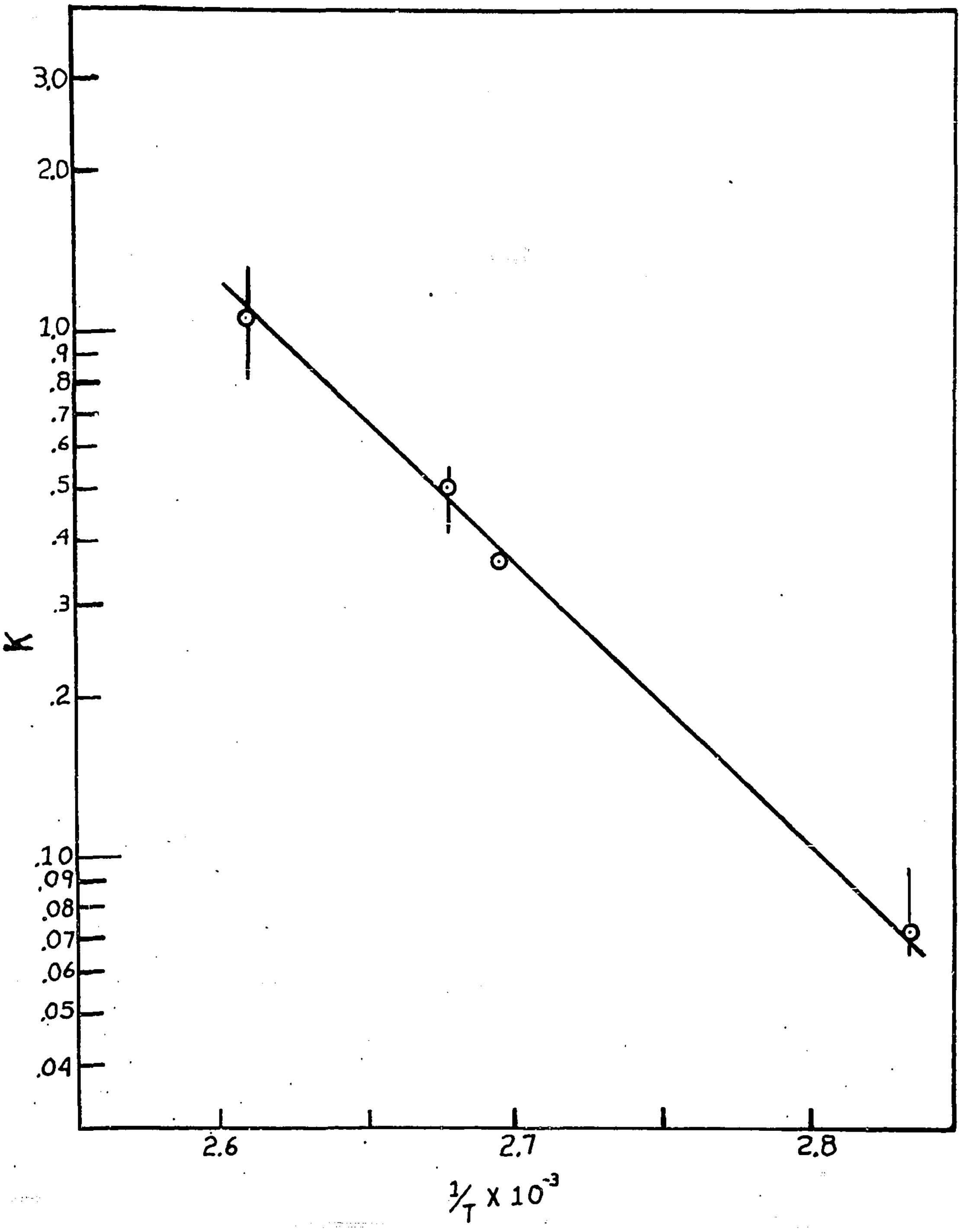


FIGURE 1 ARRHENIUS PLOT OF THE FIRST ORDER RATE CONSTANTS

Tetraborane Carbonyl

Physical properties

Tetraborane carbonyl was a thermally unstable liquid at room temperature decomposing to give carbon monoxide and other boron hydrides. It spontaneously ignited in air and burned with a green flame as do most of the other boron hydrides. The vapor pressure was measured and is compared with the literature value in the following table.

Table 5. Vapor pressures of tetraborane carbonyl at various temperatures

Temp. (°C.)	$P_{obs.}$ (mm.)	$P_{lit.}$ (mm.)[a]
-63.5	1.12	1.07
-49.5	3.24	3.61
-45.0	4.24	4.78
-30.5	11.48	12.65
0.0	69.4	71.3

[a] Data from (9)

The slight disagreement of vapor pressures in the two instances may be an indication of the instability of the compound since at 0°C. the observed value was only a rough estimate of the vapor pressure (carbon monoxide being slowly formed at this temperature).

From the manner of preparation and the agreement of physical properties between the compound formed in this kinetic study and that reported by Burg for tetraborane carbonyl, the compounds were assumed identical.

The infrared spectrum, Figure 2, was obtained in a five cm. Pyrex cell with potassium bromide windows. The sample pressure was about 100 mm. Some decomposition probably occurred while the spectrum was being taken, but the gas phase decomposition of the compound has not been studied and therefore a qualitative estimate as to the extent of sample decomposition could not be made. Extra carbon monoxide pressure was not present in the cell with the sample.

The mass spectrum of the carbonyl derivative is given in Table 6. The largest mass/charge value present in the spectrum was 52 corresponding to $B_4H_8^+$ instead of the possible parent peak value of 80($B_4H_8CO^+$). The spectrum of tetraborane carbonyl would be nearly indistinguishable from the tetraborane-10 spectrum if the 28 peak corresponding to the CO fragment were removed.

The mass spectrum always showed small amounts of diborane-6 and a hydride containing five boron atoms present in purified tetraborane carbonyl. Whether these were formed in the mass spectrometer or were not completely removed during the fractionation procedure has not been determined. There-

Figure 2. Infrared spectrum of tetraborane carbonyl. Top curve is for the empty cell.

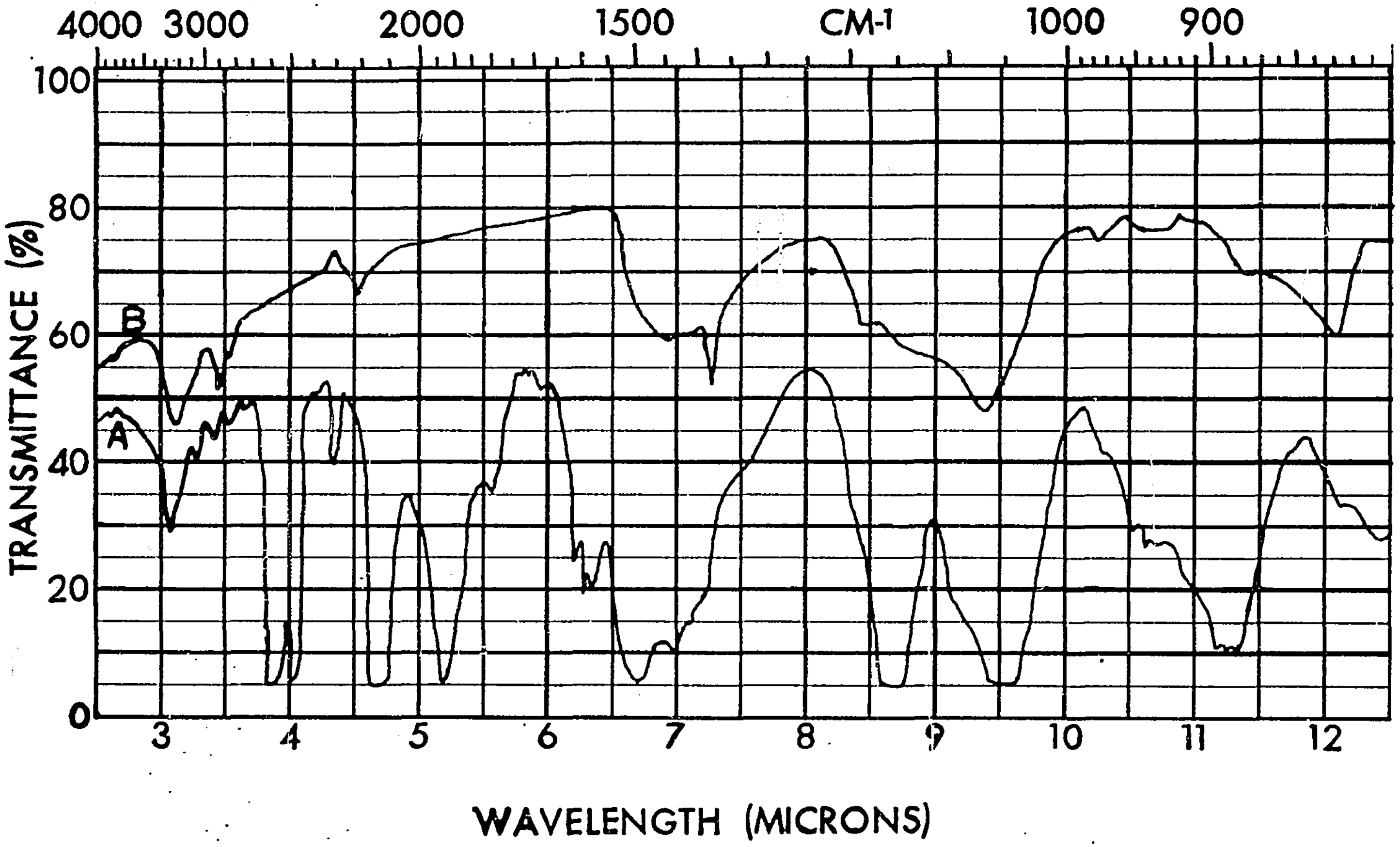

4000
3000
2000
1500
CM-1
1000
900
100
80
60
40
20
0
TRANSMITTANCE (%)
B
A
3
4
5
6
7
8
9
10
11
12
WAVELENGTH (MICRONS)

FIGURE 2

Table 6. Polyisotopic mass spectrum of B_4H_8CO at 40 microamperes current; the sensitivity was 14.4 div/ for m/e = 48 compared to 238.3 div/ for m/e = 41 for butene^{-1}

m/e	Intensity	m/e	Intensity
52	3.40	28	100
51	9.07	27	12.9
50	48.9	26	12.0
49	50.2	25	7.65
48	50.9	24	11.0
47	39.3	23	5.85
46	22.5	22	1.70
45	12.7	21	.34
44	7.94	14	3.22
43	4.30	13	15.7
42	1.14	12	10.3
41	.68	11	24.2
40	----	10	6.45
39	1.93	--	--
38	17.4	--	--
37	16.0	--	--
36	14.8	--	--
35	12.8	--	--
34	6.91	--	--
33	2.78	--	--
32	1.36	--	--
31	--	--	--
30	--	--	--
29	1.58	--	--

fore the mass spectrum of the sample was corrected for the small amount of B_5 hydride, but not for diborane-6 since there was no single m/e value which was contributed exclusively by this molecule.

The nuclear magnetic resonance spectrum is found in Figure 3. The B^{11} spectrum is composed of a triplet on the low field side and a doublet on the high field side. The proton spectrum shows five intense peaks.

Chemical reactions

Tetraborane carbonyl had been observed to liberate carbon monoxide on warming to about room temperature. If B_4H_8 is formed in this decomposition and if it is in fact the intermediate in the conversion of tetraborane-10 to pentaborane-11, pentaborane-11 should be formed by decomposition of tetraborane carbonyl in the presence of diborane-6. Therefore the interaction of diborane-6 with tetraborane carbonyl was investigated.

An excess quantity of diborane-6 (5.17 mmoles) was allowed to warm to room temperature for 18 minutes with 0.99 mmoles of tetraborane carbonyl in a sealed Pyrex bulb (65.3 ml. volume). While the reaction vessel was at room temperature, the diborane-6 was in the gas phase and the tetraborane carbonyl in both liquid and gas phase. At the end of the re-

Figure 3. Nuclear magnetic resonance spectra of tetraborane carbonyl.

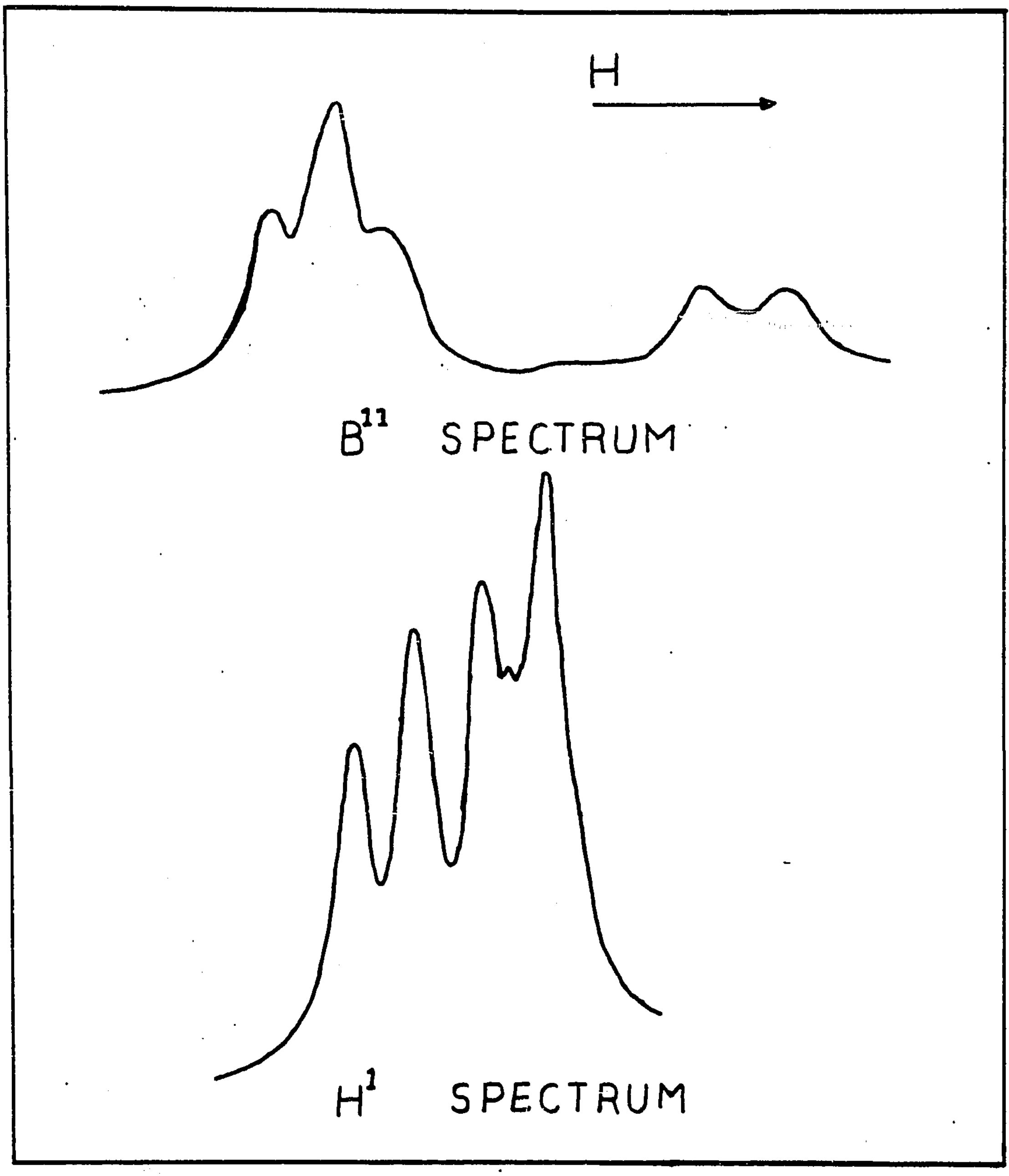


FIGURE 3

action time the reaction vessel was frozen to -196°C., attached to the vacuum system and opened with a magnetic breaker. The noncondensable gases were transferred into a small measuring system of known volume with an automatic Toepler pump and 0.07 mmoles of these gases were found. The condensable materials were transferred to the fractionating system and passed without pumping through a -135°C. trap four times. Mass spectra were run on (1) the noncondensable gases, (2) the fraction which went through the -135°C. trap, and (3) that fraction which stopped in this -135°C. trap.

The noncondensable fraction was found to be a mixture of carbon monoxide and hydrogen. The most volatile fraction of the condensable material was diborane-6 with a trace of borane carbonyl. The least volatile condensable fraction was tetraborane carbonyl with the same amount of B_5 impurity as in the original tetraborane carbonyl. The diborane-6 recovered amounted to 5.08 mmoles which constitutes nearly complete recovery of the initial diborane-6.

When only tetraborane carbonyl was allowed to warm to room temperature, more noncondensable gas was produced than when diborane-6 was present. Thus, 2.5 mmoles of tetraborane carbonyl was condensed into a Pyrex reaction vessel (49 ml. volume), sealed off and allowed to warm to room temperature for 25 minutes. The noncondensable gas recovered was 0.54

mmoles. The liquid tetraborane carbonyl had slowly become pale yellow in color. When the noncondensable gases and volatile undecomposed tetraborane carbonyl were removed, a pale orange liquid of low volatility remained in the reaction vessel. Thus nearly 0.22 mmoles of noncondensables were formed per mmole of carbonyl compared to only 0.07 for the decomposition with diborane-6 present. The tetraborane carbonyl was found, therefore, to be unreactive with diborane-6 at room temperature and more thermally stable in the presence of two atmospheres of diborane-6 gas.

The possibility of forming an octaborane or other higher molecular weight hydride by the reaction of tetraborane carbonyl and tetraborane-10 was studied. An excess amount of tetraborane-10 (3.72 mmoles) was allowed to warm to room temperature for 15 minutes with tetraborane carbonyl (0.82 mmoles) in a sealed (volume of 44.9 ml.) bulb. At the end of this period the reaction vessel was cooled to -196°C. and attached to the vacuum system. After opening the vessel with a magnetic breaker, the noncondensable gases were transferred to a small known volume with an automatic Toepler pump and measured. Only 0.03 mmoles of noncondensable gases were found. The mass spectrum showed them to be a mixture of carbon monoxide and hydrogen. The condensable materials were transferred to the fractionation system and passed through a -95°C. trap until the vapor pressure of the material remaining in this trap was constant (5-6 mm. at -45°C.). The more volatile material stopped in a -196°C. trap and was found to be pure tetraborane-10 after one more quick pass through a -95°C. trap. The amount of tetraborane-10 recovered (3.71 mmoles) was nearly identical with that put in the reaction vessel. Apparently no reaction had occurred.

Since tetraborane carbonyl did not react with diborane-6 and decomposed only slightly in the presence of it, the exchange with deuterodiborane-6 seemed to warrant investigation. This exchange study could give valuable evidence as to the structure of the molecule. For example, the exchange reaction could reveal the number of equivalent hydrogen atoms in the molecule. Another advantage of obtaining the partially or completely deuterated compound would come in interpreting the B^{11} nuclear magnetic spectrum. Since there is small spin-spin interaction between deuterium and boron atoms which are connected, the B^{11} spectrum would be simplified making the interpretation much easier. Therefore this exchange reaction was attempted. Deuterodiborane-6 (2.15 mmoles) was condensed into a weighed 50 ml. bulb attached to a four millimeter vacuum stopcock. Tetraborane carbonyl was introduced and the vessel weighed at room temperature. The amount of carbonyl in the vessel was calculated by difference. The tetraborane carbonyl was in both the liquid and gaseous phases whereas deuterodiborane-6 was in the gas phase. After 15 minutes, the deuterodiborane-6 was removed from the reaction flask and 2.33 mmoles of fresh deuterodiborane-6 were allowed to react for another 15 minutes. This step was carried out once more with 2.30 mmoles of deuterodiborane-6. All the recovered deuterodiborane-6 (6.78 mmoles) was put together and a portion was decomposed over iron turnings at 1000°C. The hydrogen-deuterium mixture was heated with a glowing platinum wire and then quantitatively analyzed with a calibrated mass spectrometer. The analysis showed that 1.37 mmoles of deuterium atoms were lost from the deuterodiborane-6 for 1.12 mmoles of tetraborane carbonyl.

The partially deuterated tetraborane carbonyl was allowed to warm once more for 15 minutes with fresh deuterodiborane-6 (2.02 mmoles). Part of the deuterodiborane-6 recovered was analyzed as previously described and 0.27 mmoles of deuterium atom were lost for 1.12 mmoles tetraborane carbonyl used. Thus a total of 1.63 mmoles of deuterium atoms entered tetraborane carbonyl.

The deuterated tetraborane carbonyl was introduced back into the fractionation system and the compound and impurities were pumped into -135° and -196°C. traps. The tetraborane carbonyl stopped in the -135°C. trap and impurities such as deuterodiborane-6 and borane carbonyl stopped in the -196°C. trap.

Since the rate of exchange was very slow in the liquid-gas phase experiment described above, the two reactants were allowed to warm to room temperature in a bulb large enough so that they were entirely in the gas phase. The purified partially deuterated tetraborane carbonyl obtained from the liquid phase exchange reaction was condensed into a previously weighed flask containing 1.05 mmoles of fresh deuterodiborane-6. The two reactants were sealed in this vessel (168 ml. volume) and weighed and by difference 0.76 mmoles tetraborane carbonyl were shown to be present. After 15 minutes, the reaction vessel was frozen to -196°C., a portion of the deuterodiborane-6 was separated and decomposed and the hydrogen-deuterium mixture equilibrated and then analyzed. In this case 0.71 mmoles of deuterium atoms were lost to 0.76 mmoles of deuterated tetraborane carbonyl. Thus one more deuterium atom had entered the molecule. However, under these conditions extensive decomposition of the tetraborane carbonyl was evident from the large amounts of noncondensable gases and nonvolatile oil produced. Since the rate of exchange was slow and the conditions of the reaction led to extensive decomposition of the tetraborane carbonyl, the exchange reaction did not warrant further study.

Some preliminary investigations of the displacement of the carbonyl group in the tetraborane carbonyl by other basic groups were undertaken. Because the compound BH_3PF_3 had physical properties closely similar to those of BH_3CO (47) and also because phosphorus trifluoride would replace the carbonyl group from borane carbonyl, the displacement of the carbonyl group in tetraborane carbonyl by phosphorus trifluoride was investigated.

A known quantity of phosphorus trifluoride (3.08 mmoles) was condensed into a weighed 50 ml. reaction vessel equipped with a four millimeter vacuum stopcock. Next, a quantity of tetraborane carbonyl was condensed into the vessel and it was removed from the vacuum system and weighed at room temperature. By difference the quantity of tetraborane carbonyl was found to be 0.68 mmoles. At the end of 15 minutes the vessel was frozen to -196°C. and the carbon monoxide transferred to a small system of known volume and 0.56 mmoles were found. The condensable components were transferred to the fractionating system and passed through a -157°C. trap and into a -196°C. trap. The quantity of phosphorus trifluoride in the -196°C. trap was 2.54 mmoles indicating that 0.54 had been consumed. The mass spectrum of the tetraborane phosphorus trifluoride molecule indicated that some tetraborane carbonyl was still present and no mass/charge value corresponding to the parent peak ($B_4H_8PF_3^+$) was present. To drive the reaction to completion an excess phosphorus trifluoride (2.33 mmoles) was condensed into the original reaction vessel along with the mixture of tetraborane-8 derivatives. The vessel was allowed to warm to room temperature for ten minutes and at the end of this time it was frozen to -196°C. and the noncondensable material was transferred to a small measuring system of known volume. When all the noncondensables had been removed, the stopcock was closed and the vessel allowed to warm to 0°C. for ten minutes. After noncondensables were removed as in the preceding step, the flask was again warmed to 0°C. for ten more minutes. The total amount of noncondensable gases recovered in these last three steps was 0.17 mmoles and 0.1 mmoles of phosphorus trifluoride were consumed. In summary, a total of 0.64 mmoles of phosphorus trifluoride reacted with 0.68 mmoles of tetraborane carbonyl with elimination of 0.73 mmoles of noncondensable gases. More than one millimole of noncondensable gas was formed per millimole of carbonyl used since some hydrogen was formed by decomposition of one of the B_4H_8 derivatives. The mass spectrum of the carbon monoxide given off during the initial reaction with phosphorus trifluoride contained almost no hydrogen, but in each succeeding reaction the hydrogen content increased. Thus, the reason for keeping the reaction at 0°C. in the last two steps was to prevent decomposition of the B_4H_8 derivative. Therefore within experimental error the following reaction took place:

$$B_4H_8CO + PF_3 \longrightarrow B_4H_8PF_3 + CO$$

The $B_4H_8PF_3$ was purified by pumping the material through a -80°C. trap into one at -112°C. The B_4H_8 derivative stopped in the -112°C. trap and traces of more volatile material passed to a -196°C. trap. The vapor pressures of tetraborane phosphorus trifluoride are found in Table 7.

Table 7. Vapor pressures of $B_4H_8PF_3$ at various temperatures

Temp. (°C.)	$P_{obs.}$ (mm.)
-80	0.4
62.5	2.0
-45.0	6.5

However they are not very accurate because the compound decomposed to give phosphorus trifluoride at -30°C. and above, but the values denoted the relative volatility of the compound.

In a search for a suitable solvent for the tetraborane carbonyl, its compatibility with acetonitrile was investigated. Approximately one-half millimole of tetraborane carbonyl was condensed into an evacuated flask along with one-half milliliter (about 10 millimoles) of liquid acetonitrile. The mixture was gradually warmed from -196°C., but while still below room temperature, the solution started bubbling, turned pale yellow and got warm to the touch. After less than five minutes, the solution had turned to an immobile, yellow gum. A noncondensable gas was evolved during this period and the mixture identified with a mass spectrometer as carbon monoxide and hydrogen. The sample was allowed to warm to room temperature while the condensable excess acetonitrile was pumped off. When it appeared to be dry (i.e. greenish-yellow solid chunks), the mercury valve was closed. The pressure increased slightly over the solid and almost immediately the solid started to expand to inch-long pale brown strips looking very much like Styrofoam. This expansion was accompanied by evolution of more noncondensables and acetonitrile. The solid was completely nonvolatile and apparently stable in air. The material was insoluble in anhydrous ether, carbon tetrachloride and even acetonitrile. In hot water and hot absolute ethanol, hydrolysis and ethanolysis occurred with the evolution of a small amount of gas.

It is quite evident from the quantity of tetraborane carbonyl used and solid obtained that the acetonitrile had undergone a condensation reaction. In view of the fact that the solid compound formed was impossible to recyrstallize, no pure product was obtained from the reaction and therefore the reaction did not warrant further study.

DISCUSSION

The thermal decomposition of tetraborane-10 at temperatures between 80° and 110°C. has been studied kinetically in the presence of the weak base carbon monoxide. The reaction was found to be first order in tetraborane-10 and approximately zero order with respect to carbon monoxide. The reaction found to be taking place was the following:

$$B_4H_{10} + CO \longrightarrow B_4H_8CO + H_2$$

The heat of activation of this reaction was calculated as 24,560 calories per mole in comparison with 23,400 calories obtained by Dupont for the conversion of tetraborane-10 to pentaborane-11 and with 23,400 calories for the decomposition of tetraborane-10 found by Pearson and Edwards. Figure 4 shows a plot of first order rate constants _versus_ the reciprocal of the temperature for the decomposition of tetraborane-10. Curve A shows the values obtained by Pearson and Edwards for the decomposition in the absence of any other added compound. Curve B shows values obtained by Dupont and by this study for the decomposition in the presence of diborane-6 and carbon monoxide respectively. The agreement between values obtained by Dupont and this study is clearly seen from this graph since only one straight line fits both data quite well.

It would appear that the reaction intermediate in each case was the same. Dupont postulated that the first step of

Figure 4. Arrhenius plot of first order rate constants; Curve A, values obtained by Pearson and Edwards; Curve B, crosses represent values obtained by Dupont and solid dots, values from this study.

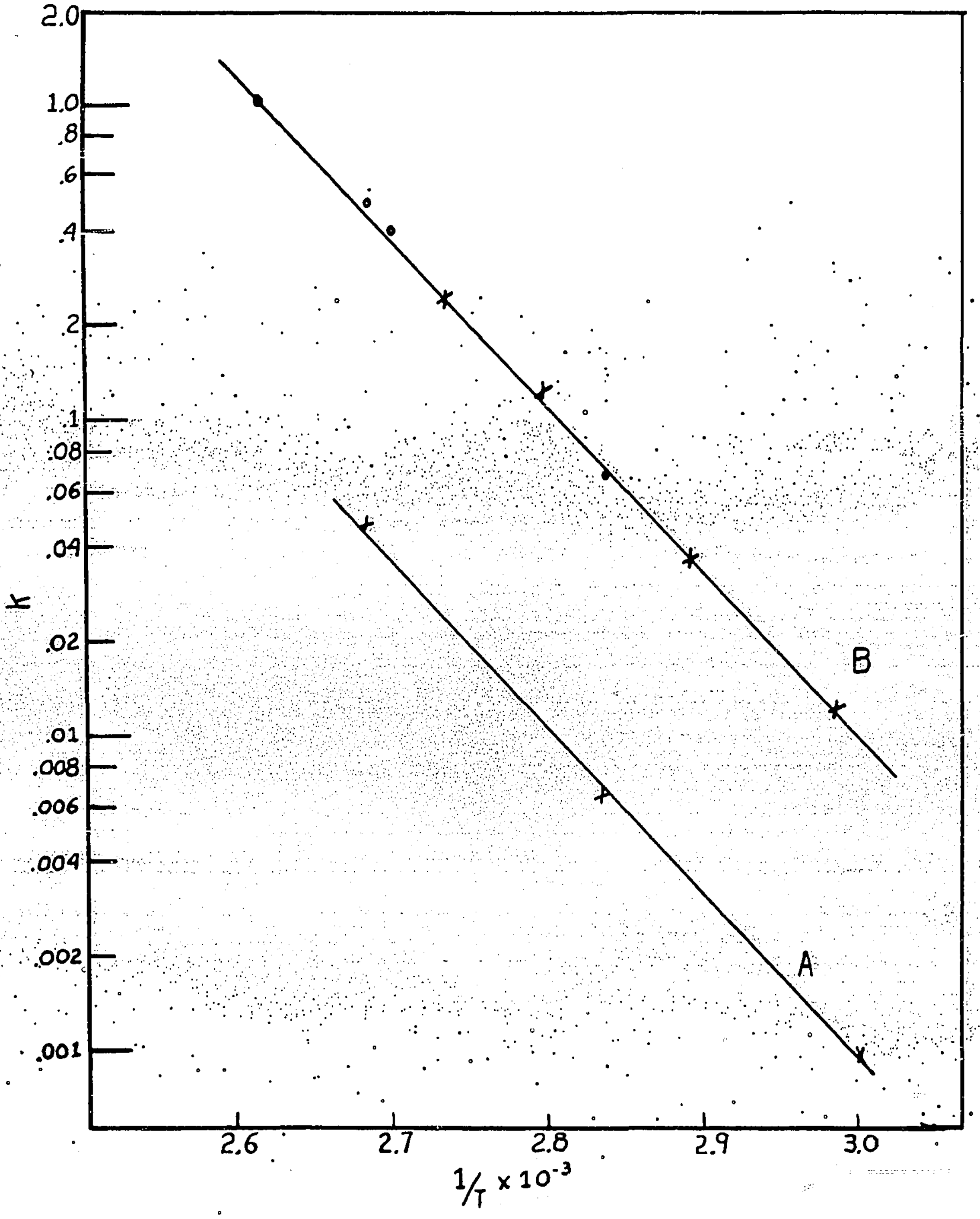

2.0
1.0
.8
.6
.4
.2
.1
.08
.06
.04
.02
.01
.008
.006
.004
.002
.001
k
B
A
2.6
2.7
2.8
2.9
3.0
1/T x 10⁻³

FIGURE 4

the mechanism involved the formation of a B_4H_8 molecule with subsequent reaction with borane to form pentaborane-11 as:

$$B_4H_{10} \longrightarrow B_4H_8 + H_2$$

$$B_4H_8 + BH_3 \longrightarrow B_5H_{11}$$

Hence, this study supported the intermediate postulated by Dupont for the interconversion reaction since tetraborane carbonyl was the major condensable reaction product.

No structure for a filled shell B_4H_8 based on an icosahedral fragment could be devised. The structure proposed for the B_4H_8 molecule by Dupont and Schaeffer was derived from the semitopological approach to the boron hydrides as first suggested by Dickerson and Lipscomb (16). However, the equations were revised to consider molecules with a vacant orbital. Using the same notation that was originally presented:

s = number of B-H-B bridge bonds in the molecule.

t = number of B-B-B bonds, either central or open.

y = number of conventional two center B-B bonds.

x = number of single B-H bonds in excess of one per boron.

The general boron hydride then has the formula: B_pH_{p+q}.

Now the equations for electron, orbital and hydrogen balance are the following for a boron hydride with a vacant orbital:

Electron balance:

$$2s + 2t + 2y + 2x + 2p = 3p + p + q$$

$$2s + 2t + 2y + 2x = 2p + q$$

Orbital balance:

$$3s + 3t + 2y + 2x + 2p = 4p + p + q - 1$$

$$3s + 3t + 2y + 2x = 3p + q - 1$$

Hydrogen balance:

$$s + x = q$$

Solving these equations one obtains three equations and four unknowns:

$$s + x = q$$

$$s + t = p - 1$$

$$t + y = p - q/2$$

For the B_4H_8 molecule one obtains:

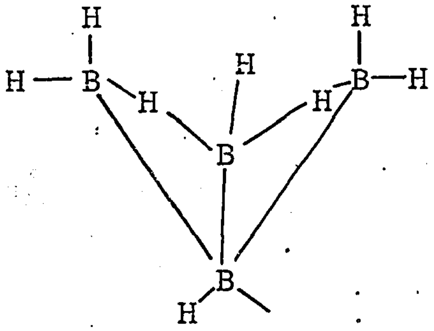
$$s + x = 4$$

$$s + t = 3$$

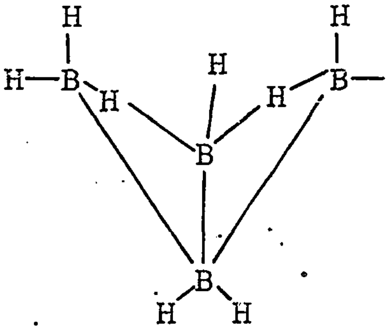
$$t + y = 2$$

Solving these equations for all possible combinations of s t y x, one finds that three are possible: 1203, 2112 and 3021. However, upon investigation of the possibilities one finds that the structures based upon the icosahedron cannot be drawn for the 1203 structure. Furthermore, upon loss of a molecule of hydrogen the tetraborane-10 molecule would not be expected to rearrange to form one more BH_2 group than it already had. Neither can satisfactory structures be found for the 3021 type.

Two structures for the 2112 combination are shown below:



(1)



(2)

Only the first follows all the assumptions presented by Dickerson and Lipscomb for postulating a new structure. The second violates the assumption that a plane of symmetry must be present in the molecule. In the first, the vacant orbital is at the basal boron atom and on the "apex" boron atom in the second.

Now the problem becomes one of rationalizing which of the two structures is correct. Several observations were made to indicate that the carbon monoxide was present as a carbonyl group. Firstly, the compound decomposed with the evolution of carbon monoxide, and secondly the mass spectrum showed the presence of the carbonyl group with 28 mass units as the most intense peak. Finally, the infrared spectrum showed no OH, or CH groups present, but did show a carbonyl group and CO stretching frequency at 1925 cm.$^{-1}$. This assignment is a little lower than the CO stretching frequency

(2164 cm.$^{-1}$) in borane carbonyl (15) and also lower than in metal carbonyl compounds (10) (values between 1994 and 2080 cm.$^{-1}$ have been reported).

The B^{11} nuclear magnetic resonance spectrum as shown in Figure 3 for tetraborane carbonyl shows two distinct differences from that of tetraborane-10 (77, 78) Figure 5. The doublet on the high field side of the tetraborane-10 spectrum results from the spin-spin interaction of a single proton on the two basal atoms. The doublet in the tetraborane carbonyl spectrum is only one-half the intensity of the doublet in the tetraborane-10 spectrum indicating the presence of only one BH group. This doublet is also shifted to a higher field strength, higher than for any known boron hydride.

The triplet present in the tetraborane-10 spectrum on the low field side has to account for only two boron atoms and arises from the spin-spin interaction of a pair of protons connected to two boron atoms. However, for the tetraborane carbonyl spectrum, the triplet must account for three boron atoms.

If one assumes that the carbonyl group is attached to the "apex" boron atom, then there must be accidental overlap of the two triplets caused by the pair of hydrogen atoms on the basal and "apex" boron atoms. If the carbonyl group is attached to a basal boron atom, then the triplet would not

Figure 5. Nuclear magnetic resonance spectra of tetraborane-10.

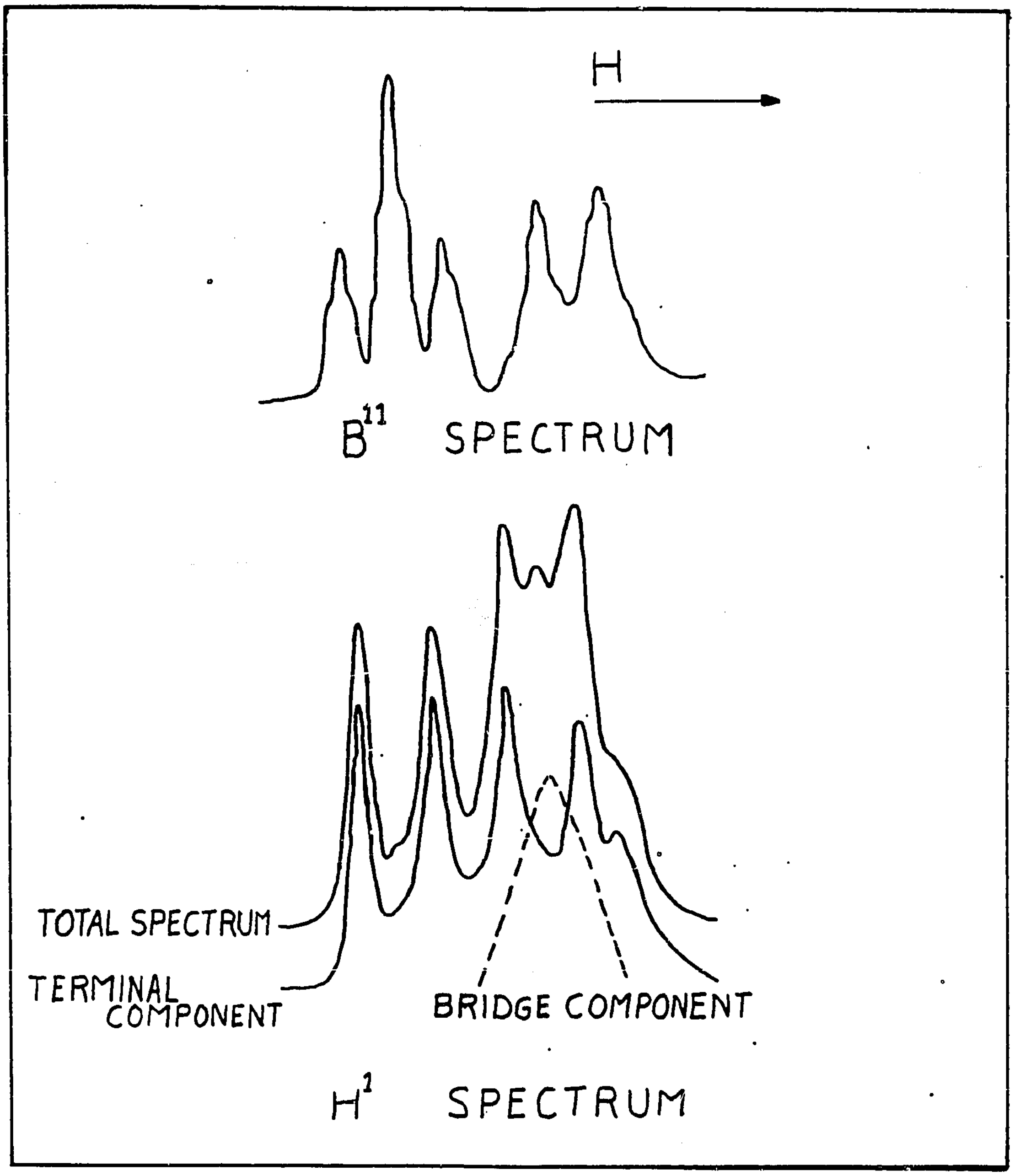

H
B11 SPECTRUM
TOTAL SPECTRUM
TERMINAL COMPONENT
BRIDGE COMPONENT
H1 SPECTRUM

FIGURE 5

be the result of accidental overlap of two triplets but the result of identical chemical shift resulting from the symmetrical positions of these atoms in the molecule. The triplet at the low field is less resolved for the carbonyl derivative than for tetraborane-10. If a doublet, arising from a second BH group in the carbonyl derivative, has been shifted to the left (lower field) so that it now lies under the left side of the triplet of the tetraborane carbonyl spectrum, this doublet then can be considered to cause the asymmetry of the triplet resulting from the spin-spin interaction of a pair of protons connected to two boron atoms.

The proton spectrum for tetraborane carbonyl was very similar to that of tetraborane-10. In both cases four peaks arise from the terminal protons and spin-spin interaction with B^{11}. A fifth peak arising from the bridge protons falls beneath the quadruplet on the high field side of the spectrum. These proton spectra were taken at 40 mc. However, if the frequency could be increased to 60 mc., the bridge protons would probably be shifted to a higher field and the spectrum could be resolved. This resolution or use of the spin saturation technique would allow the determination of the number of protons in the terminal and bridge positions.

The simplest and possibly best explanation of the results of the nuclear magnetic resonance spectrum is that the carbon monoxide is in the molecule as the carbonyl group at one of the basal boron positions. This gives the molecule a plane of symmetry through the carbonyl group and basal boron atoms. The requirements of the 2112 structure previously proposed are fulfilled with this interpretation.

The other structure which would fit the requirements of the 2112 molecule, would place the carbonyl group at one of the two "apex" positions and the two BH_2 groups at basal and "apex" positions. This structure, although not entirely eliminated by the nuclear magnetic resonance spectrum, lacks a plane or axis of symmetry normally found in the structures of the boron hydrides. Furthermore this structure may be completely eliminated if one accepts the fact that a mirror plane of symmetry is required in the molecule.

Since the deuteration of tetraborane carbonyl was slow, extensive decomposition of the tetraborane carbonyl occurred before the compound was completely deuterated. Therefore evidence for the equivalence of the hydrogen positions could not be obtained. The B^{11} nuclear magnetic spectrum of the completely deuterated tetraborane would have given very valuable evidence about the structure. Since there is only a very small amount of spin-spin interaction between boron and the deuterium nuclei, even though the deuterium nuclei has a spin of one, the spectrum would have been simple and easy to interpret. For example, if the carbonyl group is attached to the basal atom as predicted the B^{11} spectrum should consist of three peaks in the ratio of 2 : 1 : 1. One would expect the two "apex" boron atoms to have the same chemical shift and therefore they would overlap with the intensity of two. The two different basal atoms should have different chemical shifts and cause the other two peaks with equal intensity. If the carbonyl were at the "apex" boron position, the spectrum would probably consist of four peaks in the ratio of 1 : 1 : 1 : 1 unless accidental overlap occurred. Unfortunately, to prepare quantities of completely deuterated tetraborane carbonyl from deuterotetraborane-10 would be an extremely difficult and a time consuming task.

The preparation of the phosphorus trifluoride tetraborane-8 by reaction of tetraborane carbonyl and phosphorus trifluoride seems to have been formed by a displacement reaction. The observed stoichiometry for the reaction indicated that nearly all the carbon monoxide was replaced, but it was necessary to do this by a stepwise procedure. It was shown by Parry (47) in 1956 that borane carbonyl and phosphorus trifluoride borane had physical and chemical properties that were almost identical. Therefore the same two derivatives of the tetraborane-8 molecule were expected to be very similar and are.

The three observed vapor pressures of the phosphorus trifluoride derivative are only slightly higher than those for the corresponding carbonyl derivative. Table 8 shows the relative volatility of the two compounds. The phosphorus trifluoride derivative is thermally more unstable than the corresponding carbonyl derivative in contrast to the corresponding borane derivatives. The values in the above table for carbonyl derivatives were calculated using vapor pressures at -49.5° and -30.5°C. whereas vapor pressures at -63.5° and -45°C. were used for the phosphorus trifluoride derivative. The values for this latter compound are only to be construed as giving an idea of its volatility since only three vapor pressures were observed.

Table 8. Physical constants for the stabilized tetraborane-8 derivatives

	B_4H_8CO		$B_4H_8PF_3$
	Calculated from Burg's data	This study	
ΔH_v (calories/mole)	7120	7183	6436
Calculated boiling point (°C.)	62.6	64.4	70
Trouton constant	21.2	21.3	18.7

It was shown by Burg and Spielman (9) that tetraborane carbonyl reacted with trimethyl amine without liberation of carbon monoxide to form a nonvolatile solid material. Since phosphorus trifluoride was found to displace the carbonyl, the reaction between trimethyl amine and the phosphorus trifluoride derivative to form the amine adduct of tetraborane-8 seemed to warrant investigation. A very preliminary study of the reaction with deficiency of trimethylamine indicated that an exothermic reaction took place below 0°C. with elimination of a volatile gas and white sublimable solid and possibly a nonvolatile solid. Further investigation of this reaction would be desirable, especially the identification of the reaction products.

It is interesting to note that Parry _et_ _al_. (48) tried unsuccessfully to identify triborane phosphorus trifluoride compound as a product of the interaction of tetraborane-10 and phosphorus trifluoride:

$$B_4H_{10} + PF_3 \text{ (excess)} \longrightarrow F_3PBH_3 + F_3PB_3H_7$$

The reaction was carried out in sealed bulbs at pressures of five atmospheres or above at room temperature for three days. Diborane-6 and phosphorus trifluoride borane were two of the identified products, but there were other unidentified compounds formed in small amounts.

Finally, the failure of acetonitrile to be a useful solvent for tetraborane carbonyl was evident by its reaction with this compound. Since it was impossible to recrystallize the solid material, the composition is unknown. It would be interesting to find out if it has incorporated any boron atoms in this structure and why this derivative caused the apparent polymerization.

SUMMARY

The kinetic study of the thermal decomposition of tetraborane-10 in the presence of carbon monoxide revealed that the reaction was first order in tetraborane-10 and zero in carbon monoxide. The heat of activation of the reaction was found to be 24,560 calories per mole in comparison with the value observed by Dupont who obtained 23,400 calories per mole for the conversion of tetraborane-10 to pentaborane-11. Tetraborane carbonyl was found to be the major condensable product of the reaction. The carbonyl group was proposed from theoretical viewpoint to be attached to a basal boron atom and this structure was correlated with the infrared, mass and nuclear magnetic resonance spectra. Chemical and physical properties of this compound were investigated and the new compound phosphorus trifluoride tetraborane was prepared by the reaction of tetraborane carbonyl with phosphorus trifluoride.

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