BORAX

TO BORANES

A collection of papers comprising the Symposium—From Borax to Boranes, presented before the Division of Inorganic Chemistry at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1958, together with three papers from the 135th ACS Meeting in Boston, Mass., April 1959.

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Preface

Over the past decade boron has been accorded a treatment of which most of the other elements might well be envious. Acting on more or less qualitative indications that certain boron compounds held considerable promise as "superfuels" for jet craft and rockets, the Government of the United States invested many millions of dollars in a program of research and development which encompassed almost all aspects of boron chemistry. A not insignificant segment of American scientific manpower responded to the need for personnel, and, by 1955, boron was enjoying a level of popularity in university and industrial research that it could not have aspired to ten years earlier. Although prior contributions had been made largely by inorganic chemists, active investigations in the field were now also being conducted by workers in all of the other branches.

The industrial effort was concentrated largely in two firms (the Callery Chemical Co. and the Olin Mathieson Chemical Corp.) but quite a few companies were engaged in the program on a smaller scale. On the academic side, there were few major chemistry departments which did not number among their staff members at least one person engaged in work on boron compounds. Interest became so general that, in 1957, the ACS Division of Inorganic Chemistry established a Boron Committee to handle the steadily increasing flow of boron papers that were being submitted for presentation at national meetings.

Now, in 1961, the Boron Committee has been discharged and government support of the industrial program has dwindled to a small fraction of its former level. The boron "superfuels," while not discredited, now appear less spectacularly promising than they once did. Factors such as lower-than-expected performance, high cost, and high toxicity have combined to dampen enthusiasm for the program. Yet, disappointing though this showing may be, we cannot help but be encouraged by the resulting tremendous progress in the fundamental chemistry of boron—progress which might have required several decades had it not been for the great concentration of effort that the boron program provided. Our understanding of the nature and behavior of boron compounds has grown immeasurably during the past ten years, and the unique character of many of these substances is certain to lead to applications unforeseen when the program got under way. Finally, interest in the high-energy aspects of boron compounds is far from dead. Work is continuing, and boranes or their derivatives may yet emerge triumphant in the area of chemical fuels.

Perhaps the year of peak interest in boron chemistry came in 1958, when the symposium "From Borax to Boranes" was presented at the 133rd ACS Meeting in San Francisco. This volume is composed of papers presented at that meeting and was to have been edited by the late Professor George W. Schaeffer who organized still another symposium on boron at the Boston ACS Meeting in 1959. Professor Schaeffer's untimely death, in 1959, represented a serious loss to boron chemistry. He had been one of the most active workers in the field and had made many important contributions. It is to Professor Schaeffer's memory that this volume is dedicated.

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Introduction

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As a consequence of events which occurred in the closing years of World War II, the need for an aircraft fuel containing more energy was recognized. Military operations were requiring greater efficiencies from their air-borne weapons in terms of either a greater distance or a larger pay load per unit of fuel. The high energy available in boron compounds was known and the British in 1947 evaluated some of these compounds for use as ramjet fuels.

The United States Department of Defense, seeking a better fuel, initiated Project ZIP in 1952. The objective of ZIP was to develop a fuel having properties similar to JP-4 (a hydrocarbon jet fuel) but having a higher density, a faster flame speed, a lower vapor pressure, and more energy per pound.

Project ZIP was large and had as its two prime contractors the Callery Chemical Co. and the Olin Mathieson Chemical Corp. Many universities, research institutes, government laboratories, and private companies were subcontractors on the project. After a careful evaluation of the high energy-containing, light weight elements, it was decided that the fuel objective of Project ZIP should contain a borane or a modified borane. Consequently, research in boron chemistry was pursued feverishly by the many scientists working on the project.

To facilitate the exchange of experimental results obtained on these programs and to stimulate interest among those not on the project, the Division of Inorganic Chemistry of the American Chemical Society appointed a Committee on Boron Chemistry in 1957. This committee [composed of G. W. Schaeffer, St. Louis University (deceased), R. W. Parry, University of Michigan, and D. R. Martin, Olin Mathieson Chemical Corp., Chairman] sponsored a number of programs on boron chemistry at the national meetings of the American Chemical Society. Symposia were held at two of these meetings at which the papers in this book were presented: "From Borax to Boranes" in April 1958 in San Francisco, and "Boron and Binary Boron Compounds" in April 1959 in Boston. The relationship of these papers to the probable steps in making a *H*igh *E*nergy *F*uel (HEF) is self-evident in the following description of a composite of possible processes for going "From Borax (an ore) to Boranes (a fuel)."

The three most common and stable boranes known at the inception of the project were diborane, pentaborane(9), and decaborane. Under ambient conditions, diborane is a gas, decaborane is a solid, and pentaborane(9) is a liquid possessing certain objectionable properties. It is pyrophoric and toxic, has a low density and a comparatively high vapor pressure. However, the heat of combustion (Table I) of each of these boranes was attractive and a logical procedure would be to attempt to modify these molecules sufficiently to give the desired properties without sacrificing the greatly desired high heat of combustion.

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Table I. Heat of Combustion of Fuels

Fuel	B.t.u./Lb.
Hydrogen	51,571
Diborane	31,078
Pentaborane(9)	29,070
Decaborane	27,850
Methyldiborane	26,420
JP-4	18,400

After inspection of Table I, it is obvious that most of the heating value of a fuel comes from the captive hydrogen. Therefore, a high energy fuel should contain boron, as much hydrogen as possible, and a third element to modify its properties. The modifying element selected was carbon, inasmuch as it was a component of hydrocarbon fuels and inasmuch as the materials, reactions, and techniques of organic chemistry could be utilized. The process of modifying the boranes would not be easy, as can be seen from Table I. For example, the replacement of one hydrogen atom in a diborane molecule by the smallest organic radical, the methyl group, results in a diminution of the heat of combustion by at least 15% (compare diborane with methyldiborane). Because of the sensitivity of the heat of combustion of a borane molecule to the replacement of hydrogen by hydrocarbon groups, the ternary diagram (Figure 1) for boron, hydrogen, and carbon was constructed to serve as a guide for research.

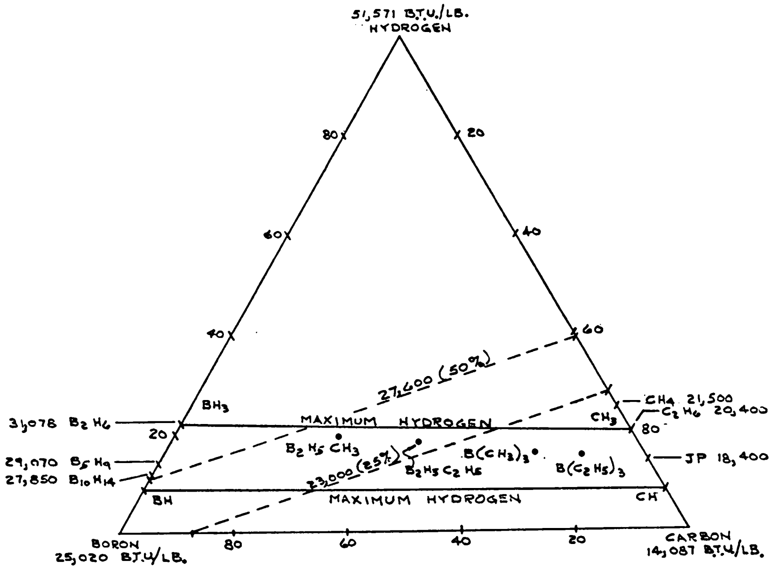

Figure 1. Ternary diagram for boron, hydrogen, and carbon

In the ternary diagram, the heats of combustion for known hydrocarbons and boranes were indicated on the appropriate axes. Recalling that the fuel should contain as much hydrogen as possible, and leaving one of the four sp^3 bonds of boron and of carbon for bonding, a tie line was drawn on the diagram from a point representing the composition of BH_3 on the borane axis to a point representing the composition of CH_3 on the hydrocarbon axis. Obviously, this line represents the maximum amount of hydrogen that the resulting fuel molecule can have. By similar reasoning, and insisting that at least one hydrogen atom must remain attached to each boron and carbon atom in the fuel molecule, a tie line was drawn from the composition representing BH on the boron-hydrogen axis to the point representing the composition of CH on the carbon-hydrogen axis. This tie line represents the minimum amount of hydrogen in the synthetic fuel molecule. The next step was to plot on the diagram the points for the heats of combustion for known organoboranes. Isotherms (dashed lines) were then drawn through compositions whose heats of combustion were 25 and 50% greater than JP-4. By this procedure, a parallelogram was described on the diagram, within which were compositions for possible organoboranes having heats of combustion which would be 25 to 50% greater than JP-4. The objective of ZIP was then to synthesize molecules whose compositions fell within the area described by the parallelogram.

Figure 2 is a flow chart for a composite of processes for converting the ores of boron into a high energy fuel.

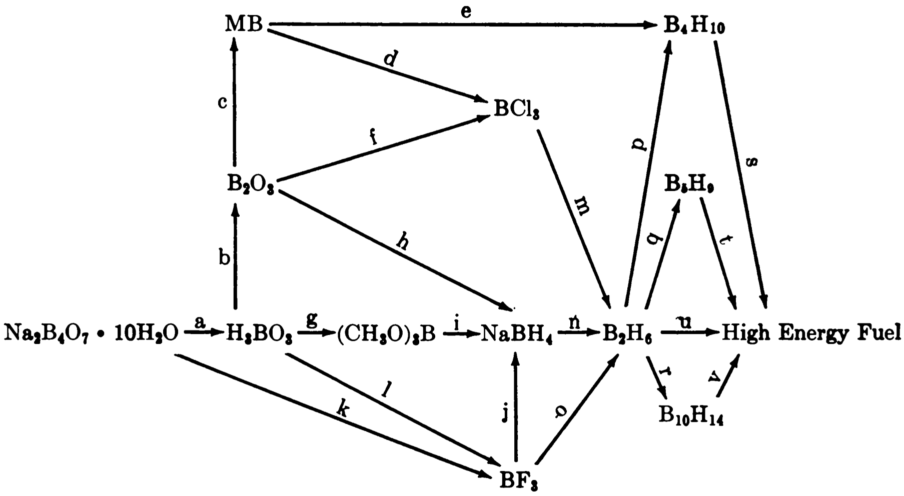

Figure 2. Borax to borane flow chart

The processes may be classified into four main steps: conversion of boron ores to boron halides or sodium borohydride, preparation of diborane from boron halides or sodium borohydride, conversion of diborane to higher boranes, and alkylation of boranes to organoboranes.

Conversion of Boron Ores to Boron Halides or Sodium Borohydride

Not only borax, but the other ores of boron, may be converted to boric acid by various processes involving the use of acids—e.g., sulfuric acid (step a) (*1*). Boric acid may be calcined to give boric oxide (b). Boric oxide may be converted to borides or boron carbide by heating with metals or carbon (c). These borides may be chlorinated to give boron trichloride (d) or treated with an acid such as hydrochloric acid, to give boranes—e.g., tetraborane (e). Boron trichloride also may be prepared from boric oxide by chlorination in the presence of carbon (f).

Trimethoxyborane is readily prepared by esterification of boric acid with methanol (g). Sodium borohydride is prepared by a reaction involving sodium and hydrogen or sodium hydride with boric oxide (h), trimethoxyborane (i), or boron trifluoride (j).

Boron trifluoride is readily prepared from boron ores or boric acid by reaction with an acid—e.g., sulfuric acid—in the presence of a fluoride, or with hydrogen fluoride (k,l).

Preparation of Diborane from Boron Halides or Sodium Borohydride

Diborane, the key intermediate, may be prepared by the reaction of boron halides with active metal hydrides, aluminohydrides, or borohydrides (m,n,o). Boron trichloride may be hydrogenated in the presence of an active metal (zinc, magnesium) (m) to produce diborane. Boron trifluoride may be converted by the Ziegler process to diborane (o). Sodium borohydride will yield diborane if treated with a Lewis acid or a protonic nonoxidizing acid (n).

Conversion of Diborane to Higher Boranes

The higher boranes may be obtained by controlled pyrolysis of diborane (p,q,r).

Alkylation of Boranes to Organoboranes

The appropriate borane or boranes may be alkylated to produce the desired high energy fuel (s,t,u,v) by a Grignard reaction or by the reaction of an alkyl halide with a metalloborane or a metal alkyl with haloborane.

The chapters which follow discuss the chemistry related to some of the problems involved in making and handling a high energy fuel.

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Pioneer Personalities in Borane Chemistry

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In the last 15 years an old problem and a chemical curiosity have been changed into a modern contemporary miracle.

For centuries only the compound borax was known, as a saline substance thought to be made artificially and called by the name derived from Sanskrit, "tincal." The roots of borane chemistry extend back to this tincal mentioned by the Arab, Geber, in the 8th century, although it is difficult to determine whether Geber actually referred to modern borax. Tincal was found in the lake waters of Asia Minor, Tibet, India, Ceylon, and China. It was located in Chile and Peru after the discovery of the New World and later recognized in small quantities in mineral waters of Italy and Saxony. Imported into Europe mainly by the Dutch by way of the East Indies, tincal was always covered with a soapy material made from soda and a fatty body which could be separated by acid before the substance was refined in such seaport cities as Venice, where tincal was used to manufacture hard glass.

Early Chemical Investigators

True chemical investigation of tincal began in 1702, when William Homberg, a distinguished man in his day, combined it with ferrous sulfate and obtained boric acid which was erroneously given the name of "sedative salt" and thought to contain sulfur. Born in 1652 at Batavia, the son of a Dutch East India official, Homberg went to Europe to study law. After he became an advocate in Madgeburg, where Otto von Guericke produced an electrical effect by rubbing sulfur and constructed his noted evacuated spheres which proved that air had weight, Homberg was captivated by science and abandoned law. To learn more, his travels took him to England to become a friend of Boyle, to visit Kunckel, the discoverer of phosphorus, and to Rome to study medicine. After his return to Paris, Homberg was appointed the personal physician of the Duke of Orleans and a member of the Academy of Science. Elizabeth Charlotte of Orleans said of him, "One cannot know Homberg without admiring him for his clear mind—not at all confused as the highly educated usually are, but always jolly. Everything he knows, even the most difficult of arts, seems to him just as if he were playing tricks." The next step to make sedative salt with any kind of mineral acid from tincal was taken by Louis Lemery.

The name "borax," a term used by the Greeks and Romans in connection with the preparation of hard glass, appears in the 18th century texts by Peter Shaw (1734) and Richard Watson (1789). Meanwhile, Baron (1747) identified borax as a combination of sedative salt and soda. Geoffroy, the Younger, found that it colored an alcohol flame green. In that same century, the relationship of borax to alum as another earth was accepted. Torbern Bergman, "the father of analytical chemistry," suggested that sedative salt was actually an acid. In his "Nomenclature Chimique," Lavoisier, whose intent was to eliminate meaningless names in chemistry, suggested "radical boracique" for sedative salt and listed it with the undecomposed radicals of muriatique and fluorique in his table of elementary substances. Commercially, Muspratt's "Industrial Dictionary," in 1860, mentions borax as a flux in metallurgy and borax tinged with metal oxides as a glaze and means of identification of metals in qualitative analy-

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sis. A single English refinery was a profitable producer of borax, although the cost had been lowered from £350 in 1815 to £48 per ton in 1850. Oddly, the clear, large crystals made in England were not acceptable to the trade, which was familiar with the gray broken Dutch import. Grinding the pure crystals in a rotating cask made them marketable. Meanwhile, the discovery of boric acid in the natural steam near Florence was an operative source which remains to the present day.one of the remarkable feats in chemical engineering.

Humphry Davy

In England, the isolation of boron was reported on June 30, 1808, by Humphry Davy, who called the element "boracium." He was said to be delirious with joy over his newly discovered elements, potassium and sodium. The former was the new reagent with which Davy displaced the element boron. The French investigators, Gay-Lussac and Thenard, had a huge voltaic pile constructed for them by the order of Napoleon, who was impressed by the research of Davy, to whom a prize had been given by the French for the best paper on the galvanic fluid, in spite of the fact that France and England were at war. The Frenchmen found that potassium might be prepared by reducing caustic alkali with metallic iron at a high temperature. Employing the same method followed by Davy, although quite independently, the French obtained the new element from borax, reported to the French Academy on June 21, 1808, and called the element "bore." By November 30, 1808, the French had recomposed the element into boric acid by oxidation. Subsequent tests indicated that neither effort had produced uncontaminated boron. Not until one hundred years later was pure boron made by Weintraub in 1909.

Although the element boron was little more than a chemical curiosity, determination of its chemical properties led eventually to the production of boranes through a long tortuous route. The investigators for one hundred years either obtained impure boron or produced too little borane and in such an impure state that conclusive results could not be presented. Invention of special high vacuum equipment adequate for the fractionation of gaseous products was not possible in this period. The early workers cannot be discredited for their failures. They were in many cases famous men, including three Nobel Prize winners, who turned to other more promising fields.

To ascertain its chemical properties, Davy treated boron with hydrochloric acid; this produced a gas which Davy first believed to be hydrogen with a disagreeable odor. He noticed that the gas burned with a bluish flame tinged with green, which led to his assumption that he had prepared a mixture of hydrogen and a boron hydride which he named borane. He could do nothing more. This man, who discovered the alkali metals and proved that chlorine was an element and that acids did not all contain oxygen contrary to the categorical statement of Lavoisier, would be famous in chemical history forever.

In 1858, Friedrich Wöhler and Henri St. Claire Deville made a vain effort to collect and identify the gas produced by direct combination of boron and hydrogen and the action of acid on aluminum boride. Wöhler, one of the founders of modern organic chemistry, and St. Claire Deville, the skilled producer of aluminum, were likewise discouraged and relinquished the unprofitable search for a boron hydride. In 1869, the enunciation of the Periodic Law by Mendeleef and Lothar Meyer emphasized the relationship between boron and carbon as nonmetals. The rapidly growing chemistry of carbon-hydrogen compounds made it probable that a comparable boron-hydrogen system could exist.

Forty more years pass. Who were some of the men who believed that boron hydrides could and should exist? One group attempted to isolate a solid borane in the residues from the reactions of boron compounds. In 1880, Benjamin Reinitzen was convinced that boron trioxide with potassium under sodium chloride produced a mixture of inseparable boranes. Ludwig Gatterman, in 1889, in a long article on silicon and boron, assumed that he had a borane when magnesium boride and hydro-

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chloric acid interacted. Clemens Winkler, the discoverer of germanium, used magnesium boride with boiling hydrochloric acid. His conclusion that he had B_8H would have had no acceptance in the light of modern theory. Richard Lorenz, in 1888, wrote an article entitled, "The Valence of Boron," in which he stated that he had prepared solid boranes which he could not isolate. Others recalled Davy's paper and searched for a gas. Gustafson, in 1870, tried sodium amalgam with boron trichloride at 150°C. When Francis Jones and R. L. Taylor, between 1879 and 1881, added concentrated hydrochloric acid to magnesium boride, spectroscopic analysis proved boron to be in the gas formed. This gas produced boron by thermal decomposition, appeared to have H_3 units from its density, and was surmised to have a formula BH_3. Meanwhile, H. B. Baker and H. B. Dixon discovered that boron could occlude considerable hydrogen. Moissan, in 1891, corroborated the work of Jones without extending the research. The discoverer of fluorine and the designer of the electric furnace which won for him the Nobel Prize found greater satisfaction elsewhere. In the same year, Sabatier, Nobel Prize laureate for his method of hydrogenating organic compounds in the presence of finely divided metals, confirmed Jones by some quantitative tests. Ten years later, the wizard of gas manipulation and Nobel Prize man, Sir William Ramsay, with H. S. Hatfield repeated Jones' work with utmost care to provide pure magnesium bromide and concentrated hydrochloric acid. Working in a vacuum, Ramsay obtained two gases which had densities that suggested to him a more stable ring form with the formula B_3H_3 and a less stable linear molecule. Twenty-five subsequent attempts by Ramsay to repeat his own work were unsuccessful. After Ramsay deserted the field, he turned, as had all the others, to more rewarding problems.

Alfred Stock

The man with the vision, the determination, the patience, and the persistence to prepare and characterize boranes, was Alfred Stock. A span of a century after Davy intervened before Stock's high vacuum equipment produced boranes which could be separated and identified. That story need not be repeated, for it is known to all who have read Stock's "Hydrides of Silicon and Boron." The biography by Wiberg, one of Stock's closest friends, and himself an expert in the borane field, portrays Stock's life and significant place in the history of German chemistry.

Alfred Eduard Stock was born July 16, 1876, in the old Hansa town of Danzig. His father was a bank official and his grandfather was a court secretary and subdirector of an insurance company, descended from a line of guild workers and farmers. His mother was the daughter of a record office worker and director of the ducal art museum, whose forebears had been officers in trade and official service. Stock was a "Sunday child," who rose to fortunate heights, yet endured as well the depths of earthly existence. After a rich life, his strength literally sacrified for chemistry, Stock was forced to flee in the closing days of World War II with the loss of all his possessions to the tiny Elbe mariner's village of Aken, where he died.

Stock's life extended through four German epochs, the Empire, the Weimar Republic, the Third Reich, and the postwar period. His activities coincided with the slump of inorganic chemistry in the late nineteenth century to the renaissance of the twentieth in which Stock was one of the leaders. From 1882 to 1884, Stock was a scholar in the Friedrich-Werderschen Gymnasium in Berlin, where his parents had moved. His interest in science began in his boyhood with catching salamanders and butterflies and pressing plants. It continued with chemistry and physics. Stock's father would have preferred what to him seemed a more secure future, but acceded to his son's wishes and bought him scientific books and laboratory equipment. A sympathetic teacher gave him a well earned "Sehr Gut," for his "Reife-prüfing," which partly enabled him to win a stipend for advanced study for which he matriculated at the University of Berlin. Of the two chemical institutes under Hans Landolt and Emil Fischer, Stock chose the magnetic Fischer, whose laboratory was so crowded that

Stock did not have a work bench until the third semester. The fumes pestered the neighboring streets, but to the students it seemed a promised land. Stock worked briefly with van't Hoff, who had just arrived in Berlin, after which he assisted Piloty. Stock's doctoral dissertation was entitled "A Quantitative Separation of Arsenic from Antimony. Monobromacrolien and Tribrompropionaldehyde. Bromnitroso Hydrocarbons and Their Transformation into Pseudonitrole." Because the acrolien preparations were such a tearful affair, Stock and his laboratory neighbors wept in the ill-ventilated room. Stock became Fischer's lecture assistant in 1898–1899 and from this opportunity stemmed Stock's pleasure in fine experiments, because Fischer's lecture demonstrations were always like a three-ringed circus. On May 10, 1899, Stock was awarded the doctor's degree with a magna cum laude.

At this time two circumstances made a lasting impression on Stock and influenced his career. In the presence of the Kaiser and Kaiserin, Stock heard an extraordinary experimental lecture by Sir William Ramsay on the noble gases. The remarks by the presiding president of the German chemical society on the iron endurance, the far-reaching self-criticism, the breadth of knowledge, and the use of physical as well as chemical aids in Ramsay's research aroused in Stock the wish to do something as significant as this British scientist had done. Ramsay's efforts in 1901 to prepare borane were the inspiration for Stock, who in this field both achieved his hopes and surpassed Ramsay and all other predecessors. The other fateful move was instigated by Emil Fischer, who felt that inorganic chemistry was being neglected in Germany, so he sent two of his best students where they might be trained to improve the situation.

Stock was sent to Moissan in Paris and Otto Ruffe to Ostwald. Later, Ruffe remarked with reason, if not with modesty, that he knew of but two famous inorganic chemists in Germany and the other one was Alfred Stock! For Moissan, who defied pressure to enter the popular organic field in order to develop inorganic problems, chemistry was not just the dirty side of physics. With Moissan as a model of order, preciseness, and ability as a clear fluent speaker, Stock returned after a year to Berlin imbued with the French chemist's spirit of exactness and rectitude. During this second sojourn in Berlin, Stock started the investigation of phosphorus, arsenic, and antimony compounds with unusual composition. He turned to the study of hydrides and sulfides of antimony and phosphorus and the mechanism of their preparation. Simultaneously, Stock began to design equipment. A modified vapor pressure thermometer was called Stock's tension thermometer and a vacuum pump was called Stock's pump. He became interested in the sun's rays as a source of energy which he later sidetracked for cathode rays, which were as effective and more reliable. At this time, Stock wrote a text for quantitative analysis which reached its sixth edition in 1949. Associated with Otto Diels, Stock's interest turned in 1904 to the hydrides of the metals. By 1907, a lecturer in the Great Hall of the Institute, Stock was entrusted with the building of an inorganic research laboratory. However, an attractive invitation from Breslau to be the professor at the Technische Hochschule promised opportunity to do independent work. It was there that Stock established a new institute for inorganic chemistry and meanwhile wrote an inorganic survey for 1909.

Stock's work on boranes, which was to continue for a quarter of a century, was started in Breslau, for he asked himself if this element so near to carbon in the Periodic Table was really so monotonous and lazy as it appeared to be. Fischer, at Stock's request, learned from Ramsay that he had abandoned his work on boranes. This left Stock free to apply to the problem his unique technique and inventiveness which brought success where the previous attempts had failed. Stock investigated C_3S_2, CSTe, and CSSe as possible poison gases at the same time.

When Willstätter went to Munich, Stock was called back to Berlin for his third stay in that city, this time at the four-year-old Kaiser-Wilhelm Institute at Berlin-Dahlem. Since Bechmann headed inorganic and physical chemistry, and Otto Hahn radioactivity, organic chemistry virtually disappeared upon Stock's arrival. By now, Stock was chronically ill with mercury poisoning which had started in Moissan's laboratory, although the symptoms of headaches, catarrh, and vertigo were not under-

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stood. Stock could not take an active part in World War I, but at its end he was free to return to his research on silicon and boron hydrides and his passionate interest in the essential rebuilding of German chemistry. Even as early as 1918, Stock advocated the restoration of the chemical courses at the Technische Hochschule. With the sympathy and influence of Carl Duisberg, 15,000,000 marks were set aside and an organization of which Stock was an officer was founded to establish scientific training once again.

Stock, at this time, was lecturing for himself, for Emil Fischer, and for Will. He joined many scientific societies, in all of which he felt obliged to share the work. He was not like the man of whom Schiller said, "I have here just an occupation but no meaning." He was on the committee which was responsible for meeting the requirements of the Versailles Treaty for control of chemical work, and later on the German committee to establish re-entrance into the International Union of Pure and Applied Chemistry. Stock was struck with the value of the new atomic theories, in support of which he wrote a small book for German chemists called "Das Atom." An earnest advocate of simplified nomenclature, he remarked, "Poor and ununderstandable records would enter a mass grave in which the results of chemical work would disappear." He invented a type of lecture demonstration by which manipulation with small manageable amounts could be enlarged for all to see in a big hall. Stock undertook consulting work, but while these activities were continuing, his work on boranes and silanes, carbon suboxide, sulfides, nitrides, halides of boron, and alkyl borides never ceased. The halides were used by Otto Hönigschmidt to obtain his excellent value for the atomic weight of boron. With the assistance of the Siemans-Halske Co., Stock studied beryllium and its alloys.

By 1923–24, Stock's symptoms grew much worse. During the war, in order to free larger laboratories for the war effort, he had worked in small unventilated rooms without precaution. He tried operations, massages, electrical treatments, and mountain climbing at Berchtesgaden. He seemed to be losing his mind. Only with the help of very complete notes could he carry on a lecture. He reported that he forgot telephone numbers, what he had memorized, the content of books and plays which he had recently read and seen, and even his own book just published. Mathematical computation was out of the question and he doubted if he could continue scientific work. Suddenly, when an assistant developed an ulcer which could be definitely traced to the effect of mercury, the puzzle was solved.

Leaving all work for six months, Stock returned, fired with the ambition to study mercurial poisoning which he now indicated had victimized Faraday, Pascal, Berzelius, Liebig, Wöhler, and to some extent, Hertz and Ostwald. Stock published his earliest paper on the subject in 1926, to be followed by many others. His introduction began with an account of his personal illness, so that his experience might give the warning which would prevent others from enduring the affliction which he had had all of his scientific life. He developed the means for detection of 0.00001 mg. of mercury, because of the minute amount which is the threshold for poisoning. He developed a micrometric process for deposition of mercury and subsequent distillation from a cathode. By a special method to determine this element in nature, Stock made an extended search in all common reagents, minerals, earthy materials, carbon, illuminating gas, soot, brick, filter paper, spring, river, sea and rain waters, and plant and animal food. He determined the vapor pressures and solubilities in inorganic and organic solvents of mercury and its compounds under many conditions. He examined the route mercury poisoning appears to take in the body, its accumulation in the kidneys, and the greater injury to the nervous system compared to the digestive or circulatory system. In addition to experimental animals, he used himself when he squirted a very dilute solution of $HgCl_2$ into his nostrils to establish without question the typical symptoms of the poison. All this information was presented by addresses and papers to the medical and dental societies. At the Paris Fair in 1937, Stock discovered a meter-wide vat filled with mercury in the Spanish pavilion. He wrote in dismay to the French Secretary General of the Fair, earnestly suggesting that the building be open on all four sides or the entire personnel in charge might be poisoned. Later, his sensitivity to mercury vapor was such that Stock always worked with open windows or on a terrace, even in weather so cold that his assistants had to be provided with lined boots as well as other warm clothing.

In 1926, Stock accepted a call to Karlsruhe, where a year later Egon Wiberg joined him in a laboratory which Wiberg described as a glass primeval forest constructed for experiments with high vacuum technique. At first appalled, Wiberg soon mastered the details and wrote that he was "overjoyed by the exactness and elegance of the neat methods used by Stock."

Wiberg pictured Stock, whose ability brought him the Rectorship of the school in two and a half years, as a man who favored curriculum changes to emphasize fundamental science, less pedantic instruction, and a spirit of free discussion with "wit and enjoyment." Because Stock was so punctual that he never came to any lecture or meeting so much as a minute early or late, students set their watches by his appearance. With the use of a pen, which wrote a line as fine as a hair, Stock answered all his letters within an hour. No matter how pressed for time, he never lost his calm and patience, even if what he was doing taxed all his powers. In the evening, he was a friend to all who enjoyed good company, probably true to the admonition of Goethe, "By day, work. In the evening, entertain guests." Many a summer gathering was held in Stock's garden with his wife offering the hospitality of the house.

His philosophy for work made him an experimental scientist. Enthusiastic about the discovery of new compounds and operation of new transformations, Stock gladly left to others the unexplained relationships that led to the postulations of new hypotheses. He was not inclined to speculative observations and theoretical juxtapositions. He said, "The worth of a theory should not become overshadowed, but it also must not corrupt. Often it is only old wine in a new flask. The good in it is not new and the new in it is not good." In the words of Leonardo da Vinci, "The experiment does not err. The interpretations are erroneous. The glittering changes in theory dare not scorn experimental work." Material interests were never a stimulation for Stock's research. To quote Wiberg directly, "he was more interested in finding a bed of ore than in working it. Science was a goddess and not the good able cow who provided him with milk. Only the splendid sun goddess gives the grass that the faithful cow eats. If the sun should be eclipsed, the grass would wither and the cow would give neither milk or butter."

Among the many honors bestowed upon Stock was the election to the presidency of the Verein Deutscher Chemiker and the Deutsche Chemische Gesellschaft. In them, he strove for the welfare of the organization without political direction. It is said that like Bunsen, he relied on his deafness, for if he had managed affairs as he thought proper, when other suggestions were made, he simply did not hear them. He was representative at the celebration in France for the 100th anniversary of Bertholet and in Moscow for the same honor for Mendeleef. When George Fisher Baker lecturer at Cornell University in 1932, Stock spoke of it as an opportunity to sit once more on the school boy's bench to review his English and critically examine his work on boranes. The volume which contains those lectures represents the summation of the pioneer work in the field.

In 1936, Stock retired from Karlsruhe and moved back to Berlin for the fourth time, where he was assigned to work on mercurial poisoning in two small rooms at the Kaiser Wilhelm Institute. He still frequently lectured on boranes, traveled to Rome in 1938 to the International Congress, to Vienna, and to Sweden. In 1943, when his two small rooms were needed for the war effort, Stock withdrew and with his wife left Berlin for the home of his brother-in-law at Bad Warmbrunn in Silesia. In 1945, the oncoming march of the Russians was heralded by distant disquieting cannon roar. When the Stocks were ordered to leave, the railroads were in such shape that they could not go to a daughter, but took refuge with one of his early students, Ernst Kuss, who was then at Dessau working at a magnesium plant at Aken. With only what he could carry in a brief case, Stock and his wife arrived after thirteen train changes.

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Soon he learned that his home at Berlin-Dahlem was badly bombed and that his possessions in Silesia were lost. Nevertheless, after the war, he gradually resumed communication with his daughters and his friends. He wrote to Wiberg, "Enjoy what God gives you. Do willingly without what you do not have." Early in 1946 he gave what was probably his last lecture on borane chemistry to chemists at the Bitterfeld works. He also sent out a stirring appeal to his scientific friends, just as he had done at the end of World War I, to "save German chemistry." He died on August 12, 1946, perhaps having lost the will to live, as he saw all the chemical world which he had tried so hard to build in ruins around him. Wiberg vividly records the far-reaching bodily incapacity of Stock before he died. It was tragic to see this man who had been so active or, to use a double meaning, "this mercurial man," formerly in activity now in fact.

Among Stock's 274 publications 18 are on organic compounds, 43 on phosphorus, arsenic, and antimony, 50 on boron and boron hydrides, 29 on silicon and silicon hydrides, 50 on mercury, 30 on apparatus, and 18 on educational topics, which well summarizes his interests. At the end of his first Cornell lecture, Stock stated his philosophy: "The most important problem for the scientific mind to solve will be how to free mankind from political, social, and economic limitations and how to give it a purer, broader-minded understanding of humanity and sympathetic cooperation."

H. I. Schlesinger

In America, H. I. Schlesinger and his students were attracted to the hydrides of boron which had been made with great effort and expense by Stock. His formulas, which had been established without doubt, did not conform to the accepted theories of valence and molecular structure. To resolve this problem, the Americans improved the methods of preparation of boranes and a favorable period of study was inaugurated with expanding value to theoretical concepts and practical applications. The last 25-year period begins with the work at Chicago under Schlesinger.

Dr. Schlesinger, who accepted the challenge created by borane chemistry, received his baccalaureate degree in 1903 and his doctor's degree in 1905 from the University of Chicago under the direction of Julius Stieglitz with an organic thesis which was a discussion of the catalysis of the imide esters. Before returning to his alma mater in 1907, where he remained until his retirement in 1948, Dr. Schlesinger studied first under Nernst in Berlin, and with Thiele at Strasbourg, and occupied a position for a brief time at the Johns Hopkins University. His research for the first 20 years in the physical organic field includes absorption spectra, conduction of electrolytes in nonaqueous solvents such as formic acid, complex compounds of cobalt, chromium, and the platinum metals, manganates and permanganates, inorganic sulfur compounds, equilibrium relations in complex ions, nitrososulfonic acid, and complex salts containing NO. With a well established reputation for exact research, Schlesinger was asked to be a consultant for the International Critical Tables.

In 1929, a second 20-year era began when Schlesinger was attracted to Stock's work. Like some of the compounds which he had studied already, the structure problem was unusual. No American had considered the boron field and Schlesinger could visualize in it interesting relationships between inorganic and organic chemistry. With Anton Burg, a simpler more effective method to obtain diborane was devised. Later modifications made with H. C. Brown provided production on an even larger scale. Expansion of these studies to the hydrides of aluminum, silicon, cadmium, magnesium, and beryllium, the use of boranes as reducing agents and sodium borohydrate as an excellent source of portable hydrogen in war time, borine, and diborines extended the knowledge of the field.

Dr. Schlesinger, like Stock, was a very versatile man. All this research was performed in spite of heavy departmental and teaching responsibility. In 1912, he assumed the direction of the general chemistry courses, for which he wrote a widely used text and laboratory manual. He contributed much to the strength of the chemistry department of the University of Chicago as secretary, 1922–33, and executive secretary, 1933–48. The multitudinous details of such a position, particularly during the depression and the war years, were managed with a quick sure grasp of the solution of the problems. His administrative ability was evident as a member of an advisory committee of seven for the faculty of the entire university.

Deeply interested in educational problems of the elementary chemistry student, Schlesinger believed in the importance of basic teaching. He was a pioneer in the establishment of introductory courses in the physical sciences. As producer of seven motion pictures, he promoted visual aids for instruction of fundamental chemical theory. His lectures were clearly and deftly presented with infectious enthusiasm. His students appreciated his sincere helpful criticism. To quote an anonymous writer, "He can pick out an error in an experiment which he has never seen, much less done, a half mile away." He served the American Chemical Society in many capacities, as chairman and councilor of the Chicago Section, and as assistant editor of *Chemical Abstracts*. He worked with the Atomic Energy Commission, the Office of Scientific Research and Development, and as a director of Navy Research Projects. In 1950, Schlesinger was the George Fisher Baker lecturer at Cornell. His membership in the National Academy of Sciences and the Chicago Literary Club gives ample proof of his scholarly attainments and catholic interests outside of chemistry.

Special mention should be given to Egon Gustav Martin Wiberg, born June 3, 1901, at Güstrow, who received his Ph.D. at Karlsruhe in 1927. Devoted to Stock, Wiberg's papers on boron halides, and hydrides, their structure, their valence problems, and the constitution of polyborates constitute the portion of his research which makes him a worthy successor to Stock. Wiberg's interest in Germany is contemporaneous to that of Schlesinger in America.

Chemically speaking Stock, Schlesinger, Wiberg, and their students descend from Liebig through a line of organic chemists. Stock connects to Liebig by student-teacher relationships through Emil Fischer and Baeyer. Schlesinger was trained under Stieglitz, who is related to Liebig through Tiemann and A. W. Hofmann. Wiberg is the sixth in line from Liebig through Stefan Goldschmidt, Dimroth, Thiele with whom Schlesinger also studied, Volhard, and Heinrich Will. Liebig himself studied with Gay-Lussac, the discoverer of boron, and his forebears extend through a long series of French chemists to William Homberg, who first prepared boric acid.

How clearly the study of borax to boranes shows the slow development of chemistry until the last 150 years. An even greater rate of advancement marks the last 25 years. Progress depends upon accumulation of facts, design of equipment, and theoretical concepts. Each man extends knowledge only so far as the conditions which he knows suggest advancements to his mind. The present breath-taking achievements rise from the foresight, ingenuity, and courage of the pioneers. Tincal to rocket fuels and structural chemistry is a long but arresting narrative.

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Development and Present Status of the Borax Industry

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The borax industry in the U. S. may be divided into four periods: discovery of borax in California in 1856 and the recovery of borax from Borax Lake in Lake County from 1864 to 1868; starting in 1872, recovery of borax from surface crusts of playa (marsh) deposits in Nevada and California; underground mining of colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) in the Calico Mountains of California starting in 1887; and direct recovery of sodium tetraborate from the brines of Searles Lake starting in 1919, and from the borate ores of the Kramer deposit of Kern County, California, starting in 1927, to supply the major portions of the world's borax requirements. South America was a major producer of borate ores from 1881 to 1887, but in recent years mining has been very limited. Italy and Turkey have their own domestic industries, while the development of the Inder deposits in Russia in 1936 has seemingly made that country also self-sufficient in this regard.

The element boron is widespread in nature and is estimated to constitute about 0.001% of the earth's crust (*5*). Besides being present to the extent of a few parts per million in sea water, it occurs as a trace element in most soils and is an essential constituent of several rock-forming silicate minerals such as tourmaline and datolite (*9*). The presence of boron in extremely small amounts seems to be necessary in nearly all forms of plant life, but in larger concentrations it becomes toxic to vegetation.

However, in only a limited number of localities are high concentrations of boron or large deposits of boron minerals found in nature, and the more important of these seem to be primarily of volcanic origin.

Usually spring waters, issuing from the depths of the earth, ultimately find their way into streams and rivers to be carried away to the oceans. However, in many arid areas, soluble minerals brought to the surface by hot springs are not always continually removed. These waters may soon be evaporated, either in the immediate vicinity of the springs, or after subsequent accumulation as lakes in closed basins without overflow. This latter situation apparently occurred in certain localities on a large scale during past ages of intensive volcanic activity, particularly in Tertiary and Quaternary times. Large quantities of boron-bearing waters from subterranean sources flowed from hot springs in these areas for long periods. At least a portion of such waters became entrapped in landlocked depressions and was subsequently evap-

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orated. The borates carried by these waters, following probable reaction with surface minerals such as carbonate rocks and the salines of such basins, gradually accumulated as beds of alkali and/or alkaline earth borates. Subsequently, various changes and alterations may have occurred in these borate deposits down through the ages, but the important factor has been the continuation of conditions of very limited rainfall. Of necessity, this had to be insufficient to wash away the more soluble borate minerals into rivers destined to reach the oceans, or to cause the more or less complete removal by erosion of former deposits of the less soluble calcium borate minerals such as colemanite. Thus, the gradual accumulation of large deposits of borate minerals on the surface of the earth in previous geologic eras and their subsequent survival down through the ages, even with partial protection by burial under other sedimentary or alluvial deposits, have been possible only in extremely arid regions. As a result, the world's important commercial deposits of borates are to be found only in such localities as the barren wastes of south-central and southwest Asia, portions of Asia Minor, the pampas of South America, and the desert areas of the southwestern United States, all of which are immediately adjacent to regions of former intensive volcanic activity.

Borax in Early Times

It is not known when borax was first discovered, but legend has it that the ancient Babylonians more than 4000 years ago sent emissaries to bring strange crystals from across the Himalayas for use in the working and welding of gold (*16*). The Egyptians are believed to have been familiar with borax and it is said that, during the first century A.D., the Roman emperors Caligula and Nero used to scatter "borax" on the ground after gladiator combats. However, this may have been a calcium borate, because there is evidence that the early Romans had stumbled upon the pandermite deposits in Asia Minor and had done some mining there.

Some time before 300 A.D., borax glazes made their appearance in China. About 400 years later an Arabian alchemist, named Geber, used the word "baurach," the arabic name for borax, in his manuscripts. However, it was seemingly Marco Polo who brought the first authentic specimens of borax to Europe from Mongolia in the late 13th century. This material had the Sanskrit name of "tincana," from which we have obtained the mineral name tincal. By the middle of the 16th century, according to Agricola in his "De Re Metallica" (*1*), the use of borax as a flux had become well known throughout Europe, although there was still considerable confusion as to its nature.

Except for the small amounts of borate materials from Asia Minor, most of the ancient trade in borax seems to have come from the Ladakh district of Kashmir, and to the east from the desert regions of Tibet. In these areas, the borax occurs as masses of opaque crystals and surface crusts on the beds of several dry lakes at elevations up to about 15,000 feet. The source of the borax is said to be the waters of hot springs at numerous locations in this area (*19*).

Crude borax from these Tibetan sources is said to have been gathered by natives and transported to Lhasa to be bartered for cowrie shells and other commodities. Traders then carried the borax 500 miles over the Himalayas to Calcutta in packages of 20 to 40 pounds each, lashed to the backs of sheep. From Calcutta, caravans and later sailing vessels distributed the product to the west along the various trade routes from the Orient. Refineries were established first in Venice and later in other European cities.

Italian Borate Industry

In 1777, the presence of boric acid, then known as "sal sedativum," was noted in the waters of some of the hot springs, "soffioni," of Tuscany, and about 1818, Francois de Larderel, a Frenchman living in Italy, began recovering boric acid by evaporating these waters. By 1827, this source was supplying most of the European borax and boric acid markets and continued to do so for approximately 45 years, until about 1872, when borax from the Western Hemisphere began to take over much of the trade (*7*).

Discovery of Borax in California

On January 8, 1856, John A. Veatch found that the waters of a spring in Tehama County, about 8 miles east of Red Bluff, Calif., contained small amounts of borate. During the months that followed, he found traces of boron in a number of other springs in various parts of northern California. This lent encouragement for further search, and in September of the same year, he found crystalline borax in the muddy bed of a small shallow lake, now known as Borax Lake, in Lake County, about 75 miles north of Petaluma. A second visit to this lake the following year disclosed the possibility of recovering commercial quantities of borax from this source.

As a result of Dr. Veatch's discoveries, the California Borax Co. was formed under the direction of W. O. Ayers, and in 1864 the commercial recovery of borax from Borax Lake was started. The mud was taken from the lake bottom through cofferdams, which could be moved from place to place and then bailed out. The crystals of borax were separated from the mud, washed, dissolved in hot water, and recrystallized (*21*). For the next four years these operations produced an average of about 150 tons per year and supplied the limited borax needs of the United States. However, a rise in water level in 1868 made the operations unprofitable.

Playa (Marsh) Deposits

About 1870 or 1871, small amounts of ulexite were found in Nevada a few miles east of Mono Lake. However, this attracted little attention, and the real U. S. borax industry may be said to have actually started in 1872, with the discovery of crystalline borax (tincal) at Teel's marsh, in the same locality. This was the first commercially profitable borax deposit in the U. S., and may be regarded as the beginning of the second period in the borax industry of the West (*21*). About the same time similar playa deposits were discovered at nearby Rhode's marsh, at Columbus marsh, and in Fish Lake Valley, all in Esmeralda County, Nevada. In California, John W. Searles began operations on the mud flats surrounding a dry lake, now known as Searles Lake, in northwestern San Bernardino County, and a few years later, borax recovery also began in Saline Valley in Inyo County.

The method of recovery used in most of these marsh operations was relatively simple, although crude. The incrustations on the surface of the mud flats were harvested and leached with hot water in dissolving tanks, and the mud was allowed to settle. The clear solution was then run to cooling vats, where borax crystals formed slowly on the bottom and sides, to be later removed, recrystallized, and packed for shipment. In most cases, the product had to be hauled by mule teams, either all the way to the coast, or many miles to the nearest railroad.

Similar operations began about 1882 in Death Valley and in nearby Amargosa Valley. However, the surface crusts of these deposits, together with most of those being worked in Nevada, contained numerous lumps of a fibrous form of ulexite, known as "cotton ball." In fact, in many of the deposits the borate present was entirely in this form. At first this was discarded by the average prospector, but it was soon found that this material could be treated with soda in the boiling and leaching operations, to give a moderate yield of borax. Also, it was soon recognized that the borate content of these salt crusts was secondary in nature, having been formed by evaporation of borate-bearing waters (*3*). The search for the primary sources of the borate soon led prospectors to the mountains east of Death Valley, where a small deposit of bedded ulexite was found in place in the Tertiary lake

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sediments that constituted many of the rock formations of that region. Here also in October 1882 a new mineral, colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), was discovered (*12*).

Colemanite Mining

In the following year the discovery of a large and more readily accessible bedded deposit of colemanite in the Calico Mountains near Daggett, Calif., resulted in 1887 in the transfer of borax mining activities to that locality, which was soon providing the greater part of the world's requirements. This discovery was the beginning of the third, or colemanite, period of the borax industry which thus became revolutionized. These deposits were much more extensive, more easily accessible, and in purer state than the marsh (playa) deposits. Most of the latter in Nevada and Death Valley were gradually abandoned as no longer economical. In California, the playa operations at Searles Lake ceased in 1896, but those in Saline Valley continued to about 1908.

In handling the major portion of the colemanite in the Calico District, the mined ore from underground workings was first crushed and then calcined in a roasting operation sufficient to dehydrate the colemanite and cause it to fall away to a powder, thus permitting it to be separated from the coarser gangue material by simple screening (*21*). These concentrates were then shipped to refineries to be converted to borax by digesting with hot sodium carbonate solutions, followed by filtration and crystallization.

After these deposits began to approach exhaustion a few years later, colemanite mining operations were transferred in 1903 to the mountains immediately east of Death Valley, where additional deposits of calcium borates had meantime been found in the Furnace Creek area and in the nearby district around Ryan. These proved to be extensive and far excelled those previously worked in the Calico Mountains. At first, all mining operations were by means of shafts and underground drifts, but in the years that followed, several "glory hole" type of mines were developed. The ore was mainly colemanite, but lesser amounts of other borates were present which did not decrepitate on roasting. This necessitated the modification of the concentration methods originally used. This was done by incorporating gravity separation methods, such as Wilfley tables, on the recrushed residue from the roasting and screening operations (*21*).

Although these mines supplied the greater part of the world's requirements of borate ores during this period, the operators were not alone in the field. Several other bedded deposits of calcium borates, mainly colemanite, had been discovered in the southwest, and were mined on a fairly large scale.

Direct Recovery from Sodium Borate Deposits

However, the industry was due for another revolution, with the discovery of an enormous ore body of sodium borate, buried beneath the sands of the Mohave Desert in the Kramer District in southeastern Kern County, California, in 1925 (*18*). This deposit came into production in 1927, marking a new era in the California borax industry. This has since become the world's largest single source of borax. All colemanite operations in Death Valley and elsewhere in this country were soon closed down because they could no longer compete with the more economical direct production of sodium borates at Kramer, and at Searles Lake.

This huge deposit at Kramer, or Boron as it is now called, is about one mile wide and four miles long, with an ore body varying from 80 to about 250 feet in thickness (*10*). The run-of-mine ore averages about 25% shale and 75% hydrated sodium tetraborate in the form of both the decahydrate (tincal) and a previously unknown compound, the tetrahydrate (kernite, $Na_2B_4O_7 \cdot 4H_2O$). Underground mining methods have been used by the Pacific Coast Borax Co. (now a division of U. S. Borax and

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Chemical Corp.) for the past 30 years, but at present, open-pit mining is being developed. However, this necessitates a herculean task of removing from 300 to 400 feet or more of overburden.

A variety of ore-dressing methods are used in processing the ore, depending primarily upon the type of concentrates desired, whether for domestic use as such, for direct refining by recrystallization, or for export as a crude product. Much of the shale can be removed by high intensity magnetic separation, while calcining, screening, tabling, air classification, etc., all find their place in the various beneficiation steps (*6, 16*).

Searles Lake Brines

Following the abandonment of John Searles' operations at Searles Lake in 1896, no borax was recovered from that source until 1919, when borax became a by-product of potash recovery. Starting in 1916, potassium chloride was recovered from the brines of the main salt body of Searles Lake. This deposit extends over an area of between 30 and 40 square miles, with a depth of 60 to 130 feet. The salt body is porous and the interstices contain a saturated brine which makes up over 40% of the volume of the deposit. This brine is pumped from wells sunk into the lake bed, and is evaporated to produce a hot concentrated liquor which can be cooled to crystallize crude potassium salts. However, these salts were soon found to be seriously contaminated with borax and it became obvious that this impurity would have to be separated as a necessary by-product (*17*). Late in 1918 it was found that rapid cooling would cause the potassium chloride to crystallize free of borax, which would remain in solution in a supersaturated state to be recovered later as a separate crop. This could then be recrystallized as refined borax. Since that time the American Trona Corp., and its successor, the American Potash and Chemical Corp., have been producing a substantial proportion of the world's supply of borax (*20*).

In addition, another type of process for the recovery of borax is now in operation at two plants on Searles Lake, the West End Chemical Co. (a division of the Stauffer Chemical Co.), and the carbonation plant of the American Potash and Chemical Corp. In general, this method (*13*) consists in carbonating the alkaline brine with carbon dioxide gas to precipitate sodium bicarbonate as a means of sodium carbonate recovery. At the same time the borax content of the brine becomes partially acidified to form the highly soluble sodium pentaborate ($Na_2B_{10}O_{16}$). After the bicarbonate crop has been filtered off, a portion of fresh raw brine is added to adjust the alkalinity back to that of the tetraborate. The mixture is then cooled to bring about the crystallization of a substantial crop of borax. These methods now contribute greatly to the total output of borax from Searles Lake.

A small amount of borax has also been recovered at times as a by-product of sodium carbonate operations on Owens Lake, but this quantity has been insignificant and the major portion of the world's supply is now coming from the two localities in the Mohave Desert, the Kramer deposits and Searles Lake, about 50 miles apart.

The Borate Industry in Other Countries

The Italian operations in Tuscany have been mentioned. Besides recovery of increased amounts of boric acid, ammonium salts, and carbon dioxide from the steam vents, considerable electric power has been developed in recent years. The plants were destroyed during World War II, but have since been rebuilt and are now operating on a sufficient scale to supply most of Italy's domestic borate needs (*8*), while the power output is in excess of 100,000 kw. (*14*).

Little authentic information is available concerning the present status of the borax industry in the U.S.S.R. Prior to 1936, all the borax and boric acid were made from imported materials, but the development of the borate deposits of the Inder Lake region in western Kagakstan (north of the Caspian Sea) resulted in the country's becoming more or less self-sufficient in this regard (*2*). However, some boric acid was imported during and immediately after World War II.

The Inder deposits contain a whole series of calcium and magnesium borates, and considerable work has appeared in the Russian chemical literature in recent years on the phase relations involved. Official figures are lacking, but an estimate (*4*) made in 1940 indicated a production of 25,000 to 30,000 tons of boron compounds annually. In addition to the borate minerals, the so-called "deep brines" which permeate the 36-meter thickness of salt bed of Inder Lake, also contain recoverable amounts of boron (*11*). The occurrence of boron minerals has been reported from time to time in various parts of Siberia, but there are no indications that any of these have commercial possibilities. The original sources of borax in Tibet are now available to the Russians through Red China.

The Turkish deposits in Asia Minor were worked since ancient times. Modern mining began in 1865 and has been carried on more or less continuously. ever since. The principal mineral has been pandermite, but considerable colemanite and other calcium borates have been found by recent drilling operations. The U. S. Bureau of Mines Minerals Year Book shows the production of 13,730 metric tons of ore for the year 1953.

In South America the mining of borate ores began in Chile in 1852, but did not develop on a large scale until 1881, when for a while South America was the principal source of world supply, prior to the colemanite developments in California. Peru also produced ulexite for many years, but since 1917 output has been very limited.

The salt pans or dry lakes of northwestern Argentina were also a source of borates in years past; however, an interesting deposit has been developed in this locality in recent years (*15*): the Tincalayu borax mine, in the province of Salta. In addition to massive tincal, this deposit also contains kernite, together with a new sodium borate mineral, ezcurrite ($Na_4B_{10}O_{17} \cdot 7H_2O$).

Small amounts of magnesium borate minerals occur in Korea, and in oceanic salt deposits, such as the Stassfurt deposits in Germany, where the mineral boracite ($Mg_6B_{16}O_{30} \cdot MgCl_2$) has been a minor commercial source of borates since the early days of the German potash industry.

Small borate deposits have been worked in a very limited manner from time to time in various other countries; however, the complex and usually poor quality of the ores and the remote and usually inaccessible locations have rendered these operations unprofitable in comparison with the rich and easily accessible deposits of California, which now produce the greater part of the world's boron requirements.

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Production of Ammonium Pentaborate and Boric Oxide from Borax

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A process for the production of ammonium pentaborate and boric oxide is described. The first phase involves separation of ammonium pentaborate from the reaction of borax with 10% aqueous ammonium chloride. The second phase consists of thermal decomposition of ammonium pentaborate to boric oxide.

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The goal of this work was to develop an economical process for converting boron ores to boric acid and/or its derivatives without the use of sulfuric acid. Ammonium chloride was considered as a neutralizing agent because it is a readily available by-product (as a 10% aqueous solution) of the Solvay process. Additionally, ammonium chloride was reported (*3*) as an alternative (but untried) acid in the production of boric acid from borax and ammonium sulfate. The reaction of borax and ammonium chloride, however, produces ammonia and ammonium pentaborate which can be decomposed thermally to ammonia and boric oxide.

Conversion of Borax to Ammonium Pentaborate

Borax and ammonium chloride (10% aqueous solution) are mixed and heated. Water and ammonia are distilled from the solution at 98° to 100°C. until a white, crystalline precipitate appears in the distilling flask. The slurry then is cooled to 0°C. and filtered. The filter cake (unwashed), dried at 90°C., is ammonium pentaborate. The filtrate (mother liquor) is reserved for the next cycle.

In a typical experiment, borax (190.7 grams, 0.50 mole) and a 10% solution of ammonium chloride (54.5 grams, 1.02 moles, dissolved in 490.5 grams of water) were

Table I. Data Summary for Development of

			Data for $NH_4B_5O_8 \cdot 4H_2O$ Precipitate					
Cycle No.	Borax, Mole	Ammonium Chloride (10% Aq.), Moles	Ppt., grams	B, %	$NH_4B_5O_8 \cdot 4H_2O$, grams	Purity, %	Yield, %	NaCl in ppt., grams
I	0.50	1.02	79.0	19.65	73.1	98.8	72.0	1.3
II	0.50	1.02	114.8	18.50	106.6	93.0	96.3	5.4
III	0.50	1.02	110.3	19.35	107.5	97.5	98.9	4.3
IV	0.50	1.02	112.3	19.35	109.2	97.3	100.5	3.2
V	0.50	1.02	105.8	19.97	106.0	100.0	97.6	3.2

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In BORAX TO BORANES;
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mixed in a flask. A 1% excess over the stoichiometric amount of ammonium chloride was used. The solution was stirred and heated, and about 200 grams of water and ammonia was distilled into a receiver which contained 100 ml. of 6.025*N* hydrochloric acid. A color change of the methylene blue–methyl red indicator from purple to green indicated a quantitative yield of ammonia (10.2 grams). Care was taken that no ammonia escaped from the system. The remaining solution was cooled to 60°C. and concentrated further by passage of an air stream over its surface. When an additional 50 grams of water had been removed, the solution became cloudy because of the formation of a white, crystalline precipitate. The slurry was stirred, cooled to 0°C., and filtered. The product, ammonium pentaborate (tetrahydrate), was dried in an oven at 90°C.

The mother liquor from the filtration was concentrated further in the same manner until about 75 ml. of supernatant liquid remained over the newly precipitated salts (sodium chloride and ammonium pentaborate). A solution containing 450 ml. of ethyl alcohol (denatured formula A-30) and 50 ml. of ethyl acetate was divided equally into two portions. The first 250-ml. portion was added dropwise with stirring to the aqueous slurry, and the resultant mixture was digested at 60°C. for a half hour. The second portion was added; then the slurry was cooled to 20°C. and filtered. (The alcohol-ester mixture was used to increase the solubility of ammonium pentaborate and decrease the solubility of sodium chloride.) The unwashed filter cake, dried at 110°C., proved to be essentially sodium chloride. The mother liquor containing some of both salts dissolved was added to the reaction mixture remaining after the removal of water and ammonia from the next cycle. The ethyl alcohol and ethyl acetate were distilled together over a temperature range of 78° to 82°C. and reserved for use in precipitating sodium chloride in the next cycle. This procedure was repeated for several cycles.

Table I summarizes the results of five cycles, and Figure 1 shows a flow chart for the process.

Conversion of Ammonium Pentaborate to Boric Oxide

Ammonium pentaborate (tetrahydrate) when heated from 500° to 900°C. liberates ammonia and water, and boric oxide remains as the residue.

A sample of ammonium pentaborate from the first cycle of the process was analyzed and found to contain 19.65% boron, 4.96% nitrogen, and 31.02% water (see Table II for theoretical values). The product (78 grams) contained 1.6% sodium chloride.

A 0.865-gram sample of the salt from the first cycle was placed in a porcelain crucible and heated over a Meker burner for 2 hours. The volatile materials were allowed to escape. The loss in weight was 0.328 gram, corresponding to quantitative removal of ammonia and water and, possibly, some steam-distilled boric acid. The glassy residue, which weighed 0.537 gram, was washed from the crucible with hot

Ammonium Pentaborate Process

Data for NaCl Precipitate

Ppt., grams	Cl, %	NaCl, grams	Purity, %	Yield, %	$NH_4B_5O_8 \cdot 4H_2O$ in ppt., grams
57.0	41.28	37.7	66.3	64.4	21.6
...	...	...	...	...	...
89.5	58.40	86.3	96.4	75.6	3.5
69.5	54.64	62.5	90.0	106.8	7.1
...	...	...	...	...	...

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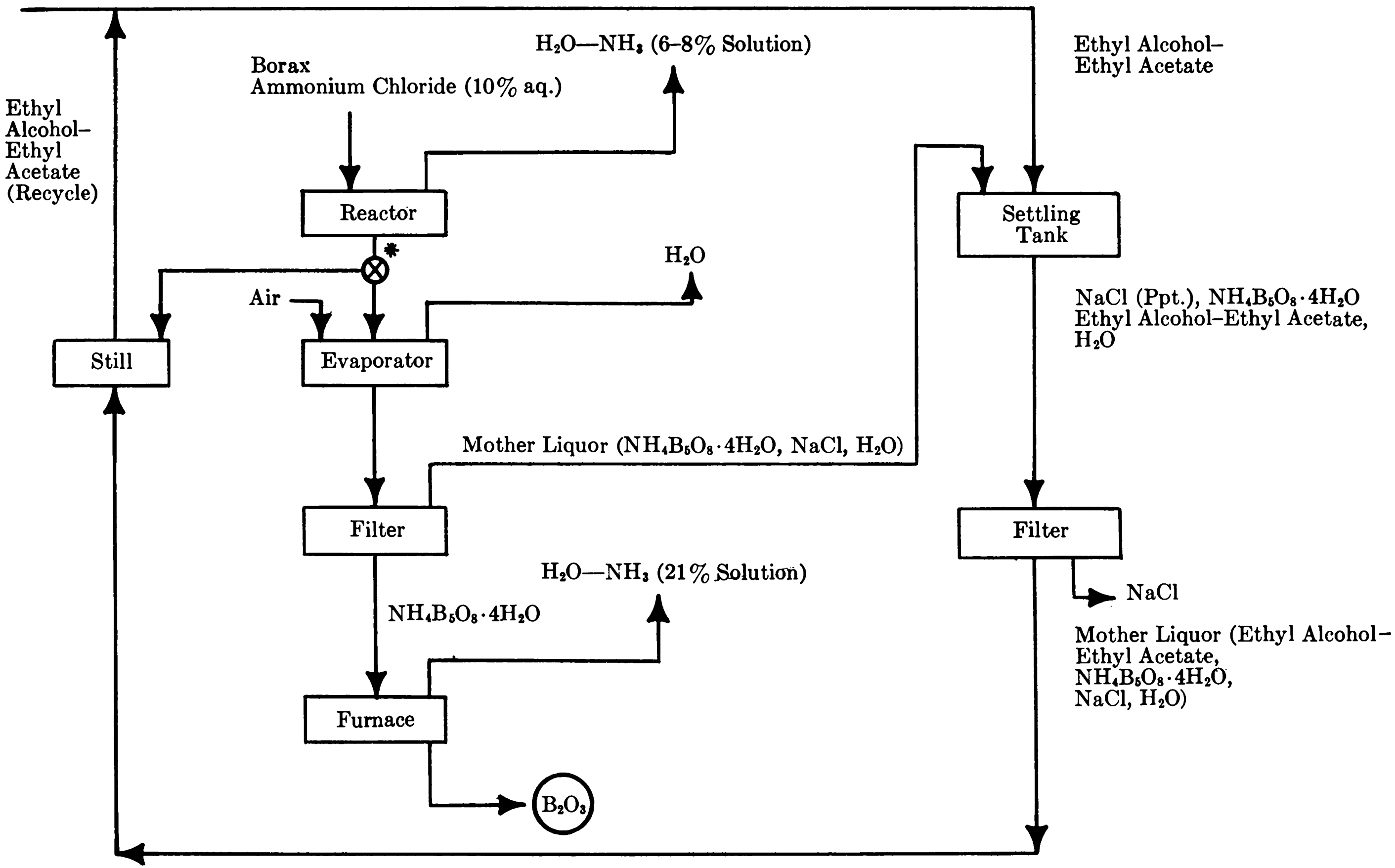

* Valve open for first cycle only.

Figure 1. Process flow chart for production of boric oxide from borax

water. Titration of the solution with mannitol and standard acid showed the presence of 0.91 gram of boric acid, which is equivalent to 0.51 gram of boric oxide. This represents a 93% yield of boric oxide.

Commercial ammonium pentaborate also was analyzed as a standard for the product from the process. A sample contained 20.20% boron and 5.15% nitrogen (see Table II). Another sample (10.0 grams, 0.037 mole) was spread in a thin layer along the bottom of a Vycor tube, which was heated over a temperature range of 550° to 900°C. in an electric furnace for 7 hours. Boric oxide "glass" formed inside the tube. The volatile materials were passed into standard acid. Back-titration of the unreacted standard acid with standard base indicated that 0.68 gram of ammonia was evolved, representing a quantitative yield. The yield of boric oxide was not determined.

Table II. Summary of Analytical Data

Source of Ammonium Borate	Formula	Composition, %						Remarks
		Calcd. from Formula			Detd. by Analysis			
		B	N	H_2O	B	N	H_2O	
Pacific Coast Borax Co.	$(NH_4)_2B_4O_7 \cdot 3H_2O$	17.60	11.42	22.05	17.17	10.82	...	Salt has V.P. of ammonia
Fisher Scientific Co.	$NH_4HB_4O_7 \cdot 3H_2O$	18.90	6.13	23.67	20.20	5.19	31.71	
City Chemical Co., New York, N. Y.	$NH_4B_5O_8 \cdot 4H_2O$	19.89	5.15	26.46	20.30	5.15	30.76	
City Chemical Co., New York, N. Y., Expt. 89D-21	$NH_4B_5O_8 \cdot 4H_2O$	19.89	5.15	26.46	21.58	4.00	...	Salt recrystallized from boiling water
Expt. 89D-18	...	...	...	...	20.20	4.11	..	
Expt. 89D-25	...	...	...	...	19.14	4.87	26.08	
Expt. 89D-56-1	...	...	...	...	19.65	4.96	31.02	

X-Ray Analysis of Ammonium Borates

A sample of the salt from the first cycle of the reaction of borax and ammonium chloride was recrystallized from water twice and analyzed. It contained 19.14% boron, 4.87% nitrogen, 26.08% water, and negligible chloride, in close agreement with the theoretical values for ammonium pentaborate (see Table II). X-ray diffraction patterns of a sample of the recrystallized ammonium pentaborate from the process, commercial ammonium pentaborate ($NH_4B_5O_8 \cdot 4H_2O$), and commercial ammonium hydrogen tetraborate ($NH_4HB_4O_7 \cdot 3H_2O$) were identical (*2*).

Discussion

Boric acid was the expected product from the reaction of borax with ammonium chloride, paralleling its reported (*3*) reaction with ammonium sulfate. However, these experiments showed only 60% of the theoretical amount of ammonia was evolved, based on Equation 1.

$$Na_2B_4O_7 \cdot 10H_2O + 2NH_4Cl \rightarrow 4H_3BO_3 + 2NaCl + 2NH_3 + 5H_2O \tag{1}$$

A study was not made of the effect of using borax or ammonium chloride in excess of more than 1% of stoichiometric amounts. It was proposed that the other 40% of ammonia was involved in the formation of an ammonium borate. Equation 2

$$5Na_2B_4O_7 \cdot 10H_2O + 10NH_4Cl \rightarrow 4NH_4B_5O_8 \cdot 4H_2O + 10NaCl + 6NH_3 + 37H_2O \tag{2}$$

most accurately represented the results of several experiments, in that the yield of ammonia was quantitative. Nevertheless, the close correlation between Equation 2 and the amount of ammonia evolved was not accepted as final proof that the product was ammonium pentaborate.

Three ammonium borates were considered as possible products: $(NH_4)_2B_4O_7\cdot 3H_2O$, $NH_4HB_4O_7\cdot 3H_2O$, and $NH_4B_5O_8\cdot 4H_2O$. Elemental analyses and x-ray diffraction patterns of the product and the commercial salts were obtained for comparative purposes (Table II). Ammonium tetraborate was eliminated as a possible product on the basis of the nitrogen analysis (twice that of the product) of the commercial salt. On the other hand, it has been impossible to differentiate between ammonium pentaborate and ammonium hydrogen tetraborate on the basis of elemental analysis. It was supposed that the difference could be ascertained by determination of water of hydration; however, no quantitative method was devised for distinguishing between water of hydration and adsorbed water. In addition, identical solutions of each commercial salt gave the same pH value of 7.6. If ammonium hydrogen tetraborate had been the product, Equation 3

Table III. Solubility Data for Sodium Chloride and Ammonium Pentaborate (*4*)

	Grams, Per 100 Grams Satd. Solution	
T, °C.	NaCl	$NH_4B_5O_8$
A. Solubility of Sodium Chloride and Ammonium Pentaborate in Water		
0	26.28	3.95
10	26.29	5.39
20	26.37	7.07
25	26.43	...
30	26.49	9.10
35	...	10.02
40	...	11.40
45	...	12.81
50	26.83	...
60	...	18.25
70	27.27	...
75	...	24.40
80	27.54	...
90	27.80	30.29
100	28.12	...
B. Solubility of Sodium Chloride in Aqueous Solutions of Methyl and Ethyl Alcohols (at 25°C.)		
Solvent, G./1000 G. H_2O,		
CH_3OH		
8.01	26.29	
16.02	26.02	
32.04	25.50	
96.12	23.50	
C_2H_5OH		
0	26.55	
11.51	2.606	
23.03	25.63	
46.06	24.75	
92.12	23.29	
230.3	19.35	

$$Na_2B_4O_7\cdot 10H_2O + 2NH_4Cl \rightarrow NH_4HB_4O_7\cdot 3H_2O + 2NaCl + NH_3 + 7H_2O \qquad (3)$$

would represent the reaction. Based on Equation 3 the yields of ammonia averaged 120%. Therefore, as the experimental results corresponded closely to Equation 2, ammonium pentaborate was considered to be the product. Yield data in Table I were based on Equation 2.

The x-ray diffraction patterns gave no conclusive proof of the identity of a particular ammonium borate. The patterns of commercial ammonium pentaborate and ammonium hydrogen tetraborate were identical with the x-ray diffraction pattern of the ammonium borate from the process.

The ammonium pentaborate (from the process) which was thermally decomposed had a purity of 98.4%. Yet, as reported, the yield of boric oxide was only 93% (based on Equation 4).

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$$2NH_4B_5O_8 \cdot 4H_2O \rightarrow 5B_2O_3 + 2NH_3 + 9H_2O \quad (4)$$

Perhaps the low yield was due to the volatility of boric acid with steam. As the heated ammonium pentaborate decomposed, boric acid, a possible intermediate product, may have steam-distilled with the evolving ammonia and water. The minimum temperature for the complete decomposition of ammonium pentaborate was not determined. The melting point of boric oxide was reported as 577°C. (*1*).

1. After distillation at 100°C. of water and a stoichiometric amount of ammonia from the aqueous solution of ammonium chloride and borax, the temperature is lowered to 60°C. for further evaporation. This procedure is followed to minimize the decomposition of dissolved ammonium pentaborate.

2. Near-quantitative yields of ammonium pentaborate are shown in Table I for the second to the fifth cycles. At least one cycle is required for the recycle solution to become saturated with the product(s).

3. A mixture of ethyl acetate and denatured alcohol is added to the slurry containing the coprecipitates sodium chloride and ammonium pentaborate. Ethyl alcohol (A-30, denatured) decreases the solubility of sodium chloride and, at the digestion temperature of 60°C., dissolves the ammonium pentaborate. Ethyl acetate maintains the sodium chloride as a finely divided, filterable precipitate.

Methanol proved unsatisfactory as a precipitant, because sodium chloride is appreciably soluble in it (see Table III). Isopropyl alcohol also proved to be undesirable because it is immiscible with aqueous sodium chloride solutions at most concentrations.

4. The chief difficulty in the process is that some ammonium pentaborate is occluded and lost in the precipitated sodium chloride. The problem could probably be resolved if a better technique of digestion were devised. Or perhaps washing the filter cakes would purify the product. If not, the boron values in the salt could be recovered by conversion of the ammonium pentaborate to trimethyl borate by reaction with methanol. Hydrolysis of the trimethyl borate would give boric acid, which could be converted to boric oxide on heating.

5. Unlike the ammonium pentaborate, near-quantitative removal of sodium chloride did not become constant. Nevertheless, recycled sodium chloride did not appreciably affect the yields of ammonium pentaborate. The yields of sodium chloride in the third and fourth cycles approached quantitative consistency. Perhaps subsequent cycles would have given maximum yields of sodium chloride.

6. Sodium chloride and ammonium pentaborate have an inverse solubility effect on one another in aqueous solution. Sodium chloride increases the solubility (at 90°C.) of ammonium pentaborate by a factor of 5%. On the other hand, ammonium pentaborate decreases the solubility of sodium chloride by a factor of 10% (see Table III).

7. After the sixth or seventh cycles, the mother liquor would probably contain 450 ml. of denatured alcohol, 50 ml. of ethyl acetate, 15 to 20 grams of ammonium pentaborate, 5 to 10 grams of sodium chloride, and 30 to 50 grams of water.

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Preparation and Chemistry of Elementary Boron

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Obtaining pure elementary boron of high quality is complicated not only by difficulties of analysis, but also because it exists in amorphous form and in at least three crystalline modifications whose stability ranges are not yet clearly delineated. Products containing mixtures of these forms appear to be common. Progress in the preparation and determination of the properties of boron was reviewed by Laubengayer *et al.* in 1942; the major emphasis in this paper is on information appearing since that time. An attempt is made to correlate the conditions of preparation with the known crystalline modifications: tetragonal, low temperature rhombohedral, and high temperature rhombohedral. The rather limited information on the chemistry of elementary boron is summarized.

Elementary boron was first isolated and identified as such 152 years ago by the English chemist Davy and the French chemists Gay-Lussac and Thenard. Late in 1807, Davy announced the formation of a dark colored combustible material by the electrization of boracic acid moistened with water, and in June 1808, only 9 days apart, both Davy and the French chemists announced the formation of a black combustible substance by the reaction between boric acid and potassium. The products thus obtained probably contained less than 50% elementary boron, and it was not until nearly 100 years later that samples containing over 80% boron were made.

In the years since its discovery, the problem of obtaining elementary boron of high quality has been complicated not only by analytical difficulties, but also by the fact that it can exist in amorphous form and in at least three crystalline modifications whose stability ranges are not yet precisely delineated. The analytical difficulties were exposed clearly by Winslow and Liebhafsky in 1942, when they showed that a commercial boron, claimed to be 99% pure, contained no more than 92% boron, and that four different analytical methods gave four widely different results for the boron content of three different commercial samples (*125*). The structural difficulties became apparent only after the discovery of x-ray diffraction, but unlike the case of carbon, there were no natural crystals to serve as a guide. Everyone who has worked with x-ray powder diffraction patterns of boron has been dismayed by the great abundance of reflections. This abundance is due to both the complexity of some of the forms of boron and the coexistence of several forms in many samples.

Some idea of the effort which has been made to prepare and study the chemistry

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of elementary boron may be gained from Figure 1, which shows the number of publications and patents appearing in each quarter century since 1800. When one considers the current interest and potential utility of boron for semiconductors and high energy fuels, and as a component of high melting–hard materials, it seems likely that the recent high rate of publication will continue.

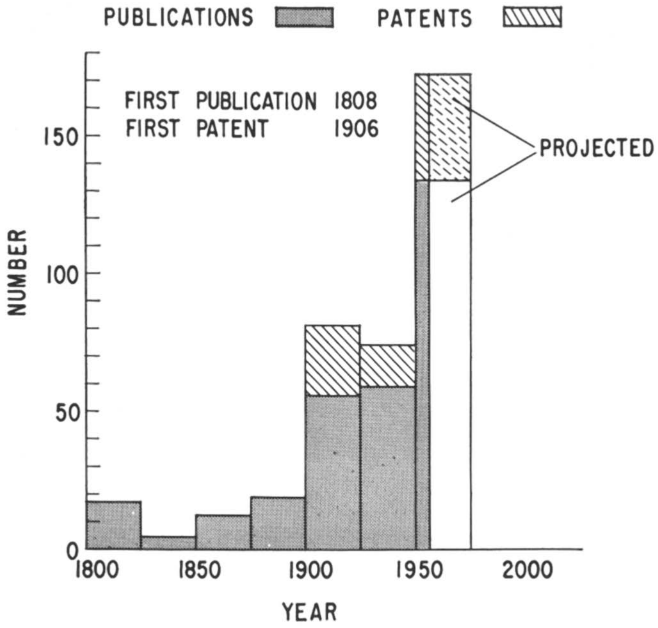

Figure 1. Publications and patents on elementary boron

Progress in the preparation and determination of the properties of boron was reviewed by Laubengayer *et al.* in 1942 (*59*). Other summaries may be found in Gmelin's Handbook (*27*), which covers the literature through 1949, and in the "Rare Metals Handbook" published in 1954 (*9*).

Major emphasis here is on the over 90 papers and patents that have appeared since Laubengayer's review. An attempt is made to correlate the method of preparation with the structure, purity, and chemical properties of the product.

Structure

For the purposes of this review, it is assumed that boron may exist in three crystalline modifications (Table I). The low temperature rhombohedral form, surprisingly, is the simplest, and the high temperature rhombohedral form the most complex. The stability ranges are highly approximate, and the form of boron obtained is influenced by the method of preparation.

Table I. Boron Structure

Temp., °C.[a]	Structure	Atoms/Unit Cell	Density
>1300	High temperature rhombohedral	108	2.35
1100–1300	Tetragonal	50	2.31
800–1100	Low temperature rhombohedral	12	2.46
<800	Amorphous	...	<2.3

[a] Highly approximate.

The powder diffraction patterns used for identification are shown in Table II.

Table II. Powder Diffraction Patterns

Rhombohedral				Tetragonal			
Low Temperature[a]		High Temperature[b]		Observed[c]		Calculated[d]	
d, A.	*I*	*d*, A.	*I*	*d*, A.	*I*	*d*, A.	*hkl*
		8.00	ms				
		7.50	m				
						6.173	110
		5.50	w				
		5.05	s				
		4.65	ms				
		4.50	m			4.365	200
		4.40	m	4.40	m	4.358	101
4.247	45	4.25	m				
4.066	100						
		4.00	m				
				3.90	s	3.899	111
		3.70	m				
3.544	2	3.55	m				
		3.42	mw				
						3.297	201
		3.21	vw				
		3.09	vw	3.05	w	3.087	220
						3.084	211
		2.95	w				
		2.87	m				
		2.75	w			2.761	310
		2.62	m			2.631	221
		2.60	w				
		2.57	mw				
2.545	70						
		2.52	m	2.53	m	2.519	301
2.479	10	2.47	ms				
		2.40	m	2.42	m	2.421	311
						2.417	102
		2.36	ms				
		2.32	w			2.329	112
		2.26	vw			2.182	400
2.180	4	2.20	mw	2.20	m	2.182	321
2.132	4					2.179	202
2.113	55					2.114	212
						2.103	002
		2.08	w				
						2.058	330
		2.04	m				
2.029	<2						
						2.002	401
						1.952	420
				1.94	w	1.951	411
						1.950	222
						1.904	331
						1.903	302
						1.859	312
		1.83	w				
						1.820	421
		1.76	m			1.744	322
		1.71	w			1.712	510
1.666	4	1.68	m			1.649	501
						1.649	431
						1.648	402
						1.647	103

[a] See (*16*) for observed spacings to 0.778.

[b] See (*42*) for observed spacings to 0.859.

[c] Sample prepared by W. L. Robb.

[d] Calculated by L. H. Vogt, Jr., using a_0 = 8.73 A. and c_0 = 5.03 A. (*39*), with absences characteristic of the space group selected by Hoard, Hughes, and Sands (*40*), who discuss the variability of axes in this form. Further work is necessary to provide a definitive pattern for the tetragonal modification.

That for the tetragonal form is the least well known. The pattern for the high temperature rhombohedral form is the most complex and contains a number of lines coincident with or close to those for the other forms.

In a number of instances powder patterns contain lines other than those shown, even when samples have been prepared under rigorously clean conditions. It thus seems likely that still other crystalline phases exist for boron, but for this review we assume only the existence of the three phases shown. The structure problem is discussed in detail by Hoard (*38A*) and by others (*28, 39, 40, 60, 96, 99*).

Preparation of Boron

Methods for the preparation of boron may be divided into four major groups shown in Table III, which lists typical reagents for each method. The order is also

Table III. Preparation of Boron

1. Reduction		
A. Metals and misc. agents	B_2O_3	Mg
B. Electrolysis	KBF_4—KCl	
C. Hydrogen	BBr_3	H_2
2. Thermal decomposition	B_2H_6, BI_3	

approximately the order of increasing product purity, the best boron being made by the last two methods.

Reduction of Boron Compounds by Metals and Miscellaneous Agents. Reduction methods using metals or other chemical agents are summarized in Table IV. The boron source compound has usually been from the group boric oxide, borax, boron halides, or metal fluoborates. Boron is obtained as a powder and is purified by leaching with aqueous reagents such as hydrochloric or hydrofluoric acid, and alkalies. While boron is reputed to be inert to these reagents, Eggersgluess, Monroe, and Parker (*18*) have reported that powdered boron prepared by the reduction of B_2O_3 with magnesium is subject to a slow and progressive oxidation by hot water, and Mikheeva and coworkers (*71–73*, *107*) have reported that acid treatment lowers the quality of boron. If this is generally true for powdered products, it would mean that when aqueous reagents are used for leaching, oxygen will always be present as an impurity even when carefully excluded from the starting materials.

Table IV. Reduction of Boron Compounds by Metals and Miscellaneous Agents

Elements	Li	Be				C	
	Na	$\boxed{\text{Mg}}$	Al			Si	P
	K	Ca		Fe	Zn Hg		
Compounds	$B_2O_3 + CaC_2$ $LiBH_4 + FeCl_3$ $BN + HCO_2Na$						

The method most commonly used in the past to prepare boron in quantity involves the action of magnesium on boric oxide, which takes place with considerable evolution of heat when a mixture of the two is ignited. The black powder thus obtained is referred to as "Moissan's boron" because Moissan worked out the conditions most favorable for its production. The product may contain 95 to 98% boron after purification, but is often of much poorer quality. The commercial production of boron by E. Merck Chemische Fabrik using this method is described in a FIAT report by Smatko (*112*). The product was said to contain 90 to 93% boron, BN, silicon, and B_4C. Eggersgluess (*18*) found, in addition, 5.2% H_3BO_3 and significant amounts of magnesium.

A complete re-examination of the boric oxide–metal reaction for preparing boron was reported by Mikheeva and coworkers in Russia in 1957 (*71–73*, *107*). They confirmed previous experience that reduction by magnesium was best for technical preparation, but proposed a two-stage vacuum treatment at 1400° to 1500° and 1600° to 1800°C. for final purification rather than the conventional acid treatment. In this way they claim to increase purity from 80% boron after one acid treatment to about 98% boron. The chief impurity in the crude product is magnesium, which is vaporized during the vacuum treatment.

Reduction of borax or boric oxide by aluminum occupies a special place in the history of the boron problem because of the great confusion it has caused. This reaction gives rise to a variety of crystalline products at first thought to be boron but later shown, in most instances, to be aluminum borides. Merck's commercial production of "crystalline boron" by this method is described by Smatko (*112*). Kohn, Katz, and Giardini (*51*, *52*) have recently worked out the lattice constants for two forms of AlB_{12} and for AlB_{10}, thus helping to clear up some of the confusion, but they and Parthe and Norton (*89*) have also shown that a reported monoclinic form of

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AlB_{12} is in reality high temperature rhombohedral boron. Thus we have gone full circle. The only safe conclusion to draw from all this, however, is not to use aluminum as a reducing agent to prepare pure boron.

In the period under review there have been five patents for the preparation of boron involving as a preferred procedure the reaction of an alkali or alkaline earth metal or alloy, but preferably sodium with a boron halide or a fluoborate (*35, 36, 110, 113, 114*). The claimed purity of the products ranges from 50 to 98%. While these methods produce technically acceptable material, they are unlikely to be suitable for the preparation of high purity boron.

Boron and/or borides are also formed by the reaction of borohydrides with aqueous inorganic salts. These reactions [reviewed by Gaylord (*25*)] have not been used for the preparation of boron.

All the reduction methods using metals and miscellaneous agents yield powders which are usually referred to as amorphous. Except for the identification of the high temperature rhombohedral form in an aluminothermic product, no other sample has been positively identified as a crystalline form of boron. The few powder patterns available for Moissan's boron cannot be matched with those for the known forms of boron, nor with the recent data reported for the magnesium borides (*46, 68, 69, 98*). These data, however, are incomplete and upon further examination Moissan's boron may be found to contain substantial amounts of magnesium borides as the source of the diffraction patterns.

Reduction of Boron Compounds by Electrolysis. Boron may be prepared by the electrolysis of fused melts containing a metallic borate or fluoborate as the source of boron, and metal or carbon electrodes. It seems generally agreed that the boron is not produced directly but is formed by the chemical reaction between the borate and the active metal produced in the primary electrochemical process. Thus when molten borax is electrolyzed, the primary cathodic product is thought to be sodium, which reacts with the melt to form boron. The product is usually a finely divided powder distributed in the melt near the cathode and is extracted by digestion with hot water and with hydrochloric acid, then washing and air drying at 100° to 120°C.

The purity of boron prepared by several different electrolytic processes is shown in Table V. To eliminate the effect of changing cation, only melts containing potassium salts are shown. Before 1925, no one had claimed to prepare boron of good quality by electrolysis. Table V represents about one tenth of the available data and gives the best purity obtained for the melts shown. From these and the other data, the following seem worthy of note.

Table V. Purity of Boron

Purity of Electrolytic Boron from Melt of	Kahlenberg	Andrieux	Cooper	A. and Deiss	Murphy *et al.*	Nies *et al.*
B_2O_3—K_2O		57				
B_2O_3—K_2O—KCl	100					65
KBF_4—KCl			99.4	93	97	
B_2O_3—KBF_4—KCl			99.7	91	91	96
B_2O_3—KF—KCl				87		91
B_2O_3—KF—KCl—HCl						97.5
Year	'25	'29	'51	'55	'57	'58

The electrolysis of alkali or alkaline earth borates generally yields a very poor product, the best purity, 88%, having been obtained by Andrieux in the electrolysis of magnesium borate (*3*).

The addition of halide salts to boric oxide results in a purer product. This was suggested by Kahlenberg (*47*), although his work could not be duplicated by Nies, McIntyre, and Fajans (*84*). It was also suggested by Andrieux, who prepared boron in 92% purity by adding magnesium fluoride to an $MgO \cdot B_2O_3$ melt.

High purity electrolytic boron dates from the work of Cooper, who first used an oxide-free melt, but showed that boric oxide could be used in this melt without harm (*10, 11*).

Cooper's high purity products have not been duplicated by later workers, although their products are of good quality (*2, 78, 84*).

Because of the dissociation of KBF_4, Nies and coworkers used an HCl-acidified B_2O_3—KF—KCl melt and were able to make products of as good quality as with oxide-free electrolyte (*84*).

The chief impurities in the samples thus made are oxygen, carbon from the reaction vessel, and iron from the electrodes.

When alkaline earth borates are used as electrolyte, the main impurity is the alkaline earth boride.

The only x-ray work on electrolytic boron is that of Cooper (*9*), who reported that a faint diffraction pattern was obtained whose lines matched those for tetragonal boron.

As a general conclusion from a review of electrolytic processes for the preparation of boron, it seems unlikely that pure boron will be prepared by the electrolytic processes that have been used to date or minor modifications of them.

The electrolytic processes have been reviewed and discussed in detail (*2, 3, 9, 78, 84*) [see also (*1, 8, 10, 11, 19, 41, 77, 83, 85, 122, 123*)].

Reduction of Boron Compounds by Hydrogen. Reduction of nonvolatile boron compounds by hydrogen was tried experimentally many years ago, but with negative results. Success with such typical starting materials as boric acid, borates, or boron nitride can now be shown to be improbable, because the calculated free energy changes have large positive values.

The reduction of volatile boron compounds has been limited almost exclusively to boron trichloride and boron tribromide as the boron source. Most recent work has been done with the tribromide, because it is easier to handle and reacts more readily than the trichloride (*23*). The free energy as a function of temperature for the reactions of BF_3, BCl_3, and BBr_3 with hydrogen has been given by Stern and Lynds (*115*). For these reductions, the experimental apparatus has been one of three main types:

1. A reactor containing an electric arc or spark.
2. A hot tube reactor.
3. A reactor containing a hot filament or rod.

It is convenient to use this classification for discussion.

Reactors Containing an Arc or Spark. The first sample of boron of really good quality was probably made by Weintraub in 1909 by passing several high potential alternating current arcs through a mixture of boron chloride and hydrogen, using water-cooled copper electrodes (*124*). Some boron deposited on the electrodes, fused to beads, and fell off. These analyzed 99.8 to 100.2% boron and contained traces of silica but no copper. Several people repeated this work and confirmed that pure boron was obtained. A very extensive series of investigations on this method and on boron prepared by it was carried out in France by Hackspill and Cueilleron and reported in 1944 (*13–15, 37, 38*). They claimed a purity of 99%.

The boron produced by the arc process ranges from amorphous to crystalline to x-rays. Cueilleron (*13*) states that the x-ray spectrum of the crystalline material is similar to that obtained by fusing the amorphous form in an atomic hydrogen blowpipe. This suggests that the product of the arc process was the high temperature rhombohedral form of boron.

Hot Tube Reactors. The preparation of boron by the boron halide–hydrogen reaction in a hot tube might generally be considered unattractive because of the possibility of contamination of the boron by the tube material. Early work indeed showed that reduction of boron chloride in tubes of silica or carbon led to poor yields or considerable contamination, but recent workers have done better. Goss (*29*) and McKinley (*65*) disclose in patents the use of this reaction for preparing pure powdered boron. Robertson (*95*) and Kiessling (*49*) independently used the reduction of the bromide at 750° to 800°C. as a means of preparing several grams of powdered boron. Kiessling reported the purity as 98.9%, and Robertson gave an x-ray diffraction pat-

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tern which we can now identify as largely that of the low temperature rhombohedral form of boron.

Hot Filament Reactors. The method of preparing elements by thermal decomposition or hydrogen reduction of a simple volatile compound on an electrically heated refractory filament is ideal for obtaining samples of high purity. The free element deposits on the filament in massive form and the other products of the reaction are removed as gases. This "filament method" is known in German as "Aufwachsverfahren" and was first described by Koref in 1922. The experimental techniques as well as the wide variety of metals and refractory compounds that can be made by this method are described by Powell, Campbell, and Gonser (*91*) and by Becker (*7*).

Warth (*121*) used the filament method to prepare boron in 1923, but his paper seems not to be well known, as it appeared in a journal of relatively limited circulation. Warth used a tungsten filament 10 to 12 inches long and 30 mils in diameter. He found that boron could be deposited from boron chloride and hydrogen at temperatures of 1300° to 1850°C. without alloying with the filament and that the product could be stripped easily from it. The boron thus obtained had a smooth crystalline appearance and was silvery gray in color.

The filament reduction of boron chloride or boron bromide by hydrogen was used by a number of investigators during the 1930's to prepare boron for studying its properties, but very little work was done on its structure or on determining its purity, this being assumed as high. In the period under review, however, a number of papers devoted to the structural problem have appeared.

The filament method is usually thought of as being useful for preparing only small quantities of boron, but hundreds of grams per run can be made. Details of the process on this scale are given by Stern and Lynds (*115*), and the AEC report by Fetterley and Hazel (*21*) describes a plant for making 300 pounds per month of greater than 97% purity boron using 2-inch-diameter graphite rods as filaments. The apparatus is patented (*20*).

PURITY. The filament method appears to be satisfactory for making high purity boron, high purity being defined as 99.0 to 100%. Purity in materials is often subject more to folklore than fact, and boron is no exception. It has been said that a purity of 99.999% has been achieved for boron or approximately 1 part per 100,000. This is rather remarkable as we know the chemical atomic weight to only about 1 part per 1000. The problem of proving purity of boron samples has been discussed in detail by Laubengayer (*58*).

The chief sources of impurity in the filament method are oxygen and nitrogen in the hydrogen, silicon tetrahalides in the boron halides, carbon from the apparatus, and contamination from the filament. Of these the choice of filament material is the most important, because contact with it cannot be avoided whereas the reactants may be subjected to exhaustive purification. Of the filament materials which have been tried, iron and platinum are not satisfactory because they form low melting borides or eutectics; carbon, molybdenum, tungsten, niobium, tantalum, and titanium have been used fairly successfully. Tantalum has been used by a number of investigators and seems to be particularly good if hydrided before use, although it is then brittle. Stern and Lynds (*115*) used titanium with considerable success, and developed a low temperature chlorination process for removing titanium and titanium borides from the product. Powell (*91*) has noted some compound formation from boron trichloride and hydrogen with different substrates as follows: iron, 600° to 700°; titanium, zirconium, and molybdenum, 1000°; tantalum and tungsten, 1500° to 1600°. Compound formation was found to predominate as follows: titanium and zirconium, 1300° to 1400°; molybdenum $> 1500°$; tantalum and tungsten, 2000°. Some of the analyses reported for boron prepared by the filament method are given in Table VI (see also *32*). Extensive additional data are given by Stern and Lynds (*115*). As might be expected, the boron at the exterior surface of the deposit is generally much less contaminated than that near the filament, although the separation is surprisingly good in some cases.

Table VI. Purity of Filament Boron

Filament	Boron	Filament Material	Fe	Si	Ref.
C	98.4	1.13	0.02	0.08	(*21*)
Mo	99.2–99.7	<0.0045 Sp			(*23*)
W	99–100	<0.1		— Sp	(*58*)
W		0.7	Tr. Sp.	0.02	(*117*)
Ta	99–100	— Sp		— Sp	(*58*)
Ta[a]	97.5		2.1		(*115*)
Ta[b]	96.7	3.2			(*115*)
Ti	95.0	2.03	0.03	0.13	(*115*)

Sp = spectroscopic. [a] 1225°C. [b] 1000°C.

CRYSTALLINITY. The available results on crystallinity are shown in Table VII. The identifications in brackets are the estimate of the present author. From 600° to 1000°C. amorphous deposits are obtained. This is interesting, when it is recalled that in a hot tube the low temperature rhombohedral form was obtained at 750° to 800°C. Náray-Szabó and Tobias (*79*) have also published powder data. There are indications that their "graphitic" boron contains the low temperature rhombohedral form and their "crystalline" boron contains the high temperature rhombohedral form, but both powder patterns contain many extraneous lines, so that positive identification is difficult. Their data and those from one of the samples of Stern and Lynds (*115*) would seem to require other than known forms of boron. The tetragonal form was probably obtained by Hackspill in 1933 by reaction of $BCl_3 + H_2$ in a spark, and a mixture of this and the high temperature rhombohedral form by decomposing BBr_3. These samples were studied later by Lagrenaudie (*55*).

Table VII. Crystalline Form of Boron from Filament Reaction $BX_3 + H_2$

°C.	X	Form		Source
1400–1450	Cl	Tetragonal		Fetterley (*21*)
1350	Br	HTR-massive, and	T-XL	Hoard (*40*), Laubengayer (*58*)
1150–1300	Br	tetragonal		Uno (*119, 120*)
1100–1200	Cl		[HTR]	Stern (*115*)
1100	Br		[HTR]	Uno (*119, 120*)
1075–1125	Cl		[+]	Stern (*115*)
850–1000	Br	Massive amorphous		Laubengayer (*58*)
600– 800	Br	Amorphous powder		Laubengayer (*58*)

HTR = high temperature rhombohedral, T = tetragonal, + = unknown phase.

The position of the tetragonal form seems anomalous, but the reported temperatures are probably misleading. The tetragonal needles are always observed to grow normal to the surface of the filament. Shinn (*109*) has reported observing such growth in the temperature range 1400° to 1800°C., with best results at 1700°C. The temperatures are those of the massive surface, however, and the growing needles, which in the author's experience always appear darker than the filament, are probably at a considerably lower temperature.

The effect of reaction conditions on crystallinity has received some attention. It seems generally agreed that under otherwise equal conditions reduction of boron bromide gives more crystalline deposits than reduction of the chloride, and with the bromide there is a concentration effect, deposits tending to become less crystalline as the partial pressure of the bromide is increased above about 10 to 15 mm. Shinn (*109*) has reported the peculiar and inexplicable result that better crystals are obtained with direct current–heated filaments than with alternating current–heated filaments.

Boron prepared by the filament method has been discussed (*95, 108, 116*).

Thermal Decomposition of Boron Compounds. Prior to 1940, boron had been prepared by the thermal decomposition of BN, by the decomposition of BCl_3 on a hot iron surface and subsequent thermal decomposition of the iron boride thus formed, and by the decomposition of BBr_3 or B_2H_6 on a hot tungsten filament. The products were not highly pure, and x-ray work was carried out only on the hydride product, which Brandaur showed to be amorphous. Recently Ostroff and Sanderson (*87*) have decomposed $NaBH_4$ and KBH_4 in nitrogen, hydrogen, and air. The residue from heating in nitrogen and hydrogen is a black solid of varying composition. This solid dissolves partly in water with gas evolution, and is evidently composed of boron and the alkali metal either mixed or combined. The formation of boron by the decomposition of other borohydrides is reviewed by Gaylord (*25*). The boron thus formed is incidental and has not been separately studied. Boron coatings for ion chambers have been made by decomposing trialkyl boron compounds (Me, Et, or Pr) at 500° to 550°C. and 1-mm. pressure on various metal substrates. The deposits were reasonably adherent but were about 50/50 boron and carbon (*70, 76*), as might be expected. Intermediate compound formation in the decomposition of trimethylboron has recently been studied by Goubeau and Epple (*30*).

Good quality boron may be made by the thermal decomposition of boron hydrides or boron trihalides. The filament method is preferred, although arc or hot tube reactors have been used.

Decomposition of Boron Hydrides. A number of investigators have used the decomposition of diborane or other hydrides on hot glass, metallic elements, or alloys to prepare boron films but have given no data on crystallinity or composition of the film (*17, 31, 54, 102, 104, 105*). The effects of experimental variables are discussed in detail by Schlesinger *et al.* (*104*) and by Robb and Landauer (*94*). By using sufficiently high temperatures, borides can be formed directly (*82, 91, 97*). With iron this reaction begins at 425° to 500°C. (*53, 76, 105*).

Boron hydrides from diborane to decaborane have been decomposed at temperatures from 300° to 900° to yield films amorphous to x-rays (*4, 45, 55, 92, 103, 111, 118*). A few spectroscopic examinations have shown traces of silicon, magnesium, and copper, but extensive analyses have not been made nor have the deposits been analyzed for boron. Friedrich and Jacobsmeyer and Badar and Jacobsmeyer (*6, 24*) claim to obtain large crystals at 1000°, fine crystals at 1300°, and large crystals at 1500°, but do not give x-ray data. It is surprising how little is known about boron prepared by decomposing boron hydrides, despite the many times the method has been used.

The low temperature rhombohedral form of boron has recently been made by Robb and Landauer by decomposing diborane at 1000°C. (*94*). They also studied the decomposition of pentaborane and decaborane. The chief impurity was carbon, and methods for its removal from the starting materials are given.

Decomposition of Boron Halides. The thermal decomposition of boron halides can be used to prepare boron and boron coatings, but there is surprisingly little information on the structure or purity of the products (*41, 56, 75*). Two patents by Gross (*33*) and Fitzer (*22*) specify purifying boron or coating articles with boron from the lower halides such as BF, BCl, and BBr. These are formed and vaporized by passing the corresponding boron halide over elemental boron and then decomposed without separation or purification in a different part of the apparatus. Klynchnikov (*50*) claims to purify boron by a related process in which the impurities are evaporated as volatile chlorides, leaving the pure element behind. Lagrenaudie (*55*) studied boron prepared by Hackspill by decomposing BBr_3 in an arc. This material gives a complex pattern which is probably a mixture of the tetragonal and high temperature rhombohedral forms.

Uno (*119*) prepared boron by the thermal decomposition of boron bromide on tungsten or tantalum in vacuum and his sample appears to have been the high temperature rhombohedral modification. Some boron recently prepared for this laboratory by the same method (*106*) contained 0.05% carbon, 0.02% tantalum, and less than 0.05% of oxygen, hydrogen, nitrogen, and other impurities.

The first recognized sample of the low temperature rhombohedral form of boron was recently prepared by McCarty by decomposing boron triiodide at 800° to 1000° on tantalum (*61, 63*). This material contained $C = 0.003\%$, $I = 0.04\%$, and no impurities of $Z \geqslant 13$ present to more than 0.001%.

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Purification of Boron

The methods commonly used for purifying powdered boron—boiling with water, treatment with hydrochloric acid, treatment with aqueous alkalies, etc.—would seem to be of questionable value for the purification of high purity boron, because they tend to introduce oxygen. The extent of such contamination has not been extensively investigated. Such treatments are, however, useful for removing gross impurities from such boron and from massive deposits on filaments. Formstecher and Ryškevic, for example, remove molybdenum filaments successfully with dilute nitric acid and 30% hydrogen peroxide (*23*).

Filament boron can usually be separated successfully from the filament by hand sorting, and for large amounts, crushing and magnetic separation have been used (*21*). One chemical treatment which seems to have been successful is the low temperature chlorination process of Stern and Lynds (*115*). Samples ground to −100 mesh and treated with chlorine at 300° to 350°C. were consistently upgraded from about 96% to better than 99.5% boron.

High temperature vacuum firing or fusion, if carefully done, can result in considerable purification. Aluminum, copper, magnesium, and tin tend to vaporize completely; iron, silicon, and titanium vaporize partially; and molybdenum, carbon, and tungsten are retained (*64*). A two-stage firing at 1400° to 1500° and at 1600° to 1800° is recommended by Mikheeva *et al.* (*71–73, 107*) for upgrading Moissan boron from 80% to about 98% boron. Haag (*36*) improves the purity of boron from 90–95% to 97–99% by a similar treatment.

Richter (*93*) states that thin layers of evaporated boron are amorphous to electrons. Johnston, Hersh, and Kerr (*45*) have made the tetragonal modification by heating amorphous boron 10 minutes at 1700°C.

Recently Horn (*42*) has succeeded in zone refining boron using boron nitride boats and a protective atmosphere of helium or argon. The impurities were reduced in one sample from 1% to 0.1% in five to eight passes. The product had the high temperature rhombohedral structure, and it appears that fused boron generally has this structure (*13, 55, 100*).

Horn has also prepared the low temperature rhombohedral form by crystallization from platinum-boron melts at 1200° to 800°C. (*43*).

Chemical Properties of Elementary Boron

The chemical reactions of elementary boron appear not to have been systematically studied since the work of Moissan (*74*) in 1895. Moissan's boron was a fine powder, not highly pure. Both these factors influence the chemical properties. It appears not to have been recognized for many years that finely divided boron reacts with the oxygen and water vapor of the atmosphere and samples were stored without protection against this attack. While it seems likely that Moissan's observations of the properties of boron will be proved correct in the main when the massive material is carefully studied, finely divided boron prepared with care to protect its surface will probably be more highly reactive than has generally been observed.

The chemical reactions of Moissan's boron are given in all the standard reference works and need not be repeated here. Early references are indexed by Jacobsen (*44*).

Hydrogen. Cueilleron (*13*) observed no reaction between colloidal boron and nascent hydrogen, but Newkirk and Hurd (*81*) observed diborane as the product of the reaction between 96.9% commercial boron and hydrogen at 840°.

Metals. Boron reacts with most metals to form borides. Two topics that need further work to obtain even an elementary knowledge are the preparation and properties of alkali metal borides [recently reviewed by Markovskiĭ and Kondrashev (*67*)], and the relation between boride structures and their hydrolytic reactions.

Carbon. Glasser and his colleagues have made the interesting observation that boron carbide behaves more like a reactive mixture of B and C than an inert compound B_4C (*26*).

Nitrogen. Richter (*93*) has observed that evaporated boron films are stable in oxygen for many hours, but by the slightest contact with air immediately form crystalline BN.

Oxygen. Interest in high energy fuels has led to the study of the oxidation of boron powders and such powders mixed with liquids. The results have been summarized by Olson and Setze (*86*). Despite the high heat of oxidation, high combustion efficiencies have not been obtained in practical equipment with boron slurries containing particles 1 to a few microns in size. Boron required 10 times as long to burn as magnesium, and 20 times as long as iso-octane. It is suggested that a viscous film of boric oxide delays or prevents combustion (*101*). Similar difficulties have beset all attempts to determine the heat of oxidation of boron directly (*18, 95, 118*).

Under more ordinary conditions a consistent picture of the oxidation behavior can be obtained. Cooper (*9*) reports that 1- to 10-micron particles oxidize slowly at room temperature, in one case purity dropping from 99 to 92% after a few months' exposure in a laboratory. Particles above 40-mesh size were unaffected by such exposure. On heating, powdered boron will take fire and burn in air at 700° (*74*), but the massive pressed element appears stable to about 750°C. At 800°, a black glaze forms and the attack is more rapid above 1000°C. (*9*). Single crystals of boron or massive fused pieces are even more resistant (*58*).

Halogens. Boron reacts spontaneously with fluorine at room temperature, presumably forming BF_3. The reaction has not been studied in detail.

In chlorine, massive boron is reported to be inert to 500°C., but to react at 550°C. (*9, 125*). Stern and Lynds have successfully purified massive boron by chlorination of impurities at 300° to 350°C. (*115*). Finely divided boron from the thermal decomposition of boron hydrides chlorinates completely at 400° (*92*).

Powdered boron (commercial, 75% B) pressed into pellets reacts with bromine very very slowly at 600° and much more rapidly at 800°C., to yield boron tribromide. Silica or Vycor tubes are used (*49, 80*).

The reaction between boron and iodine requires a temperature of at least 900° for an adequate reaction rate. This process has been described in detail by McCarty and Carpenter (*62*).

Amorphous boron does not react with ICl near its boiling point, 97.4°C. (*34*).

Nitryl fluoride and boron react at room temperature with considerable evolution of heat to form $(NO_2)BF_4$ (*5*).

Water. Eggersgluess *et al.* (*18*) have reported that boiling with water caused a slow and progressive oxidation of powdered Merck boron.

Acids. Boron in colloidal or massive form is not attacked by nonoxidizing acids such as hydrochloric, hydrofluoric, or hydriodic (*13, 58*), although Latimer and Hildebrand note (*57*) that it should be.

Colloidal or powdered boron is soluble to some extent in cold concentrated nitric acid and vigorously soluble in the hot acid (*13, 49*). The massive form is unattacked by dilute nitric acid and is only slowly soluble in hot concentrated nitric acid (*23, 58*) although it will dissolve completely in time in 1 to 1 nitric acid (*49*). The effect of the surface area is shown clearly on filament deposits of iodide boron containing red sandy areas, black massive areas, and red crystals. The sandy-appearing areas are rapidly attacked by warm concentrated nitric acid; the other zones are attacked much more slowly (*63*, and personal observation).

Hot sulfuric acid or sulfuric-chromic acid mixtures attack boron only very slowly (*58*).

Bases. Crystalline boron is unattacked by boiling concentrated or fused sodium hydroxide up to 500°C. Above this temperature the crystals are slowly etched (*58*). This reaction has also been studied at 537° and 815°C. (*12*). Boron is commonly dissolved for analysis by fusion in sodium carbonate or carbonate-nitrate mixtures

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(*21, 88, 115, 125*). It appears essential to fuse the mixture to a clear melt, $T >$ 850°C., to ensure complete reaction. The reaction has not otherwise been studied.

Oxidizing Agents

Agent	Form of Boron	Reaction	Ref.
H_2O_2 + dil. HNO_3	Crystalline	None	(*23*)
$KMnO_4$	Powder	Ignites with shock or friction	(*13*)
Lead oxides	Powder	Ignites with shock or friction	(*13*)
Tin oxides	Powder	Ignites with shock or friction	(*13*)
$Pb(NO_3)_2$	Powder	Ignites with shock or friction	(*13*)
Sb_2O_3	Powder	Ignites on heating	(*13*)
HI	Powder	Explodes	(*13*)
$AgNO_3$ (aq.)	Powder	Reacts	(*13*)
H_2O_2 concd.	Powdered crystals	Slow	(*58*)
Ammonium persulfate (aq.)	Powdered crystals	Very slow	(*58*)
Na_2O_2	Powder	Dissolves when fused	(*18, 125*)
Na_2CO_3—$NaNO_3$	Powder	Dissolves when fused	(*125*)
KIO_4 (aq.)	Powder	Dissolves	(*66*)

Miscellaneous

BN	Molten	None	(*42, 89*)
ThO_2, BeO	Molten	Reacts	(*64*)
BF_3, BCl_3, BBr_3	Powder	Forms lower halides (?)	(*33*)
B_2O_3	Powder	Volatile suboxides	(*48, 90*)

Some Important Problems

The preparation and chemistry of elementary boron still contain some important problems, and recent developments make it possible to attack some of these problems with a reasonable chance of success. First, there is need to prepare boron of very high purity, and this need may be divided into two parts. On the one hand we should have boron of 99.9+% purity for chemical work, and on the other, we need boron with a much lower level of electrically active impurities for study of its electrical properties. Boron to satisfy both these needs can probably be made by decomposing boron iodide on hot boron. A second problem related to the first is the development of an analytical method good to at least ± 0.05%. A third problem is the establishment of the stability ranges for the different allotropic modifications of boron, some of which are probably still unknown. This problem can be attacked by vacuum heat treating of boron in boron nitride crucibles. Finally, we need a systematic study of the chemical properties of boron, and for this purpose pure fused boron with the high temperature rhombohedral structure is the most reproducible starting material at the present time.

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Structure and Polymorphism in Elemental Boron

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The structures of α-rhombohedral boron, tetragonal boron, and the boron carbide phase are three-dimensional frameworks containing linked B_{12} icosahedra. The structure formed at lowest temperatures, α-rhombohedral boron, is unique in using half of its atoms to form delta linkages between icosahedra; the structure then satisfies the electron counting of the essentially molecular Longuet-Higgins and Roberts bonding theory. Linkages to icosahedra are generally strong in tetragonal boron and boron carbide. Deposition at 1000° to 1500°C. onto various more or less heavily attacked substrates furnishes other possible boron polymorphs. At these and lower temperatures appropriate kinetic mechanism, rather than any thermodynamic consideration, probably dictates the choice of crystalline pattern. At higher temperatures the growth kinetics generally allow formation of the most complex but thermodynamically stable β-rhombohedral polymorph.

Recent successes in growing pure single crystals of boron are largely responsible for the certain identification and characterization of three polymorphic modifications. Single crystals prepared following Laubengayer and coworkers (*13*) are tetragonal, boron crystallized from the melt is rhombohedral (*19*), and the phase obtained at 800° to 1100°C. by McCarty and coworkers (*15*) also is rhombohedral. Critical examination (*10*) of reported powder diffraction patterns shows that several preparations, old and new, not involving fusion were largely or wholly (high temperature) β-rhombohedral boron; this modification appears to be thermodynamically stable from the melting point down to 1500°C., quite possibly to much lower temperatures. Crystallization of (low temperature) α-rhombohedral boron from boron-platinum melts (*12*) at 1200° to 800°C. and its consistent preparation by deposition from the vapor onto several different substrates at 800° to 1100°C. provide evidence of the possible temperature range for stability of this polymorph. And because 1100° to 1300°C. is a reasonable estimate for the temperature range of spontaneous single crystal growth of tetragonal boron (from a substrate of different structure), a rather satisfactory alignment of polymorphs seems to shape up. This, however, is by no means the end of the tale.

Several powder diffraction patterns from boron preparations of apparently reasonable purity are not interpretable in terms of any combination of patterns given by the established polymorphs (*10*). For example, the newest and perhaps the

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strongest claimant to recognition as a distinctive polymorph is a preparation by Talley (*22*) employing the pyrolytic decomposition of boron tribromide on a filament (tungsten, molybdenum) at approximately 1250°C. to give boron of better than 99.0% purity. The evidence that this preparation is a homogeneous material at present rests upon Post's (*18*) successful indexing of some 50 powder lines from the diffractometer trace (Cu$K\alpha$ radiation) in terms of a large (ca. 192 atoms) tetragonal unit with $a = 10.10$, $c = 14.28$ A. Although impressive, this evidence lacks the decisive character of single crystal data, and no firm appraisal of status is feasible for the Talley preparation.

Nevertheless, it is highly probable that reasonably pure boron can be prepared in what must initially appear as a bewildering variety of crystalline polymorphs. Several have been prepared within a rather narrow band of temperatures (*10*). Generally they have been formed by deposition of boron from various reaction mixtures onto heated substrates, and these latter usually have been more or less severely attacked. But because the deposition of boron has ordinarily been at too rapid a rate to be matched by the radial diffusion of substrate atoms, it has been possible to recover essentially pure crystalline boron from the outer layers. If the crystalline boron thus obtained be homogeneous, it still need not be a thermodynamically stable or even metastable polymorph: It may be a monotropic form fundamentally unstable at all temperatures and pressures with respect to transformation into a stable polymorph.

There is much to be said for the hypothesis (*10*) that boron is peculiarly susceptible to formation of monotropes when prepared by deposition methods. Boron atoms in the known structural types form strongly linked and rather complex three-dimensional networks usually containing regularly disposed holes of adequate size to accommodate foreign atoms. It is clear that (perhaps many) other frameworks obeying the same general structural principles are possible, some of which will correspond to plausible monotropic forms. Moreover, either the thermodynamically stable or a kinetically favored form of a higher boride (or solid solution) may utilize the framework of a boron monotrope. Because of usually heavy attack upon the substrate during initial deposition, the structural pattern first established is likely to be that of a boride containing a boron framework which, as determined by the character of the substrate (and sometimes other impurity) atoms, may be that of a monotropic form. Continued deposition without phase change will then permit recovery from the outer layers of essentially pure boron as the crystalline monotrope. Thermodynamically, this monotrope is correctly and more logically regarded as the extreme case of a nonstoichiometric boride. Should a second (outer) phase develop at a later stage of deposition, the new pattern may but is probably much less likely to be that of a nonstoichiometric boride.

The formation of monotropes which are not properly classified as nonstoichiometric borides may also be favored by the deposition technique, especially when employed in the lower range of temperatures. What is involved here is the comparison of growth kinetics for structural frameworks of radically different complexity, a subject better taken up following presentation of the established structural results. The somewhat speculative analysis of this introductory section is intended to provide a rationale for the otherwise mysteriously conflicting reports on boron polymorphism.

Known Structural Frameworks

The atomic arrangements within the tetragonal (*8*, *9*) and the α-rhombohedral (*4*, *15*) modifications of boron are definitely established by x-ray diffraction studies, while that of the far more complex β-rhombohedral polymorph is now under investigation (*11*). All of the structural results are based upon general *hkl* data from single crystals with, in the studies of tetragonal and β-rhombohedral boron, intensity measurement by counter recording using both Cu$K\alpha$ and Mo$K\alpha$ radiations. The observation in each case that half or more of all significant reflections are beyond the reach of Cu*Kα* radiation at once implies the existence in the crystal of a strongly bonded three-dimensional network having at room temperature little thermal motion beyond the required zero-point vibrations.

Also pertinent to this discussion is the boron carbide phase of a long known (*3*, *25*) rhombohedral structural type containing a three-dimensional framework intimately related to that of α-rhombohedral boron (*4*). This phase has been studied within the range 4 to 28 atomic % carbon by Glaser, Moskowitz, and Post (*7*), who found no experimental evidence of extrema in lattice constants, electrical resistivity, or density at any stoichiometric composition. Apparently their samples were not well annealed nor of particularly high purity; according to Finlay (*6*), carbon in excess of the 20 atomic % corresponding to the theoretical $B_{12}C_3$ always separates as graphite when a sample is cooled slowly enough from fusion down to room temperature. Allen (*1*) made a careful study of the boron carbide phase in the composition range, B_4C to B_7C, but failed to comment on the possibilities of going to even lower carbon content. There is general agreement that the density and lattice spacing data require boron enrichment to be largely the result of direct replacement of carbon by boron atoms. These experimental data have important implications for the later discussion, particularly in connection with bonding theory.

The three established frameworks have a common structural entity—the group of 12 boron atoms arranged at the vertices of a nearly regular icosahedron. This polyhedron (Figure 1) has 20 equilateral triangles as faces, 12 vertices, and 30 edges; it has six fivefold, ten threefold, and 15 twofold symmetry axes, 15 mirror planes, and a center of inversion, all of which are readily identified by inspection of Figure 1. The symmetry operations constitute a (noncrystallographic) point group of order 120, to be compared with the crystallographic point group of highest symmetry, O_h—*m3m*, of order 48. The full symmetry of the regular icosahedron, more specifically, its fivefold axes cannot be required of a B_{12} complex within a crystal. What can be required in a favorable case within each crystal system is: cubic, T_h—*m3* of order 24; trigonal or hexagonal, D_{3d}—$\bar{3}m$ (*12*); tetragonal or orthorhombic, D_{2h}—*mmm* (*8*); monoclinic, C_{2h}—*2/m* (*4*); triclinic, C_i—$\bar{1}$ (*2*). In α-rhombohedral boron and in boron carbide, the symmetry required of the B_{12} group is

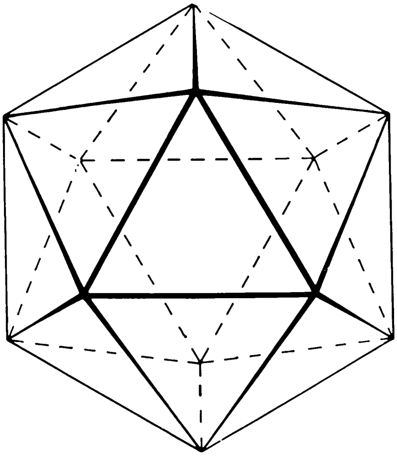

Figure 1. Regular icosahedron viewed along one of its ten threefold axes. Impression of perspective makes easy the identification of all symmetry elements

indeed $\bar{3}m$, but in tetragonal boron it is only $2/m$. The departure from dimensional regularity is not large in any of these structures.

The electron density of a real B_{12} icosahedron for the most illuminating case of projection along a quasi-fivefold axis, here exemplified by the (001) projection in tetragonal boron (*9*), is reproduced in Figure 2. The B_{12} group appears as a central doubled peak centered within a circular pattern of ten single peaks. A quasi-fivefold axis of a B_{12} icosahedron is very nearly parallel to the unique *c*-axis in tetragonal boron, and to each rhombohedral axis in α-rhombohedral boron and in boron carbide; the distance on centers between adjacent directly connected icosahedra is given by the lattice translation, respectively, 5.06, 5.07, 5.19 A. A boron atom used for such intericosahedral linkage forms six bonds, five within the same B_{12} group, the sixth along the quasi-fivefold axis to an external atom; these bonds are directed toward the vertices of the pentagonal pyramid defined by the six neighboring atoms. Taking this as the preferred bonding pattern for a boron atom, the geometry of connecting icosahedra into three-dimensional networks may then be examined.

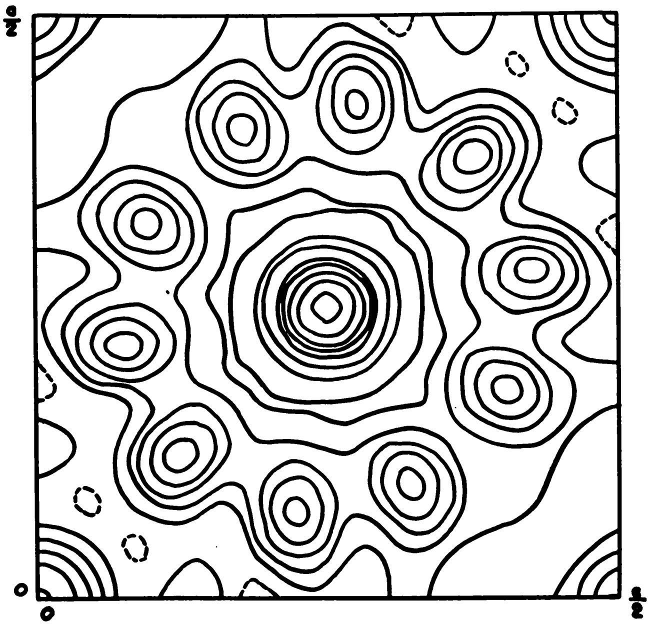

Figure 2. Electron density of an icosahedral boron-12 group projected nearly along a quasi-fivefold axis. This is the (001) projection from tetragonal boron

It is most convenient to discuss network formation in terms of dimensionally regular icosahedra. The structure analysis of tetragonal boron (*9*) gives 1.805 ± 0.015 and 1.68 ± 0.03 A. as the most probable values for, respectively, the edge of a regular B_{12} group and the B—B length for direct intericosahedral connection. The corresponding but probably less accurately determined values from the α-rhombohedral data (*4*) are 1.77 and 1.71 A.; the bond linking icosahedra is in any case significantly the shorter and presumably the stronger of the two. An icosahedron of edge 1.805 A. inscribes within a sphere of radius 1.715 A.; two such icosahedra directly connected along a common fivefold axis have a center to center separation of $2(1.715) + 1.68 = 5.11$ A. The angle subtended at the center of the icosahedron by an edge is 63.5°. It follows that if dimensionally regular icosahedra are centered at the points of a rhombohedral lattice having $a = 5.11$ A.. $\alpha = 63.5°$, each icosahedron of symmetry $\bar{3}m$ is linked to six others along three of its (six) quasi-fivefold axes which, for this idealized case, also coincide with the rhombohedral axes. Just half of the boron atoms are thereby used for linking B_{12} groups, yet the result is an undistorted though still incomplete version of the three-dimensional frameworks present in the α-rhombohedral boron and boron carbide structures. The description of a specific structural type is completed by specifying how the remaining six atoms of each icosahedron form outwardly directed bonds tying laterally into the three-dimensional network. The bonds in question are termed "lateral" because they are approximately (boron carbide) or exactly (α-rhombohedral boron) perpendicular to the threefold axes of the rhombohedral crystals.

Table I. Cell Data for Boron and Boron Carbide

α-Rhombohedral boron.
$a = 5.057$ A., $\alpha = 58.06°$. B_{12}/unit. $R\bar{3}m$.[a]
Boron carbide.
$a = 5.19$ A., $\alpha = 65.3°$. $B_{12}C_3$/unit. $R\bar{3}m$.[a]
Tetragonal boron.
$a = 8.75$, $c = 5.06$ A. $(4B_{12} + 2B)$/unit. $P4_2/nnm$.[a]
β-Rhombohedral boron.
$a = 10.14$ A., $\alpha = 65°3'$. 108B/unit. $R\bar{3}m$.[a]

[a] Space group of the structure.

Unit cell data on the phases of immediate structural interest are given in Table I. The formation of lateral connections between icosahedra in α-rhombohedral boron is accompanied by lateral shrinkage of the idealized framework, as shown by the decrease from 63.5° to 58.1° in the rhombohedral angle. Insertion of a linear C_3 chain at the center of each rhombohedral cell in the idealized framework to give the boron carbide structural type produces small increases in both α and a. The whole pattern of connecting icosahedra to give a three-dimensional network, excepting along the short c-axis, is much more complex for tetragonal boron.

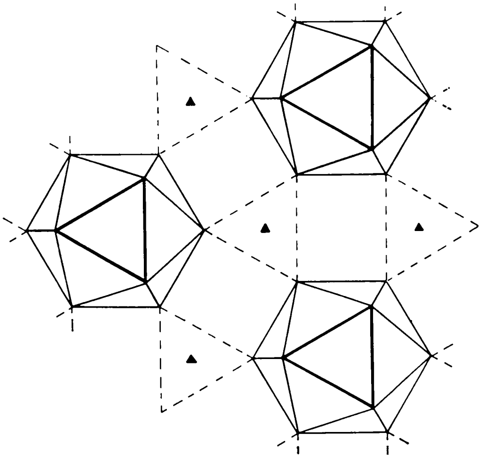

Figure 3. Slice through the α-rhombohedral boron structure to include three icosahedra centered in the (111) plane. Dotted lines indicate delta bonds which provide lateral connection of icosahedra

Figure 3 represents a slice through the structure of α-rhombohedral boron to include three icosahedra centered in the rhombohedral (111). The lateral ties,

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shown as dotted lines, bear little similarity to the intericosahedral linkages already discussed or, for that matter, to those which remain to be discussed for boron carbide and tetragonal boron. The equilateral triangle formed by three atoms from three different icosahedra is considered by Decker and Kasper (*4*) to represent a three-center or delta bond of the sort freely employed by Eberhardt, Crawford, and Lipscomb (*5*) in their treatment of the boron hydrides. Indeed, α-rhombohedral boron would appear to be the simplest three-dimensional crystalline "anhydrogenide" of the boron hydrides, put together from icosahedral fragments present in the vapor by a mechanism suited to low temperature deposition. In view of its excessive length (2.025 A.), the delta bond appears to be a relatively weak example of the type, hence especially susceptible to attack by various reagents at elevated temperatures. Since a three-center bond requires just two electrons (*5*), each participating boron atom need supply on the average but two thirds of an electron, and each B_{12} group is called on for $6(2/3) = 4$ electrons (*4*).

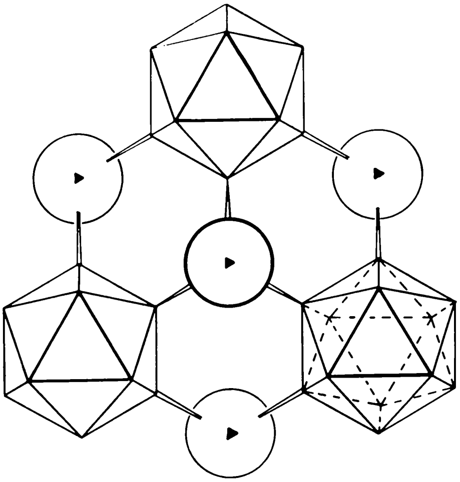

Figure 4. Slice through boron carbide structure to include three icosahedra centered in the (111) plane. Approximately lateral bonds connecting icosahedra to terminal carbon atoms of carbon chains are shown

Figure 4, in complete analogy with Figure 3, represents a slice through the structure of boron carbide to include three icosahedra centered in the plane (111) of the rhombohedral cell. The lower terminal atom of the C_3 chain centered at the midpoint of the cell is represented by the central heavy circle in Figure 4. This atom is seen to form four tetrahedrally distributed bonds, one upward along the threefold axis to the central carbon atom, three others gently inclined downward to three equidistant boron atoms of the three neighboring icosahedra. Thus the "lateral" bonds formed by boron, one per atom and six per icosahedron, are to terminal atoms of C_3 chains, and are also very nearly along quasi-fivefold axes of the icosahedra. The boron atoms of the framework divide into two structurally distinct but equally populated classes. The configuration of the six bonds to any boron atom is pentagonal pyramidal; the two classes are distinguished accordingly as the axial bond is to boron of another icosahedron or to carbon of a chain.

There are holes, two per cell, along the principal diagonal between icosahedra and carbon chains, large enough to accommodate extra atoms (*3*). Filling of these holes with carbon atoms is indicated by the density and lattice parameter data of

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Glaser and coworkers (*7*) for their carbon-rich (though presumably quenched) preparations of boron carbide. However, it is mainly replacement of carbon by boron atoms in the chains which must be called upon to account for the highly boron-rich phases. There is, indeed, direct evidence for such replacement from Bray's (*2*) nuclear magnetic resonance study of a boron carbide (of unspecified composition). The persistence of the three-dimensional network under extreme conditions of maltreatment is amply demonstrated by Tucker and Senio's (*23*) study of neutron irradiation of boron carbide.

The primitive unit of the tetragonal boron structure (*9*) contains four B_{12} icosahedra and two "tetrahedral" atoms (each forming four bonds directed toward the corners of a flattened tetrahedron), all linked together into a continuous framework. By taking this rather complex arrangement it becomes possible for every boron atom of an icosahedron to preserve more or less satisfactorily the pentagonal pyramidal configuration of six bonds characteristic of every icosahedral atom in boron carbide, but of only half of all atoms in the α-rhombohedral structure. Of the twelve external bonds from one icosahedron, ten are direct links to other icosahedra, two are with tetrahedral atoms. Six of the intericosahedral links (1.68 ± 0.03 A.) enjoy highly favorable geometry, the remaining four (1.845 ± 0.03 A.) are certainly much strained, but are still substantially shorter than the delta bonds (2.025 A.) in α-rhombohedral boron. Some sort of internal compensation may be present, because the links to tetrahedral atoms are shortest of all, 1.601 ± 0.005 A., in the best single crystal specimen available for study. The length of a true B—B single bond is presumably $\lesssim 1.601 \pm 0.005$ A. [The possibility that the tetrahedral positions were filled to any significant degree by carbon, nitrogen, or oxygen instead of boron atoms is definitely excluded (*9*).]

The persistence of the tetragonal framework under adverse conditions is demonstrated by internal evidence (*9*). The single crystals as grown in a steep thermal gradient (*13*) are subject to a large and variable degree of internal disorder, showing up in the diffraction data through a notable diversity in the strength of diffuse scattering, the distribution of Bragg intensities, and even the lattice constants. The dominant type of structural defect is almost certainly "substitutional vacancies" in the fundamental framework (*9*). Nevertheless, data from the poorest specimen establish the persistence of a framework slightly modified in degree but not in kind from that of a clearly superior crystal. The quoted bond data are weighted values corresponding nearly or exactly to results given by the best available specimen.

The tetragonal framework contains holes, two per cell, large enough to accommodate tantalum atoms (from the filament) so that a stoichiometric boride, TaB_{25}, is a theoretical possibility. The detailed structure analysis places an upper limit of 1/1400 on the atom fraction of tantalum in these holes for the tiny single crystals providing the diffraction data. The crystals grew out from a microcrystalline matrix of different structure (*10*) ensheathing the heated filament, and study of the preparative details (*13*) leaves the impression that single crystal growth was initiated in a region of very low tantalum concentration. Even so, it remains uncertain (*10*) whether the crystals were formed as a nonstoichiometric boride of tantalum.

Another set of regularly disposed but smaller holes in the tetragonal framework appear to be partially filled ($\lesssim 1/4$ occupancy) by boron atoms (*9*). The fractional occupancy is least ($< 1/8$) for the specimen showing least evidence for substitutional vacancies in the basic framework. This suggests that a perfectly established framework might tolerate rather than welcome occasional extra atoms in holes.

The present status of our structural investigation (*11*) of the very complex β-rhombohedral boron may be summarized as follows. The single crystals provide data of superior quality: We anticipate that nearly one half of the more than six thousand forms theoretically recordable with Mo$K\alpha$ radiation will give measurable intensities with counter recording using a specimen about 0.3 mm. in diameter. It is certain that the β-rhombohedral structure is not merely a distorted and elaborated version of the idealized framework described for α-rhombohedral boron and boron carbide. On the contrary, it is almost certain that at least one third of the boron atoms (108 per cell) cannot be present as icosahedra, and it is even doubtful whether such groups play any important role within the structure.

Bonding Theory

One theoretical approach to the bonding of three-dimensional boron networks derives from the Longuet-Higgins and Roberts (*14*) molecular orbital treatment of the regular B_{12} icosahedron. These authors employ elegant group-theoretical methods to obtain symmetry orbitals for the irreducible representations of the icosahedral group (of order 120), and are then in position to construct the (48) molecular orbitals and to compute the (14, mostly degenerate) energy parameters on the usual approximate basis for the B_{12} group. Some 36 of the molecular orbitals have amplitudes concentrated mostly on or within the icosahedron; the remaining 12 tend to concentrate outside. On the basis of energy parameters, the first group divides sharply into 23 antibonding and 13 bonding orbitals. Energy parameters for the twelve externally concentrated orbitals are perhaps not uniformly favorable, but these orbitals are considered to uncouple from the icosahedron to give 12 localized *sp* hybrids suitable for external bond formation. In order that a B_{12} group forming 12 external bonds may have a closed shell structure according to this theory, the bonding orbitals must be filled with $2(13 + 12) = 50$ electrons; or, assuming the attached atoms or groups to supply 12 electrons for the external bonds, a B_{12} icosahedron must still claim $26 + 12 = 38$ electrons.

Since 12 boron atoms can furnish but 36 valence electrons, a $B_{12}H_{12}$ molecule must lack two electrons of achieving a closed shell structure and is presumed to be unstable (*14*). No such species has ever been isolated, although recent work by Shapiro and Williams (*20*) perhaps indicates that the possibility of doing so should be further investigated. The theory clearly predicts stability for the anion, $B_{12}H_{12}^{--}$.

Longuet-Higgins and Roberts' application of their theory to tetragonal boron and boron carbide takes these framework structures as aggregates of regular icosahedra and either tetrahedral boron atoms or C_3 chains linked together by standard single bonds. They ignore any effect of the necessarily lowered symmetry of the icosahedra and, probably more important, possible conjugation throughout the network; the evidence from interatomic distances is that the direct intericosahedral links are of fractional order, with bond number $\lesssim \frac{3}{4}$. When applied to the tetragonal framework, the theory would like to have $2(4) + 4(38) = 160$ electrons per cell, whereas 50 boron atoms can supply only 150 of these. The average deficit, 0.2 electron per B, is larger than in $C_{12}H_{12}$—i.e., $\frac{1}{6}$ electron per B. The theory as applied differs in no essential respect from that for a molecular crystal: The same electron deficit distributed according to a similar pattern is obtained for a unit cell containing four icosahedral $B_{12}H_{12}$ and two tetrahedral BH_4 molecules [or for the partially condensed $B_2(B_{12}H_{10})_4$, etc.].

The electron counting for boron carbide of ideal stoichiometry and structure works out nicely (*14*) provided two electrons from the central atom of the C_3 chain, where they are not needed (except to maintain approximate electrical neutrality!), are transferred to the B_{12} group. Thus for $C_3^{++}B_{12}^{--}$ the electron counting is summarized by $2 + 2(4) + 38 = 48 = 3(4) + 12(3)$. With replacement of carbon by boron in the chains this counting is no longer achieved. For the limiting case of B_3B_{12}, probably never fully attainable experimentally, the average deficit is 0.2 electron per B.

Decker and Kasper point out (*4*) that the electron counting in the α-rhombohedral structure agrees with the theory adapted to use six outward pointing orbitals of the 12 per icosahedron in delta linkages to other B_{12} groups. The counting then is $6(\frac{2}{3}) + 6 + 26 = 36$ valence electrons per cell.

At the opposite extreme of theory, Pauling's (*16*) treatment places great weight

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on variations in bond lengths while ignoring essential peculiarities of configuration—e.g., the icosahedral geometry in the framework; it does not provide so interestingly specific a model for testing as does the Longuet-Higgins and Roberts theory. Pauling's treatment of the tetragonal boron network is as follows (*17*): Of the 148 B—B links within one cell, the eight to tetrahedral atoms are assigned bond number ¾, the remaining 140 bond number ½, corresponding to a theoretical total of 152 electrons. The respective bond distances given by experiment (weighed averages from two specimens) are 1.617 and 1.797 A., by Pauling's calculation 1.695 and 1.80 A. Lacking an *a priori* basis for fixing bond numbers, the cited assignment is not unique; it would appear that the 12 unstrained intericosahedral links (1.68 ± 0.03 A.) qualify, according to calculation, as ¾ bonds, the tetrahedral links more nearly as single bonds.

Yamazaki (*24*) has used the tight binding approximation in a theoretical calculation of the electronic band structure for boron carbide. The largest computed energy gap divides the 60 Bloch orbitals into groups of 24 and 36 corresponding to the respective valence and conduction bands. The energy separation is satisfactorily large, 2.6 e.v., at the center, doubtfully so in view of the approximations, 0.9 e.v., at the boundary (111) point of the Brillouin zone. The 48 valence electrons from one $B_{12}C_3$ should just fill the valence band to render stoichiometric boron carbide nonconducting. Substitution of boron for carbon in the chains should result in decreased electrical resistivity. However, Glaser and coworkers (*7*) report that hot-pressed powders (of debatable purity) give a smooth decrease of resistivity with increasing carbon content in the range 4 to 28 atomic % of carbon. The conclusion derived from studying the spectrum of published work on the boron carbide phase is that accurately quantitative studies, to include chemical, x-ray diffraction, and nuclear-magnetic resonance analyses, density and resistivity measurements, all on the same well-defined single crystals, are badly needed.

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Polymorphism in Boron

That deposition from the vapor onto attacked substrates may yield a variety of boron monotropes more properly classified as nonstoichiometric borides seems plausible enough in terms of the structural characteristics of known boron frameworks. Where attack upon the substrate is either absent or unimportant, the growth of boron monotropes (except at the highest temperatures) still seems more than usually probable, analogous, for example, to the deposition from the vapor of the monotropic white phosphorus in preference to the structurally more complex violet phosphorus. The evidence is convincing that β-rhombohedral boron is thermodynamically stable from the melting point down to some at present undetermined temperature which, indeed, may be much lower than has been tentatively assumed. However, it is probable that below some effective temperature the kinetics of growth will always favor a modification, be it monotrope or stable polymorph, of relatively simple structure in preference to the most complex β-rhombohedral framework.

Even if neither α-rhombohedral nor tetragonal boron be formed as a nonstoichiometric boride, one or both may still be monotropic, formed in consequence of favorable growth kinetics. Prospects for direct observation of reversible phase transformations (apart from fusion) are dismal. It is observed (*4*) that α-rhombohedral boron is unstable to prolonged heating above 1200°C., transforming irreversibly to β-rhombohedral boron at 1500°C., and giving unidentified material in the 1200° to 1500°C. interval. These data suggest, but do not prove, that tetragonal boron is monotropic; they suggest, very probably erroneously, that the β-rhombohedral phase is not stable below 1500°C.; they suggest, but do not prove, that the α-rhombohedral polymorph is thermodynamically stable below 1200°C.; they suggest most strongly kinetically sluggish transformation, especially pronounced for direct growth below 1500°C. of the pure β-rhombohedral polymorph.

The difficulties barring the way to unambiguous conclusions are further illustrated by Stern and Lynds' (*21*) preparations using a mixture of boron trichloride and hydrogen as the boron source for deposition. Boron deposited onto a strongly attacked titanium substrate at 1100° to 1200°C. is definitely identified (*10*) as the β-rhombohedral polymorph. Neither of the quite dissimilar materials deposited, respectively, on titanium and carbon at 1075° to 1125°C. (note the curious temperature overlap with the preceding report!) give powder data interpretable in terms of known patterns. The formation of β-rhombohedral boron at 1100° to 1200°C. suggests, but does not prove, thermodynamic stability at these temperatures; a more favorable growth mechanism than usual certainly is indicated. That this polymorph is no longer formed on titanium below about 1100°C. may be wholly attributable to kinetic factors; the material deposited at the lower temperature is not related (*10*) to any other reported preparation, and is very probably formed as a nonstoichiometric boride (or possibly a mixture thereof). A similar conclusion is probable for the different material (not the ordinary boron carbide phase) deposited on carbon in the same temperature range. It is further to be emphasized that 1075° to 1200°C. represents a temperature range in which formation of α-rhombohedral and possibly also of tetragonal boron would have been anticipated. In view of its vulnerable delta bonds, establishment of the α-rhombohedral pattern during initial heavy attack upon the substrate may be deemed unlikely. Although it might still be expected at a later stage of deposition, if thermodynamically stable, it is not identifiable in the products (*10*). Stern and Lynds' results indicate that a variety of usable boron frameworks do exist; they appear also to establish the overwhelming importance of kinetic factors in determining what material is obtained by deposition at relatively low temperatures.

The examples discussed are perhaps sufficient to indicate why reasonably pure boron is likely to be reported in an initially astonishing variety of crystalline "polymorphs." In total contrast to this diverse exhibit, the impression left with this writer is that a single polymorph, the β-rhombohedral modification, may turn out to be thermodynamically stable over the whole range of temperatures (and more or less normal pressures). This impression would be strengthened were it certain, rather than just strongly suspected, that B_{12} icosahedra play no essential role in the β-rhombohedral structure.

The integrated effect from several reported preparations (*10*) containing β-rhombohedral boron is to indicate thermodynamic stability of this phase within the temperature range in which it has been possible to prepare tetragonal boron. Comparing the tetragonal and α-rhombohedral frameworks, the latter appears to be higher in energy and probably also higher in entropy. Should the relative entropy content become controlling, it ought to favor the α-rhombohedral framework at higher rather than lower temperatures. The chemical reactions and the structural characteristics of the boron hydrides indicate that boron icosahedra, or at least fragments thereof, are fairly readily synthesized at relatively low temperatures. Kinetically speaking, the α-rhombohedral framework seems a highly plausible and particularly simple result of low temperature combination of icosahedral fragments. As compared with tetragonal boron, the α-rhombohedral framework retains the weak delta bonds between icosahedra and thus obeys the electron counting required by the essentially molecular Longuet-Higgins and Roberts theory (*14*). If, indeed, icosahedra play no important role in the β-rhombohedral structure, one could infer that under conditions of sufficiently high kinetic mobility, (linked) icosahedra are abandoned in favor of an energetically more favorable, but simultaneously much more complex arrangement. In this case, the β-rhombohedral framework would not appear, as does that of α-rhombohedral boron, to be an obvious structural "anhydrogenide" of the higher boron hydrides.

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High Temperature Chemistry of the Binary Compounds of Boron

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The refractory binary compounds of boron with some of the transition metals have many attractive properties. They are high melting, high boiling, good conducting, chemically inert, and thermodynamically very stable compounds. Their methods of preparation, their thermodynamic, chemical, and physical properties, and their uses are listed, described, and discussed. Their phase relationships are unusual, for there are frequent cases of extensive solid solubility and narrow temperature ranges of stability. The present status of the field is assessed.

The high melting points, the high boiling points, the extreme hardness, the chemical inertness, the high electrical and thermal conductivity, the high thermal neutron cross section for boron-10, and the low cross section for boron-11 make the metallic borides materials of great current interest.

Most of the metals form binary compounds with boron, and many of them are of high temperature interest. This discussion is concerned with the properties of these refractory borides, most of which contain the transition elements. They are sometimes called "refractory hard metals," and are frequently discussed along with carbides, nitrides, silicides, sulfides, and sometimes oxides. Boron carbide and boron nitride have refractory properties and frequently are discussed with the metallic borides.

As one examines the literature, he finds that the refractory borides have been studied in a systematic fashion only in the past two decades and that many of their properties are not known very well. For example, the compositions of many of the phases may not be known even at the present time, and many of the melting points may be uncertain by several hundred degrees.

Reviews of the preparation and properties of the refractory borides have been written by Schwarzkopf and Kieffer (*25*), Powell (*21*), Powell, Campbell, and Gonser (*22*), and Samsonov and Markovskiĭ (*24*). The important phase relationships and crystallographical data have been collected by Hansen (*8*) and by Pearson (*17*). The present discussion reviews some of the important chemistry of the metallic borides and indicates areas of present and future work.

General Features

The characteristic properties of these refractory borides, in addition to those mentioned earlier, are that they are good electron emitters; they are thermodynamically very stable compounds; they are generally not soluble in acids but are soluble in

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alkaline or fused alkaline media; they are fairly resistant to oxygen attack; and the systems show a wide variety of phases with occasional wide solid solubility.

The phases that have been reported are indicated in Table I, and some of the properties are listed in Table II.

Table I. Phases of Metallic Borides (*8, 16, 21, 24, 25*)

	M_4B	M_3B	M_2B	M_3B_2	MB	M_3B_4	MB_2	M_2B_5	MB_4	MB_6	MB_{12}	Other
Be			x				x			x		
Mg							x			x?	x?	
Ca										x		
Sr										x		
Ba										x		
Al							x				x	
Y										x		
La										x		
RE									x	x		
Ac									x	x		
U							x		x	x		
Ti			x		x		x	x				
Zr					x		x				x	
Hf					x		x					
V			x		x	x	x					
Nb		x	x	x	x	x	x					
Ta		x	x	x	x	x	x					
Cr	x		x		x	x	x					Cr_5B_3
Mo			x	x	x		x	x				
W			x		x		x	x				
Mn	x		x		x	x	x					
Re								x?				
Fe			x		x							
Ru			x		x		x					Ru_2B_3
Os					x		x					Os_4B_9?
Co			x		x							
Rh			x		x?							
Ir				x	x		x					
Ni		x?	x	x	x							Ni_2B_3?
Pd				x?								
Pt				x?	x?							
Cu												CuB_{22}

Preparation

The metallic borides are almost always prepared in the laboratory by synthesis from the elements or by the reduction of the metal oxide with boron. Most generally, laboratory preparations of pure material from the elements are accomplished by heating pressed mixtures of powdered metal and boron. Considerable care must be exercised in the preparation of borides in this fashion. The reaction is strongly exothermic, and at temperatures ranging from 900° to 1200°C. reaction begins, and there is a very rapid rise in temperature. Very frequently the materials are scattered throughout the apparatus, and the crucible is destroyed.

The purity of samples prepared in this way varies with the purity of the starting materials. Many of the more volatile impurities, such as iron, which is present in commercially available pure boron, will distill out of a sample if the product is heated to 2000°C. On the other hand, other impurities, such as carbon, cannot be removed simply by evaporative techniques.

Another way of preparing pure borides in the laboratory is by the boron reduction of oxides, provided that there are no ternary compounds. The reaction proceeds smoothly with the loss of $B_2O_2(g)$ or $B_2O_3(g)$. Boron carbide may be used as the reducing agent, but contamination by carbon probably occurs.

Commercial preparation of metallic borides is very well summarized and described by Powell (*21*). The methods include the reduction of metal oxide–boric oxide mixtures by carbon or active metals; the vapor plating of the boride on a hot metallic surface from a boron-containing gas; the vapor plating of the boride on a hot surface

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Table II. Properties of Refractory Borides (*8, 21, 24, 25*)

Phase	Melting Point, °C.	Resistivity,[a] μohm-Cm.	Hardness[b]	
MgB_2	<1000			
MgB_{12}	<1700		—————.	
CaB_6	2235	123.5	2740 ± 220	V-1
SrB_6	2235			
BaB_6	2270	306	3000 ± 290	V-1
AlB_2	1400 ± 50			
LaB_6	2210	27	2770 ± 160	V-1
CeB_6	2190		3140 ± 190	V-1
ThB_4	>2500?			
ThB_6	2195			
CB_4	2200	4×10^{10}	4950	V
Ti_2B	2200 ± 50			
TiB		40		
TiB_2	2790	15.2–28.4	2710	K-1
ZrB		30–35	69–72	R_A
ZrB_2	3040 ± 50	9.2–38.8	1560	K-1
ZrB_{12}	2680	100; 60–80	92–95.5	R_A
HfB_2	3250 ± 100	10		
VB	1900	35–40		
VB_2	2400 ± 50	16	2800	K-1
Nb_2B	1930?			
NbB	>2000	64.5		
NbB_2	3050	28.4–65.5	2595	V-3
Ta_2B	2040			
TaB	2040	100		
TaB_2	3100 ± 50	68–86.5	2615 ± 120	K-1
Cr_3B_2	1960			
CrB	2000	64		
CrB_2	1900	21	1800	V-1
Mo_2B	2120	40	2500	V-2
M_3B_2	2250			
MoB	2350	45–50	2350	V-2
MoB_2	2250 ± 60	22.5–45	1200	V-2
Mo_2B_5		25	2350	V-2
W_2B	2770 ± 80			
WB	2860 ± 80			
W_2B_5	2200	21	2663	V-3
Fe_2B	1389			
FeB	1550			
Co_2B	1265			
CoB	1400			
Ni_2B	1230			
Ni_3B_2	1160			
NiB	1020			
Ni_2B_3	1280			

[a] Measured at room temperature.
[b] Knoop Hardness No.

Vickers Microhardness, Kg./Sq. Mm.

R_A = **Rockwell A**

K-1 = K-100g, KHN
K-2 = K-50g, KHN
K-3 = K-30g, KHN

V-1 = K-100g, VHN
V-2 = K-50g, VHN
V-3 = K-30g, VHN

from the thermal decomposition of a boron halide and metal halide gaseous mixtures, or from hydrogen reduction of the mixed gases; and the electrolysis of fused mixtures of metal oxide, metal fluoride, and boric oxide.

Structures

The structures of the various metallic borides have been worked out by Hägg (*7*), Kiessling (*12*), Post and coworkers (*19, 20*), Brewer and coworkers (*2*), Zalkin and Templeton (*28*), and several other investigators. The structures are of various types with some showing isolated boron atoms, some showing boron chains, some showing two-dimensional boron networks, and some showing three-dimensional boron networks. These structures are discussed by Schwarzkopf and Kieffer (*25*), and Post (*18*) describes these structures in detail.

Phase Relationships

The outstanding features of the constitution diagrams for the metallic borides are the large number of phases, the high melting points, the occasional extensive solid solubility, the surprisingly many examples of disproportionation in the solid, and the several examples of phases having a narrow temperature range of stability. Hansen (*8*) has collected phase diagrams for the various systems involving boron. To illustrate the various unusual features of these diagrams, a few of them showing intermediate phases are mentioned.

One of the simplest is that of the boron-aluminum system in which there are two intermediate phases, AlB_2 and AlB_{12} (*8*). At 1350° to 1450°C. AlB_2 melts incongruently, giving an aluminum-rich liquid and AlB_{12}. The latter phase was originally thought to be crystalline boron. Its melting properties are not well known.

In the boron-iron system, there are again two intermediate phases, Fe_2B and FeB (*8*). The former melts incongruently at 1389° to give a liquid and FeB; and FeB melts, probably congruently, at about 1550°C.

In the boron-nickel system there are at least three and possibly four intermediate phases (*8*). Two of them, Ni_2B and Ni_3B_2, melt congruently at about 1225° and 1160°C., respectively. The third, NiB, melts incongruently at 1020°C. to give a liquid and Ni_2B_3 (?). It is thought that Ni_2B_3 may melt congruently at about 1275°C.

A more complicated system is that of boron and titanium (*8*). There are four intermediate phases, Ti_2B, TiB, TiB_2, and Ti_2B_5. Ti_2B is believed to disproportionate both at temperatures below 1800°C. and above 2200°C. In both cases a titanium-rich liquid is formed, and the other phase is TiB at low temperature and TiB_2 at the higher temperature. TiB disproportionates at 2060°C. into Ti_2B and TiB_2. TiB_2 is thought to melt congruently at about 2800°C., but the behavior of Ti_2B_5 is not known.

One of the most complex boron metal systems is that of boron and molybdenum. There are six phases in this system: Mo_2B, Mo_3B_2, α-MoB, β-MoB, and two phases between MoB_2 and Mo_2B_5. The MoB phases show solid solutions of several atomic per cent on each side of the stoichiometric composition. The phases between MoB_2 and Mo_2B_5 are interesting because the low temperature one has a structure typical of M_2B_5 borides, and the higher temperature one has a structure typical of MB_2 borides. Yet neither of these stoichiometric compositions lies within the solid solution region of the observed phases which is of the order of a few atomic per cent. The phase, Mo_3B_2, was shown by Steinitz, Binder, and Moskowitz (*27*) to disproportionate at lower temperatures into Mo_2B and MoB. According to Gilles and Pollock (*5*), the minimum temperature of stability is 1950°C. It melts incongruently at about 2250°C. to form a molybdenum-rich liquid and MoB. This phase is unusual in having this limited temperature range of stability.

An even more unusual kind of behavior is reported in the boron-zirconium system (*8*). The phases are ZrB, ZrB_2, and ZrB_{12}. ZrB_2 and ZrB_{12} apparently melt congruently at about 3040° and 2680°C., respectively. ZrB is reported to disproportionate into zirconium and ZrB_2 below 800° and also above 1250°C. It is interesting to examine the thermodynamic consequences of this behavior.

Consider the reaction,

$$Zr(s) + ZrB_2(s) = 2ZrB(s) \tag{1}$$

The free energy change for this reaction is positive at temperatures below 800°C., but then it becomes negative. Because the reaction involves only solids, the entropy change will be close to zero; and the heat content change will also be nearly zero, because the free energy change is so small.

Consider first that there is negligible solid solubility of the phases. The disproportionation of ZrB at temperatures above 1250°C. implies that $\Delta F°$ for the above reaction shows a minimum between 800° and 1250°C. and becomes positive again above 1250°C. Since

$$d\Delta F°/dT = -\Delta S° \tag{2}$$

the entropy change is positive at low temperatures, becomes zero at the temperature

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of the minimum in the ΔF° curve, and is negative at higher temperatures. The expression,

$$d\Delta S^\circ/dT = \Delta C_p/T \tag{3}$$

indicates that the heat capacity of the products of the above reaction is less than that of the reactants. Similarly, ΔH° decreases with increasing temperature and passes through zero.

Suppose, on the other hand, that with increasing temperature the solubility of boron in zirconium metal increases sharply or that there is a sharp decrease in the boron content at the metal-saturated edge of the ZrB_2 phase. Under such circumstances the activity of zirconium in the metal phase or that of the boron in the compound would be reduced significantly with increasing temperature. In these circumstances the above reaction is not precisely the correct one, for the phases are not pure at all temperatures. The margin of disproportionation stability of ZrB is so slight that these lowered activities could cause its disappearance with increasing temperature.

There are insufficient data to ascertain which of these sets of conditions exists. In either case, the lower disproportionation limit implies that ΔS° is positive below 800°C.

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Thermodynamic Properties

Very few thermodynamic data are available for the refractory borides. The low temperature heat capacity and entropy have been obtained by Kelley (*11*) for boron carbide, and King (*13*) has measured the high temperature heat capacity, but very few other determinations have been made.

The chemical inertness of the refractory borides precludes the measurement of heats of solution by conventional techniques. Smith, Dworkin, and VanArtsdalen (*26*) have measured the heat of formation of B_4C by combustion techniques. Holley and coworkers (*9*) and Hubbard and coworkers (*10*) are undertaking measurement of the heats of formation of some of the refractory borides by oxygen combustion techniques and by fluorine combustion techniques, respectively. Margrave and coworkers (*15*) have measured high temperature heat capacities for some borides.

Brewer, Sawyer, Templeton, and Dauben (*2*) have obtained some relative stabilities, and Brewer and Haraldsen (*1*) have obtained some heats of formation by two kinds of measurements. Systems containing boron and two metals were heated, and the resulting samples were studied by x-ray diffraction techniques. From such experiments it is possible to ascertain the relative stability of the various metallic borides with respect to one another. The results indicate that the most stable borides are in groups IV and V of the transition elements.

The other kind of experiment involves heating together a metal, elemental boron, and a third nonmetal component such as carbon or nitrogen. Alternatively, the starting materials could be metal boride and the third component or metal carbide and boron. From these experiments it is possible to set limits on the values for some of the thermodynamic properties of the borides by using the available values for carbides and nitrides. It was pointed out that the replacement of boron in a metallic boride with nitrogen occurs with large negative ΔS° and ΔH° values. Consequently, the boride reacts with nitrogen at low temperature, but becomes stable in the presence of nitrogen at a high temperature.

Experiments such as this are not always successful because solid solution among various phases may occur and because ternary phases may also appear.

The difficulty of measuring heats of formation and obtaining reactions sufficiently close to equilibrium to fix precisely thermodynamic values makes it desirable to find other ways of obtaining thermodynamic values. One of the most satisfactory ways is that of the study of vaporization reactions. Gilles and Pollock (*6*) have studied the evaporation characteristics of the various molybdenum borides and have obtained heats of formation for those phases. Robson and Gilles (*23*) have measured the vaporization properties of boron carbide and have used them, together with the heat of formation of boron carbide, to obtain the heat of sublimation of boron. Eick and Gilles (*4*) have studied evaporation properties of the rare earth tetra- and hexaborides.

No gaseous metallic borides have yet been identified.

Chemical Properties

Most of the refractory borides are very slowly soluble, if soluble at all, in acids but dissolve in alkaline media. Some of the alkaline earth borides react with acids to form borohydrides. The reactions of the refractory borides are so slow or complicated that the analysis of compounds is a most troublesome problem.

At high temperatures, many of the borides are fairly resistant to oxygen attack. When the reaction occurs, $B_2O_3(g)$ and $B_2O_2(g)$ are probably formed along with the metal oxide.

The reaction with nitrogen was discussed in the previous section. The reaction of ammonia with the borides is related to that for nitrogen. It is to be expected that reaction of borides with ammonia will be favored over reaction with nitrogen.

Generally speaking, carbon does not react readily with the refractory borides, especially if they are boron-rich (*1*). If, of course, samples contain excess boron, boron carbide will be produced until the excess boron is removed. If the boride is rich in metal, then metal carbide and a phase richer in boron will result. Boron usually reacts with carbides.

The reaction of water at high temperature with the metallic borides has not been studied systematically. A study of this interaction may reveal some interesting reactions involving gaseous molecules. On the basis of work by Chupka and Berkowitz (*3*), White and coworkers (*29*), and Margrave (*15*), it might be supposed that HBO_2 and perhaps others may be produced.

Physical Properties

The melting points of some of the borides are extremely high. Some values obtained from Hansen (*8*), Samsonov and Markovskiĭ (*24*), Powell (*21*), and Schwarzkopf and Kieffer (*25*) are listed in Table II. Some borides of elements in groups IV and V have melting points above 3000°C.

Boron carbide has long been thought to have a hardness next to that of diamond. Some of the other borides are extremely hard, also, and values can be found in tabulations by Powell (*21*), Schwarzkopf and Kieffer (*25*), and Samsonov and Markovskiĭ (*24*). Some values are given in Table II. Typical values range from 2250 to 3000.

The conductivity of the various metallic borides is almost metallic. The resistivity values are tabulated by Powell (*21*), Samsonov and Markovskiĭ (*24*), and Schwarzkopf and Kieffer (*25*) and typically run between 10 and 100 μohm-cm. Some of the values are given in Table II.

One of the interesting properties of the metallic borides is their superconductivity. This property has been observed for some of the nickel, tantalum, and molybdenum borides. Some of the phases have rather high curie points.

Lafferty (*14*) has pointed out that the thermionic emission of some of the refractory borides is very good and has suggested that this property may make them excellent cathodes.

Some work has been done on the Hall coefficient and the magnetism of the borides, but considerably more needs to be done.

Uses

The potential uses of refractory borides depend mostly on the nuclear properties of boron, the thermal stability, the high conductivity, the high hardness, and the

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chemical inertness of the various phases. They have been suggested as possible nuclear control rods, turbine blades, rocket motors, tools, sliding contacts, high temperature crucibles, chemical apparatus, catalysts, abrasives, thermocouples, and thermistors. Their use has not been extensive, but the future may see greatly increased application.

Present Status

Our present knowledge concerning the refractory borides is very incomplete, and the possibilities for future use are not clear. These compounds have many attractive features for high temperature application, but the promise suggested by these properties has not yet been fulfilled. The relationships among their structures and their bonding are very interesting problems. There are enormous gaps in our knowledge of their properties, especially their thermodynamic properties, their chemical reactions at high temperature, and their mechanical, electrical, and magnetic behavior. Very little work has been performed on ternary systems.

The borides should prove to be a fertile field for much needed fundamental research. Not a great amount of research is being performed, but among the most active are the Russian workers.

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Preparation of Diborane

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Diborane was first isolated by Stock from the pyrolysis product of tetraborane, prepared by acid hydrolysis of magnesium boride. In 1931 Schlesinger and Burg prepared diborane by passing hydrogen and boron trichloride through an electric discharge. About 1944 the first essentially quantitative process for preparing diborane was developed by Schlesinger and Brown. It used lithium hydride to reduce boron trifluoride in diethyl ether. This method was used by Callery to prepare the first commercial quantities of diborane. In 1947 Hurd prepared diborane by passing a stream of boron halide and hydrogen through beds of active metals. Several methods using sodium borohydride were later developed. The method preferred at present involves its reaction with boron fluoride in the dimethyl ether of diethylene glycol.

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Flammable hydroboron gases were first observed at least a century ago. Some of the early workers assigned a formula BH_3 to the products. However, diborane was first isolated and characterized by Alfred Stock in his ingenious vacuum apparatus in 1912. In his preparation boric oxide was reduced with excess magnesium to form magnesium boride. This was hydrolyzed to give chiefly tetraborane, with yields of the order of 5%. This in turn was decomposed or disproportionated to all the other known boranes (*19*).

$$\text{Mg (excess)} + B_2O_3 \rightarrow MgB_2 + Mg + 3MgO$$

$$MgB_2 + Mg + HCl \rightarrow B_4H_{10} + H_2 + MgCl_2$$

$$B_4H_{10} \rightarrow B_2H_6 + \text{other boranes}$$

About 1930 work on the boron hydrides was begun at the University of Chicago under the direction of H. I. Schlesinger. His first publication in the field reported the first direct method of preparing diborane. Boron trichloride and hydrogen were passed through an electric discharge to give some diborane, but chiefly hydrogen chloride and chlorodiborane. This in turn reversibly disproportionated to boron trichloride and diborane, and the diborane was removed by low temperature fractional distillation (*16*):

$$2BCl_3 + 5H_2 \xrightarrow[\text{discharge}]{\text{electric}} B_2H_5Cl + 5HCl$$

$$6B_2H_5Cl \leftrightarrows 5B_2H_6 + 2BCl_3$$

Boron trichloride is generally prepared from boric oxide as follows:

$$2B_2O_3 + 7C \xrightarrow{2000°C.} B_4C + 6CO$$

$$B_4C + 8Cl_2 \rightarrow 4BCl_3 + CCl_4$$

A plausible reaction mechanism was postulated according to the following equations (*17*):

$$BCl_3 \rightarrow BCl_2 + Cl$$

$$H_2 + 2Cl \rightarrow 2HCl$$

$$(2BCl_2 + H_2 \rightarrow 2BCl_2H \rightarrow B_2Cl_4H_2)$$

or

$$2BCl_2 \rightarrow B_2Cl_4 \xrightarrow{H_2} B_2Cl_4H_2$$

$$3B_2Cl_4H_2 \rightarrow B_2H_6 + 4BCl_3$$

By this method yields based on boron trichloride were boosted to the order of 50% and production rates were increased from grams per year to grams per week.

This was the method of choice until the years of World War II, when work on the alkali metal borohydrides by Schlesinger and Brown's group at Chicago led to the use of boron trifluoride–etherate with lithium borohydride or lithium hydride in the first relatively quantitative preparations of diborane (*12*, *15*). This reaction was studied at a number of laboratories. It was found necessary to add a catalyst to avoid a "surge" reaction. All the catalysts were such as to cause a smoother rate of solution of the lithium hydride to form an intermediate borohydride or substituted borohydride.

$$4LiH + BF_3 \xrightarrow{\text{catalyst}} LiBH_4 + 3LiF$$

$$\text{Catalysts: } B_2H_6 + 2LiH \rightarrow 2LiBH_4$$

$$B(OCH_3)_3 + LiH \rightarrow LiB(OCH_3)_3H$$

$$3LiBH_4 + BF_3 \rightarrow 2B_2H_6 + 3LiF$$

If the reaction was not kept under pressure or left uncatalyzed, the by-product was generally lithium fluoborate, resulting in a much greater consumption of boron fluoride (*3*):

$$6LiH + 8BF_3 \rightarrow B_2H_6 + 6LiBF_4$$

This method was used by Jackson and coworkers at Callery to produce in glassware the first pound quantities of diborane. The work was done for Mine Safety Appliances Co. A pilot plant was then set up which used ether saturated with diborane to dissolve the lithium hydride. The solution was allowed to react with boron trifluoride–etherate. Yields of about 90% were obtained, with about 95% purity. The major impurity was ethane from some cleavage of the ether.

In 1947 Hurd reported (*9*) and patented (*10*, *11*) a synthetic method in which mixtures of hydrogen and boron halide were passed through beds of active metals at 200° to 400°C., the chief products being diborane and monohalodiborane. Metals used included alkali metals, alkaline earths, magnesium, zinc, and aluminum. The boron hydrides were separated from the gaseous products by fractional distillation at −190°C. A suggested modification (*10*) included the addition of a salt to form a liquid eutectic with the halide of the active metal. The eutectic drained away from the contact mass and was easily separated from the reaction products. Conversion was about 30%, with yields of diborane plus monohalodiborane totaling about 50%.

Price (*6*) reported that the reaction of boron chloride, hydrogen, and aluminum proceeds smoothly above 350°C., with conversion not exceeding 30%. The presence of the metal makes the reaction thermodynamically favorable.

Modifications of the metal hydride–boron halide method include the use of magnesium borohydride (*21*), lithium aluminum hydride (*5, 18*), calcium aluminum hydride (*4, 13*), or aluminum hydride as reducing agents, boron trichloride as the boron carrier (*7*), and dioxane (*4, 7*) and tetrahydrofuran (*3*) as the solvents; the use of the latter solvent requires an efficient stripping column to recover the diborane.

$$3Mg(BH_4)_2 + 2BCl_3 \rightarrow 3MgCl_2 + 4B_2H_6$$

$$3Ca(AlH_4)_2 + 8BCl_3 \rightarrow 3CaCl_2 + 6AlCl_3 + 4B_2H_6$$

$$3LiAlH_4 + 4BCl_3 \rightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$$

$$2AlH_3 + 2BCl_3 \rightarrow 2AlCl_3 + B_2H_6$$

$$6LiH + 2BCl_3 \rightarrow 6LiCl + B_2H_6$$

The last reaction gives 70 to 77% yields of diborane and is of interest because lithium is more readily recovered from lithium chloride than from lithium fluoride for recycling (*1*).

With the establishment of Callery Chemical efforts were soon begun to develop improved methods for the preparation of diborane. The logical first step appeared to be the substitution of sodium hydride for the more expensive lithium hydride. A study of the reaction of sodium hydride with various boron compounds showed that elevated temperatures were necessary for reaction; the major hydrogen-containing product was invariably sodium borohydride. Boron halides, fluoborates, borate esters, and boric oxide were used as the boron source. The sodium hydride could be either preformed or formed *in situ*. However, in no case were more than trace quantities of volatile hydrides found.

$$4Na + 2H_2 + BF_3 \rightarrow NaBH_4 + 3NaF$$

$$4Na + 2H_2 + NaBF_4 \rightarrow NaBH_4 + 4NaF$$

$$4Na + 2H_2 + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$$

$$4Na + 2H_2 + 2B_2O_3 \rightarrow NaBH_4 + 3NaBO_2$$

While Schlesinger's group had earlier reported the preparation of diborane from sodium borohydride, yields were generally poor from the sodium borohydride produced at high temperatures. The sodium borohydride produced at Chicago had been made by the reaction of diborane with sodium hydrotrimethoxyborate and was possibly of a more open crystal form:

$$2NaBH(OCH_3)_3 + B_2H_6 \rightarrow 2NaBH_4 + 2B(OCH_3)_3$$

After considerable time spent on an almost Edisonian approach, it was found that sodium borohydride and anhydrous ferric chloride gave off appreciable quantities of volatile hydrides when heated together. This reaction also could be carried out in ether, for reasons which are still not understood. Optimum conditions included addition of the ferric chloride–ether solution in 10% excess at −5°C. followed by refluxing to disengage the diborane. In similar studies with lithium borohydride, Schaeffer found that at lower temperatures ferrous borohydride is stable and at higher temperatures iron boride is formed (*14*).

$$2FeCl_3 + 6LiBH_4 \rightarrow 2Fe(BH_4)_2 + 6LiCl + B_2H_6 + H_2$$

$$FeCl_3 + LiBH_4 \rightarrow FeB_2? + LiCl + H_2$$

Cupric chloride reacted similarly. Hydrogen chloride or the boron halides alone or in the presence of aluminum chloride would not react with sodium borohydride in ethyl ether.

Search was continued for suitable conditions for the reaction of sodium borohydride with either hydrogen chloride or the boron halides. The first success followed an experiment which involved overnight stirring of a charge of hydrogen chloride and sodium borohydride in a glass ball mill (*20*); a good yield of diborane was obtained. Boron trichloride also reacted to give good yields of diborane under these conditions.

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Meanwhile exploratory work continued in other areas. Attempts had been made to electrolyze sodium borohydride to yield diborane by anodic oxidation. However, the known solvents for sodium borohydride were ammonia derivatives (which reacted with the nascent borane to form amine-boranes) or hydroxyl compounds which solvolyzed the nascent borane.

$$2BH_4^- \xrightarrow{\text{anode}} B_2H_6 + H_2 + 2e$$

$$BH_3 + NR_3 \rightarrow R_3N{:}BH_3$$

$$BH_3 + 3HOR \rightarrow B(OR)_3 + 3H_2$$

Melts of mixed borohydrides and low-melting mixtures of alkali metal halides with aluminum halides were investigated. Although lithium borohydride is the only alkali metal borohydride melting with little decomposition, a eutectic of lithium and potassium borohydride was found to melt at 100°C. and a ternary eutectic with sodium borohydride at 95°C., certainly unusually low for salt melts (Figures 1 and 2).

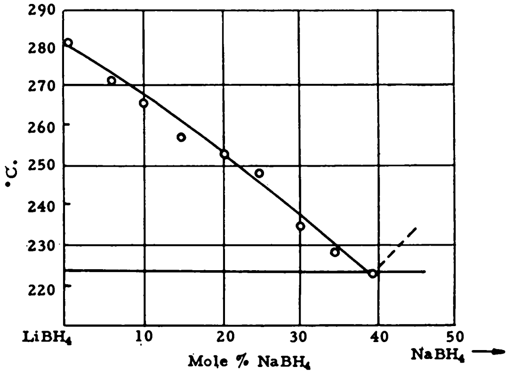

Figure 1. Phase diagram of $LiBH_4$-$NaBH_4$

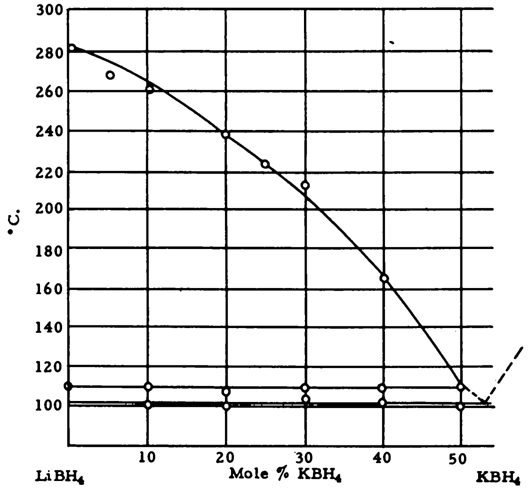

Figure 2. Phase diagram of $LiBH_4$-KBH_4 system

Electrolysis of these eutectic melts gave good current yields of diborane. However, at least part of the cathode product was lithium, which was undesirable for recycle. Reaction of these melts with hydrogen chloride also gave good yields of diborane.

During this period Ansul Chemical began production of the dimethyl ethers of the polyethylene glycols. The dimethyl ether of ethylene glycol had been tried earlier for the reaction of sodium borohydride and hydrogen chloride, and gave about 35% yield of diborane. Since sodium borohydride formed a diammoniate and a dihydrate and was unusually soluble in ethylenediamine, the sodium ion was apparently coordinating these solvents. Further encouragement came from the known greater reactivity of sodium aluminum hydride in dimethyl ether than in diethyl ether. Although work in this field has been published by others (*2*), the work at Callery was entirely independent and is recounted here.

Samples of the ethers were obtained for experiments. The code names are listed below.

Ansul	Callery	Ether	Brown (*2*)
E-121	M1M	Ethylene glycol dimethyl ether	Glyme
E-1414	M2M	Diethylene glycol dimethyl ether	Diglyme
E-161	M3M	Triethylene glycol dimethyl ether	Triglyme
E-181	M4M	Tetraethylene glycol dimethyl ether	Tetraglyme
	E2E[a]	Ethylene glycol diethyl ether	Diglyet
	M3E[a]	Triethylene glycol methyl ethyl ether	

[a] Carbide & Carbon.

The first sample received was M3M, and on reaction with hydrogen chloride or electrolysis, it showed abundant qualitative evidence of diborane formation. To determine the best ethers for investigation, the solubility of sodium borohydride in the

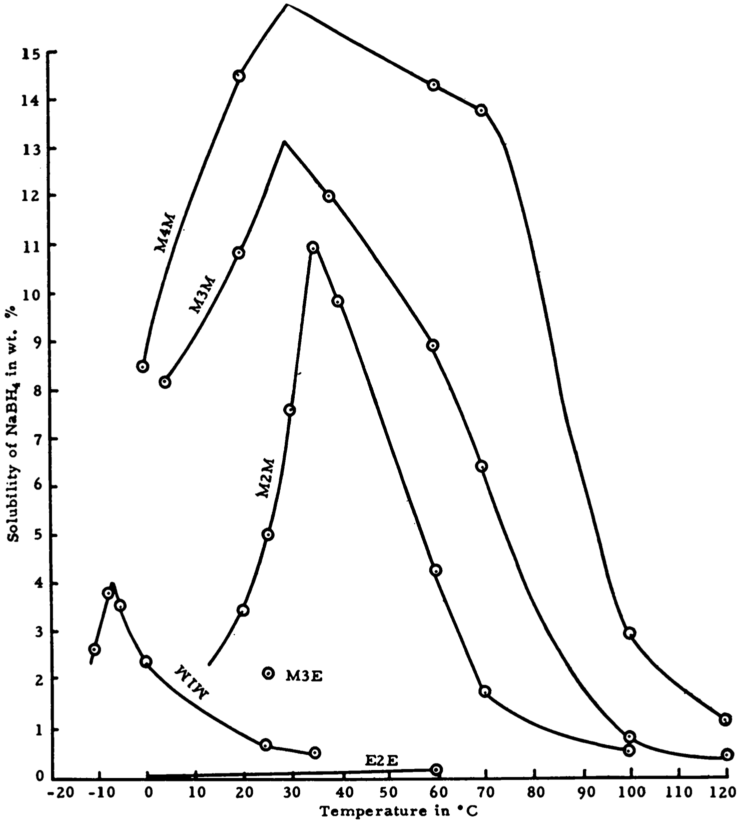

Figure 3. Solubility of sodium borohydride in polyethylene glycol ethers

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different ethers was investigated (Figure 3). Because M2M showed good solubility characteristics near room temperature, it was chosen for extensive investigation.

The electrolysis of sodium borohydride in M3M was also studied. While sodium plated out readily, it tended to float on the surface of the M3M and short out a simple cell. Hence, mercury was used as the cathode. An appreciable time lag was noticed between the start of electrolysis and the release of appreciable quantities of diborane. A plot of time *vs.* yield (Figure 4) indicated that approximately half the theoretical current was passed before diborane was evolved and that then it was released at twice the theoretical rate. The formation of an intermediate, $NaBH_4 \cdot BH_3$, was postulated, and its solution was found to be a considerably better conductor than that of sodium borohydride alone. A possible explanation is that sodium borohydride may be more highly associated in M2M solution than the adduct. In support of this thesis the low-temperature forms of all the alkali metal borohydrides are associated into long chains (*1*).

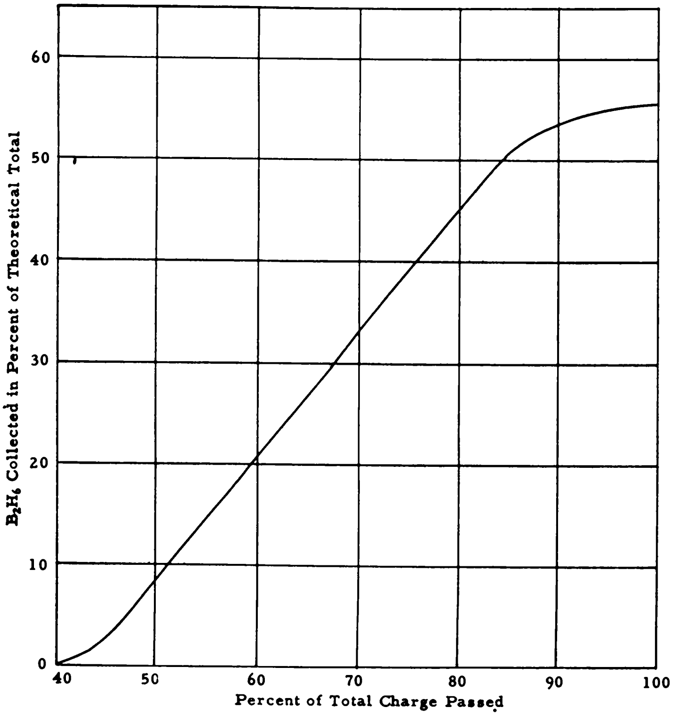
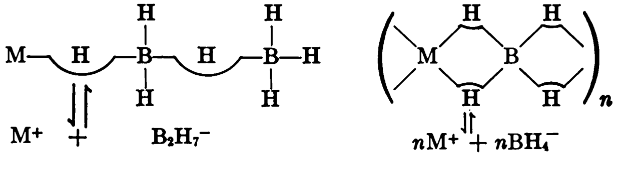


Figure 4. Electrolysis of $NaBH_4$ in tetraethylene glycol dimethyl ether with rotating graphite anode

Temperature < 60°C.



Because the reaction of hydrogen chloride with sodium borohydride "wastes" one of the four hydridic hydrogens, the use of the boron halides was tried. Boron fluoride, much the cheapest of the boron halides per mole, was investigated rather thoroughly.

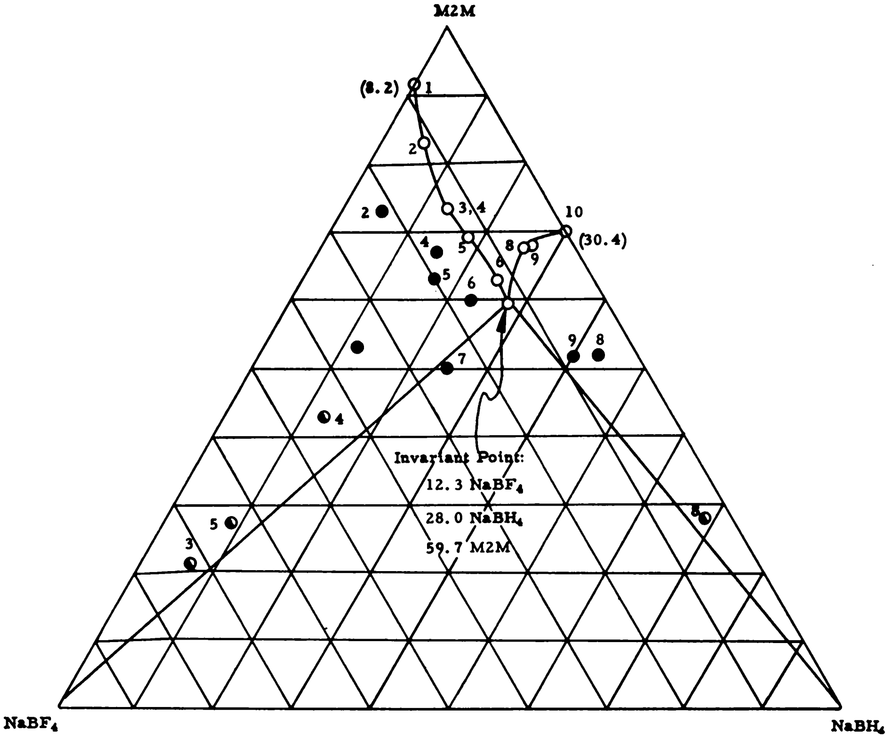


Figure 5. $NaBF_4$-$NaBH_4$-M2M system at 30°C. plotted in mole per cent

The reaction yields sodium fluoborate as a by-product, so the ternary system $NaBH_4$-$NaBF_4$-M2M was investigated for the area of maximum solubility (Figure 5).

The original engineering effort to utilize these solvents used E2E. However, it

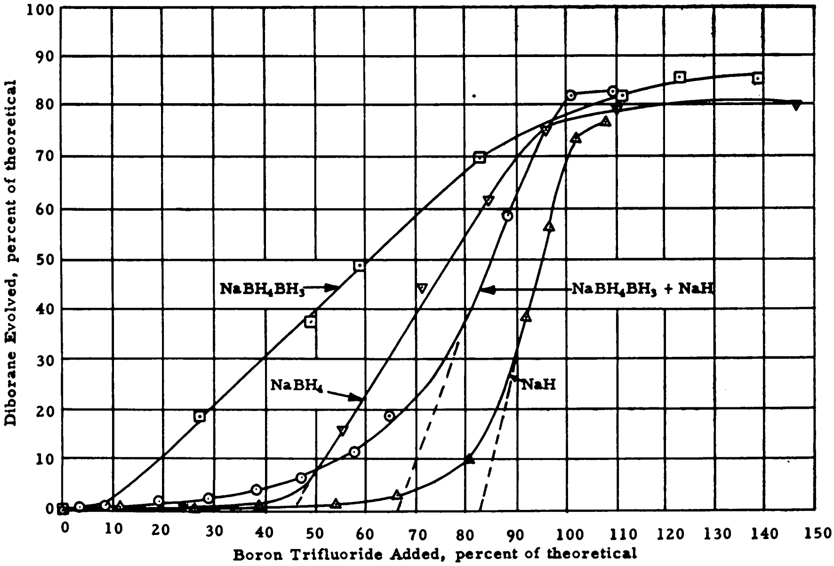


Figure 6. Evolution of diborane

was found to be unsatisfactory. The use of mineral oil as a diluent was permissible only so long as sufficient M2M was present to dissolve the by-product sodium fluoborate. In the engineering processing, the same intermediate, $NaBH_4 \cdot BH_3$, was encountered (Figure 6). The use of boron trichloride was found to be satisfactory in the laboratory, but in pilot plant units it caused too much ether cleavage.

The possibility of using sodium hydride directly with the boron halides in the polyethers was investigated. With boron fluoride good yields of diborane were obtained, but there was a steady build-up of dioxane in the ether medium, indicating attack on the ethers.

Recent experiments have shown that potassium borohydride works as well as sodium borohydride in these solvents. Since the solubility of potassium borohydride is only 0.013 gram per 100 grams of M2M, an explanation of this phenomenon is still needed. Figure 7 indicates that no intermediate KB_2H_7 is formed.

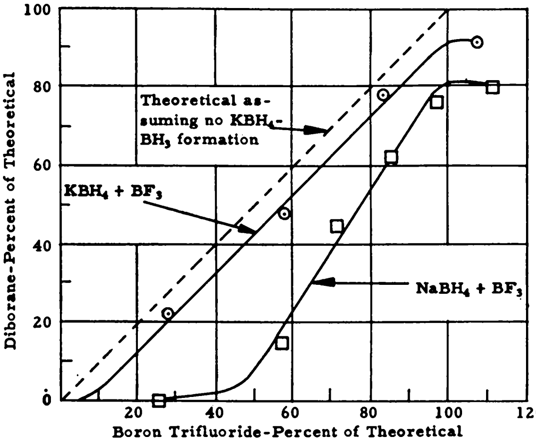


Figure 7. Reaction of potassium borohydride with boron trifluoride

A recent German patent reports a radically new approach. Formaldehyde is used to reduce tribromoborane over a copper catalyst at 400°C. (*8*).

$$HCHO + 2BBr_3 \xrightarrow[Cu]{400^\circ} B_2H_6 + HBr + CO + \text{side products}$$
$$25\% \text{ yield}$$

Other new and improved methods will doubtless be forthcoming.

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Tetraborane, a Review

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Tetraborane can be prepared by several methods which involve the action of acids on magnesium, aluminum, or beryllium borides, the hydrolysis of magnesium boride, the hydrogenation of a boron halide at elevated temperatures or in an electric discharge, and the pyrolysis of diborane at normal or at higher pressures. The physical and chemical properties as well as its structure are evaluated on the basis of the experimental data available.

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Tetraborane, B_4H_{10}, was the first of the boron hydrides definitely characterized as a chemical compound by Stock and Massenez (*20*) in 1912 in Germany. They prepared the compound by the action of hydrochloric acid on magnesium boride. The other boron hydrides were prepared and characterized later, also by Stock, the pioneer in this field. The American research in this field was started by Schlesinger and his coworkers at the University of Chicago. The more important of the boron hydrides, or boranes, with their physical properties are listed in Table I.

Table I. Physical Constants of the Boranes

Name	Formula	Melting Point, °C.	Boiling Point, °C.
Diborane	B_2H_6	−165.5	−92.5
Tetraborane	B_4H_{10}	−120	18
Pentaborane(9)	B_5H_9	−46.6	58
Pentaborane(11)	B_5H_{11}	−123	63
Decaborane	$B_{10}H_{14}$	99	213

Tetraborane is a liquid boiling slightly below room temperature, diborane is a gas, the two pentaboranes are liquids, and decaborane is a solid. Pentaborane(9) is often defined as stable pentaborane and pentaborane(11) is called unstable pentaborane.

This discussion reviews some of the properties of tetraborane and methods of preparation. The structure of tetraborane is first considered. Its infrared spectrum is depicted in Figure 1. There are absorption maxima indicating boron-boron bonds (8.754 microns), hydrogen-boron bonds (3.9 and 4.04 microns), and bridged hydrogen atoms (4.654 microns). These were verified in a later study by Lipscomb (*8*), who established its structure (Figure 2).

The diagram indicates how the components are bonded. One can note the bridged and nonbridged atoms in the molecule.

Stock's first reaction of hydrochloric acid on magnesium boride gave low yields of an impure product; nevertheless, it furnished limited quantities of tetraborane for initial studies.

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To provide larger quantities of material, Stock and Kuss (*19*) devised a semiautomatic electric apparatus to decompose kilogram quantities of magnesium boride with hydrochloric acid (Figure 3).

In an effort to increase the yields and purity of tetraborane, Stock and other workers investigated alternate reaction systems. Stock, Wiberg, and Martini (*23*) used phosphoric acid with borides and increased the yield of tetraborane to approximately 11%. Steele and Mills (*17*) also used phosphoric acid, but with aluminum borides, and obtained some tetraborane. This had the advantage of avoiding the formation of silicon hydrides, but the yields were not high. Wiberg and Schuster (*25*) added phosphoric acid to a mixture of magnesium and boric oxide and obtained 11% yields of tetraborane. In other work, Stock, Wiberg, and Martini (*24*) found that hydrochloric acid reacted with beryllium boride to give higher yields of tetraborane than the corresponding reaction with magnesium boride and it also avoided the silicon hydride by-product.

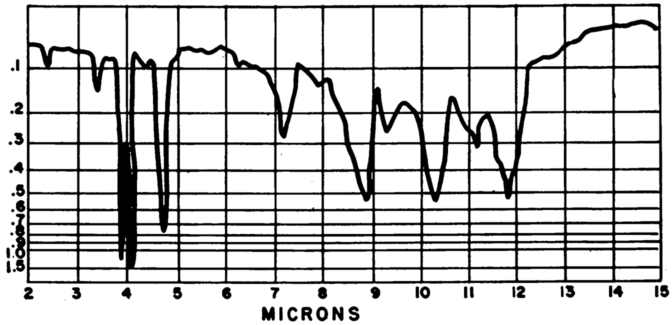

Figure 1. Infrared spectrum of tetraborane

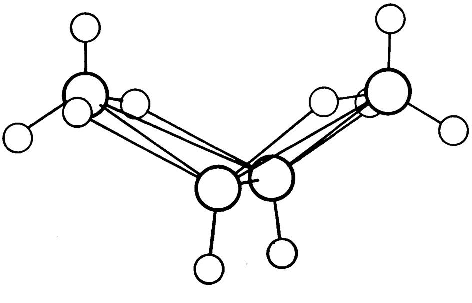

Figure 2. The molecular structure of tetraborane

Recently two Russian workers (*10*) made a comprehensive study of the reaction of borides with acid. They reduced boric oxide with sodium, lithium, beryllium, magnesium, and calcium, to prepare the borides. They also studied the borides of aluminum, iron, nickel, and manganese. The best yields of tetraborane were obtained from magnesium boride, by the reaction of boric oxide with magnesium.

These investigators also mixed magnesium and boron to obtain magnesium boride, and found that on hydrolysis it led to the highest yield of tetraborane, 14.5%, obtained so far. They also studied the effect of using various acids, including sulfuric,

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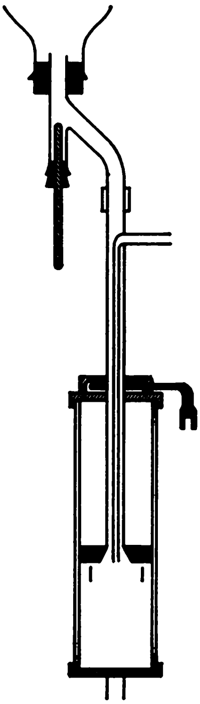

Figure 3. Apparatus for the mechanical transfer of boride into acid

hydrochloric, and phosphoric. With phosphoric acid the 14.5% yield of tetraborane was obtained. The equations follow:

$$2B + 3Mg \rightarrow Mg_3B_2$$

Mg_3B_2 + acid →	tetraborane, %
HCl	3
H_2SO_4	1
H_3PO_4	14.5

In a different approach to the problem, Stock and Pohland (*22*) synthesized tetraborane by the reaction:

$$2B_2H_5I + 2Na \rightarrow B_4H_{10} + NaI$$

The reaction, however, is not suitable for the preparation of large quantities of the compound.

In 1952, a patent was issued to Hurd (*6*) for the preparation of boron hydrides, including tetraborane. His method involved the reduction of a boron halide with hydrogen at 150° to 400°C. in the presence of an active metal hydride.

Boron halide + hydrogen + metal hydride → boron hydride + metal halide

BF_3	LiH
BCl_3	NaH
BBr_3	KH
BI_3	BaH_2
	CaH_2
	SiH_4

At the temperatures used, it is probable that diborane was the first borane formed, which then was pyrolyzed to tetraborane, pentaborane, etc., rather than having the higher hydrides directly synthesized.

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One of the major steps in the study of boranes was the hydrogenation of boron trichloride or bromide in an electric discharge (*15*). In this method, pure hydrogen is allowed to bubble through liquid boron trichloride at —40°C. and the resulting mixture is led through a 12- to 15-kv. discharge at a pressure of 10 mm. The apparatus is shown in Figure 4. The resulting mixture is condensed, the hydrogen is removed, and the other products are fractionated. Diborane was the principal product from which the unstable pentaborane(11) was made; the latter reacted in turn to form the tetraborane (*1*).

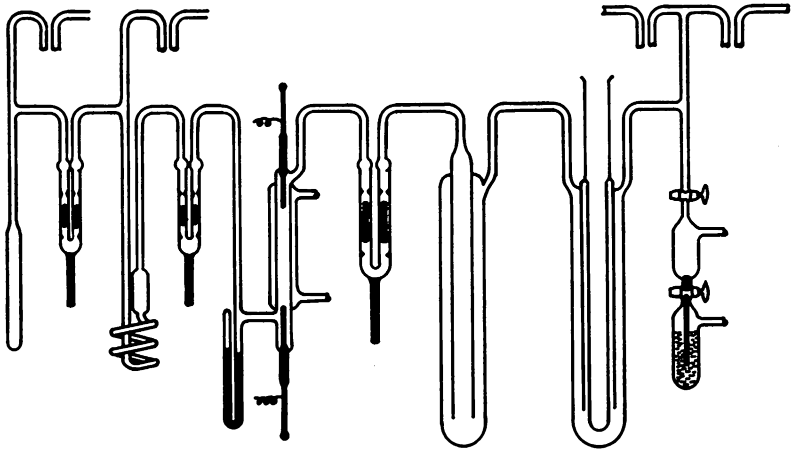

Figure 4. Electric discharge apparatus

This was accomplished by allowing the diborane to flow through a U-tube heated at 115°C. The flow of diborane was controlled by a capillary tube so as to make the treatment equivalent to a 3-minute heating of a stationary sample. This procedure gave the unstable pentaborane(11). Tetraborane was obtained by heating a 10 to 1 mixture of hydrogen and pentaborane(11) for 10 minutes in a bulb at 100°C.

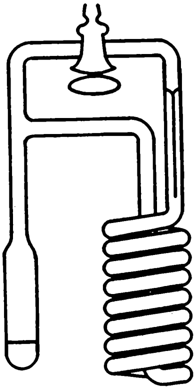

Figure 5. Pyrolysis apparatus (Burg and Stone)

Burg and Stone (*2*) more recently developed an apparatus for conveniently preparing pentaborane(11) (Figure 5). The diborane passes from the tube at —78°C. through the coil at 120°C. and is trapped in the vacuum system beyond it. The pentaborane(11) is then transferred from the coil to a bulb for treatment with hydrogen to yield the tetraborane.

Still another method for the preparation of tetraborane was discovered by Schlesinger (*16*) and his coworkers at the University of Chicago. They reduced tetrachlorodiborane (*4*) with lithium or aluminum borohydrides. The equation can be written:

$$B_2Cl_4 + 4LiBH_4 \rightarrow B_4H_{10} + B_2H_6 + 4LiCl$$

The diborane can be readily separated from the tetraborane. One of the chief difficulties with the method is the preparation of the tetrachlorodiborane (*4*). This compound is difficult to obtain and no satisfactory method has yet been reported for its preparation on a large scale.

Stock and Mathing (*21*) were among the first to prepare tetraborane by the pyrolysis of diborane. They used the system shown in Figure 6, consisting of a heated tube, a circulating pump, and a trapping system. At 180°C., for 21-hour reaction time, the yield of tetraborane was 22% with a 56% conversion of diborane.

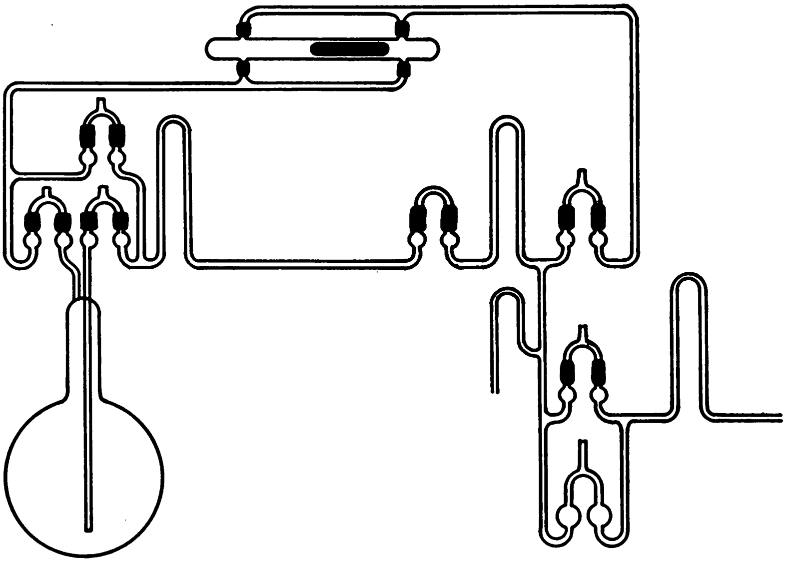

Figure 6. Pyrolysis apparatus (Stock and Mathing)

McCarty and DiGiorgio (*9*), in a study on pyrolysis, obtained some information on the preparation of tetraborane, although preparation of this material was not the primary object of the work. The apparatus they employed (Figure 7) consisted of an 11.5-liter elongated bulb, a bellows pump, heated reactor, and a trapping system. It appears from their data that lower temperatures favor the formation of tetraborane.

A variation of the heated tube method, for tetraborane preparation, was reported by Klein, Harrison, and Solomon (*7*). Their system employed a hot zone at 120°C. and a cold zone at −78°C. for the treatment of diborane. With this apparatus they realized a yield of 80 to 95% of tetraborane. In this pyrolysis, some pentaborane(11) was formed as a by-product.

The high pressure pyrolysis of diborane was another method explored for the preparation of tetraborane. Dillard (*3*) was the first investigator to do a significant amount of work using this approach. He observed that at room temperature, after 5 to 9 days, from 20 to 35% yields of tetraborane were obtained under pressures of approximately 50 atm. Similar yields could be obtained in a much shorter time—e.g., 8 hours—by heating the autoclaves to 50° to 75°C.

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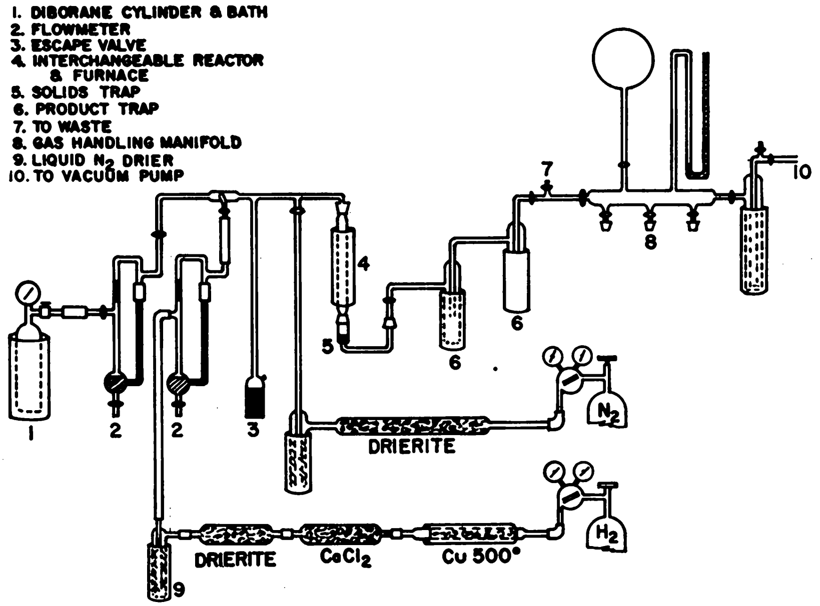

Figure 7. Pyrolysis apparatus (McCarty and DiGiorgio)

In studies at the Olin Mathieson Chemical Corp. laboratory (*11*) some of the work of Dillard was repeated and additional research was carried out.

A slightly different technique was employed, in that micro series autoclaves were used. These autoclaves and the auxiliary equipment are miniatures of standard high pressure apparatus. They enable one to perform experiments at high pressures with minimum quantities of materials. The chief advantage is, however, that expensive and elaborate equipment with controls, barricaded booths, etc., can be avoided. This technique has been found very useful. Figure 8 shows a diagram of the micro high pressure apparatus.

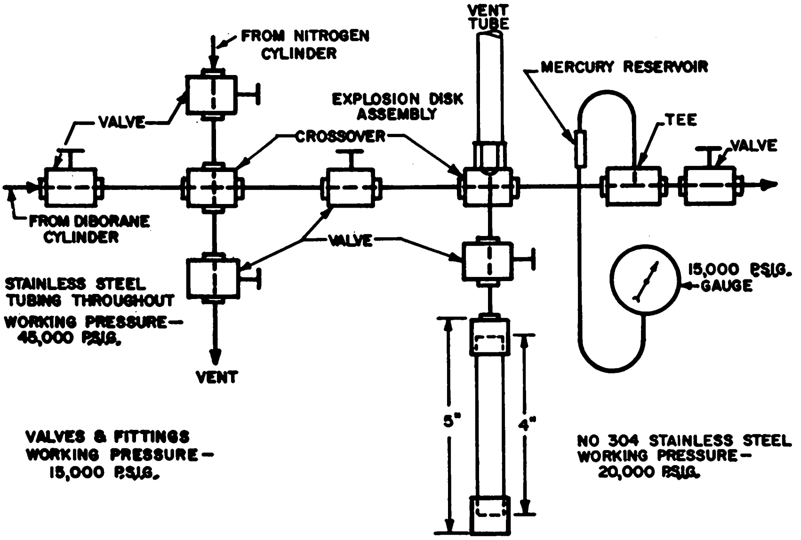

Figure 8. Micro high pressure apparatus

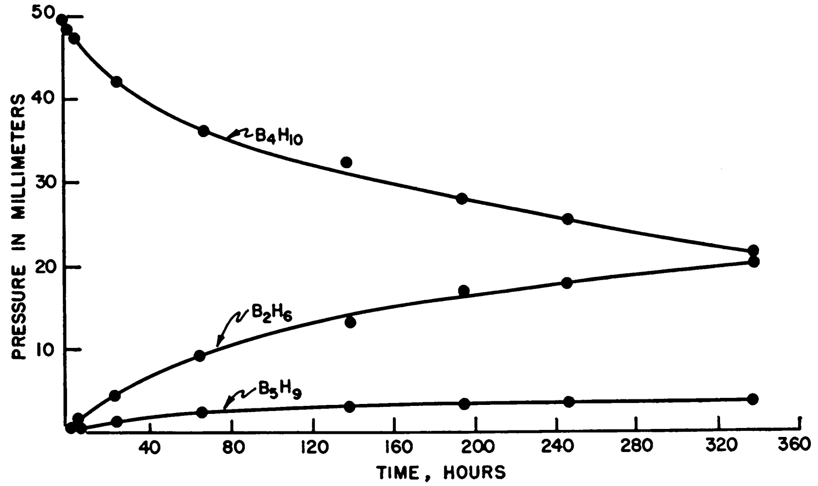

Figure 9. Conversion of tetraborane at 20°C.

Some of the other properties of tetraborane are of interest. Tetraborane has been reported by Stock (*18*) to be unstable at room temperature and to decompose slowly into diborane, the stable pentaborane(9), and some nonvolatile materials. This was verified by an experiment lasting 340 hours (*24*), in which tetraborane was placed in an infrared cell kept at 20°C. and its spectrum was recorded periodically. The data are presented in Table II and diagrammatically in Figure 9.

Table II. Conversion of Tetraborane at 20° C.

	Pressure, Mm.		
Time, Hours	B_4H_{10}	B_2H_6	B_5H_9
0	49	0	0
1.5	48	0.5	0
5[a]	47	1.5	0.5
22	42.5	4.3	1.5
68	36	9	2
140	32	13	2.5
195	28	16.5	3
245	25.5	17.5	3
340	21	20	3

[a] Solid deposits began to appear.

Pearson and Edwards (*13*) investigated the decomposition of tetraborane at higher temperatures, from 60° to 100°C. They noticed that the initial reaction products were diborane, pentaborane(11), hydrogen, and yellow solids, with pentaborane(9), decaborane, and hexaborane.

Tetraborane hydrolyzes slowly in water to form boric acid, and rapidly in alcohols such as methanol, to form trimethyl borate. It reacts with hydrogen chloride to form the unstable B_4H_9Cl.

Stock (*23*) reported that it forms an addition compound with ammonia, $B_4H_{10} \cdot 4NH_3$. Besides these and a few other reactions, the chemistry of tetraborane has not been reported to a great extent. In the last few years, however, its chemistry has been explored more widely. Parry (*12*) and coworkers have investigated the reaction of tetraborane with ammonia and have observed some interesting results. They reported a series of compounds of tetraborane with two, three, six, and seven molecules of ammonia, although there seems to be some doubt about the last material. To date, no tetraammonia derivative has been observed, corresponding to that reported by Stock.

The most interesting aspect of this work and of other recent work by Hough, Ford, and Edwards (*5*) on the reaction of Lewis bases with tetraborane, is the fact that it can be cleaved in a symmetrical or nonsymmetrical manner.

Figure 10 shows a diagram of diborane and tetraborane being cleaved in a symmetrical manner; the tetraborane is also being cleaved in a nonsymmetrical manner.

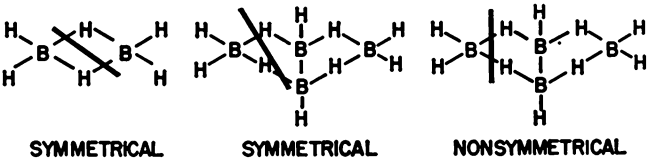

Figure 10. Cleavage of diborane and tetraborane

The symmetrical cleavage of tetraborane leads to H_3B and B_3H_7 fragments, while the nonsymmetrical cleavage produces H_2B^+ and $B_3H_8^-$. The materials $[H_2B(NH_3)_2]B_3H_8$ and $B_3H_7 \cdot NH_3$ have been prepared. They correspond to both the nonsymmetrical and symmetrical cleavage of tetraborane:

$B_3H_7 \cdot NH_3$	$[H_2B(NH_3)_2]B_3H_8$
Symmetrical cleavage	Nonsymmetrical cleavage

To prepare $B_3H_7 \cdot NH_3$, corresponding to the symmetrical cleavage, the reactions shown below were used.

$$B_4H_{10} + NaH \rightarrow BH_3 + NaB_3H_8$$

$$NH_4Cl + NaB_3H_8 \rightarrow NH_3B_3H_7 + NaCl + H_2$$

The compound NaB_3H_8 had been reported by Hough, Edwards, and McElroy (*4*) and the $NH_3B_3H_7$ was prepared by Parry.

Hough, Ford, and Edwards observed that compounds such as ethyl ether triborane, trimethylamine triborane, dimethyl sulfide triborane, and thiophene triborane could be prepared. These correspond to a symmetrical cleavage of the tetraborane. The above compounds and others whose triborane derivatives have been prepared are:

Ethyl ether
Pyridine
Trimethylamine
Dimethyl sulfide
Thiophene
Glycol ethers

In the above investigation, the reaction of trimethylamine with tetraborane led first to the formation of the amine borane and amine triborane. This latter compound reacted with additional trimethylamine to form an amine borane and a polymer. This reaction has also been investigated by Burg and Stone (*2*), who had observed that the ultimate reaction products were an amine borane and a polymer. This series of reactions is:

$$(CH_3)_3N + B_4H_{10} \rightarrow (CH_3)_3NB_3H_7 + (CH_3)_3NBH_3$$

$$(CH_3)_3NB_3H_7 \xrightarrow{(CH_3)_3N} (CH_3)_3NBH_3 + \text{polymer}$$

This type of research opens up a new field of chemistry with many possibilities of new compounds.

Finally, tetraborane appears to be an intermediate in the formation of other boranes and a great deal of work has been reported with regard to the role of tetraborane in this sequence of reactions. See, for example, (*14*).

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Mechanisms of Isotopic Exchanges in the Boron Hydrides

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The exchange of deuterium and boron-10 between diborane and several of the more common boron hydrides has been studied. Evidence has been accumulated for at least three mechanisms. In the diborane self-exchange the reaction appears to involve borane as an entity and the ratio of deuterium rate to boron rate is 3. In the B_2D_6–B_5H_9 exchange the rate-determining step is the reaction of borane with the terminal hydrogens of pentaborane. The bridge hydrogens are not involved. A similar situation exists in the diborane-decaborane exchange. In the B_2D_6–B_5H_{11} reaction the fraction-order kinetics indicate that the B_5H_{11} is fragmenting. All the borons and hydrogens in both molecules participate in the exchange. Only one rate of exchange has been observed, but there is experimental evidence that exchange can proceed by an intramolecular mechanism. In the B_2D_6–B_4H_{10} reaction one has at least two mechanisms of isotopic exchange and evidence of an exchange by an intramolecular mechanism. The intramolecular process is an indication of the lability of the hydrogens and the borons in some of the less stable boron hydrides.

During the past several years a number of isotopic exchange reactions involving the more common boron hydrides have been investigated in this laboratory to shed some light on the role of borane as an intermediate in boron hydride chemistry. It was expected that a difference in exchange reactivity would be observed on a study of the exchangeability of terminal hydrogens as contrasted with bridge hydrogens. The question of lability of hydrogens and borons in the less stable boron hydrides also arose and it was expected that evidence of intramolecular exchange studies would be helpful in answering questions associated with this phenomenon. It was also felt that the exchange studies between the various boron hydrides would be a necessary prerequisite to any further studies that might be undertaken to see how the boron hydrides are built up in pyrolysis reactions utilizing isotopes of hydrogen and boron as tracers. Some information has been obtained in answer to some of the above questions but much still remains to be done.

The evidence of three mechanisms for isotopic exchange in the boron hydrides is presented:

The exchange of boron and hydrogen in situations which appear to involve borane as an intermediate.

In BORAX TO BORANES;
Advances in Chemistry; American Chemical Society: Washington, DC, 1961.

The exchange of hydrogen in boron hydrides which proceeds by exchange between borane and terminal hydrogens and does not involve bridge hydrogens.

Cases in which exchange is brought about by an intramolecular mechanism.

Isotopic Self-Exchange in Diborane

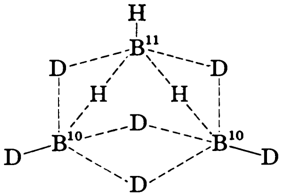
The self-exchange of deuterium in diborane was first studied by Maybury and Koski (*8*). Deuterated diborane and protonated diborane were permitted to react, and the rate of disappearance of completely protonated diborane was followed with an infrared spectrometer. The reaction was studied as a function of pressure and temperature. A total order of 1.5 and an activation energy of 21.8 ± 3 kcal. were reported.

A possible mechanism was proposed as consisting of a rapid equilibrium between diborane and borane, which was followed by a bimolecular rate-determining collision between borane and a diborane molecule. The implication was that borane was exchanging as an entity. There was some qualitative support to this view in later work by Shapiro and Keilen (*11*), who showed by mass spectroscopic measurements that there was a self-exchange of boron in diborane. However, no quantitative kinetic measurements were made.

Exchange studies with diborane and other boron hydrides showed that there was another mode of exchange of deuterium that involved only terminal hydrogen bonds and not bridge bonds. The question immediately arose whether, in the diborane self-exchange reactions, there was a mixture of exchange mechanisms which involved the exchange of borane as an entity as well as the attack of borane on the terminal hydrogen position of diborane. Such a complication could not be resolved with the above-mentioned data. The question could be answered by a quantitative kinetic comparison of the deuterium self-exchange and boron-10 self-exchange in diborane. Such experiments are under way in this laboratory; the reaction is being followed with infrared spectroscopy. Although the technique has not been completely satisfactory, it appears that the half life of the boron-10 and the deuterium exchange are the same, indicating that three deuteriums are entering the molecule for each boron-10. This, if further confirmed, would tend to exclude any appreciable amount of the deuterium self-exchange proceeding through the attack of a terminal hydrogen by a deuterated borane, at least under the experimental conditions used. However, there are still some questions about this mechanism that are not answered. One might ask, if a borane reacts with diborane

$$B^{11}H_3 + B_2{}^{10}D_6 \rightarrow B^{11}H_3 - B^{10}D_6 + B^{10}O_3 \qquad (1)$$

does it enter the diborane molecule as an entity or is an intermediate such as B_3H_9 formed?



The hydrogens and borons scramble, and on dissociation an average ratio of deuterium to boron exchange rates of 3 would still be obtained.

Exchange of Deuterium between Borane and Terminal Hydrogens in Boron Hydrides

Another type of exchange mechanism that occurs in some of the more stable boron hydrides is the exchange of deuterium between a deuterated borane derived from diborane and a terminal hydrogen of a boron hydride such as pentaborane or decaborane.

The exchange of deuterium between diborane and pentaborane was investigated by Maybury and Koski (*9*) and others. The objective of these studies was to get some insight into the mechanism of the exchange reaction and to see if there was any difference in the exchange rates involving bridge and terminal hydrogens in pentaborane. The purely chemical investigation consisted of reacting deuterated diborane and pentaborane at temperatures ranging from 40° to 100°C. and studying the rates of exchange as a function of concentration. The exchange followed the conventional rate expression

$$Rt = -\frac{ab}{a+b}\ln(1-f) \tag{2}$$

where a and b are the diborane and pentaborane concentrations, respectively, and

$$f = \frac{D_0 - D_t}{D_0 - D_\infty} \tag{3}$$

when D_0, D_t, and D_∞ are the deuterium contents in diborane at time = 0, time = t, and time = ∞, respectively. The rate, R, of the reaction is related to the concentrations by the expression

$$R = ka^\alpha b^\beta \tag{4}$$

where α and β are the orders and k is a constant. A plot of log R versus log of concentration of the appropriate species gives a line with a slope equal to the order of the reaction with respect to this species. Slopes of 0.50 and 0.97 were obtained for diborane and pentaborane, respectively, indicating that the reaction was 0.5 order with respect to diborane and first order with respect to pentaborane. An activation energy of 27 kcal. per mole was measured. The reaction showed no dependence on the surface.

Some experiments were carried out to obtain exchange between deuterium gas and pentaborane. For contact times up to 48 hours and temperatures up to 180°C., no exchange was observed. However, the exchange between deuterium and pentaborane has been achieved catalytically using chromium oxide catalysts (*1*).

Experiments using boron-10 as a tracer revealed that the borons did not participate in the exchange reaction.

If only a simple exchange reaction were involved, it would be expected that, by permitting the reaction to proceed for a long time, the deuterium content of the pentaborane would become constant and the number of hydrogen positions that were participating in the exchange could be calculated. This does not occur, for there is a complicating side reaction which arises in the formation of deuterated pentaborane from the pyrolysis of diborane. In order to get around this complication, a mass spectrometric study (*4*) was made of this exchange. By studying the distribution of the partially deuterated pentaborane species, it was possible to show that only 5 hydrogens in the pentaborane were involved in the exchange. These studies, however, did not permit the unambiguous determination of which hydrogens—bridge, terminal, or both—were involved in the exchange except by implication from the fact that 5 hydrogens were exchangeable in pentaborane.

An infrared spectral study (*3*), a technique that enabled exchange in the bridge and terminal positions to be followed readily, indicated that only the terminal hydrogens of pentaborane participated in the exchange. Bridge hydrogens were not involved at all. A similar conclusion was reached in the diborane-decaborane exchange (*2*).

A nuclear magnetic resonance study has also been made of the diborane-pentaborane exchange reaction (*5*). This study confirmed the infrared study and gave the additional information that the rate of exchange of the apex hydrogen in pentaborane with diborane was the same to within experimental error as the exchange of the base terminal hydrogens. These results suggest the following mechanism: There is a rapid

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equilibrium between borane and diborane. The rate-determining step is the bimolecular collision of deuterated borane and a pentaborane molecule.

$$B_2D_6 \rightleftarrows 2BD_3$$

$$BD_3 + B_5H_9 \rightarrow BH_2D + B_5H_8D \qquad (5)$$

During this collision the borane interacts with the terminal hydrogens of the pentaborane and the deuterium exchange results. Neither the bridge hydrogens nor the borons are involved in the exchange under the experimental conditions.

Exchange of Boron and Deuterium between Diborane and Dihydropentaborane, B_5H_{11} (6)

Dihydropentaborane is appreciably less stable than pentaborane and a number of questions arise concerning its properties: Does it dissociate into simpler fragments? Are the hydrogens and borons labile—i.e., do they interchange their positions by intramolecular exchange?

The experimental procedures used for this study were similar to those outlined

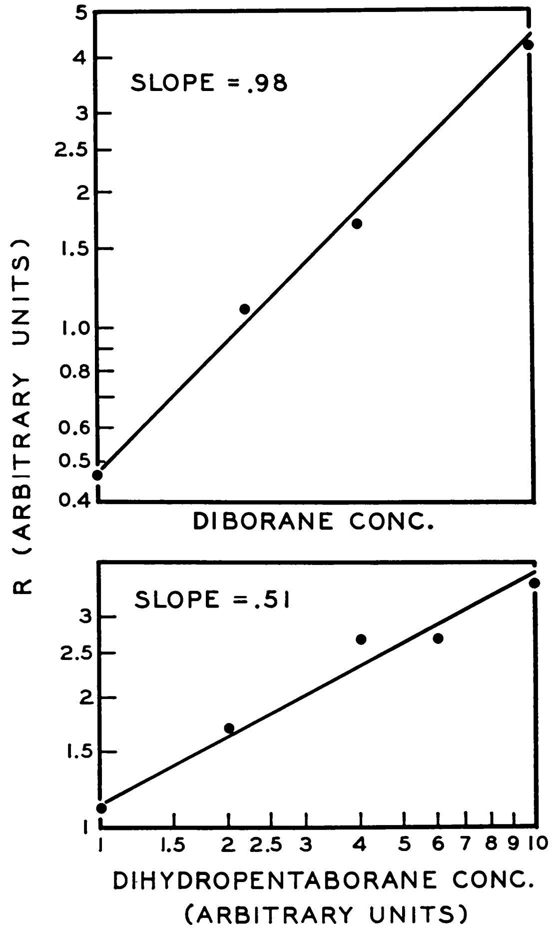

Figure 1. Plot of log *R* vs. log concentration to determine order of B_2D_6–B_5H_{11} exchange reaction

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previously. Diborane labeled with deuterium or boron-10 or both was permitted to react with dihydropentaborane, and the products were separated at various times and analyzed for their deuterium content. The rate of exchange was determined from the exchange law mentioned above. The rates were studied as a function of concentration. In both exchanges—namely, the deuterium and boron-10 reactions—the order was 1.0 with respect to diborane and 0.5 with respect to dihydropentaborane.

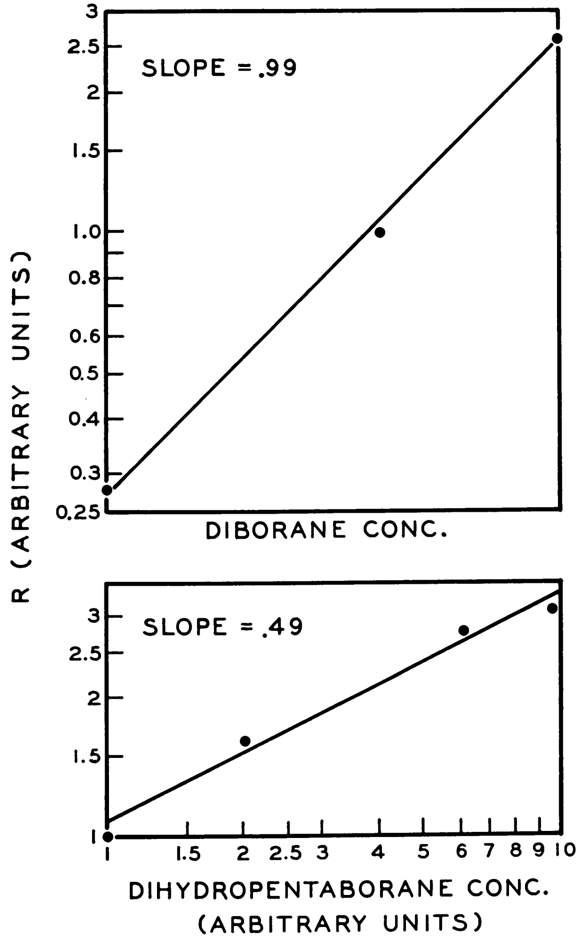

Figure 2. Plot of log *R* vs. log concentration to determine order of $B^{10}H_6$–B_5H_{11} exchange reaction

Typical results are shown in Figures 1 and 2. The reaction rate did not show any measurable dependence on the ratio of surface to volume. It was further established that in this exchange reaction all of the hydrogens and the borons in the dihydropentaborane were involved in the exchange. The exchange involving deuterium seemed to be controlled by a single rate-determining reaction—i.e., all of the deuteriums appeared to be exchanging at the same rate. A similar situation was found for the boron atoms; however, the constant, k, determined from the expression, $R = kA^{\alpha}B^{\beta}$, was about twice as large for the deuterium case as for the borons. Some

Table I. Rate Constants for Deuterium and Boron-10 Exchange Reactions between Diborane and Dihydropentaborane

Run[a]	Diborane, Moles/Liter × 10^3	Dihydropentaborane, Moles/Liter × 10^3	$R \times 10^4$	$k \times 10^2$
1	2.74	0.685	1.1	7.69
2	2.74	1.37	1.7	8.41
3	2.74	2.74	2.7	9.44
4	2.74	4.12	2.6	7.70
5	2.74	6.86	3.6	7.96
6	0.685	1.37	0.47	9.32
7	1.51	1.37	1.1	9.91
8	6.86	1.37	4.2	8.33
9	9.1	3.48	1.00	4.17
10	22.6	3.43	2.60	4.38
11	2.28	0.57	0.100	4.12
12	2.29	5.48	0.31	4.09
13	2.27	3.46	0.28	4.69
14	2.29	1.15	0.16	4.62
15	2.74	1.37	1.8	8.88
16	2.74	1.37	1.8	8.85
17	2.74	1.37	1.6	7.93

[a] Runs 1 to 8 are deuterium exchanges; runs 9 to 14 are boron-10 exchanges; runs 15 to 17 are deuterium exchanges where ratio of surface to volume is varied.

of these data are given in Table I. These experimental facts appear to be compatible with the following mechanism

$$B_5H_{11} \underset{k_4}{\overset{k_1}{\rightleftarrows}} X + Y$$

$$B_2{}^{10}D_6 + X \xrightarrow{k_2} \text{exchange} \tag{6}$$

The first reaction is a rapid equilibrium of dihydropentaborane with fragments X and Y. The X so produced undergoes a relatively slow rate-determining bimolecular collision with a deuterated diborane molecule. The exchanged fragment can then enter dihydropentaborane through the association step. The deuterium and/or boron-10 that has so entered the dihydropentaborane can distribute itself rapidly throughout the various positions of the molecule intramolecularly. This mechanism is consistent with the fact that the reaction showed a half-order dependence on dihydropentaborane concentration and a first-order dependence on diborane concentration.

If one uses the procedure recently outlined by Marcus (*7*) and applies the usual steady-state approximations to the proposed mechanisms, one can relate R to the rate constants of the elementary steps of the isotopic exchange. The result is

$$R = \frac{k_2(k_1k_4)^{1/2}\,(B_2{}^{10}D_6)(B_5H_{11})^{1/2}}{k_4 + k_2\left(\dfrac{k_4}{k_1}\right)^{1/2}\dfrac{B_2{}^{10}D_6}{(B_5H_{11})^{1/2}}} \tag{7}$$

If $k_4 >> k_2(k_4/k_1)^{1/2}\, B_2{}^{10}D_6/(B_5H_{11})^{1/2}$ and the second term in the denominator is neglected, then the expression for R gives a concentration dependence which agrees with the experimental results. This investigation sheds little light on the identity of the fragments, X and Y. In view of the important role that has been generally assigned to borane (BH_3) in boron hydride chemistry, one may be inclined to identify one of the fragments resulting from the dissociation of dihydropentaborane as borane.

In a previous study where the self-exchange of deuterium in diborane was investigated, it was postulated that the rate-determining step was a bimolecular collision between borane and a diborane molecule. If borane was the equilibrium product in the dissociation of dihydropentaborane, then the rate-determining step in the B_5H_{11}–B_2D_6 exchange would be the same as postulated in the diborane self-exchange reaction. The diborane self-exchange reaction is being re-examined and the study is being extended to include the boron exchange. The preliminary examination of the boron-10 self-exchange in diborane indicates that the half lives of the boron and deuterium exchanges are the same. The ratio of the *R* values for deuterium and boron-10 is 3 or the ratio of the *k* values would be unity.

Similar behavior might be expected in the case of the B_5H_{11}–B_2D_6 exchange as here the same rate-determining step would be involved if dihydropentaborane dissociated into borane. However, examination of the data in Table I indicates that the ratio of the rate constants is approximately 2. A possible explanation for this apparent discrepancy might be the following. When the deuterated borane recombines with an appropriate fragment to form dihydropentaborane, the deuteriums and borons exchange rapidly with the other positions in the B_5H_{11}. If in this intramolecular exchange the deuteriums exchange appreciably more rapidly (more than three times as fast) as the boron-10 atoms, one might expect to observe *R* ratios greater than 3.

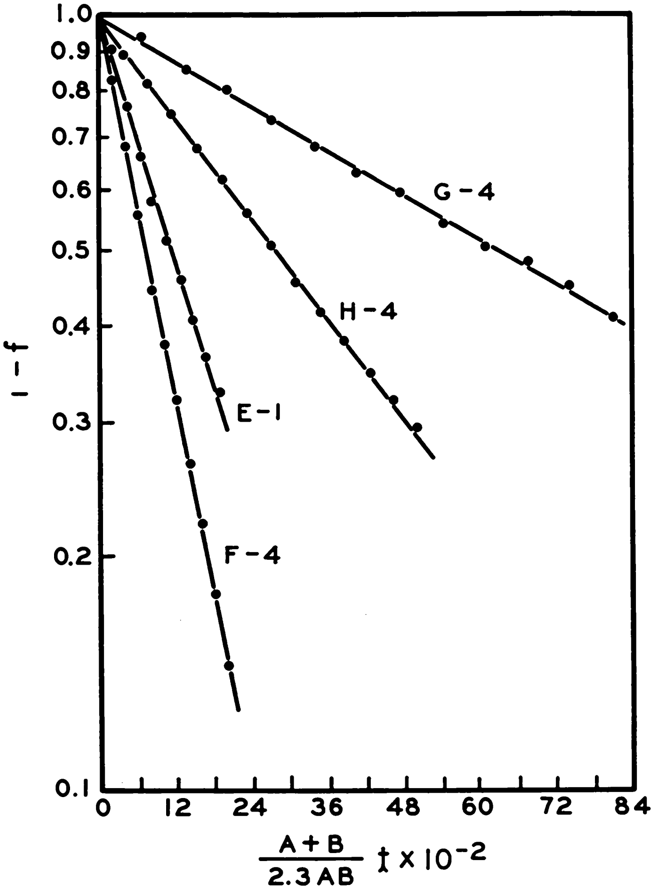

Figure 3. Typical plots of ln $(1 - f)$ vs. $\frac{A+B}{2.3AB} \times 10^{-2}$ for B_5H_{11}–B_2D_6 exchange reaction at various concentrations

G-4, 1.28 cm. B_2D_6; 2.56 cm. B_5H_{11}
H-4, 2.82 cm. B_2D_6; 2.56 cm. B_5H_{11}
E-1, 5.13 cm. B_2D_6; 5.13 cm. B_5H_{11}
F-4, 12.82 cm. B_2D_6; 2.56 cm. B_5H_{11}

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Exchange of Deuterium between Diborane and Tetraborane (12)

The B_2H_6–B_4H_{10} exchange is being studied with techniques similar to those described above. In its gross features this reaction appears to be more complicated than those mentioned above. In all of the boron hydride exchange reactions previously studied, the plot of $\ln(1-f)$ versus time was a straight line, indicating that the first-order exchange law was being obeyed and that exchange was controlled by a single rate-determining step. A typical set of plots for the B_2D_6–B_5H_{11} exchange is shown in Figure 3. In tetraborane the corresponding linear plot is not obtained (Figure 4).

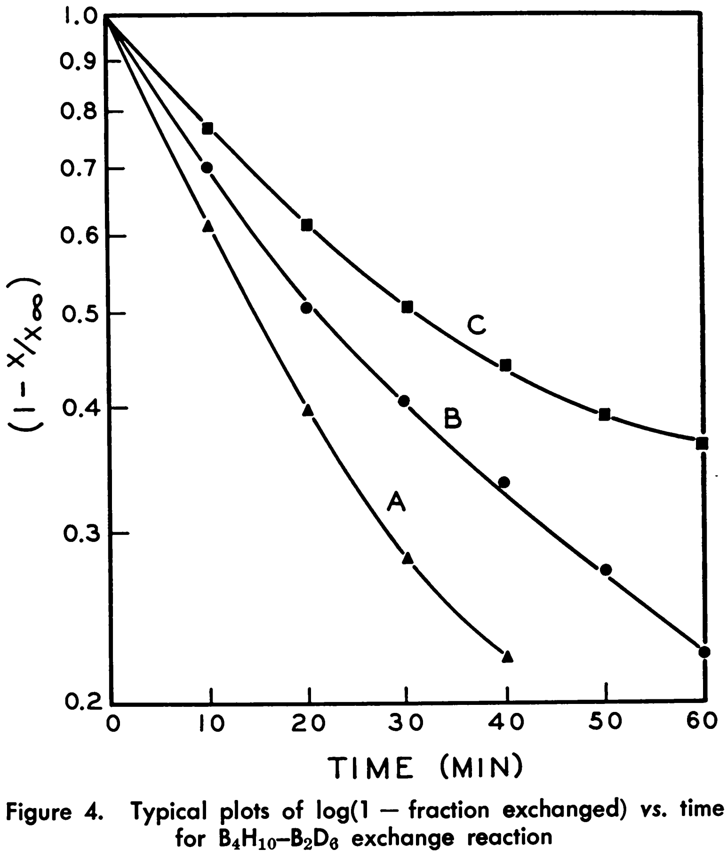

Figure 4. Typical plots of log(1 — fraction exchanged) *vs.* time for B_4H_{10}–B_2D_6 exchange reaction

B_2D_6 pressure, 10 cm.
Tetraborane pressure. *A* = 1 cm.; *B* = 3 cm.; *C* = 5 cm.

The curvatures in these plots indicate that exchange is proceeding by more than one rate-determining mechanism. The variation of the rate with concentration suggests that the more rapid exchange reaction is first order with respect to tetraborane and 0.25 order with respect to diborane. The slower reaction shows a 0.5-order dependence on diborane concentration and a first-order dependence on tetraborane. These studies to date have been made mainly at 45°C. Some boron-10 exchange studies have also been made and, although it is too early to draw final conclusions, the results in certain respects are similar to those obtained in dihydropentaborane. The ratio of deuterium to boron-10 exchange is greater than 3, indicating that deuterium is entering the tetraborane at an appreciably faster rate than the boron. The reactions show no dependence on the ratio of surface to volume and are probably homogeneous gas phase reactions. Examination of Equation 7 shows that if the second term in the denominator is greater than the first

$$k_2 \left(\frac{k_4}{k_1}\right)^{1/2} \frac{B_2{}^{10}D_6}{(B_4H_{10})^{1/2}} \gg k_4$$

then the rate should show a concentration dependence similar to that found in the tetraborane exchange. This would suggest that the rate-determining step of the fast exchange would be the dissociation of tetraborane, probably into BH_3 and B_3H_7 fragments, which have been postulated previously in boron hydride chemistry.

In some recent studies (*10*) on the decomposition of tetraborane, an equilibrium corresponding to

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

was suggested. To test if such an equilibrium might be operative under the conditions described here, an exchange was attempted between deuterium gas and tetraborane at 45°C. In running the reaction, no exchange was realized in 130 minutes, whereas under corresponding conditions appreciable exchange was realized when diborane was used as the source of deuterium. Therefore, it appears that the above equilibrium cannot be contributing significantly to the exchange. It is premature to assign a mechanism for the second slower exchange mechanism, but the attack of a BD_3 originating from diborane on the terminal hydrogens of the undissociated tetraborane cannot be ruled out at this point and would be compatible with the observations on pentaborane. The more rapid entrance of deuterium, as contrasted with boron-10, into the tetraborane would also be in harmony with these two mechanisms. The situation, however, seems to be even more complex than indicated by these two mechanisms. For example, if one permits deuterated diborane to exchange with tetraborane and then removes the diborane and studies the infrared spectra of the partially deuterated tetraborane as a function of time, one observes the following effect. The peaks which are due to terminal hydrogen vibrations drop in intensity, whereas the ones due to bridge hydrogen vibrations increase in intensity. The change in amplitudes of the peaks is small but appears to be quite outside of experimental error. If this observation is further confirmed, it would be fairly direct evidence for an intramolecular type of exchange that was mentioned in the case of the dihydropentaborane.

In summary, the exchange studies indicate the existence at least of three modes of isotopic exchange in the boron hydrides:

Exchanges where borane appears to be involved as an entity and the deuterium rate is three times the boron rate exchange. This mechanism seems to be most clearly exemplified in the self-exchange in diborane.

Exchanges where borane exchanges with terminal hydrogens and not with bridge hydrogens. This was the case in pentaborane and decaborane.

Intramolecular exchange which appears to be present in exchanges in dihydropentaborane and tetraborane.

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Kinetics and Mechanism for Acid-Base Reactions Involving Boranes

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One of the characteristic reactions of the boranes is their behavior as secondary Lewis acids. Subsequent to an initial "activation" which produces acid fragments, very rapid associations with atoms or groups which can donate electrons take place. In turn, these are followed by rearrangements and the splitting off of products. Results obtained in this laboratory and in two other laboratories on the rates of the gas phase reactions between boron trifluoride and various amine bases are discussed as model systems. Several experimental procedures have been devised which permit the estimation of the rate constants for these very fast associations. The generally accepted theory for the formation of donor-acceptor bonds is also reviewed briefly.

The exposition which is currently referred to as the "charge-transfer" theory has been presented in a number of publications by Mulliken (*63*, *67*) and is qualitatively illustrated in Figure 1. In the left diagram, as the donor-acceptor pair approach one another (r_{A-B} decreases), except for an initial weak Van der Waals type of attraction, there would be repulsion for all relative orientations, if these molecules maintained their original valence states. However, their electronic structures do change, so that, for some favorably oriented configurations, this adiabatic process does result in an attractive potential well.

One may formulate the latter as a linear combination of the ground state $[\psi_0(AB)]$ with an excited electronic state $[\psi_1(A^-B^+)]$, generated by removing an electron from the donor and placing it on the acceptor. The approach of the ion pair is controlled by an attractive potential, but at large r_{A-B} values the position of this surface lies above the ground state at a level which depends on the net energy gain $[\mathrm{I.P.}_B - \mathrm{E.A.}_A]$. Because of the readjustment of the electron configurations at small r_{A-B}, the ground state "repulsive" curve and the charge transfer "attractive" curve do not actually cross (noncrossing rule for states of same symmetry); they "combine" to produce the ψ and ψ^E curves.

The detailed shapes of the energy surfaces in the vicinity of the would-be crossover are dependent on many factors in a way which is too complicated for any available theory to predict. It is clear that a variety of stabilities for such a product are to be anticipated. One significant factor is the ionization potential of B; the larger it is for a specified electron affinity of A, the lesser the depth of the well in the $\psi(AB)$ surface. For a high enough I.P., the reaction path along the lowest electronic state may go through a maximum, as is indicated on the right in Figure 1, and under such circum-

In BORAX TO BORANES;
Advances in Chemistry; American Chemical Society: Washington, DC, 1961.

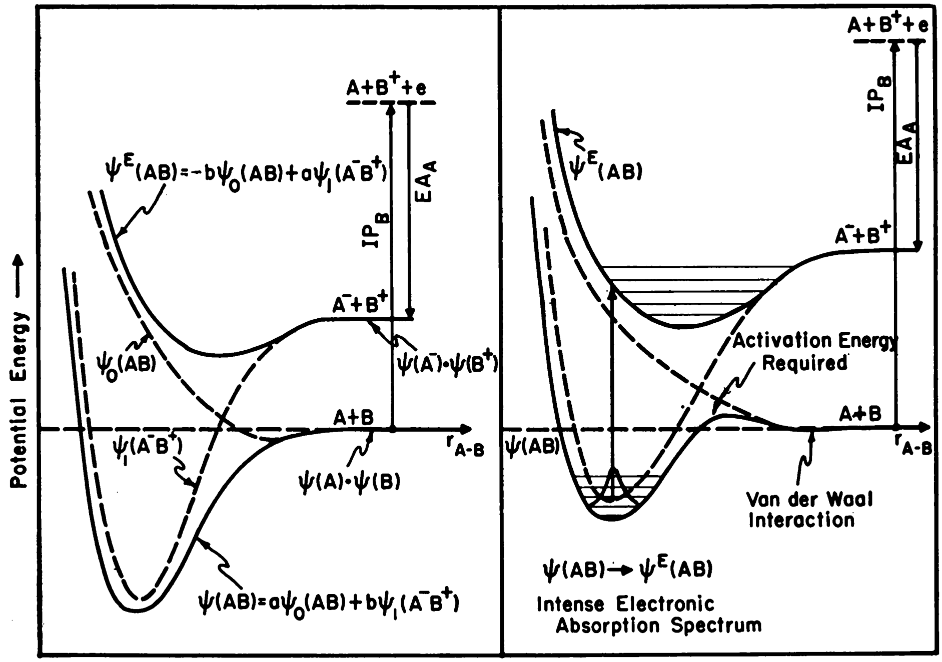

Figure 1. Schematic potential energy curves for charge-transfer compound formation

stances a heat of activation for association would be observed, paralleling a small $\Delta H^\circ_{\text{assoc.}}$. One should expect that in general the rates of association of Lewis acids and bases will be very rapid, except between relatively weak acids and weak bases. The thermodynamic relations which must be satisfied in such reactions have been discussed at length (*72*, *82*). Recent references to thermochemical data on BX_3 addition compounds are cited (*14*, *16*, *29*, *32*, *55*, *86*). Of particular interest are data on the reaction of diborane as a secondary Lewis acid (*7*, *12*, *26*).

Characteristically intense electronic spectra are to be expected (*63*) ($\psi \rightarrow \psi^E$ transition, Figure 1, right) even for very loose molecular complexes. These products have appreciable electric dipole moments, the magnitude of which depends on the coefficients *a* and *b* in the linear combination for the ground state. For example, the charge transfer complex formed between benzene and iodine has a moment of 0.70 *D*, whereas the moment of $Me_3N{:}BCl_3$ is 6.23 *D*. Many dipole moments for donor-acceptor systems have been summarized and discussed (*73*). Complex formation is accompanied by alterations in the geometrical configurations of the atoms or groups bonded to the acidic and basic centers. The changes are generally small in the basic unit but are appreciable in the acidic parent molecule; $(CH_3)_2O{:}BF_3$ (*5*) and $Me_3N{:}BF_3$ (*36*) are typical. In the formation of such complexes, the BF_3 unit becomes distorted from a planar to a pyramidal configuration, and the B—F bond distance increases from 1.295 A. to approximately 1.40 A. Finally, the infrared and Raman spectra of the addition compounds of boranes and a variety of bases have been reported recently (*25*, *27*, *75*, *87*, *94*).

Experimental Procedures

To date, three experimental procedures have been utilized to measure the rates of the very rapid association reactions. The rate constants are expected to be of the order

$$k_{\text{assoc.}} = 10^{14} \times 10^{-2} \times e^{-E_{\text{act.}}/RT} \text{ mole}^{-1} \text{ cc. sec.}^{-1}$$

with anybody's guess for an acceptable $E_{act.}$. Anticipating the conclusions, $E_{act.}$ probably ranges from 0, when both the acid and base molecules are "strong," to about 10 kcal., when one of these or both are particularly "weak."

First Method. An early and relatively unprecise method for determining rate constants depends on the measurement of a pressure drop resulting from the formation of a solid product upon the association of boron trifluoride with an amine (*6*). The decrement in pressure is followed manometrically in a diffusion-limited system. The over-all rate is thus slowed down, and the problem of properly mixing the reacting components at zero time is essentially bypassed.

The experimental arrangement consisted of a uniform-bore tube with an internal diameter in the range of 5 to 15 mm. A specially designed rapidly acting stopcock separated the boron trifluoride from the amine. Care was taken to adjust the pressures of the gases on the two sides of the stopcock so that they were exactly equal. Upon opening the stopcock, the pressure was followed as a function of time by means of a very sensitive automatic recording pressure transducer.

As the theory for this experiment is rather involved, no details are presented here. Attention is called to the need for a double extrapolation in order to evaluate the rate constant. One must extrapolate to zero time to determine the initial slope for the pressure decrement, and then extrapolate to zero pressure in the reaction vessel.

Data for the association of trimethylamine with boron trifluoride are plotted in Figure 2. It is clear that only an order of magnitude was determined, that the association rate constant is of the order of 10^{12} mole^{-1} cc. sec.$^{-1}$, suggesting that either the steric factor is perhaps 0.01, as might be anticipated from geometric con-

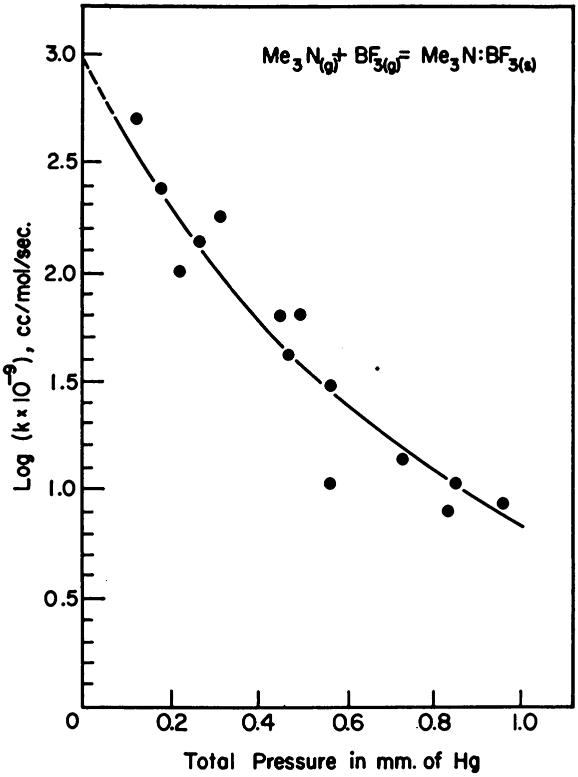

Figure 2. Extrapolation of apparent rate constant for gas phase association of Me_3N and BF_3 as deduced from the pressure decrement in a linear, diffusion-limited reactor

siderations, or a small activation energy is present. For the association of two alkyl radicals the high pressure rate constants are almost 10^{14}, suggesting a collision efficiency near unity (Table I).

Table I. Rate Constants for Bimolecular Association Reactions

(Cc. $mole^{-1}$ $sec.^{-1}$)

	k_a	t, °C.	k_a/Z	Lit. Ref.
$2CH_3$	2.0×10^{13}	165	0.2	(*81*)
	—	R.t.	0.8	(*61*)
$2CD_3$	3.8×10^{13}	165	0.4	(*81*)
$2CF_3$	2.3×10^{13}	127	0.16	(*1*)
$2C_2H_5{}^a$	4.2×10^{13}	150	0.23	(*84*)
$2C_3H_7$	(6×10^{15})	100	(25)	(*93*)
	1×10^{14}		(1)	(*41*)
$2CCl_3$	$\sim 10^{11}$	30	C_6H_{12} soln.	(*60*)

[a] Activation energy of approximately 2 kcal. is indicated; no temperature coefficient has been established for the other recombination reactions.

Second Method. The second procedure proved much more satisfactory and gave considerably more data. It also utilized a diffusion-limited process. In an ingenious adaptation of the Polanyi flame-diffusion technique, Kistiakowsky and coworkers (*42*, *85*) adjusted pressures and flow rates such that the reaction rate was limited by the spherical diffusion of one of the reactants from a point source into an excess of the other. The reaction zone was scanned with a sensitive thermocouple. By so determining the diffusion pattern and solving for the temperature distribution in terms of molecular parameters, using an idealized theory, a number of rate constants (at room temperature) have been evaluated (high pressure limits). These are summarized in Table II.

Table II. Correlation of Thermochemical Parameters with Rate Constants for the Association of Boron Trifluoride with Amines

$$BF_{3(g)} + NR_{3(g)} \xrightarrow{k_f} R_3N{:}BF_{3(g)}$$

Amine	k_f	k_f/Z (Coll. Yield)	$\Delta H°$, Kcal./Mole	I.P.$_{NR_3}$ (e.v.)	$\Delta H°_P{}^a$	$\Delta H°_B{}^b$
NH_3	2.7×10^{11}	0.001	−22.0	10.154	−12.4	....
ND_3(*43*)	1.4×10^{11}	0.0005	....	(10.15)	....	....
NH_2Me	6.7×10^{11}	0.003	−26.0	8.97	−13.1	−17.1
$NHMe_2$	5.9×10^{12}	0.02	−28.2	8.24	−11.8	−18.5
NMe_3	2.8×10^{12}	0.01	−26.6	7.82	−8.8	−17.3
C_5H_5N	9.3×10^{12}	0.03	−(27 to 30)	....	−4.1	....
n-C_4H_9-NH_2	8.9×10^{12}	0.03	....	8.71	....	....
tert-$C_4H_9NH_2$	6.3×10^{12}	0.02	....	8.64	....	....

[a] Reduced heat of protonation (*9*).
[b] Enthalpy increment for reaction (*56*) $1/2B_2H_{6(g)} + NR_{3(g)} = R_3N{:}BH_{3(g)}$.

The numbers in Table II are interesting in several respects. They are large and appear to parallel the heats of association, as reported in the literature. However, they do not correlate strictly with the heats for protonation and the heats of reaction of amines with diborane (*2*). The steric factors are about what one might expect from geometric considerations, and there is no indication except possibly in the case of the first three bases that an activation energy is present.

Two points require further comment. First, the rates of reaction do not uniformly increase with decreasing ionization potential of the bases, as would be expected if the rate directly depended on the depth of the potential well into which the associated pair sink upon addition. Second, the collision yields are high for bases as complex as *tert*-butylamine and pyridine, for which the steric factor would be expected to be considerably smaller than for the lower molecular weight donors. Unfortunately, Kistiakowsky's absolute method does not lend itself easily to a variation in temperature for the determination of activation energies.

Third Method. This was designed to measure the relative rates of association by a competitive procedure. Concurrent data were obtained by Daen and Marcus (*24*)

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and by Bauer and coworkers (4). In the latter's experiments, the association of boron trifluoride with trimethylamine was used as the reference reaction and the rate of association of another base with boron trifluoride estimated from the relative depletion rates of the amines. This was determined by analyzing via infrared the composition of the initial mixture and, after injecting a small amount of boron trifluoride, analyzing the composition of the remaining gases. The experiment must be designed to prevent local depletion and the entire system carefully controlled with respect to pressure and flow rates. Thus,

$$A_{(g)} + B_{1(g)} \xrightarrow{k_1} AB_{1(s)}$$

$$A_{(g)} + B_{2(g)} \xrightarrow{k_2} AB_{2(s)}$$

Expressed quantitatively (omit brackets to denote concentrations),

$$\frac{dB_1}{dt} = -k_1 A \times B_1 = -\frac{d(AB_1)}{dt}$$

$$\frac{dB_2}{dt} = -k_2 A \times B_2 = -\frac{d(AB_2)}{dt}$$

so that

$$\frac{d \ln B_1}{d \ln B_2} = \frac{k_1}{k_2}$$

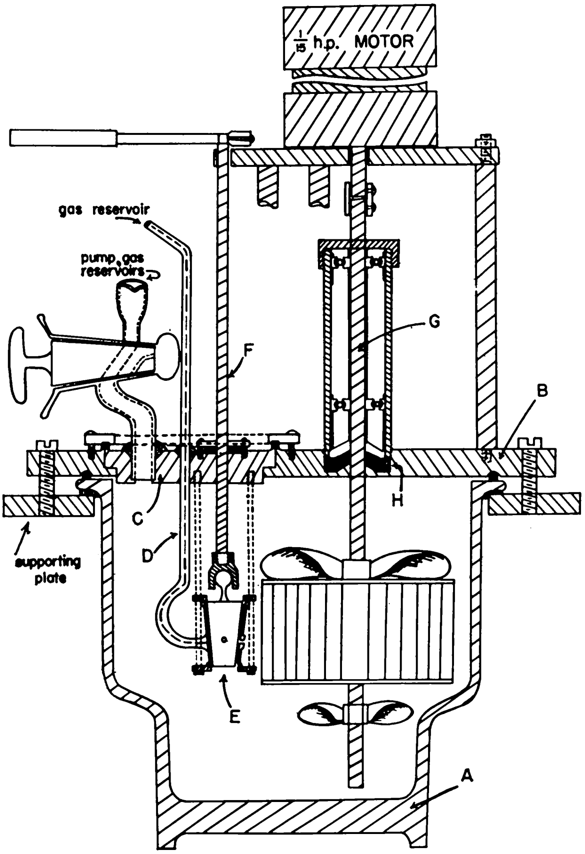

Figure 3. Reactor for measurement of relative association rate constants

Integration gives

$$\frac{\ln B_1/B_1^\circ}{\ln B_2/B_2^\circ} = \frac{k_1}{k_2}; \quad \frac{\ln [1 - (AB_1)]}{\ln [1 - (AB_2)]} = \frac{k_1 \ln B_1^\circ}{k_2 \ln B_2^\circ}$$

The relative rates for association of ammonia and trimethylamine have been determined with considerable precision in this laboratory (*4*) at three different temperatures. The reaction vessel used is shown in Figure 3. The turbine was rotated by a fast motor operating through the vacuum gland, *H*. A mixture of amines was prepared, injected into the reaction chamber, and thermostated; a sample was withdrawn for analysis through the stopcock on the left. Then, a small amount of boron trifluoride diluted with nitrogen was injected through stopcock *E*, while the turbine was rotating. Immediately, an aliquot part of the remaining gas was withdrawn for analysis, another small amount of boron trifluoride injected, a sample withdrawn for analysis, etc., until about 30% of the amines had reacted. Each of these steps gave a relative rate constant. These were averaged and compared for trends with pressures and for possible departures from a bimolecular law. The following results were obtained:

T, °K.	k_{NH_3}/k_{NMe_3}
273	0.117 ± 0.027
297	0.087 ± 0.015
333	0.111 ± 0.054

Within the experimental error, the ratio of the rate constants does not change over a temperature interval of 60°. It seemed apparent, therefore, that the activation energies for association of ammonia with boron trifluoride and of trimethylamine with boron trifluoride are equal to within 300 small calories, so that the observed differences between their rates must be due to differences in the pre-exponential terms; it appears likely that no appreciable activation energy is involved in the association of strong bases, such as the amines listed, with strong acids, such as boron trifluoride. However, one should not conclude that no acid-base association requires an activation step. For example, the reaction $BCl_3 + Cl^- \rightarrow BCl_4^-$ appears to require high temperatures as well as high pressures (*48, 62*).

Attempts in this laboratory to measure the relative association rates as functions of the temperature for other amine pairs were not successful. Since the desired ratios

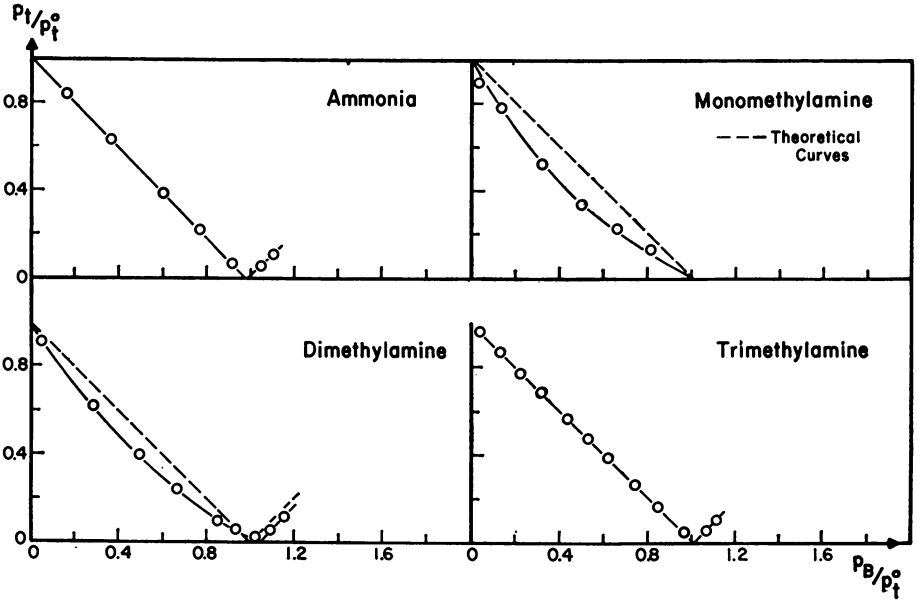

Figure 4. Gas phase titration curves with BF_3 of various amine bases
Experimental points fall on theoretical 1 to 1 curve only with NH_3 and NMe_3

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must be determined in the presence of excess amine and estimation of the extent of reaction depends on the decrement in the residual gases, it is essential that no processes other than the assumed 1 to 1 association remove any of the gases. The data obtained indicate that selective absorption of the remaining gases onto the solids generated in the reaction invalidates this analytical procedure in all cases but the pair trimethylamine and ammonia, with BF_3 as the acid (Figures 4 and 5). The experiment will have to be modified in order to take into account these absorption effects, possibly by analyzing the solids. As far as the measurements were made, the relative rates for association of the bases check with the ratios computed from˙ the absolute rates reported by Kistiakowsky.

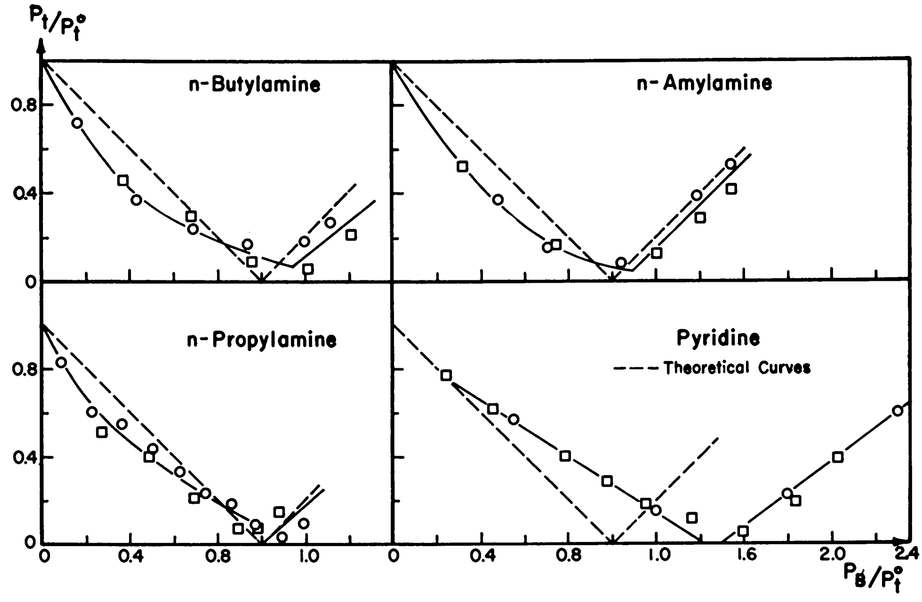


Figure 5. Gas phase titration curves with BF_3 of various amine bases

A fully satisfactory reason for the large difference in the collision efficiencies for association with BF_3 between ammonia and the several alkylamines has yet to be discovered. These differences are in a direction opposite to what one would expect from simple geometrical considerations, since the filled orbital in ammonia is superficially least shielded by the groups attached to the nitrogen atom. The three hydrogen atoms provide a less sterically hindered gate for attack by the boron trifluoride than do alkyl groups.

One may rationalize some of these observations in terms of collision theory for the reaction rates. From Kistiakowsky's data, only one in 30 to one in 100 collisions is effective for the association of BF_3 with the alkylated bases. This means that, when the donor-acceptor pair approach, the molecules do go down the potential well, but there is a very high probability, say 50 to one, that because of their mutual kinetic energy they will continue to approach along the inner repulsive part of the potential curve up to a "turn-around" point some place (on the average, kT) above the zero of potential. Then, the repulsive interaction will be sufficient to send them out again along their collision orbit. Only in a small fraction of such encounters will their mutual kinetic energy be dissipated by an intramolecular energy transfer, so that the pair will be trapped in the potential well. Clearly, the more complicated the groups attached to the nitrogen atom, the more opportunities there will be for such a transfer to occur; the more complicated the base molecule (pyridine or *n*-butylamine), the more chance there is for this stabilization to occur during the time of one collision ($\approx 10^{-11}$ second). In the case of the ammonia–boron trifluoride complex, the product produced is rather rigid, and one should anticipate considerably less opportunity for intramolecular energy transfer. In other words, the pre-exponential factor is not a geometric steric term but a transition probability. Regrettably, no quantitative theory is now available for computing its magnitude.

The above argument does not account in detail for all the available data. Thus, ND_3 is slower than NH_3, although the vibrational frequencies in the former are lower; $NHMe_2$ is faster than NMe_3, etc. Factors in addition to the relative efficiency for intramolecular energy transfer must be operative. One of these might be the effect on the collision orbit of the umbrella-type inversion which occurs at the nitrogen atom—i.e., of the reduction in accessibility of the nonbonding electron pair. Another factor is the polarizability of the base molecule and the consequent effect on the orbiting-type collisions with the acidic molecule.

Scrambling Reactions

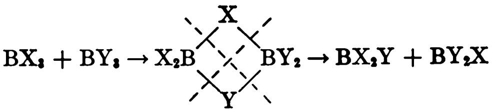
In addition to the donor-acceptor associations

$$D: + BX_3 \rightarrow D:BX_3$$

which have been established by many techniques, there is a growing body of kinetic data which indicate bridge-type associations. For the boron halides, scrambling of the halogen atoms takes place on mixing the gases. For example,

$$BF_{3(g)} + BCl_{3(g)} \leftrightarrows BF_2Cl_{(g)} + BFCl_{2(g)}$$

The equilibrium constant for this reaction is 0.53 ± 0.04 (*34*). The rates are known to be very rapid; at room temperature, less than 30 minutes is sufficient to establish equilibrium for the trifluoride-trichloride mixture. The scrambling of halide atoms between the tribromide and triiodide appears to be even more rapid. The proposed mechanism for these reactions is the intermediate formation of an unstable bridge



$$BX_3 + BY_3 \rightarrow X_2B\overset{X}{\underset{Y}{\times}}BY_2 \rightarrow BX_2Y + BY_2X$$

and the fission of that bridge in a random manner. Because the steady-state concentration of the dimers in the trihalide gases is negligibly small, one may estimate the enthalpy decrement in bridge formation to be less than 8 kcal. per mole. [Dimers have been sought in BF_3, gas (*74*) and liquid (*35*). Molecular weights of the other gaseous trihalides correspond to monomers, but the precision of the data is not sufficient to establish a significant lower limit for the possible concentration of dimers.] From the observation (*28*, *51*, *52*, *64*) that the half time for the ($BF_3 + BCl_3$) reaction is about 10 minutes, one may further estimate that the heat of activation is approximately 14 kcal.

The scrambling reaction may also proceed via a displacement mechanism, for which an appreciable activation energy is to be expected, a value comparable to one third of the bond dissociation energy. Alkyl, alkoxy, and dialkylamino groups are probably transferred from one boron to another by such a process. Establishment of equilibria such as

$$2RBF_2 + 2BCl_3 = 2RBCl_2 + 2BF_2Cl$$

requires elevated temperatures and, upon the addition of a base (trimethylamine), they are driven toward the direction in which the strongest Lewis acid has been removed (*10*). Similarly, only above 100°C. does

$$BCl_3 + 2BR_3 \rightarrow 3R_2BCl$$

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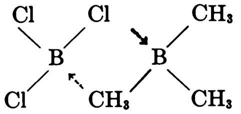
rapidly produce high yields of the dialkylchloroborane (*59*). However, it is conceivable that, with halogen atoms available, very short-lived and possibly asymmetric bridge dimers may be formed, in which a halogen atom acts as one basic center and an alkyl group, through hyperconjugation, as the other.



Careful kinetic experiments remain to be done in order to demonstrate this mechanism. In the scrambling of halogen atoms and alkyl groups between silicon and boron centers, a displacement-type process is apparently followed; no chlorine isotope exchange occurs under moderate conditions between BCl_3 and Me_3SiCl (*33*), even though a 1 to 1 addition compound of these molecules has been prepared. The comparable transfer of halogen and alkyl groups between tin and boron takes place smoothly at room temperature (*10*); this reaction merits further study.

The trialkyl, trialkoxy, and tridiamine boranes give no indication of scrambling reactions with low activation energies, although a large variety of such transfers involving mixed alkyl, alkoxy, halogens, and hydroxy boranes has been reported. [Lappert has prepared an extended summary (*49*).] Currently, Ritter (*76*) has been studying the disproportionation of monomethyldiborane. The kinetic rate laws are consistent with the mechanism in which, following dissociation to $BH_3 + BH_2Me$, two of the latter react via a displacement step to produce $BH_3 + BHMe_2$. Numerous organodichloro- and organodifluoroboranes have been prepared (*58*) in 1- or 2-mole quantities by the reaction

$$2BX_3 + (RBO)_3 = 3RBX_2 + B_2O_3 \text{ (yield, 60\% +)}$$

The products are resistant to disproportionation. Dialkylchloroboranes result in 90% yield from the reaction

$$BCl_3 + 2R_3B = 3R_2BCl$$

and do not disproportionate if distilled below 100°C. At higher temperatures, they slowly disproportionate according to the equation

$$2R_2BCl = R_3B + RBCl_2$$

The equilibrium in this reaction is far to the left, and the reverse reaction can be used for the preparation of R_2BCl from R_3B and $RBCl_2$.

Burg (*21*) reported that the compound $CH_3SB(CH_3)_2$ disproportionates moderately, giving small yields of $B(CH_3)_3$ and the new $(CH_3S)_2BCH_3$ (melting point, −59°; boiling point, est. 155°C.). The preparative sequence is:

$$(CH_3S)_3B + 2B(CH_3)_3 \leftrightharpoons 3CH_3SB(CH_3)_2$$

and $$CH_3SB(CH_3)_2 + (CH_3S)_3B \leftrightharpoons 2(CH_3S)_2BCH_3$$

These reactions require heat and a "B—H catalyst" supplied by B_2H_6. The disproportionation of $CH_3SB(CH_3)_2$ and $(CH_3S)_2BCH_3$ seldom exceeds 20%. It is probable that BH_3 plays a significant role in the mechanism.

A study of the rate of disproportionation (*90*) of dimethoxyborane in the gas phase has been made by the manometric method. The reaction

$$3(CH_3O)_2BH \leftrightharpoons 2(CH_3O)_3B + 1/2B_2H_6$$

is found to be heterogeneous; in a 1-liter spherical borosilicate glass bulb at low pressures and moderate temperatures, the rate is proportional to the square of the partial pressure of $(CH_3O)_2BH$. From the rate constant determined at 40°, 60°, and 80°C., an activation energy of 14.2 kcal. per mole of $(CH_3O)_2BH$ has been deduced.

Finally, evidence from mass spectrometric analyses (*78*) indicates that under cer-

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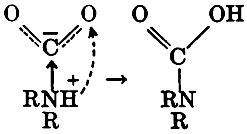
tain conditions methyl groups may migrate between boron atoms in trimethylborane. Such exchange does not occur readily in gaseous mixtures; in liquid mixtures, exchange is detectable only after prolonged standing (7 hours at −80°C. followed by 10 hours at −135°C.). The formation of a dimeric intermediate of trimethylborane may be involved in the mechanism; definitive experiments remain to be done.

Association Followed by Rearrangement or Elimination

When a Lewis acid, such as BF_3, reacts with a base—for example, an amine—the association directly produces the final product; this is followed by precipitation, which may be relatively slow due to an essential nucleation step. It has been suggested (*13*) that the 1 to 1 compound formed between triethylamine and diborane at −64°C. be formulated as a simple donor-acceptor addition, with the bridge in diborane degraded from a double to a single hydrogen link. Generally, reactions between Lewis bases and the boranes are more complex. An example in which an association is followed by an internal rearrangement is the formation of carbamide—the association of carbon dioxide with ammonia, mono-, and dimethylamines (but not with trimethylamine). In these systems, the carbon atom of the carbon dioxide acts as the acidic center for the donated electron pair. Stable salt formation must be followed by a shift of a proton from the nitrogen atom to the oxygen atom



Clearly, this cannot happen in trimethylamine. As yet, no rates for these reactions have been determined; the new techniques have not been extended to these well-known systems. It appears that, when the basic molecule is considerably weaker than ammonia, as is water or alcohol, no stable product is formed with carbon dioxide. One may interpret this, not in terms of the absence of short-lived association products, but rather that the activation energy for the second step, the transfer of a proton from the basic oxygen to the oxygen on carbon dioxide, is too high compared to the gain in bond energy by the molecule as a whole.

In the boranes, it is shown below that association generally produces a concurrent displacement of a group from the acid molecule. A particularly interesting example is the homogeneous gas phase reaction between diborane and phosphine at 0°C. It has been observed (*17*) that at the beginning of the reaction the rate of production of the solid product $H_3P{:}BH_3$ varies linearly with the pressure of each reactant, provided a certain pressure of the reactant determined by the equilibrium constant and the pressure of the other gas is exceeded. The reaction is independent of the amount of surface of the solid product or of the wall. When either reagent is in appreciable excess, the rate-time data obey a pseudo first-order equation. These facts are consistent with the mechanism:

$$\left.\begin{array}{l} PH_3 + B_2H_6 \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} BH_3 + (H_3P{:}BH_3)_g \\ PH_3 + BH_3 \underset{k_2}{\overset{k_{-2}}{\leftrightarrows}} \qquad\qquad (H_3P{:}BH_3)_g \end{array}\right\} \underset{k_3}{\overset{k_{-3}}{\leftrightarrows}} \text{solid}$$

The activation energy for the rate-controlling step is 11.4 ± 2.0 kcal. per mole; the complete expression is

$$k_1 = 10^{9.47} \exp(-11400/RT)$$

The kinetics of production of $Me_3P{:}BH_3$ will prove of considerable interest; the structure of this salt has been established (*88*).

Another reaction which is clearly of the displacement type is that between gaseous trimethylamine and diborane; regrettably, it has not been investigated in detail. Several runs in a diffusion-limited system (Method 1) have been made (*83*) at room temperature, with samples of diborane which have been in this laboratory for several years. The material was distilled according to the most recently recommended procedure (*79*); still, the purity of the material was uncertain. Preliminary results are plotted in Figure 6. The points fall into two groups, presumably because of different impurities remaining after the distillation of the two samples. Nevertheless, the order of magnitude of the rate constant is (1 to 3) × 10^8 mole^{-1} cc. sec.$^{-1}$, a value consistent with the mechanism

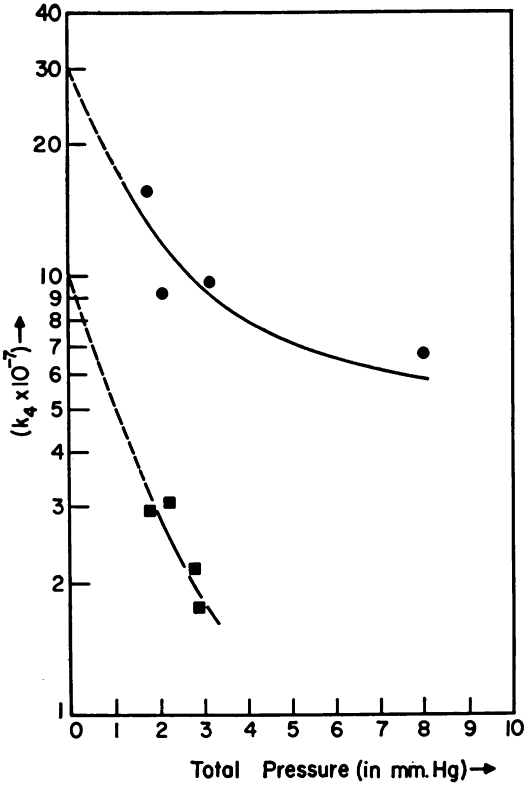


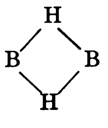
Figure 6. Extrapolation of apparent rate constant for gas phase reaction between Me_3N and B_2H_6 in linear, diffusion-limited reactor

$$Me_3N_{(g)} + B_2H_{6(g)} \xrightarrow{k_4} Me_3N{:}BH_{3(g)} + BH_{3(g)}$$

$$Me_3N_{(g)} + BH_{3(g)} \rightarrow Me_3N{:}BH_{3(g)} \qquad \text{(fast)}$$

$$Me_3N{:}BH_{3(g)} \rightarrow \text{solid} \qquad \text{nucleation limited}$$

The anticipated activation energy for the first step is 6 to 8 kcal., since the bridge



breaking energy is 28 kcal., while the donor-acceptor enthalpy decrement for N-B is about 33 kcal. (*57*). Reasonable values may be deduced for the pre-exponential factor:

$$k_4 = \begin{cases} 10^{14}\,10^{-1.7}\,e^{-E/RT}, \text{ for } E_{\text{act.}} = 6 \text{ kcal.} \\ 10^{14}\,10^{-0.2}\,e^{-E/RT}, \text{ for } E_{\text{act.}} = 8 \text{ kcal.} \end{cases}$$

No measure of the activation energy for this reaction is available. However, it is expected to be considerably less than the 11 kcal. observed for the much weaker base studied by Brumberger and Marcus.

Two other reactions between weak bases and diborane are presumed to follow a displacement-type mechanism. These are the reaction between carbon monoxide and diborane, studied by Burg (*18*), and between phosphorus trifluoride and diborane, studied by Parry and coworkers (*68*). Parry observed that the rates of decomposition of $F_3P{:}BH_3$ obeyed very closely the kinetic laws reported by Burg for $OC{:}BH_3$ and, hence, concluded that the same mechanism was followed in the decomposition of the trifluorophosphorus compound as in the carbon monoxide compound.

The mechanism proposed by Burg for the decomposition of $OC{:}BH_3$ is not consistent with his data, whereas the following mechanism is (*3*):

$$OC{:}BH_3 \underset{k_5}{\overset{k_{-5}}{\leftrightarrows}} BH_3 + CO \qquad \text{(slow)}$$

$$BH_3 + OC{:}BH_3 \underset{k_6}{\overset{k_{-6}}{\leftrightarrows}} B_2H_6 + CO \qquad \text{(fast)}$$

$$BH_3 + BH_3 \underset{k_a}{\overset{k^d}{\leftrightarrows}} B_2H_6 \qquad \text{(fast)}$$

The activation energy for dissociation (k_5) is 27.5 kcal., while that for the reverse process is 8.7 kcal. The last two reactions are comparatively rapid; the first of these is the displacement step. Granting the accuracy of Burg's data, there seems to be no way to avoid the assumption that the association of a borane with carbon monoxide, as indicated by k_{-5}, requires an activation energy, even though it is generally presumed that the association between Lewis acids and bases requires no activation. Possibly, this is an example of the case sketched in the right side of Figure 1. Carbon monoxide is a very weak base; the ionization potential for the nonbonding electrons (external to the carbon end of the molecule) has been computed to be 13.37 volts, so that the molecule is a much weaker donor than the amines and ethers. When a BH_3 and a CO approach, the crossover region must occur at a rather small intermolecular separation where the stabilization of the complex due to the C → B bonding begins to compensate for the destabilization of the carbon monoxide. Hence, the sizable hump in the adiabatic path.

In concluding this part of the discussion, one might mention, with reference to Figure 1, that the magnitudes of $\Delta H°$ for association and the corresponding $E_{\text{act.}}$ should be roughly related but not necessarily inversely proportional to one another. A large $E_{\text{act.}}$ is a consequence of a relatively high ionization potential for the nonbonding electrons in the base or a low electron affinity of the acid. A small dissociation energy in the isovalent curve may also be a consequence of the necessity for extensive configurational adjustments in the parent molecules (particularly in the acids), of the quenching of resonance energies which may be present when uncomplexed, and of steric repulsions brought about when the coordination numbers of both the acid and the base atoms are increased.

Splitting of Borane Bridges

BH_3 a Product. The two mechanisms, (*A*) splitting of a borane bridge concurrently with attack by a base molecule and (*B*) the prior dissociation to produce an

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acid fragment which subsequently associates with a base, are kinetically distinguishable. The boranes are "secondary" Lewis acids, in that one or the other of these steps is essential—that is, a significant readjustment of molecular structure must take place to produce the acid center. At this time, there are no kinetic data which are inconsistent with mechanism *A*, followed by a simple association of another base molecule with the acidic fragment thus generated. However, there is ample evidence that the hydrides of boron do dissociate thermally to produce fragments which have "kinetic" identity and are supposed to behave as "primary" Lewis acids. The latter characteristic is assigned to these fragments in view of their presumed structure and because groups with the same stoichiometry appear in Lewis salts produced when the parent hydrides are attacked by bases.

Dissociation of the simplest of the stable boranes, B_2H_6, has been studied extensively, and many attempts have been made to determine the concentration of BH_3's in equilibrium with the dimer. Indirect data, both thermochemical and kinetic, have led to an estimate of its heat of dissociation (28.4 kcal.).

$$\log_{10} K_{p(\text{atm.})} = 7.478 - 6205/T$$

Rate laws which have been determined for reactions involving gaseous diborane can be accounted for by assuming the attainment of a very rapid equilibrium for dissociation into two equal pieces, followed by a rate-controlling step between the BH_3's and the other reactant.

$$B_2H_6 \leftrightarrows 2BH_3$$

$$BH_3 + X \xrightarrow{k_x} \text{products}$$

$$\frac{d(P)}{dt} = k_x\,(X)(BH_3) = k_x\,\sqrt{K_{\text{eq.}}(B_2H_6)}(X)$$

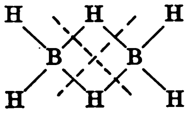
As a consequence, the rate follows in general a $(B_2H_6)^{1/2}$ dependence; where X is diborane, as in the pyrolysis of that compound, the radical B_3H_7 is produced; the concentration dependence is then $(B_2H_6)^{3/2}$. A variety of kinetic studies can all be interpreted (*3*) on the assumption that the association of two BH_3's to form the dimer occurs at nearly every collision, analogous to the association of two methyl groups. The rate constants for association and dissociation at the high pressure limit are then related by the equilibrium constant. This basic rate equation along with several others in which BH_3 participates are summarized in Table III.

Table III. Summary of Rate Constants

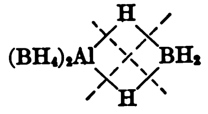
Reaction	High Pressure Limit	Based on Data in
$B_2H_6 \underset{k_d}{\overset{k_a}{\leftrightarrows}} 2BH_3$	$k_d \sim \frac{10^{19.56}}{T}$ exp. $(-28400/RT)$ $k_a \sim 10^{14}$	(*3*)
$BH_3 + B_2D_6 \rightarrow B_2H_3D_3 + BD_3$	$k = 10^{14.49}$ exp. $(-7600/RT)$	(*54*)
$BH_3 + HD \rightarrow BH_2D + H_2$	$k = 10^{11.6}$ exp. $(-7000/RT)$	(*53*)
$BH_3 + H_2O \rightarrow BH_2OH + H_2$	$k = 10^{11.28}$ exp. $(-6000/RT)$	(*91*)
$BH_3 + B_2H_6 \rightarrow B_3H_7 + H_2$	$k = 10^{11.15}$ exp. $(-11500/RT)$	(*8,23*)
$BD_3 + B_5H_9 \rightarrow BD_2H + B_5H_8D$	$k = (\quad)$ exp. $(-13000/RT)$	(*40*)

It is these and similar mechanisms which lend strong support to the assumption that the bridge in diborane is symmetrically split when the molecule dissociates in the gas phase into two fragments. This should not be confused with the possibility of unsymmetrical breaking induced by collision with reactive molecules, particularly in condensed systems.

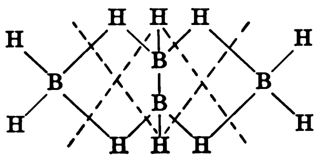
By analogy, similar splittings occur in the other boranes. These are illustrated below.



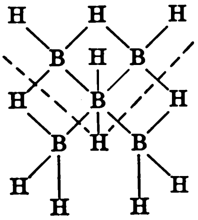
$BH_3 + BH_3$



$BH_3 + (BH_4)_2AlH$



$BH_3 + B_3H_7$



$BH_3 + B_4H_8$

Because in all cases a BH_3 group is one of the products, it is proposed that these be designated as borane splittings. The primary kinetic evidence is the observed dependence of the rates of isotope exchange on the concentrations of the parent hydrides. The aluminum borohydride has not yet been studied in this manner. However, a borane split has been postulated as the first step in the reaction of aluminum borohydride with ethylene (*11*), parallel in some ways to the reaction between diborane and ethylene (*92*). References to the literature on the isotope exchange data are cited (*39, 40, 46, 47, 50, 80, 89*).

In the exchange of deuterium between B_2D_6 and B_5H_9, the rate was found to be half order with respect to diborane and first order with respect to pentaborane. Five of the hydrogens in B_5H_9 exchanged preferentially, and these five were nonbridge hydrogens, suggesting that under the experimental conditions used the terminal hydrogens were more reactive. It was further observed that, within a factor of 2, the rate of exchange of the apical hydrogen in pentaborane was the same as that of the base terminal hydrogens. The remaining four atoms did exchange but at a very much slower rate. With B^{10} as a tracer, it was demonstrated that the boron skeleton in B_5H_9 was not involved in the exchange. The following is a satisfactory mechanism for the process:

$$B_2D_6 \leftrightarrows 2BD_3$$

$$B_5H_9 + BD_3 \xrightarrow[k_x]{} B_5H_8D + BD_2H$$

$$\frac{d}{dt}\,(\text{exchange: H—D}) = k_x \sqrt{K_{\text{eq.}}(B_2D_6)}\,(B_5H_9)$$

No B^{10}—B^{11} exchange;

$E_{\text{act.}}$ (over-all) = 27 kcal.; for k_x, $E_{\text{act.}} \cong 13$ kcal.

In the isotopic exchange reactions between diborane and pentaborane(11), all eleven of the hydrogens in the pentaborane(11) were found to undergo exchange, as did all five of the borons. Both reactions showed a half-order dependence on the B_5H_{11} concentration and the first-order dependence on the diborane concentration. The mechanism which is consistent with these facts is

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

$$\left.\begin{array}{l} BH_3 + B_2D_6 \rightarrow B_2H_3D_3 + BD_3 \\ B_4H_8 + B_2H_6 \rightarrow B_5H_5D_6 + BH_3 \end{array}\right\} \text{rate-determining}$$

$$BH_3 + BD_3 \rightarrow B_2H_3D_3$$

$$(BH_3) \cong (B_4H_8)$$

$$\frac{d}{dt}\left[\text{exchange:}\begin{matrix} \text{H—D} \\ \text{B}^{10}\text{—B}^{11} \end{matrix}\right] = k \begin{matrix} (B_2D_6) \\ (B_2{}^{10}H_6) \end{matrix} (B_5H_{11})^{1/2}$$

When the source of deuterium is D_2, the rate-controlling step appears to be

$$B_4H_8 + D_2 \rightarrow B_4H_8D_2$$

The exchange reaction between diborane and tetraborane was found to proceed in a much more complex fashion (*89*). It appears that D and B^{10} could enter tetraborane by two different routes; a fractional order dependence on B_4H_{10} was observed. It was postulated that, under the mild conditions of the exchange experiments (25° to 45°C.), vibrationally excited tetraborane exchanged, in a bimolecular collision, with deuterodiborane,

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

Also, unexcited tetraborane may react, by displacement, with BD_3,

$$B_4H_{10} + B^{10}D_3 \rightarrow B^{10}D_3B_3H_7 + BH_3$$

At higher pyrolytic temperatures, Pearson and Edwards (*71*) had to introduce the following equilibria to account for their rate laws:

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

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

A brief infrared spectroscopic study was reported on the H—D exchange between diborane and deuterated $B_{10}H_{14}$, prepared by exchanging deuterium between B_2H_6 and $B_{10}H_{14}$ at 100°. The data showed that exchange proceeds at the terminal hydrogens of $B_{10}H_{14}$ and that the bridge hydrogens are not involved in the reaction under the experimental conditions used.

Displacement of BH_3 by Base (Condensed Phase). Although no data are available on the sequence of steps initially followed when solid or liquid Lewis bases react with hydrides of boron, it is nevertheless evident that the latter do behave as acids. Until the essential experiments have been performed, one may argue that the current information relative to stoichiometry and structures of the products produced in these reactions may be accounted for, as in the few gas phase studies reported, by assuming that attack by the base produces a salt with the more acidic fragment and concurrently displaces a BH_3 group, which either reacts very rapidly with another base molecule or associates with another BH_3 to produce B_2H_6. Thus, a borane split occurs as a consequence of reaction with a base.

The large variety of compounds with the formula $D:BH_3$, generated when gaseous diborane is bubbled through a variety of liquid bases or is condensed upon solid bases, has been described by Burg (*20*). The behavior of the ammonia-diborane system, which had proved so perplexing for about three decades, finally has been analyzed in detail and its complexity accounted for (*70*). The salt, $H_3N:BH_3$, can be prepared when the temperature and medium are properly controlled.

The reaction between tetraborane and Lewis bases in the condensed phase has been recently studied in considerable detail (*38*). With Et_2O,

$$B_4H_{10} + Et_2O \xrightarrow[\text{temp.}]{\text{room}} Et_2O:B_3H_7 + 1/2B_2H_6$$

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Similar reactions occur when trimethyl phosphine or an alkali metal hydride is used as the base. The latter produces $NaHB_3H_7$. The etherate of B_3H_7 is a colorless liquid and is relatively unstable. With trimethylamine, $Me_3N{:}BH_3$ (rather than B_2H_6) and the much more stable $Me_3N{:}B_3H_7$ are produced. The trimethylamine complex is insoluble in water, only slightly soluble in ethers, thermally stable at temperatures to 300°C., and hydrolyzed only with difficulty in strong acid solution at elevated temperatures, and can be recrystallized from alcohols without decomposition. With excess Me_3N, the triborane undergoes further splitting to produce $Me_3N{:}BH_3$ and $HB(NMe_3)_x$ (*22*).

The displacement sequence strongly suggests that B_3H_7 is a stronger Lewis acid than BH_3. This is indicated by the conversion of $(CH_3)_3N{:}BH_3$ to the corresponding triborane compound by reaction with tetraborane. Sodium hydride can displace the coordinated base from the triborane complex to form NaB_3H_8. Sodium borohydride with tetraborane in ethyl ether quantitatively gives:

$$NaBH_4 + B_4H_{10} \rightarrow NaB_3H_8 + B_2H_6$$

The reaction of sodium amalgam with tetraborane also produces NaB_3H_8. Tetrahydrofuran and tetraborane reacted at room temperature to yield tetrahydrofuran-triborane quantitatively, in a few minutes, according to the equation

$$2B_4H_{10} + 2C_4H_8O \rightarrow 2C_4H_8O{:}B_3H_7 + B_2H_6$$

In the presence of an excess of tetraborane, pentaborane was obtained by the reaction

$$5B_4H_{10} \xrightarrow{C_4H_8O \cdot B_3H_7} 5B_2H_6 + 2B_5H_9 + H_2$$

The tetrahydrofuran complex $C_4H_8O{:}B_3H_7$ is a white solid, melting point 39°C. Triborane coordination complexes have been produced with such Lewis bases as dimethyl sulfide, thiophene, and ethylene glycol ethers. The compound $H_3N{:}B_3H_7$ can be prepared indirectly, either from NaB_3H_8 by treatment with NH_4Cl (in Et_2O solution at room temperature) or from $R_2O{:}B_3H_7$ by treatment with ammonia (in Et_2O solution at −78°C.) (*45*). Its structure has been determined by x-ray diffraction of the crystals (*66*).

The acid properties of B_5H_{11} have not been so extensively investigated. This pentaborane undergoes a borane split in the presence of carbon monoxide (*19*):

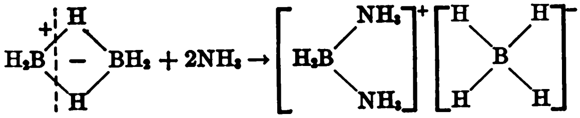
$$B_5H_{11} + 2CO \xrightarrow[\text{excess base}]{} OC{:}B_4H_8 + OC{:}BH_3$$

Hough and coworkers (*37*) have currently reported on the association of B_5H_9 with bases. In the presence of 2 moles of Me_3N per mole of the borane

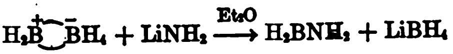
$$2Me_3N + B_5H_9 \xrightarrow{\text{rapid}} (Me_3N)_2{:}B_5H_9 \xrightarrow{\text{slow}} Me_3N{:}BH_3 + Me_3N{:}B_4H_6$$

With excess base, further borane-type splitting occurs to produce 2 moles of $Me_3N{:}BH_3$ and one $(Me_3N)_xB_3H_3$ per mole of the pentaborane.

Solvolysis of BH_2^+. Although no kinetic studies have yet been reported for the splitting of diborane unsymmetrically (to produce BH_2^+ and BH_4^-), there is much evidence that such a splitting is induced by sufficiently strong bases, in the condensed phase. Clearly, the activation energy required for such a reaction is much higher than that for the symmetric-type splitting, and hence, it does not occur as a unimolecular process in the gas phase. However, in a basic solvent (NH_3, Et_2O, etc.), concurrent solvolysis and abstraction of BH_2^+ by a sufficiently strong base (NH_3, NH_2^-, etc.) have been observed. In some respects, there are analogies between the BH_2^+ ion and carbonium ion as intermediates; hence, such reactions will be called boronium splits, in contrast to the borane split discussed above. [Parry and Edwards (*69*) refer to these as the unsymmetrical and symmetrical splittings, respectively.] Ammonia, even at low temperatures, is particularly effective in inducing boronium splittings (*70*) because of the apparent stability of the solvated ion, $H_2B(NH_3)_2^+$.

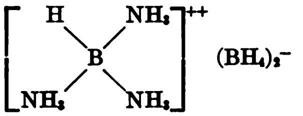


The structure of $BH_2(NH_3)_2^+Cl^-$ has been determined recently (*65*). The positive ion is that expected from the formulation of products given above; the B—N distance is 1.58 ± 0.02 A., and the ∠NBN is nearly tetrahedral. Another example (*77*) is



$$\overset{+}{H_2B}\overset{-}{BH_4} + LiNH_2 \xrightarrow{Et_2O} H_2BNH_2 + LiBH_4$$

As is well known, when the classical diammoniate-diborane is "mistreated," further reaction takes place (*69*). The available data are best accounted for by assuming further solvolysis to produce a dipositive ion



In parallel fashion, tetraborane and ammonia react in a variety of ways. Tetraborane and ammonia produce a stable, crystalline diammoniate of $B_4H_{10}\cdot 2NH_3$. The existence of a compound, $B_4H_{10}\cdot 4NH_3$, which reportedly decomposes above −20°C. with loss of hydrogen and ammonia, has not been confirmed. On the basis of reactions given below, the diammoniate of tetraborane has been assigned the structure $[H_2B(NH_3)_2]^+ [B_3H_8]^-$ (*44*).

$$[H_2B(NH_3)_2]^+ [B_3H_8]^- + Na \xrightarrow[-78°C.]{liq.\ NH_3} H_2 + NaB_3H_8 + [H_2BNH_2]_x$$

$$[H_2B(NH_3)_2]^+ [B_3H_8]^- + HCl \xrightarrow[-78°C.]{Et_2O} [H_2B(NH_3)_2]^+ Cl^- + H_2 + (C_2H_5)_2O{:}B_3H_7$$

Concluding Remarks

Since the early work of Stock, the observations that at low temperatures each of the hydrides of boron forms molecular compounds with ammonia [borane$\cdot(NH_3)_n$, with $n = 2, 4, 6$] have led to the casual surmise that the boranes behave like "acids." It is now evident that the mere stoichiometry of condensation does not demonstrate acid-base behavior. The phase rule criterion for intermolecular compound formation is much more general than the condition for donor-acceptor bond formation. Prior to asserting that a borane does behave like a Lewis acid, one must carefully fractionate and identify the products of such condensations. Determination of their structures is essential before one can obtain a clue as to the course of the reaction. A striking example of confusion resulting from attempts to deduce too much from "condensation stoichiometry" was the $B_2H_6\cdot(NH_3)_2$ system.

The behavior of boranes as Brønsted acids (proton donors) has been suggested by various writers; it has been demonstrated only for $B_{10}H_{14}$ (*30*). The latter appears to be a monoprotic acid, as judged by titration with sodium hydroxide in ethyl alcohol–water solutions. However, a total of four hydrogens rapidly exchange with deuterium from D_2O when in basic solvents (*31*); infrared data suggest that these are the bridge hydrogens. It has, therefore, been argued that all four bridge hydrogens in $B_{10}H_{14}$ are acidic but that only the first dissociation constant is sufficiently high to show up in a standard titration.

As yet, there is no clear-cut evidence that other boranes may react as Brønsted acids via their bridge hydrogens. The fact that at −120°C. ammonia and diborane form a "loose" adduct which may be carefully decomposed into its parent compounds has been cited in favor of such a model (*69*). A strong argument against this is the observation that sodium hydride and diborane add in a 1 to 1 ratio at low temperatures in diglyme (*13*). In the presence of so strong a base as H^-, it is difficult to accept that a Brønsted acid will not readily yield H_2. This aspect of the acidlike behavior of the boranes merits considerable study; perhaps the "single-bridge" model (*13*) can be justified by infrared absorption analysis.

The behavior of boranes as secondary Lewis acids has been amply demonstrated. A displacement-type mechanism, wherein a BH_3 group is released during the attack of a borane by a base, as presented above, appears to be inherently plausible.

In the presence of strong basic solvents, product analysis suggests that the abstraction of a boronium ion (BH_2^+) may occur, provided solvolysis leads to a large stable ion [in liquid ammonia, $BH_2(NH_3)_2^+$].

Acknowledgment

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Kinetics and Equilibria in the Alkylation of Diborane

Preliminary Report

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The principal characteristics of the reactions of diborane with compounds of type BX_3 have been known since the classical experiments of Schlesinger and his coworkers (*1*, *6–8*) were performed. Nevertheless numerous exact descriptions remain to be accomplished in terms of reaction velocities and equilibrium constants as well as the related mechanisms and thermodynamic quantities. Contributions have already been made through examinations of the decomposition of tetramethyldiborane (*3*) and dimethoxyborane (*9*).

What is described here is a preliminary report of work on two phases concerning the reaction between diborane and trimethylborane and the decomposition of monomethyldiborane.

Experimental

Gas partition fractometry was used for analysis in preference to infrared spectrophotometry and mass spectrometry as the method least complicated for complex mixtures. The column was loaded with a 50:50 mixture of 80-mesh firebrick and mineral oil (*4*) and the auxiliary apparatus was essentially that described previously (*5*). A typical fractometer pattern obtained at 0° is shown in Figure 1. The method proved suitable for the least stable component, monomethyldiborane, as is shown in Figure 2, where the two traces are those obtained by successive passes of the same sample through the column, in which the diborane contents were 0.3 and 0.8 mole %, respectively.

The reactor was a cylinder 4.0 cm. in diameter of 173.8-ml. volume, immersed in agitated ice water contained in a 3-liter wide-mouthed Dewar bottle. At intervals aliquots were removed for analysis by expansion into a small adjacent volume, from which they were swept directly into the fractometer.

The quantities present were estimated by graphical integration of the fractometer patterns. Where curves overlapped, the area assigned to each was estimated by comparison with curves obtained for each substance alone. The areas were corrected by factors proportional to the relative thermal conductivities with B_2H_6:B_2H_5Me:BMe_3:$B_2H_4Me_2$ as 1:1.23:1.42:1.42. The values were checked in two different ways: from comparisons between diborane and trimethylborane during induction periods when no reaction occurred and from comparison between diborane and symmetrical dimethyldiborane based upon the stoichiometry of the monomethyldiborane decomposition. The corrected areas were normalized relative to a constant total boron content, and the values were converted to units of concentration in the reactor.

The factors necessary to ensure accuracy were found to be constancy of the recorder base line and correct adjustment of areas at points of overlap. Constant

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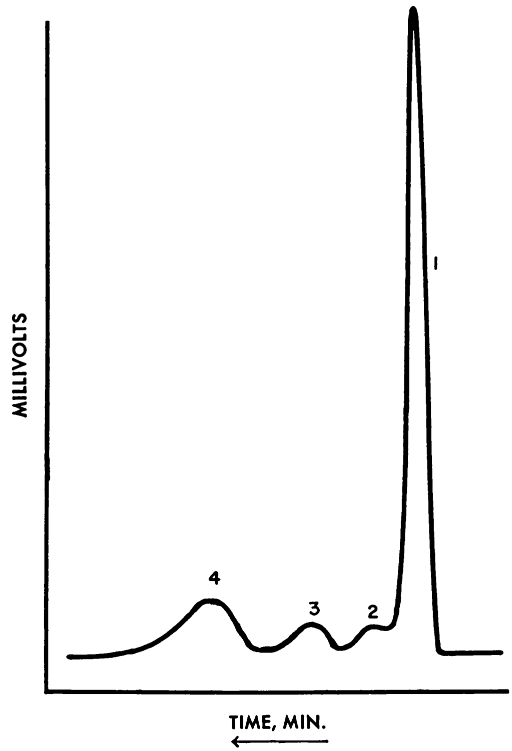

Figure 1. Fractometer pattern for mixture of diborane derivatives

1. Diborane
2. Monomethyldiborane
3. Trimethylborane
4. 1,1-Dimethyldiborane

potential across the bridge was ensured by careful attention to the storage batteries; the thermal conductivity cells were carefully insulated and immersed in oil to avoid stray current leaks. The line voltage to the recorder drive mechanism was passed through a voltage regulator. With these measures taken, a base line was obtained

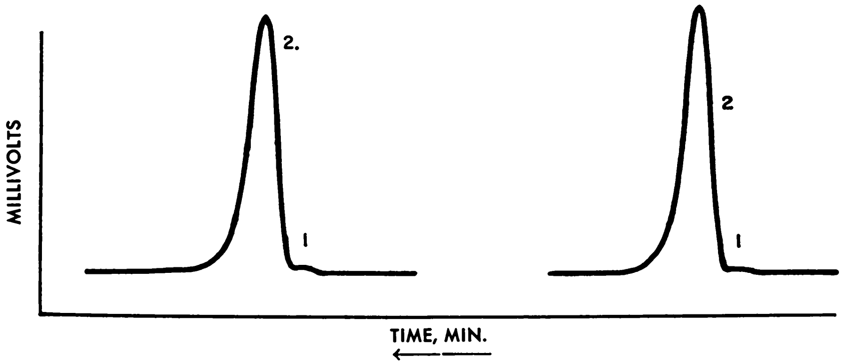

Figure 2. Fractometer pattern for monomethyldiborane

1. Diborane impurity
2. Monomethyldiborane

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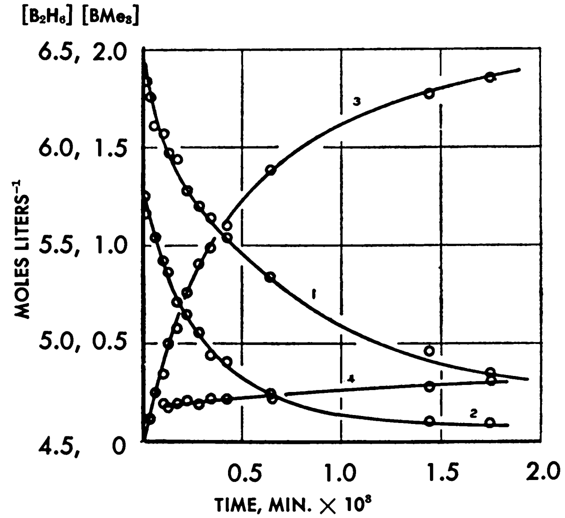

Figure 3. Integral reaction curves

1. Diborane
2. Monomethyldiborane
3. Trimethylborane
4. 1,1-Dimethyldiborane

which was stable within the line width of the recorder tracing or ±0.01 mv. on a 10-mv. scale.

Results and Discussion

Reaction of Diborane and Trimethylborane. This reaction is so complex that for orientation the integral reaction curves should be examined to discover the course of

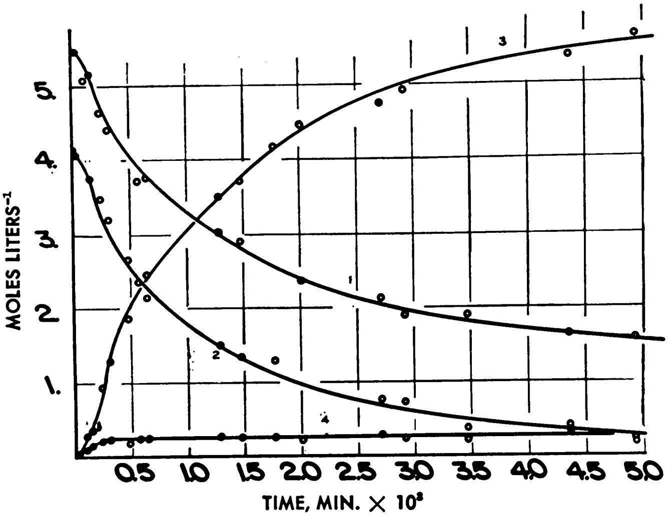

Figure 4. Integral reaction curves

1. Diborane
2. Monomethyldiborane
3. Trimethylborane
4. 1,1-Dimethyldiborane

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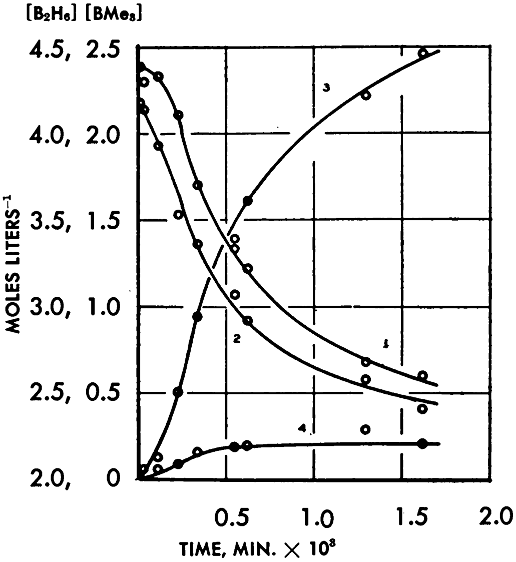

Figure 5. Integral reaction curves

1. Diborane
2. Monomethyldiborane
3. Trimethylborane
4. 1,1-Dimethyldiborane

the reaction. In Figure 3 are shown data for a fivefold excess of diborane. In Figures 4 and 5 other cases are illustrated in which the excess of diborane is about twofold. Note the S-shaped curves for disappearance of the reactants and the appearance of products in Figures 4 and 5, and the suppression of that feature as the excess diborane was increased. In several cases induction periods as long as 600 minutes were observed. These data, plotted as those belonging to a second-order process, are shown in Figure 6. One product, monomethyldiborane, reached almost its final concentration during the accelerating phase of the reaction, while the dimethyldiborane continued to

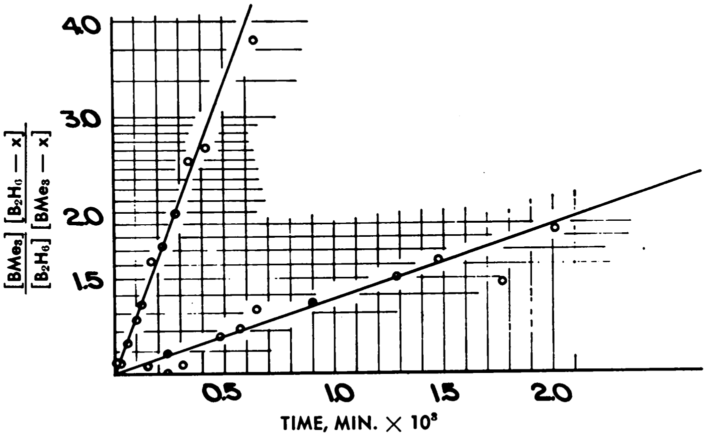

Figure 6. Second-order plots for diborane-trimethylborane reaction

○ Experimentally determined points
● Calculated from integral curves of best fit

increase greatly in amount to become the principal product. Figure 7 illustrates the fact that the S-type curve for dimethyldiborane formation is logarithmic in its early range. Of these four characteristics three are typical of chain reactions, and the second-order kinetics does not exclude chains.

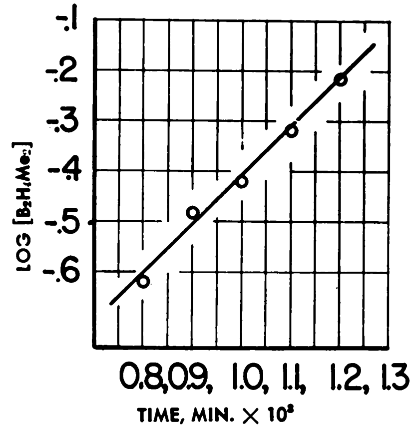

Figure 7. Logarithmic plot of early formation of dimethyldiborane

The second-order velocity constants determined graphically had the values 0.37, 0.52, 0.37, 0.39, 0.39, 0.54, 0.23, 0.41, 0.40, and 0.44, from which the second, sixth, and seventh values could be rejected as varying grossly from the mean. The constant then became 0.40 liter min.$^{-1}$ mole^{-1} with an average deviation of 0.02.

After several days the reaction mixture reached a steady state, apparently of unchanging composition, in which the components were diborane, monomethyldiborane, and 1,1-dimethyldiborane, the trimethylborane having disappeared. With respect to the reaction:

$$B_2H_6 + \tfrac{1}{2}1,1\text{-}B_2H_4Me_2 + \tfrac{1}{2}1,2\text{-}B_2H_4Me_2 \rightleftharpoons 2B_2H_5Me$$

values $K = 0.35$, 0.65 at 0° were obtained from mixtures established from B_2H_6-BMe_3 and B_2H_6-$B_2H_4Me_2$, respectively. Apparently equilibrium was not established after many days' standing at 0°.

Most reactions of diborane involve prior dissociation into borane (*1*). For the methyldiboranes it is axiomatic that borane exchangers will be found, and the crucial question concerns the steps in which methyl groups are exchanged through rupture and formation of boron-carbon bonds.

The alternative hypotheses are represented by equations:

Scheme A

$$BH_3 + BMe_3 \xrightarrow{k_6} BH_2Me + BHMe_2 \qquad (1)$$

$$BH_2Me + BMe_3 \xrightarrow{k_7} 2BHMe_2 \qquad (2)$$

and
Scheme B

$$B_2H_6 + BMe_3 \xrightarrow{a} B_2H_5Me + BHMe_2 \qquad (3)$$

$$B_2H_5Me + BMe_3 \xrightarrow{b} B_2H_4Me_2 + BHMe_2 \qquad (4)$$

In either case boranes are produced, making necessary the following reactions:

$$B_2H_6 \underset{k_w}{\overset{k_0}{\rightleftharpoons}} 2BH_3 \tag{5}$$

$$B_2H_5Me \underset{k_w}{\overset{k_1}{\rightleftharpoons}} BH_2Me + BH_3 \tag{6}$$

$$B_2H_4Me_2 \underset{k_w}{\overset{k_3}{\rightleftharpoons}} BHMe_2 + BH_3 \tag{7}$$

$$BHMe_2 + B_2H_6 \underset{k_{03}}{\overset{k_{20}}{\rightleftharpoons}} B_2H_4Me_2 + BH_3 \tag{8}$$

$$BHMe_2 + B_2H_5Me \underset{k_{13}}{\overset{k_{21}}{\rightleftharpoons}} B_2H_4Me_2 + BH_2Me \tag{9}$$

$$BH_3 + B_2H_5Me \underset{k_{10}}{\overset{k_{01}}{\rightleftharpoons}} B_2H_6 + BH_2Me \tag{10}$$

Steady-state analysis of the two schemes leads to rather different sets of differential equations, each containing members which can be integrated. In each case, however, the integrated expressions are difficult to manage algebraically. This fact makes a direct comparison difficult. For a preliminary examination direct comparison of the differential equations must suffice.

For scheme A:

$$-\frac{d(B_2H_6)}{dt} = \frac{k_{20}(k_6 + k_7r)}{2k_w(1 + r)}(BMe_3)(B_2H_6) - \frac{\frac{k_w}{Q_3}(BMe_3)[Q_1(B_2H_6) + Q_2(B_2H_5Me)]}{\left[1 + \frac{Q_4}{Q_3}\frac{(B_2H_4Me_2)}{(BMe_3)}\right]^2}$$

where

$$Q_1 = (k_6 + k_7r)^2k_{20}$$

$$Q_2 = (k_6 + k_7r)^2k_{21}$$

$$Q_3 = k_w(1 + r)(k_6 + 3k_7r)$$

$$Q_4 = 2k_w(1 + r)(k_{03} + k_{13}r)$$

$$r = \frac{(BH_2Me)}{(BH_3)}$$

initially $\frac{Q_4}{Q_3}\frac{(B_2H_4Me_2)}{(BMe_3)} \cong 0 \ll 1$ and $Q_2(B_2H_5Me) \cong 0$ and $\ll$ other terms. Thus initially

$$-\frac{d(B_2H_6)}{dt} = \left[\frac{k_{20}(k_6 + k_7r)}{2k_w(1 + r)} - \frac{k_wQ_1}{Q_3}\right](B_2H_6)(BMe_3)$$

and initially the kinetics should be pseudo second order, with ample provision for an induction period through necessity of feeding Reactions 1 and 2.

For scheme B:

$$-\frac{d(B_2H_6)}{dt} = k_1(B_2H_6) + k_a(B_2H_6)(BMe_3)$$

an expression which contains no terms related to chain components, and which upon integration yields an expression containing the constants k_1 and k_a in the logarithmic term. Only if $k_1 \ll k_a$ will a simple second-order plot describe the data. The value (*5*) of k_1 is about 7.5 × 10^{-6} sec.$^{-1}$, while the value of k_a can be taken as approximately equal to that obtained from the second-order treatment of the data. The value is 6.7 × 10^{-6} cc. sec.$^{-1}$ mole^{-1}. Thus, $k_1 \cong k_a$, and the alternative hypothesis B appears less likely than A.

Determination of wall effect and an examination of pressure dependence must be carried out. Temperature dependence of a chain reaction has less significance than for ordinary first- and second-order reactions; however, determination of the over-all net activation energy, combined with estimates for the individual steps, might permit an estimate of the number of elementary steps contributing to the over-all reaction.

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Decomposition of Monomethyldiborane. The decomposition of monomethyldiborane is seen to be a first-order reaction (Figure 8). The velocity constants are pressure-dependent, but experiments have not yet been made at sufficiently high pressures to permit extrapolation to $f(1/P) = 0$.

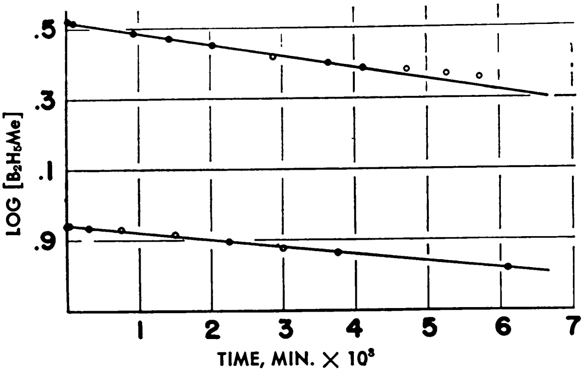

Figure 8. First-order plot for monomethyldiborane decomposition

The reaction steps in the decomposition are represented by Equation 6 and the following additional reactions:

$$(BH_2Me)_2 \underset{k_w}{\overset{k_2}{\rightleftharpoons}} 2BH_2Me \qquad (11)$$

$$BH_3 + (BH_2Me)_2 \underset{k_{11}}{\overset{k_{02}}{\rightleftharpoons}} BH_2Me + B_2H_5Me \qquad (12)$$

The rate equation is:

$$\frac{d(B_2H_5Me)}{dt} = \frac{1}{(k_{01}{}^2 + k_{01}k_{11} + k_{11}{}^2)}\,[k_{01}{}^2k_1(B_2H_5Me) - k_{02}k_{11}k_1{}^{\frac{1}{2}}(BH_2Me)_2(B_2H_5Me)^{\frac{1}{2}}]$$

which, with neglect of the second term for the reverse reaction, gives an initially first-order process. If the step represented by k_{11} (Equation 12) can be neglected, the initial process becomes dependent only upon the step represented by Equation 6. There appears latent in this development the possibility of obtaining from the reaction an experimentally determined estimate of a bridge-bond dissociation energy.

Values for the equilibrium constant for the reaction:

$$2B_2H_5Me \rightleftharpoons B_2H_6 + (BH_2Me)_2 \qquad (13)$$

were calculated from the data in Table I.

Table I. Composition of Equilibrium Mixtures from Monomethyldiborane Decomposition at 0°

Concn., Moles/L. × 10^3			$K \times 10^2$
B_2H_5Me	B_2H_6	$(BH_2Me)_2$	
1.14	0.36	0.27	7.48
0.59	0.17	0.13	6.43
3.41	1.08	0.85	7.89
2.19	0.58	0.55	6.65
6.92	1.83	1.81	6.92
6.48	1.71	1.69	6.88
4.03	1.05	1.00	6.47
1.50	0.42	0.39	7.35
		Av.	7.01

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Explosive Oxidation of Boranes

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At certain conditions of temperature and pressure, borane-oxygen mixtures are spontaneously explosive, with combustion features similar in many respects to those exhibited in the chain isothermal explosions of hydrogen-oxygen and hydrocarbon-oxygen mixtures. Pressure-temperature explosion limits for diborane and oxygen were found by Price (*4*) and Whatley and Pease (*10*) with characteristics indicating a branched chain mechanism. When oxygen was rapidly added to pentaborane, Price (*5*) found a first explosion limit region at low pressures at room temperature, as well as a glow reaction at mixture pressures below the explosion limit pressures. Stock (*9*) reported the spontaneous explosion of decaborane and oxygen at a temperature of 100°C.

Further studies of the oxidation of the boranes have been carried out in this laboratory. Initially diborane was studied because it has the simplest molecular structure of the borane series. Later, pentaborane and decaborane were investigated.

Oxidation of Diborane

Detailed studies of the combustion of diborane-oxygen mixtures at the second explosion limit were carried out by Roth and Bauer (*6, 7*) in an attempt to discover the cause of disagreement between the results of the investigations of Price and of Whatley and Pease. In general agreement with Price (*4*), well defined pressure-temperature explosion limits were found by Roth and Bauer (*6, 7*) for premixed samples of diborane-oxygen in borosilicate glass bulbs rapidly heated to the explosion temperature. Anomalous crossing over of the first limit reported by Price was found not to occur when the reaction vessels were outgassed at increased temperatures. Similar results were obtained in clean glass vessels and in vessels coated with reaction products if the coating was outgassed at temperatures above 170°C. First, second, and third explosion limits were defined, Figures 1 and 2. The second limit was virtually independent of the vessel diameter, but the position of the third limit was strongly dependent on the vessel size. The second explosion limit was studied at various mixture ratios, and analysis of explosion temperatures at 23 mm. of mercury pressure indicated that oxygen was at least 1.5 times as efficient as diborane as a third body in the chain-breaking reaction. Addition of helium and nitrogen had no significant effect on the explosion limit at 23 mm. of mercury, but argon lowered the explosion temperature. Hydrogen additions, at concentrations up to 0.10 mole fraction, lowered the explosion temperature slightly at 23 mm. of pressure. At higher hydrogen concentrations, the explosion temperature increased. Further studies of the effect of additives on the second explosion limit were made by Snyder (*8*). Nitrogen dioxide lowered the explosion temperature from 153° to 74°C. at concentrations of 1.20% of nitrogen dioxide in a stoichiometric diborane-oxygen mixture. At higher concentrations of nitrogen dioxide, up to 4.5%, the explosion temperature increased again, to 148°C.; thus all concentrations of nitrogen dioxide used sensitized the reaction. When an attempt was made to prepare a diborane-oxygen mixture with nitric oxide, NO, as an additive, immediate explosion occurred at room temperature when the nitric oxide was added. When iron carbonyl, $Fe(CO)_5$, was added, the explosion temperature of a diborane-oxygen mixture at 23 mm. was raised, and at 0.57% of iron carbonyl the

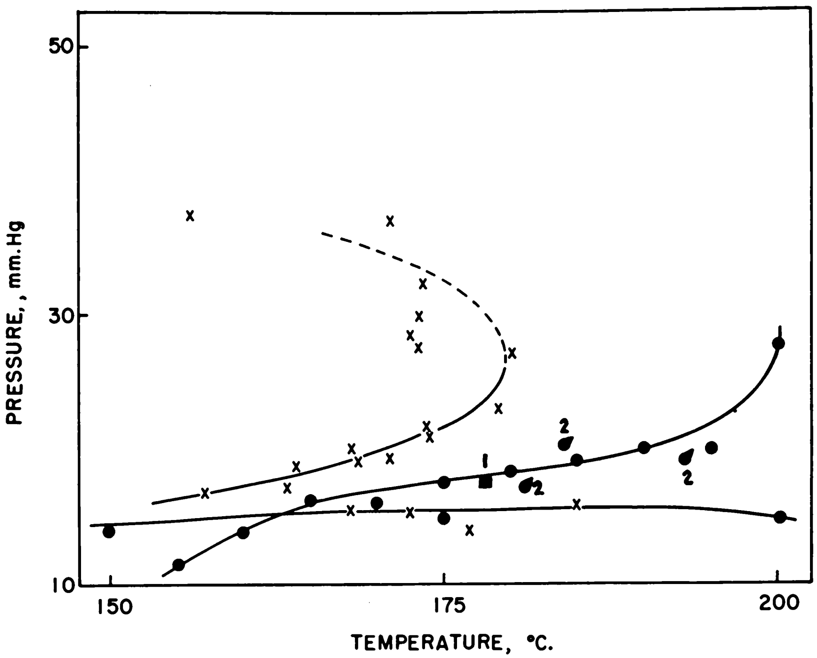

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Figure 1. Explosion limits for the stoichiometric mixture of diborane and oxygen, 3 to 1 mole ratio

- ●. Price (averaged results)
- X. This work, 4.6-cm. spherical, borosilicate glass vessel, evacuated at bath temperature, 150°-200°C.
- 1. Vessel evacuated at room temperature
- 2. Diborane decomposed in vessel prior to experiment

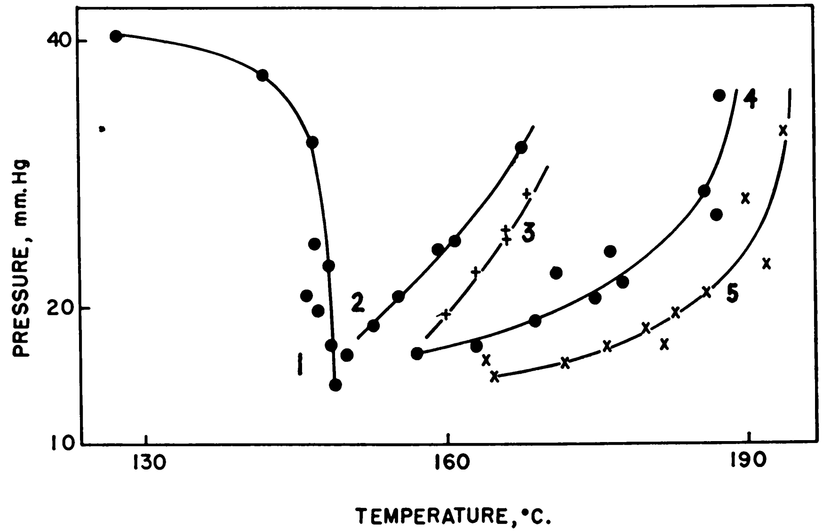

Figure 2. Second explosion limits for various mixtures of diborane and oxygen

Curve 5. $(B_2H_6)/(O_2)$ 1:4 Curve 4. 1:3 Curve 3. 1:2.5 Curve 2. 1:2 Curve 1. 1:1

explosion temperature was 190°C., at the limit of temperature of operation for the silicon oil bath.

Oxidation of Decaborane

When the oxidation of decaborane was studied, explosive mixtures were prepared by means of slow vaporization of a weighed quantity of decaborane into an oxygen atmosphere of known pressure. These mixtures were then allowed to come to equilibrium at a temperature at which the decaborane was completely vaporized and at which no slow oxidation occurred.

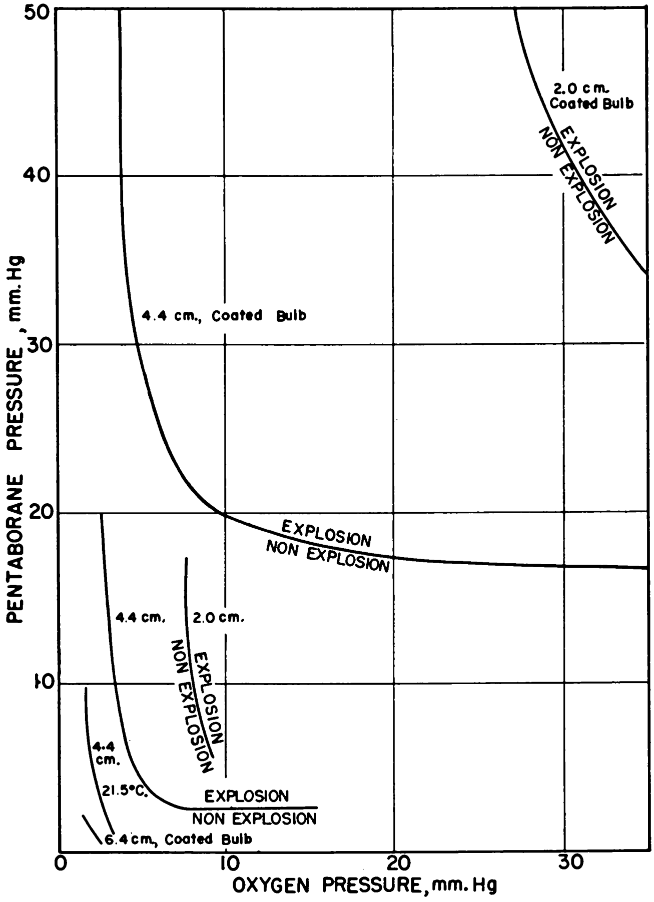

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Figure 3. Composition explosion limits for pentaborane-oxygen mixtures in clean borosilicate glass vessels and in borosilicate glass vessels coated with reaction products, at 15°C. except as otherwise noted

Explosion limits were determined for mixtures of 22 oxygens to one decaborane in borosilicate glass vessels, 6.7 cm. in diameter, coated with explosion products, by a rapid heating method. A first explosion limit for mixtures of 22 oxygens to one decaborane was found at a total pressure of 85 mm. of mercury. A second explosion limit extended from 100 to 114 mm. of mercury over a temperature range of 78° to 112°C. The peninsula tip, between the first and second limits, could not be studied since it

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was situated in a region of incomplete vaporization. The upper portion of the second explosion limit appeared to be sloping toward a third or thermal explosion limit juncture. At total pressures greater than 114 mm. explosions occurred below 80°C. When a lower mixture ratio of oxygen to decaborane was used, with the stoichiometric ratio of 11 to 1, explosions occurred before the solid decaborane could be vaporized.

Addition of nitrogen to the decaborane-oxygen mixture decreased the temperature necessary for explosion at a given total pressure. Prolonged heating of the test decaborane-oxygen mixtures did not affect the explosion temperature, indicating that very little prereaction occurred in the mixtures before the critical explosion temperature was reached. For oxygen-decaborane mixture ratios of 16.5 to 1, an erratically defined explosion limit region of from 80° to 115°C. was found at mixture pressures above 90 mm. At total pressures less than 90 mm., the 16.5 to 1 oxygen-decaborane mixtures were nonexplosive at temperatures tested, reaching to 150°C. When nitrogen was added to the 22 to 1 mixtures, the second explosion limit pressures were in-

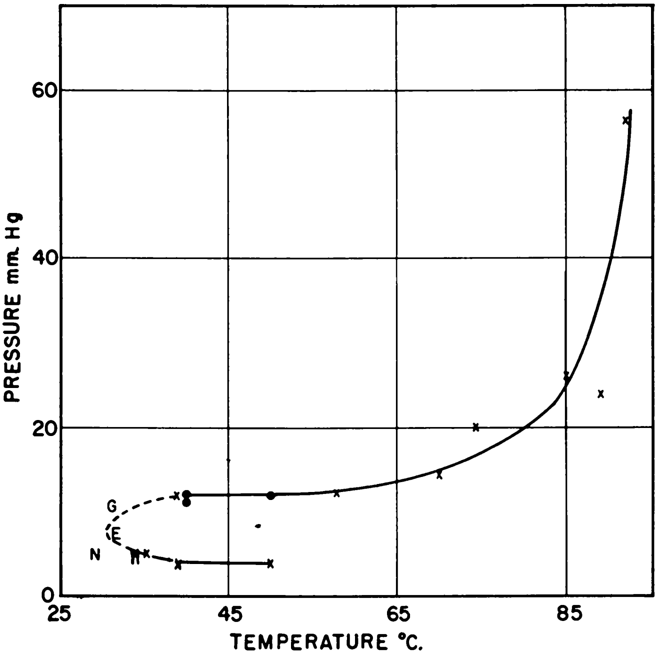

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Figure 4. Temperature-pressure explosion limits for pentaborane-oxygen, mixture ratio 1 to 3, with 0.1% iron carbonyl, in clean borosilicate glass bulbs, 4.4 cm. in diameter

X. Explosion on heating
●. Explosion on withdrawal
G. Glow on mixing
E. Explosion on mixing
N. No reaction on mixing

Table I. Second Explosion Limit Pressures for Mixtures of 22 O_2 to One $B_{10}H_{14}$ Containing Nitrogen at 100°C.

N_2, % by volume	0	10	20
Total pressure in mm. Hg	105.4	113.4	115.4

creased, over a range of explosion temperatures of from 80° to 120°C. Typical data are shown in Table I.

Oxidation of Pentaborane on Rapid Mixing

Price (*5*) studied the luminous reaction of pentaborane with oxygen below the first explosion limit and the first explosion limit at room temperature by means of a

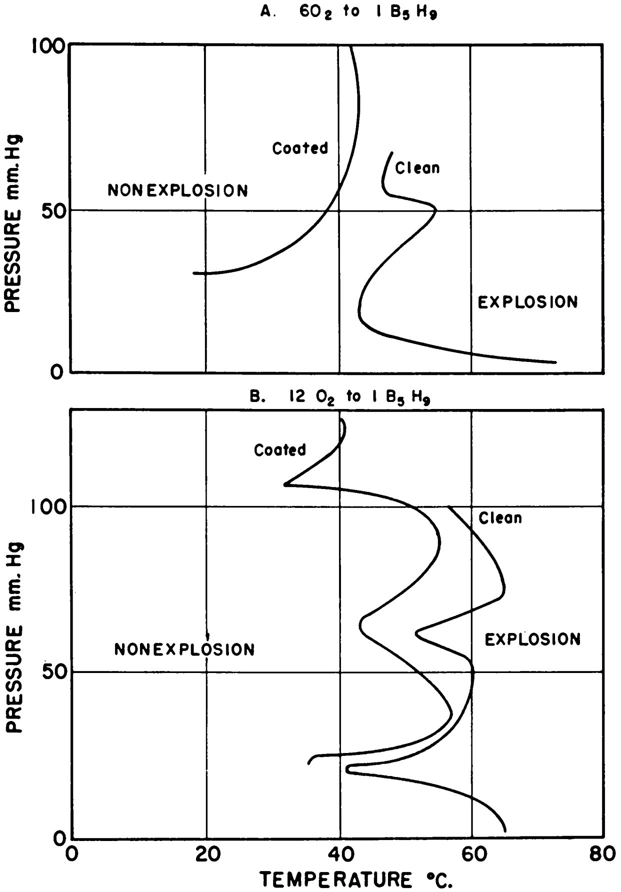

Figure 5. A. Explosion limits for pentaborane-oxygen mixtures, B_5H_9/O_2, 1:6
B. Pentaborane-oxygen mixtures, B_5H_9/O_2, 1:12

Mixtures prepared by slow addition of pentaborane to oxygen. Borosilicate glass explosion vessels (coated) contained degassed reaction products

technique in which compressed oxygen was rapidly expanded into pentaborane. A first explosion composition limit was found, showing the critical mixture pressure above which explosion occurred as a function of mixture ratio and of vessel diameter. Explosions occurred at very low pressures of 1 to 5 mm. of pentaborane. Baden, Wiberley, and Bauer (*2*) obtained results with a similar technique at 25°C., confirming those of Price. When oxygen and pentaborane were rapidly mixed at a lower

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temperature, 15°C., the pentaborane-oxygen pressure explosion limit was shifted to higher pressures, as is shown in Figure 3. The critical pressure needed for explosion was higher in coated bulbs than in clean bulbs, and decreased for both coated and clean bulbs as the vessel diameter increased. Addition of diborane and nitrogen was found to have little effect on the critical pressure limits. Addition of 1% of iron pentacarbonyl completely prevented explosion in the range of partial pressures used, extending to 140 mm. of pentaborane and 80 mm. of oxygen. With 0.1% of added iron pentacarbonyl well defined first and second temperature-mixture pressure limits were found as shown in Figure 4. In both this work and that of Price, there were high concentration gradients because the oxygen was added so rapidly.

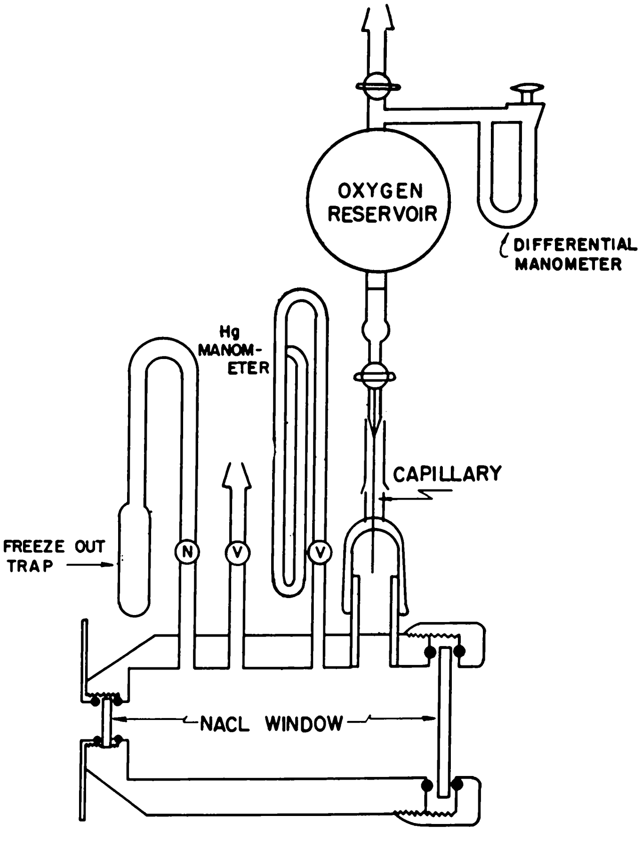

Figure 6. Infrared reaction vessel, brass cell, sodium chloride windows, borosilicate glass fittings

Slow Addition of Pentaborane to Oxygen

After Baden, Wiberley, and Bauer (*1*) found that upon slow addition of oxygen only partial oxidation of the pentaborane occurred, two methods were developed (*3*) for preparing stable mixtures of pentaborane and oxygen at much higher pressures than had originally seemed possible. In the first method pentaborane was slowly added to oxygen through a capillary tube until the desired pressures were obtained. In the second method a known amount of pentaborane was condensed in a vessel cooled by a dry ice–acetone mixture, oxygen was added to the desired pressure, and finally the mixture was allowed to warm slowly to room temperature. With either of

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these two methods mixtures of oxygen and pentaborane at a ratio of 6 to 1 or 12 to 1 could be prepared without explosion at total pressures as high as 100 mm. Infrared spectra taken of such mixtures at room temperature showed that no reaction occurred on mixing. However, when these mixtures were heated above room temperature, explosions resulted. Pressure-temperature explosion limits were determined for mixtures thus prepared of six oxygen to one pentaborane and 12 oxygen to one pentaborane, in both clean and coated bulbs. These limits are shown in Figure 5. Explosions were preceded by ignition lags, and data reported were obtained for explosions occurring within a 5-minute heating period. Mixtures at a given pressure exploded at lower temperatures in coated bulbs than in clean bulbs.

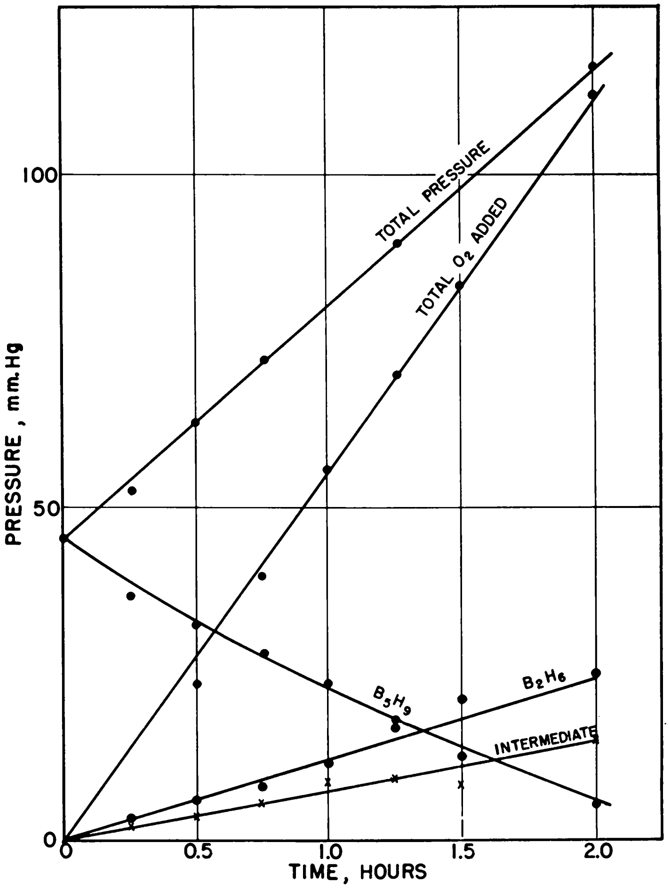

Figure 7. Analysis of reaction in infrared transmitting vessel between pentaborane and oxygen added through leak at indicated rate; compositions obtained from infrared absorption measurements; hydrogen and boric oxide formed not shown

These results obtained on mixtures of relatively high total pressures compared to the pressures used by Price (*3*) and Baden and coworkers (*2*) demonstrate clearly that the temperature at which a given pentaborane-oxygen mixture explodes is greatly dependent upon the rate at which the two reactants are mixed.

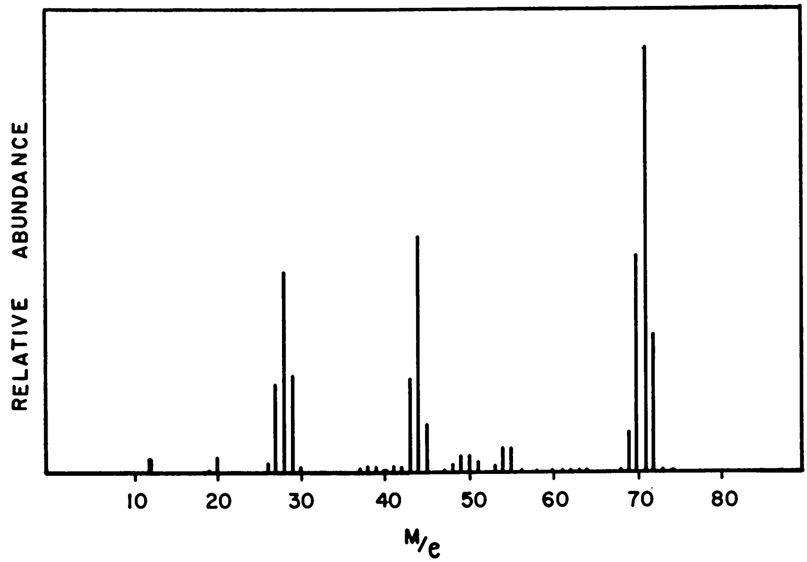

Figure 8. Mass spectrum of intermediate formed in the partial oxidation of pentaborane

Slow Addition of Oxygen to Pentaborane

On the slow addition of oxygen to a large excess of pentaborane, an immediate reaction takes place at room temperature with the final products being diborane, hydrogen, and a boron oxide. This reaction was carried out in a reaction cell with rock salt windows, shown in Figure 6. The progress of the reaction was followed by means of infrared measurements. During the reaction new absorption bands appeared which could not be assigned to diborane, pentaborane, other boron oxides, or to

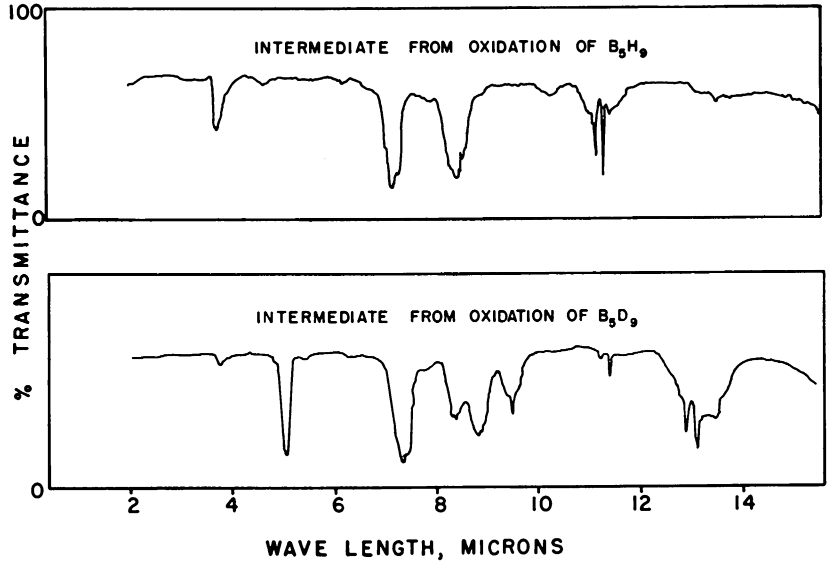

Figure 9. Infrared spectra of intermediates formed during partial oxidation of diborane and deuterated diborane

any of the known boron hydrides, showing that an intermediate was being formed, in amounts depending on the rate of oxygen addition. For example, when oxygen was slowly added at 40 to 100 × 10^{-5} mole per hour to pentaborane at 20- to 30-mm. pressure at 20°C., the intermediate was formed at a rate comparable to the rate of diborane formation. When the rate of addition was decreased to 6 × 10^{-5} mole per hour, the concentration of the intermediate found was negligible. Typical results are shown in Figure 7.

Oxidation Intermediate in Pentaborane-Oxygen Reaction

The intermediate was less volatile than diborane and more volatile than pentaborane. Its vapor pressure from −95° to −62°C. was slightly higher than that of tetraborane. Attempts to measure the vapor pressure of the liquid form accurately over a temperature range were unsuccessful because as soon as the intermediate compound was present in appreciable amounts as a liquid it decomposed violently. The molecular weight as determined by gas density measurements was 70 to 71. The amounts of orthoboric acid (H_3BO_3) formed by hydrolysis of the intermediate and

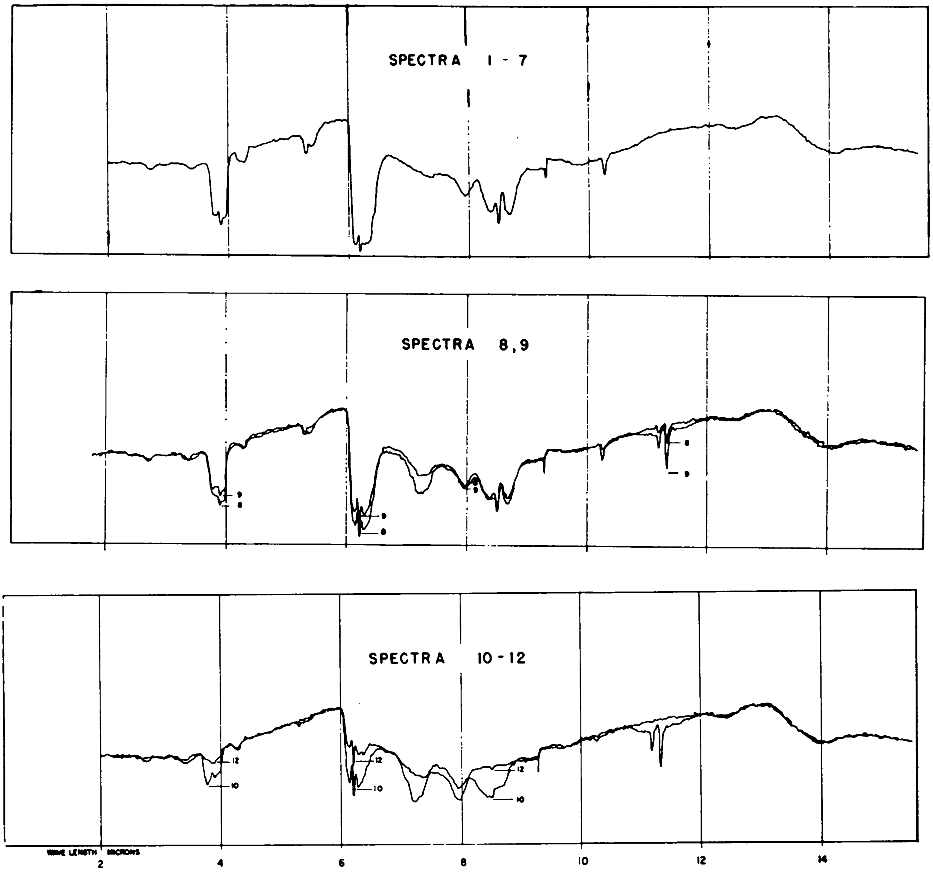

Figure 10. Spectra showing formation of intermediate by heating diborane with oxygen

Spectra 1-7. Room temperature to 122°C. for 2 hours
Spectra 8, 9. Temperature, 122° to 150°C. for 0.5 hour
Spectra 10-12. Temperature, 150°C. for 0.5 hour

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subsequently titrated corresponded to a formula with four atoms of boron per molecule.

The mass spectrum of the intermediate is shown in Figure 8. The highest mass peak occurs at mass 72. When the oxidation was carried out by slow addition of oxygen enriched 1.5% in oxygen-18 the resultant intermediate had a mass spectrum with the highest peak at 74; hence it was concluded that oxygen was present in the molecule.

The infrared spectrum of the intermediate is shown in Figure 9 and in this same figure is the spectrum of the intermediate formed when B_5D_9 was slowly oxidized. These spectra are most informative. No bands characteristic of bridge hydrogens are observed. Also, because no OH bands or OD bands were observed, the oxygen atom must be connected to boron atoms. The band at 1390 cm.$^{-1}$ corresponds to the B—O linkage. The relative simplicity of the spectrum for a molecule of so many atoms indicates that the molecule must be highly symmetrical. A plausible formula for the intermediate is $B_4H_{12}O$, if the results of hydrolysis are taken into account.

Recently this same intermediate has been detected in diborane-oxygen mixtures heated at temperatures near the third thermal limit of explosion. Infrared spectra taken during this reaction are shown in Figure 10. The characteristic bands of the intermediate at 882 and 893 cm.$^{-1}$ are evident.

In all cases the oxide formed had a characteristic absorption spectrum attributed

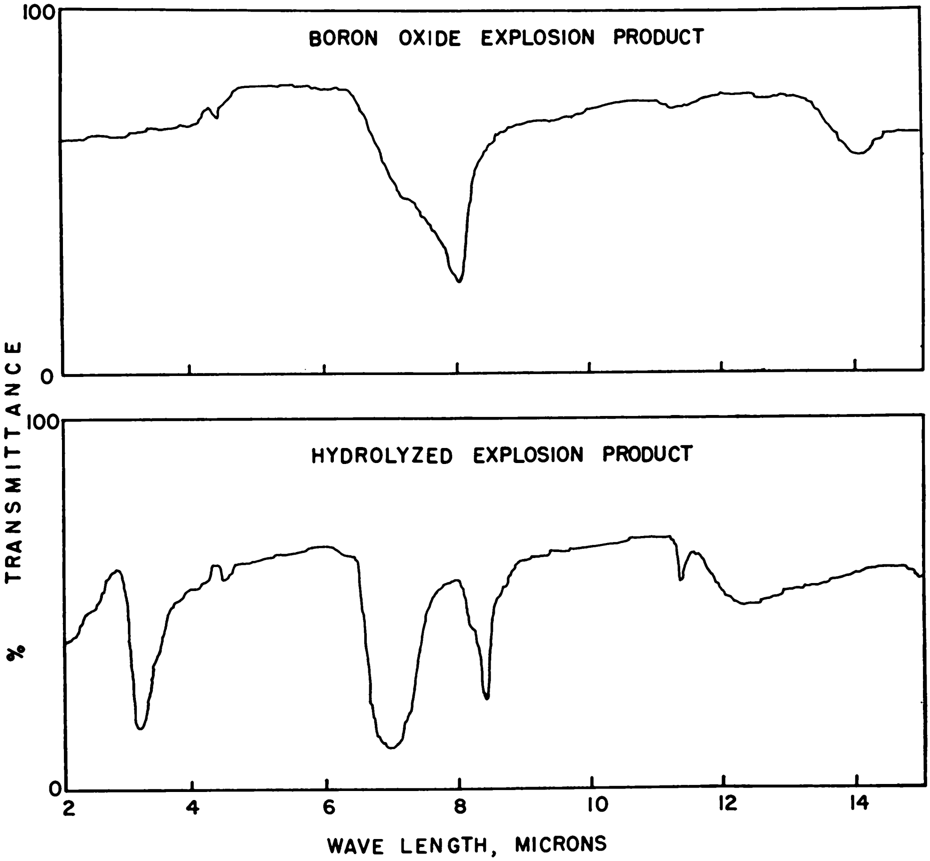

Figure 11. Infrared spectra of boron oxide explosion product formed in oxidation of diborane, and of the explosion product after hydrolysis

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to boron oxide. When water was allowed to react with this compound, even in the absence of oxygen the product was boric acid. In Figure 11 the absorption spectrum of the oxide is shown together with the spectrum of H_3BO_3 resulting from its hydrolysis.

Discussion

For the three borane hydrides studied, critical pressures and temperatures were found defining an explosive region, outside of which the mixtures of boranes and oxygen were stable or reacted nonexplosively. In the case of diborane oxidation, effects of addition of argon, nitrogen, helium, and hydrogen support a reaction involving bimolecular chain branching and trimolecular chain breaking. Sensitivity of the reaction to addition of nitrogen dioxide, nitric oxide, and iron carbonyl is in agreement with the participation of oxygen atoms in the reaction chains. A mechanism analogous to that for hydrogen oxidation at the second limit was proposed (*6*), as follows:

$$BH_3 + O_2 \rightarrow BH_2OH + O \tag{1}$$

$$\left.\begin{array}{r} O + B_2H_6 \rightarrow BH_2OH + BH_3 \quad (2) \\ BH_2OH + B_2H_6 \rightarrow BH_3 + B_2H_5OH \quad (3) \end{array}\right\} \text{chain branching}$$

$$BH_3 + O_2 + M \rightarrow HBO_2 + H_2 + M \text{ chain breaking} \tag{4}$$

$$BH_3 + B_2H_6 \rightarrow B_3H_7 + H_2 \tag{5}$$

$$B_3H_7 \rightarrow \text{higher hydrides} \tag{6}$$

$$B_2H_5OH \text{ — further oxidation} \tag{7}$$

The mechanism proposed does not explain the fact that when explosions were conducted in infrared absorption cells, the reaction products always contained water and boron trioxide, but no boric acid. This indicates that the explosive oxidation of the boranes may proceed with the direct formation of boron trioxide and that the hydrogen present in the hydrides is oxidized directly to water. In the case of the partial oxidation of pentaborane at 25° to 30°C., hydrogen and diborane are formed and are obtained as reaction products. It may be that hydrogen is first formed from the hydrides in the explosive reaction also, but that in this case the temperature soon rises above the explosive limit for hydrogen-oxygen mixtures, thus igniting the hydrogen. In the slow oxidation of diborane above the second limit and in the partial oxidation of pentaborane, the concentration of the intermediate increases to a maximum and finally falls off to zero during the reaction. From this it appears that an alternative path to the explosive oxidation is the formation of the intermediate from active fragments formed in the initial oxidation steps. The effect on the propagation of chains of the formation of nuclei of solid boron trioxide must be considered.

Even though the mechanism of the oxidation of the boranes is far from being understood, further study of the oxidation should be valuable because of the characteristics intermediate between those of the oxidations of hydrogen and carbon monoxide and those of the hydrocarbons. A notable feature is that the boranes and the intermediate thus far detected, as well as the boron trioxide found, all have distinctive infrared absorption spectra, permitting study of the progress of the oxidation in cells equipped with rock salt windows. The sensitivity of the explosive oxidations to iron carbonyl and other additives indicates the importance of further studies of the mechanism of inhibition, with the possibility of effective control of the region of pressures and temperatures of spontaneous explosion.

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In BORAX TO BORANES;
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Mass Spectrometry in Boron Chemistry

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The application of mass spectrometry to boron chemistry is particularly useful from both structural and analytical viewpoints. The technique of isotopic variation of the two stable boron isotopes as well as the hydrogen isotopes permits determination of the number of boron and hydrogen atoms in a molecule without the need to isolate the compound from a mixture. It also simplifies assignment of the various fragmentation species in the mass spectral pattern. The mass spectra of all known boron hydrides are presented, and from their monoisotopic spectra relationships in fragmentation patterns have been deduced.

Mass spectrometry is a particularly valuable tool in the chemistry of boron-containing compounds because it allows ready identification of compounds based on the two isotopes, boron-11 and boron-10. When a molecule contains several boron atoms in natural isotopic abundance, its mass spectrum has a characteristic pattern which is different from other compounds and is fairly easy to identify, a feature that is important, for example, for analysis of mixtures of hydrocarbons and boranes. The naturally occurring ratio of B^{11}/B^{10} is about 4/1, but boron can also be obtained enriched to give relatively pure boron of the lighter isotope. The use of the boron-10–enriched isotope in a compound is an additional powerful tool, because from the comparison of its mass spectrum with that prepared from isotopically normal boron one can calculate the number of boron atoms in the compound without having to isolate it. One further technique that is applicable to boron-hydrogen systems is the substitution of deuterium for hydrogen. This increases the potential use of mass spectrometry in this field, because it allows one to vary the isotopic composition of boron and hydrogen independently.

Mass Spectra of Boron Hydrides

The gross differences in mass spectra of a boron hydride and an organic compound are illustrated in Figure 1, which compares pentaborane(9) (five borons) and pentane (five carbons). The spectrum of pentane follows the usual pattern for large organic molecules; it has a low parent peak (not shown) at mass number 72 plus several predominant peaks at lower mass numbers. The large peak at *m/e* 43 corresponds to the $C_3H_7^+$ ion fragment and the peaks at *m/e* 42, 41, etc., represent loss of hydrogen atoms from this fragment, while the small peak at mass 44 is due to the carbon-13 isotope.

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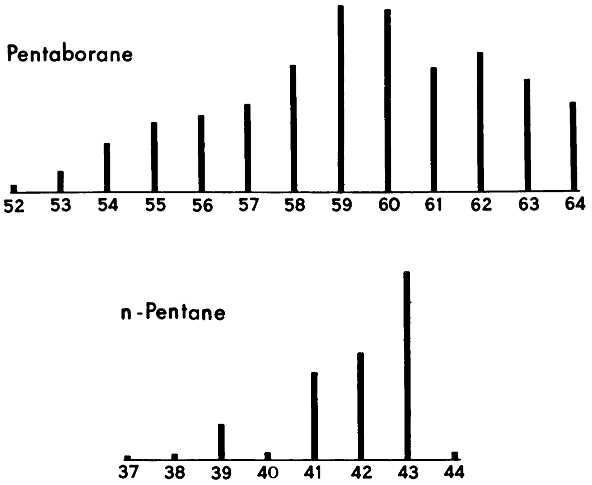

Figure 1. Comparison of principal peaks in mass spectra of a boron hydride and a hydrocarbon

The spectrum of pentaborane(9), on the other hand, is considerably different. Its parent group has a large spread that is caused by distribution of the various boron-11 and boron-10 species, such as $B_5^{11}H_9+$, $B_4^{11}B^{10}H_9+$, and $B_3^{11}B_2^{10}H_9+$, as well as by successive abstractions of hydrogens from these species. If we could resolve its spectrum so that only the parent peaks occurred—e.g., by lowering the ionizing voltage sufficiently—six different isotopic species would be visible. Because hydrogen atoms are lost readily from the parent group under normal operating conditions, the various fragment ions overlap one another to give the spectrum its pronounced spread. Although the mathematics becomes more cumbersome because of the larger number of peaks, this spread becomes useful in separating the spectrum of pentaborane(9) from that of a mixture because one can usually select a peak that is unique for pentaborane(9).

The spread that is observed in the above spectrum is characteristic of the spectra of all the known boron hydrides, the amount varying with the number of borons and hydrogens in the parent molecule. To illustrate this condition the polyisotopic mass

Table I. Normal Statistical Distribution of Boron Isotopes (80% Boron-11, 20% Boron-10) in a $B_x^{10}B_y^{11}$ System Where $x + y$ Varies from 1 to 10

	B_0^{10}	B_1^{10}	B_2^{10}	B_3^{10}	B_4^{10}	B_5^{10}	B_6^{10}	B_7^{10}	B_8^{10}	B_9^{10}	B_{10}^{10}
B_0^{11}	—	20.0	4.0	0.8	0.16	0.03	6×10^{-3}	1×10^{-3}	3×10^{-4}	5×10^{-5}	1×10^{-5}
B_1^{11}	80.0	32.0	9.6	2.56	0.60	0.15	0.04	8×10^{-3}	2×10^{-3}	4×10^{-4}	
B_2^{11}	64.0	38.4	15.4	5.1	1.54	0.43	0.11	0.03	7×10^{-3}		
B_3^{11}	51.2	41.0	20.5	8.2	2.9	0.92	0.28	0.08			
B_4^{11}	41.0	41.0	24.5	11.5	4.6	1.7	0.55				
B_5^{11}	32.8	39.2	27.5	14.7	6.6	2.6					
B_6^{11}	26.2	36.7	29.4	17.6	8.8						
B_7^{11}	21.0	33.6	30.2	20.1							
B_8^{11}	16.8	30.2	30.2								
B_9^{11}	13.4	26.8									
B_{10}^{11}	10.7										

$$B_x^{10}B_y^{11} - \frac{(x + y)!}{x!y!}(B^{10})_x(B^{11})_y$$

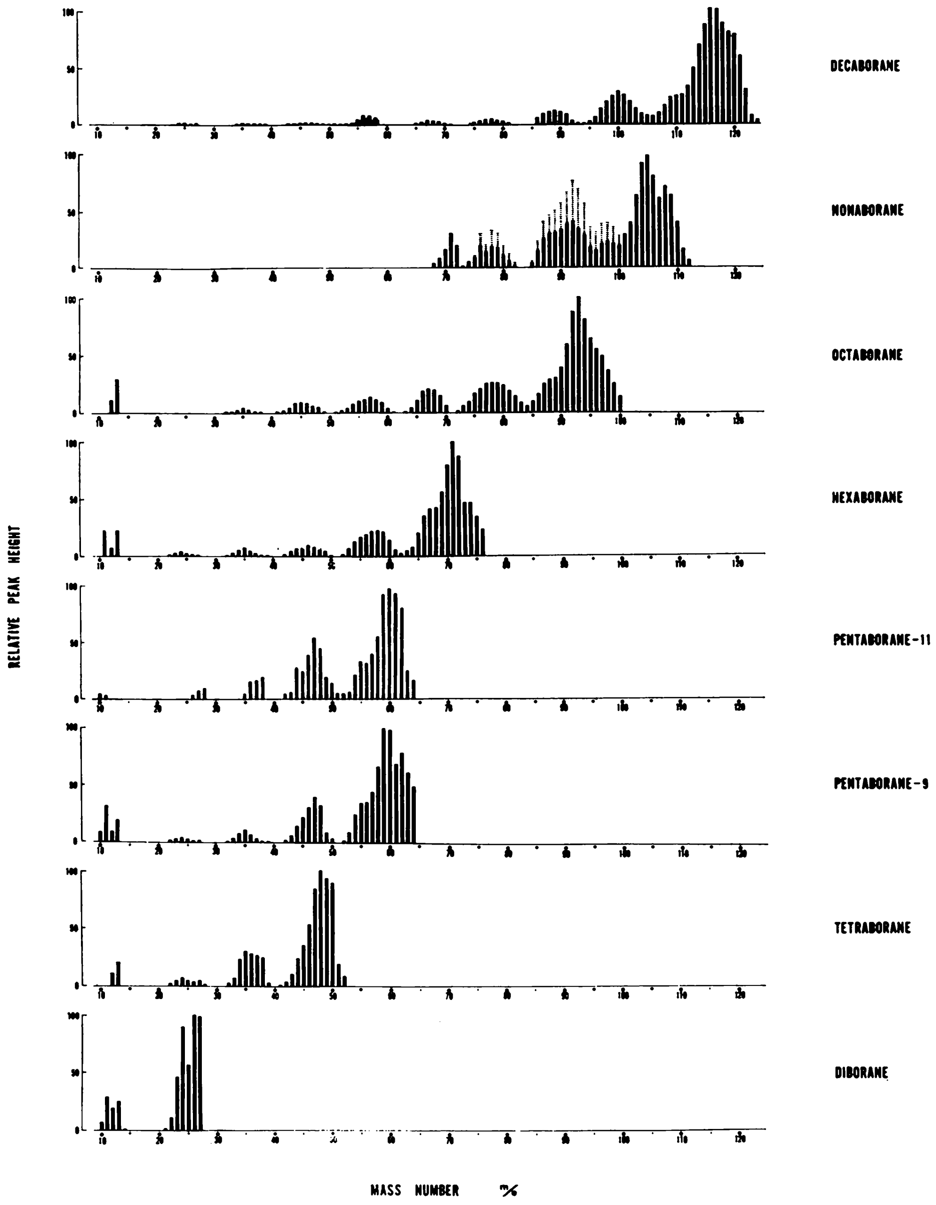

Figure 2. Mass spectra of boron hydrides

spectra of all known boron hydrides are shown in Figure 2. Although some spectra have been published (*1–4*, *13*, *14*, *18*), all those shown were prepared in this laboratory.

To show how the distribution of boron species is affected by the number of boron atoms present, Table I gives the statistical distribution for an 80–20 boron system in which the concentration of species for any compound is given along the diagonal, as indicated for pentaborane(9).

In addition to the observed increase in spread with an increase in the number of boron atoms, another useful feature of boron hydrides in dealing with mixtures is the occurrence of doubly charged ion peaks. These are not illustrated in Figure 2 because of their low intensities, but all of the boron hydrides exhibit them. The mass numbers of the doubly charged species are always less than one half the mass of the principal ion, indicating that they contain fewer hydrogen atoms.

For ordinary analytical purposes the polyisotopic spectrum is sufficient. However, if one is concerned with structure changes, such as occur in exchange work and in kinetics, it is necessary to simplify the spectrum by reducing it to its monoisotopic form, which allows direct comparison of species. The monoisotopic spectrum is calculated by simply stripping out all species that contain boron-10. This can be done without any previous knowledge of the relative concentrations of the two boron isotopes, because the correct value to use is that which gives the minimum stripping residues.

The authors and a number of other workers (*2–4*, *13*, *17*) have found that the optimum value of the ratio of the boron isotopes to use in stripping boron hydrides is 4.0, which is equivalent to 80% boron-11 and 20% boron-10. There has been considerable controversy in the past over the correct B^{11}/B^{10} ratio, and the difference between 4.0 and the "generally accepted" value of 4.3 exceeds simple experimental error. The value 4.3 was obtained (*7*) from the mass spectrum of boron trifluoride, but subsequent work (*12*, *15*) has indicated that factors such as selective desorption of $B^{11}F_3$, as well as impurities, were neglected and could account for the discrepancy. Recent work (*11*) also indicated possible selective fragmentation, so the "accepted isotopic boron ratio," 4.3, appears to be in error.

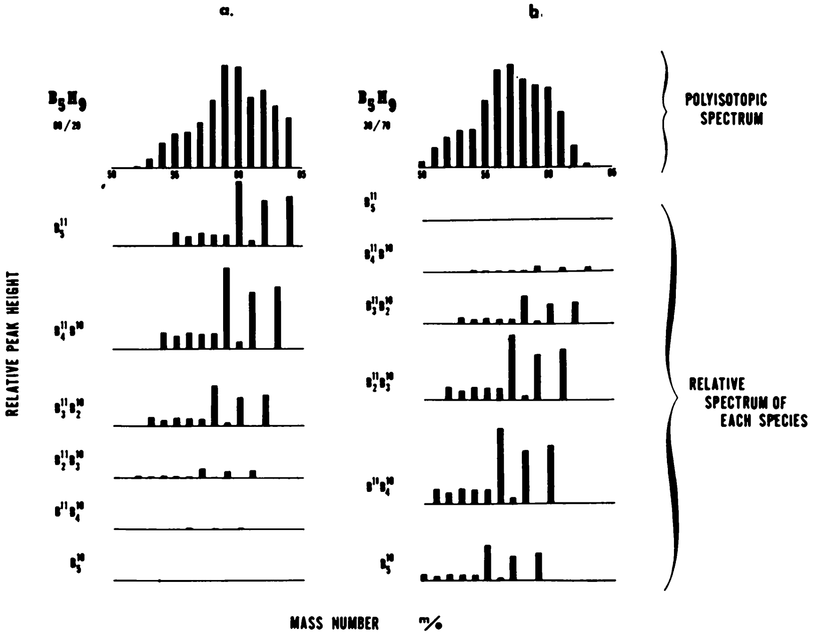

Figure 3. Effect of boron isotope content upon mass spectrum of pentaborane

a. 80% B^{11}, 20% B^{10}
b. 30% B^{11}, 70% B^{10}

Comparisons between the polyisotopic and monoisotopic spectra of pentaborane(9) are given in Figure 3 for two isotopic boron ratios, 4.0 and 0.43. The relative fragmentation pattern for each species is the same in both cases, and a critical examination of the spectra of both pentaborane(9) and diborane shows very good agreement between the boron-10 and the boron-11 monoisotopic species, at least within experi-

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mental error. If there were a measurable difference in fragmentation between a $B^{10}H$ and a $B^{11}H$, the mass spectra of hydrocarbon derivatives of the boron hydrides would be complicated by the overlap of boron and carbon species, and complete resolution of these spectra would be impossible.

Figure 4 shows the monoisotopic mass spectra (subject to revision) for the parent groups of the various boron hydrides. For comparison the spectra have been aligned

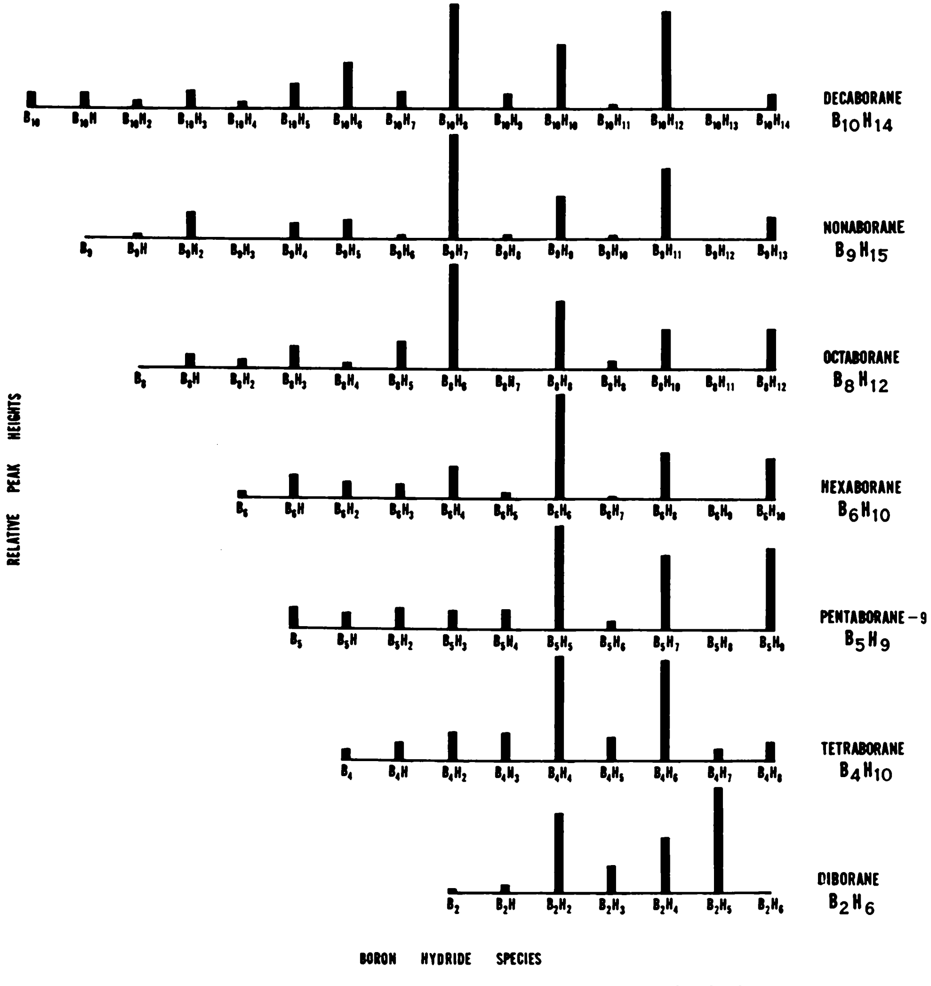

Figure 4. Monoisotopic mass spectra of boron hydrides

on the basis of B_xH_x, so that $B_{10}H_{10}$, B_9H_9, etc., lie under one another. It is noteworthy that, with the exception of diborane, the loss of hydrogens occurs first in pairs, and then singly, which is undoubtedly a consequence of their structures. It would be enlightening to be able to distinguish between the fragmentation of terminal hydrogens and bridge hydrogens and ascertain whether one or the other ruptures preferentially to yield hydrogen. In his studies on the mechanism of hydrolysis and alcoholysis of pentaborane, the senior author is working with partially deuterated pentaboranes (*9, 10*) in which the bridges are occupied predominantly by deuterium and the terminal positions by hydrogen. Another example where mass spectral information may be useful in structure studies occurs in the case of nonaborane. A proposed structure for nonaborane gives an odd number of bridge hydrogens (*5*, *6*), yet its monoisotopic spectrum bears a strong resemblance to that of decaborane, which, according to its accepted structure (*8*), contains four bridge hydrogens. Further isotopic studies on nonaborane are thus warranted.

The boron-10–enriched compounds of most of the boron hydrides have been prepared, and the monoisotopic spectra calculated from those data are in substantial agreement with the boron-11 spectra shown here. Recently published data (*17*) show that the monoisotopic spectrum of deuteropentaborane(9) follows essentially the same pattern as that for normal pentaborane(9).

Mass Spectra of the Alkyldiboranes

As part of the study of the mass spectra of boron systems, work has been extended into the organoborane field, with particular emphasis on the alkyldiboranes.

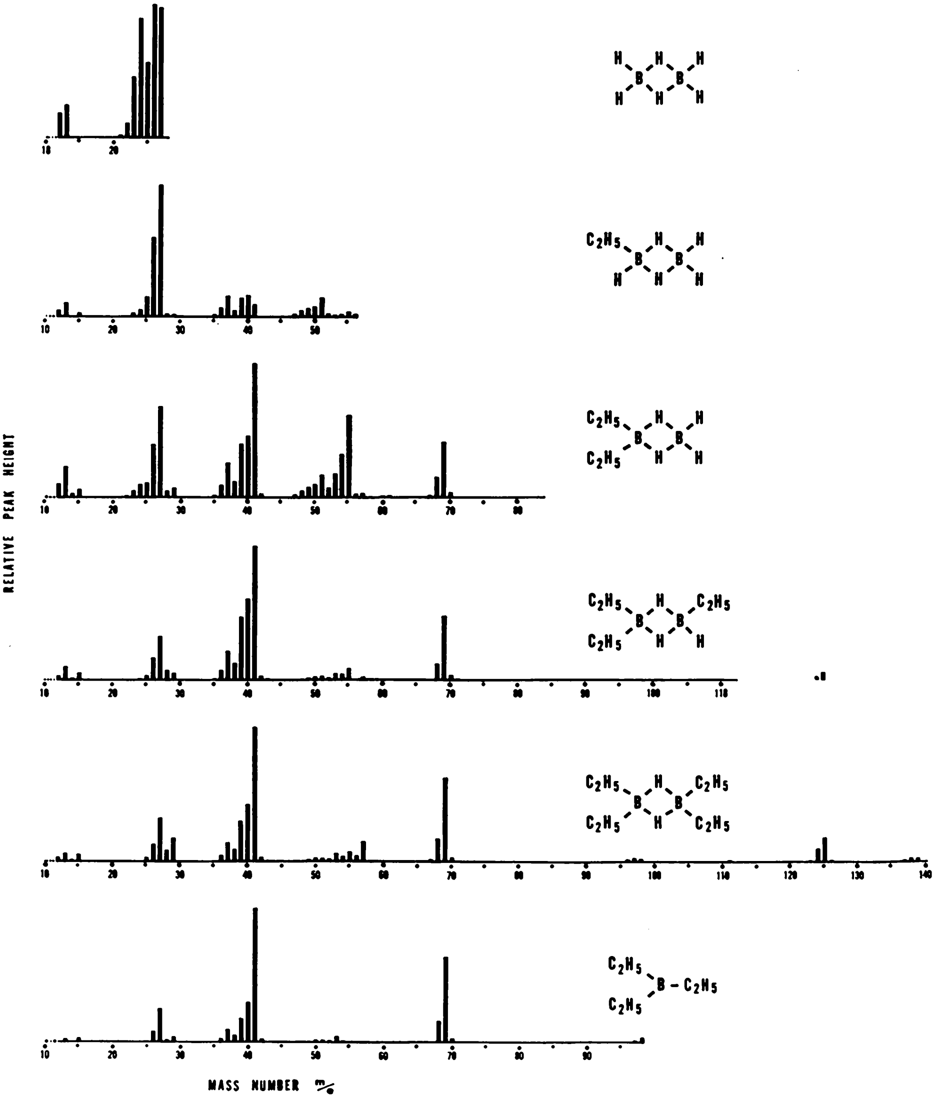

Figure 5. Mass spectra of ethyldiboranes and their parent compounds

The alkyldiboranes form an extremely interesting family of compounds, rich in mass spectral information as well as useful for isotopic exchange studies. The various alkyldiboranes (methyl and ethyl series) can be prepared easily by the Schlesinger method (*16*) of mixing diborane with the appropriate trialkylborane at different ratios of reactants, then separating the compounds according to degree of alkylation by low-temperature fractionation. The mass spectra of the ethyldiboranes have striking similarities (Figure 5). The spectrum of the parent triethylborane shows that the peak at mass 69 is due to the species $(C_2H_5)_2B^{11}$, corresponding to loss of one ethyl group, while similarly prominent peaks at mass 69 also can be observed for tetraethyl-, triethyl-, and 1,1-diethyldiborane, corresponding again to the diethylboron fragment. The mass 40 area exhibits the predominant peak at mass 41 for the same compounds that have the strong 69 peak. At first glance this seems to be straightforward, until it is realized that if two ethyl groups were cleaved from triethylborane, the residual fragment would have a top mass of 40 instead of 41. A plausible explanation is that a hydrogen atom from a cleaved ethyl group attaches itself to the boron atom to give

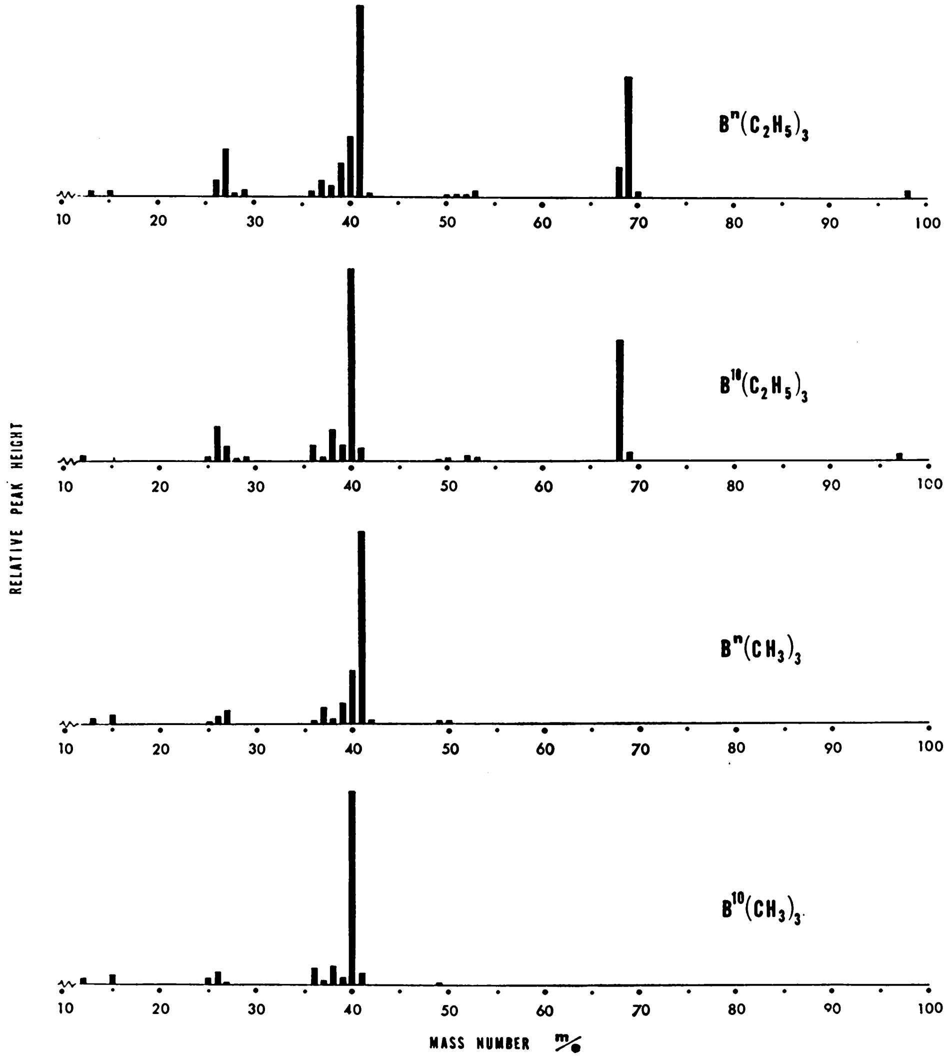

Figure 6. Mass spectra of trimethyl- and triethylboranes

$HBC_2H_5^+$. On might also speculate similarly about the species causing the high peak at mass 55 in the spectrum of 1,1-diethyldiborane. Is it simply due to loss of an ethyl group from the parent molecule, or is it due to loss of a methyl from the diethylboron group, with addition of a hydrogen atom by rearrangement? Obviously, in exchange work the particular species giving rise to each peak must be known. The use of the isotopes of boron and hydrogen can be utilized here.

The mass spectra of trimethylborane and triethylborane containing isotopically normal and boron-10–enriched boron are shown in Figure 6. For transformation of the spectra into monoisotopic form, neither 4.0 nor 4.3 could be used for the B^{11}/B^{10} ratio. To avoid residues in the stripping operation, intermediate values had to be used. Comparison of the boron-10 and boron-11 spectra of triethylborane indicated another difficulty, for, if the comparison were based on the principal peak ($HBC_2H_5^+$), discrepancies at other prominent peaks were apparent. However, if adjustments were made at these other prominent peaks, such as $(C_2H_5)_2B^+$, good agreement was obtained for all true fragmentation species by using a boron ratio of 4.13. For the addition peaks, such as at m/e 41, a ratio of 4.24 was better. The fact that the B^{11}/B^{10} ratio is higher for triethylborane than for the boron hydrides suggests slight differences in boron-isotope effect on electron impact. For the trimethyl series, because the addition peaks are not the predominant ones, the calculation was easier; the boron ratio in this case was 4.12. In the 20 to 30 mass region of the triethylborane spectrum there is an overlap of a boron-carbon species with a straight carbon species. The spectra also show half peaks and metastable peaks which have been correlated with their respective species.

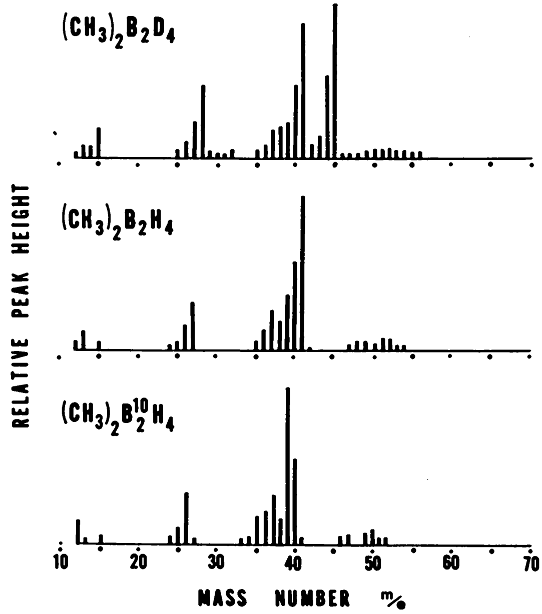

Figure 7. Mass spectra of *unsym*-dimethyldiboranes

The mono-, 1,1-di-, tri-, and tetramethyldiboranes and the corresponding ethyl series containing isotopically normal boron or boron-10–enriched boron, as well as deuterium substitution for hydrogen attached to the borons, have been prepared. The advantage of isotopic substitution in identifying the fragmentation species becomes apparent when the compound, 1,1-dimethyldiborane, is considered. From the structural formula—$(CH_3)_2B_2H_4$—the principal peak at mass 41 could be due either to $(CH_3)_2B^{11}$ or to $CH_3B_2H_4$, representing the loss of one methyl group from the parent compound, or to both. If the compound were prepared with the boron-10–enriched boron, the dimethyl-B^{10} ion would have a peak at mass 40, while the species containing two boron atoms would drop two mass units to mass 39. If instead of exchanging borons the hydrogens attached to the boron were replaced with deuterium, the dimethyl-B^{11} species would remain unchanged at mass 41, but the species containing two borons would go up four units to mass 45. Figure 7 compares the three isotopic variations of 1,1-dimethyldiborane, the center spectrum being that of the isotopically normal compound. The lower spectrum (boron-10–enriched compound) shows strong peaks at masses 40 and 39. The 40 peak is due to the dimethyl-B^{10} species, and as we know that from the trimethylborane spectrum the loss of one hydrogen from the carbon is relatively small, the high 39 peak must represent the two-boron species. The top spectrum (boron-deuterated compound) exhibits strong peaks at both masses 41 and 45, again indicating the presence of both species.

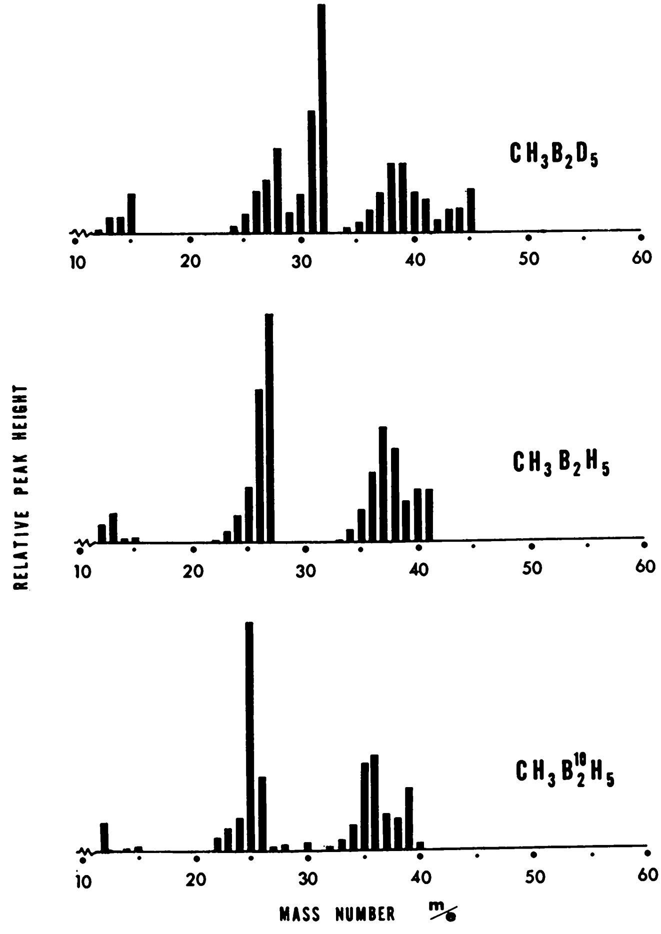

Figure 8. Mass spectra of monomethyldiboranes

In the next lower mass region, the high peak at mass 27 for the isotopically normal compound could represent the $CH_3B^{11}H$ species, or, if there were a rearrangement or addition, the species could be $B_2{}^{11}H_5$. With boron-10–enriched compound

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the high peak at mass 26 corresponds to $CH_3B^{10}H$ and the peak at mass 25 could be either the mass 26 species with one less hydrogen, or $B_2{}^{10}H_5$. However, the deutero spectrum has a prominent peak at mass 28, indicating the presence of $CH_3B^{11}D$ (not B_2D_5). The mass 28 peak clearly indicates that the hydrogen comes from the boron hydride counterpart and not from the carbon.

The mass spectra of the isotopic variations of monomethyldiboranes are given in Figure 8. As might be expected, the spectra are rather similar to the dimethyl series. The most prominent species is B_2H_5, occurring at mass 25 for the boron-10–enriched boron, at mass 27 for the $B_2{}^{11}H_5$ species, and at mass 32 for the deuterated species. The presence of the CH_3BH species also is detected in the deuterated spectrum.

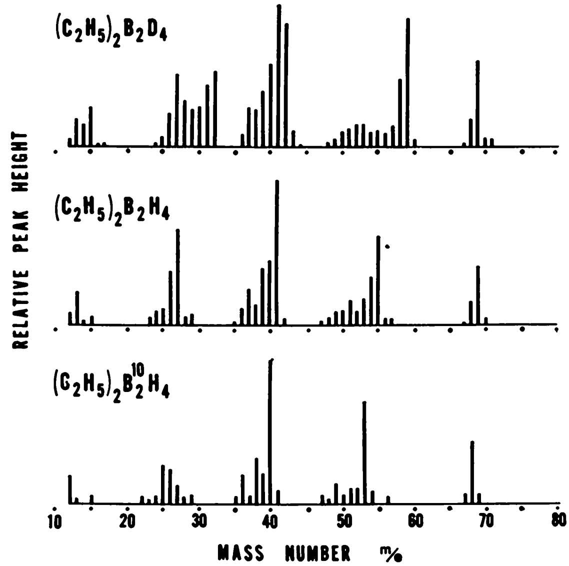

Figure 9. Mass spectra of *unsym*-diethyldiboranes

In general, the spectra for all the methyldiboranes have either an overlap or a complex species—i.e., one containing one or more carbon groups with two boron atoms. The reason for the overlap is that the boron group differs in mass units only slightly from the methyl group. Thus calculation of the concentration of species becomes difficult. On the other hand, in the ethyldiboranes the separation is more distinct, because the comparison is usually with an ethyl instead of a methyl group.

Of the ethyl series, the spectra of the *unsym*-diethyldiboranes is perhaps the most interesting (Figure 9). The peak at mass 69 for the isotopically normal and deuterated boron compounds and the peak at mass 68 for the boron-10–enriched compound are associated with the diethylboron species. The peak at mass 53 in the lower spectrum, the peak at mass 55 in the center spectrum, and the peak at mass 59 in the upper spectrum are associated with the $C_2H_5B_2H_4$ species. A similar relation exists at masses 49, 51, and 53 with the species $BHBC_2H_4$. The predominant peaks occurring at masses 40, 41, and 42, respectively, together with peaks occurring down through mass 35, are associated with the species C_2H_5BH. The peaks in the *m/e* 25 to 30 region are due to pure carbon-hydrogen species as well as boron-carbon-hydrogen species. The peaks terminating at *m/e* 32 in the deuterated compound may be due to monoethyldiborane impurity. With the triethyldiboranes (Figure 10) an analogous argument can be given, but in this case the peaks in the *m/e* 50 region are fairly small.

Once the concentrations of species for the alkyldiboranes are calculated, kinetics and exchange work become possible. Some preliminary experiments indicate, for

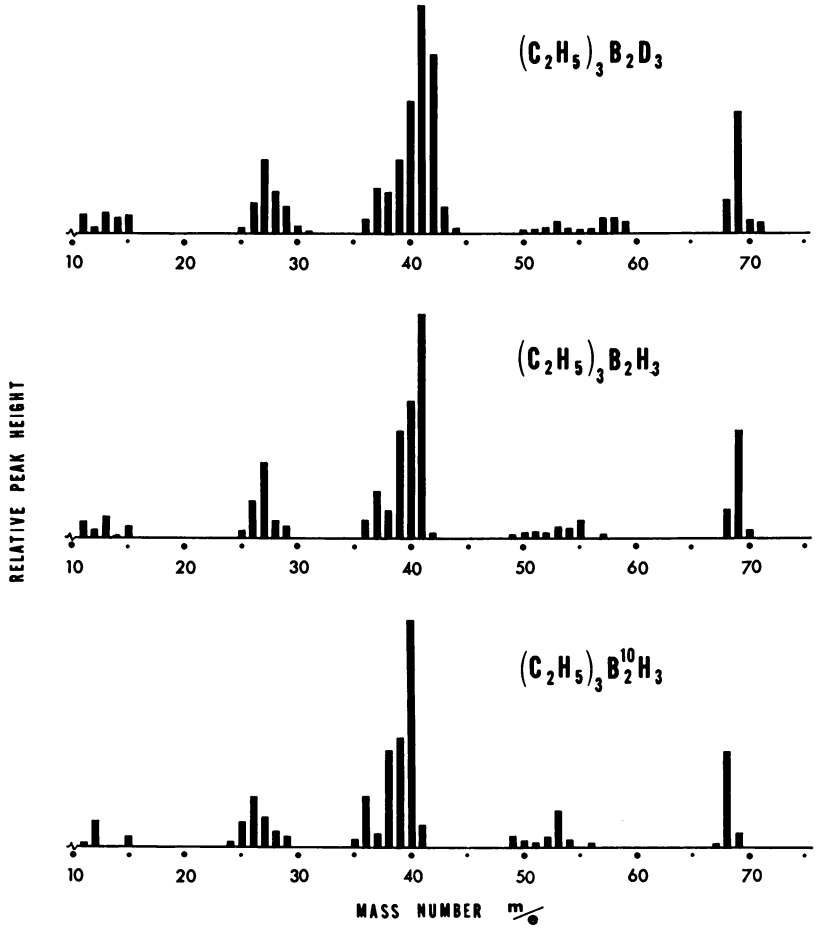

Figure 10. Mass spectra of triethyldiboranes

example, that when boron-10-enriched diborane is mixed with isotopically normal 1,1-diethyldiborane there is an immediate exchange. Close inspection reveals that the boron attached to the two ethyl groups does not exchange as rapidly as the other boron atom. This is due undoubtedly to the fact that exchange occurs primarily by making and breaking of bridge bonds, a process which would not affect the R_2BH group because of its inability to form (double) bridge bonds.

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Infrared Spectrometry in Boron Chemistry

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Various techniques in the application of infrared spectrometry to structural problems in borane chemistry are discussed. These include compensation methods with double-beam instruments, isotopic substitution techniques, and the determination of trends in series of structurally related compounds. Vibrational effects of deuterium and alkyl substitutions on diborane are discussed.

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The purpose of this discussion is to give an over-all picture of how the authors have applied infrared spectrometry in their laboratory to structural problems in borane chemistry. Rather than detailed data only the general techniques involved are considered, including topics such as compensation methods with double-beam instruments, isotopic substitution techniques, and trends in series of structurally related compounds. The paper is further limited to examination of the vibrational effects of deuteration and alkyl substitutions in diborane.

The published literature contains relatively little information about vibrational spectra of boron hydrides and their derivatives. Aside from diborane, the vibrations of which have been thoroughly investigated (*5, 13, 19, 22, 31, 34*), vibrational spectra are reported for tetraborane (*20*), stable and unstable pentaborane (*11, 20, 35*), and decaborane (*12*). The borane derivatives that have been studied by Raman and/or infrared spectroscopy are: borane carbonyl (*1, 6, 7, 32*), ether and amine borane complexes (including ammonia trimethylborane) (*9, 23, 25*), phosphorus trifluoride borane (*33*), a few trialkylboranes (*3, 17, 18, 27, 30*), some dialkoxyboranes (*14, 16*), and a number of boron halides. Dimethylaminodiborane has been studied (*4, 21, 29*), and a little has appeared on the spectra of alkyldiboranes (*6, 24, 26, 28*).

Diborane

In diborane the two boron atoms are linked by bridges consisting of two hydrogen atoms, which, according to accepted theory (*8*), are attached to the boron atoms by two three-centered bonds. It is the only known compound containing a double-hydrogen bridge. In addition, each boron has two terminal hydrogens, the four bonds around each boron being approximately tetrahedral. The two borons and the four terminal hydrogens lie in one plane, perpendicular to the plane formed by the borons and the two bridge hydrogens.

Perhaps from a chemical point of view this molecule may be considered simple; from a vibrational point of view, however, it is complex. The eight atoms of diborane have 24 degrees of freedom, 18 of which are internal vibrations (*1*). These vibrations

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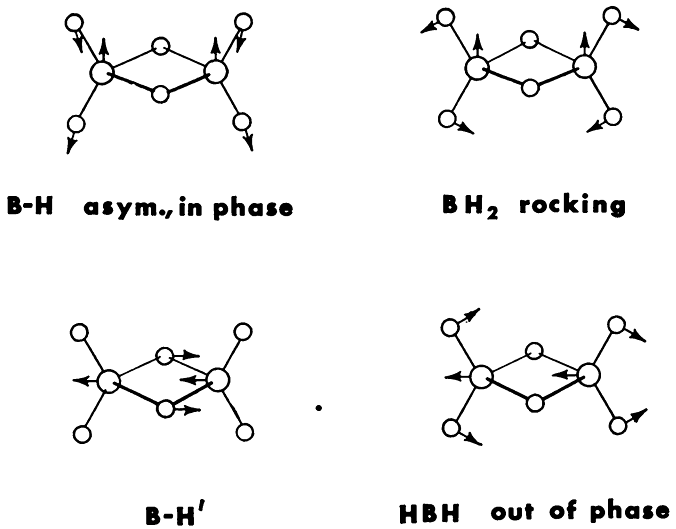

Figure 1. Four of the infrared active vibrations of B_2H_6

will cause scattering (the Raman effect) or absorption (the infrared spectrum). Whether a particular vibration appears in one or the other spectrum (or both, or neither) is determined by selection rules (*10*), which are beyond the scope of this discussion. One vibration is forbidden in both spectra—i.e., "totally inactive"—while

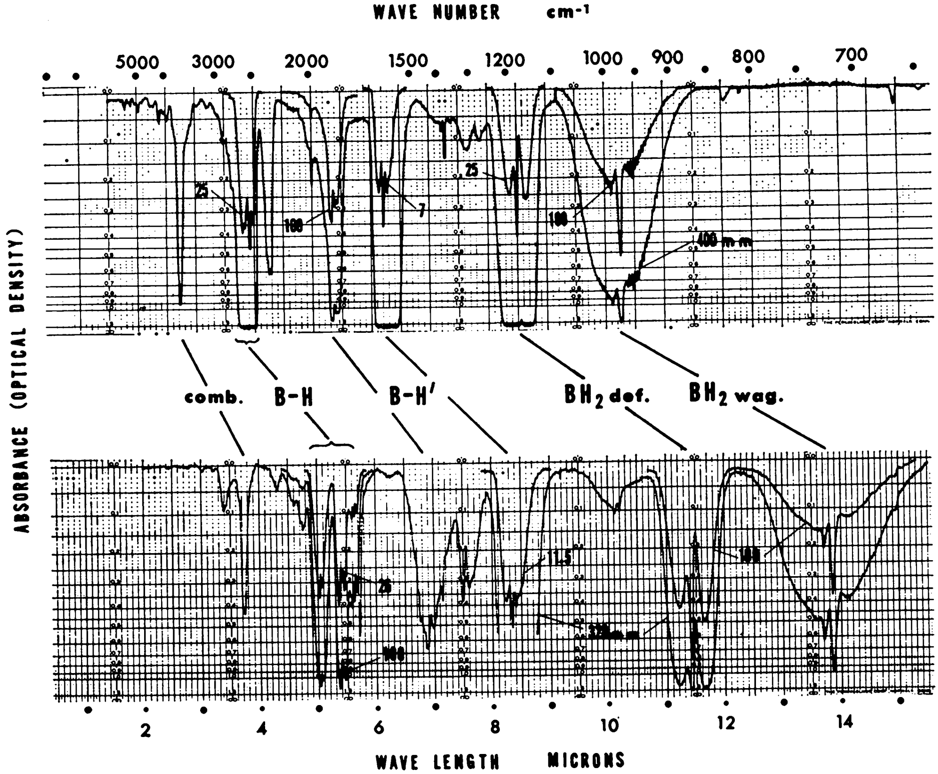

Figure 2. Frequency shifts: B_2H_6 to B_2D_6

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all the others are either infrared active or Raman active. In this case, because of the center of symmetry, the vibrations are active in one or the other but not in both.

Figure 1 shows four of these vibrations. Each involves all or most of the atoms of the molecule, yet each can be described essentially as stretching or distortion of certain bonds—i.e., they are characteristic of a certain group. The upper left vibration involves stretchings of the B—H (terminal) linkage, with the two hydrogens oscillating asymmetrically about each boron (one stretches, while one contracts) and with the two ends of the molecule vibrating in phase with each other. The upper right vibration represents an in-plane rocking of the two BH_2 parts of the molecule. The lower left vibration is one of the B—H′ (bridge) stretching modes, while the final one represents a deformation of the HBH angle, the two ends vibrating out of phase with each other. All of these vibrations involve changes of dipole moment and hence are infrared active.

It is fortunate, especially for the analyst, that whenever certain atom groups or certain bonds appear in a molecule, the characteristic frequencies associated with them usually appear in the infrared and Raman spectra. Thus there are frequencies characteristic of C—H bonds, B—H bonds, B—C bonds, etc.

It is important to be able to recognize infrared bands as being characteristic of certain bonds, for this information can then be used to identify bonds and groups and to help determine structures of new compounds. This fundamental knowledge is best obtained through the study of the simpler molecules, of which diborane is an example.

The infrared spectrum of diborane, with labels for the "characteristic" bands, is shown in the upper part of Figure 2. These same bands appear (sometimes slightly shifted) in other molecules containing the same atom groupings.

Deuterated Diboranes

The lower half of Figure 2 illustrates the effect of replacing hydrogen atoms by deuteriums. This generally causes a lowering of the frequencies—the heavier atoms

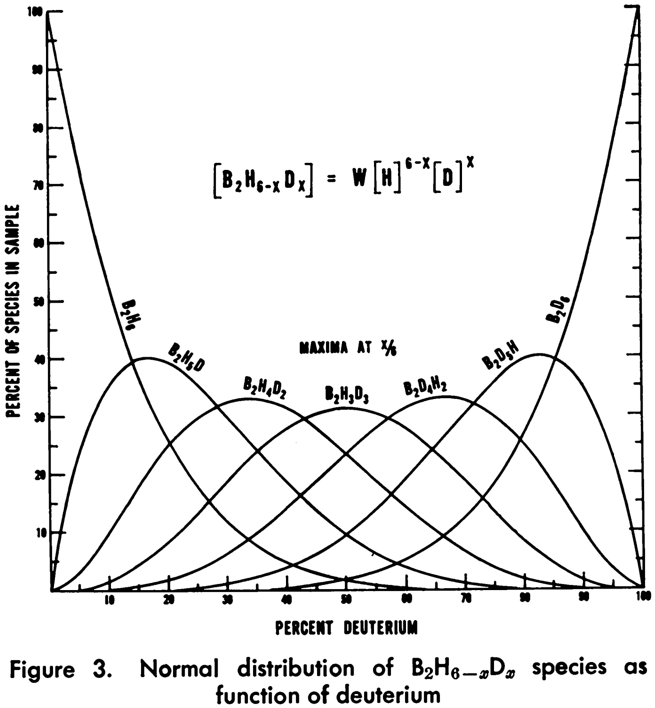

Figure 3. Normal distribution of $B_2H_{6-x}D_x$ species as function of deuterium

can be pictured simply as moving more sluggishly—and for each B_2H_6 band there is a corresponding one for B_2D_6 at a lower frequency. Whenever B_2H_6 and B_2D_6 are mixed together, there is a rapid redistribution of hydrogen and deuterium, and an equilibrium is established among B_2H_6, B_2H_5D, $B_2H_4D_2$, $B_2H_3D_3$, $B_2H_2D_4$, B_2HD_5, and B_2D_6. Their statistically calculated concentrations as functions of the deuterium content are given in Figure 3, where *W* represents the statistical weighting factors (binomial coefficients for six entities).

In order to obtain a spectrum of B_2H_5D a mixture of 95% B_2H_6 and 5% B_2D_6 was chosen. Figure 3 shows that this will result in about 74% of B_2H_6, 23% of B_2H_5D, and a small amount of $B_2H_4D_2$—a rather unhandy mixture. But in the Perkin-Elmer Model 21 double-beam spectrophotometer, one may compensate for the 74% of B_2H_6 "impurity" by using pure B_2H_6 in the compensating beam at the appropriate pressure. The small amount of $B_2H_4D_2$ present can be ignored.

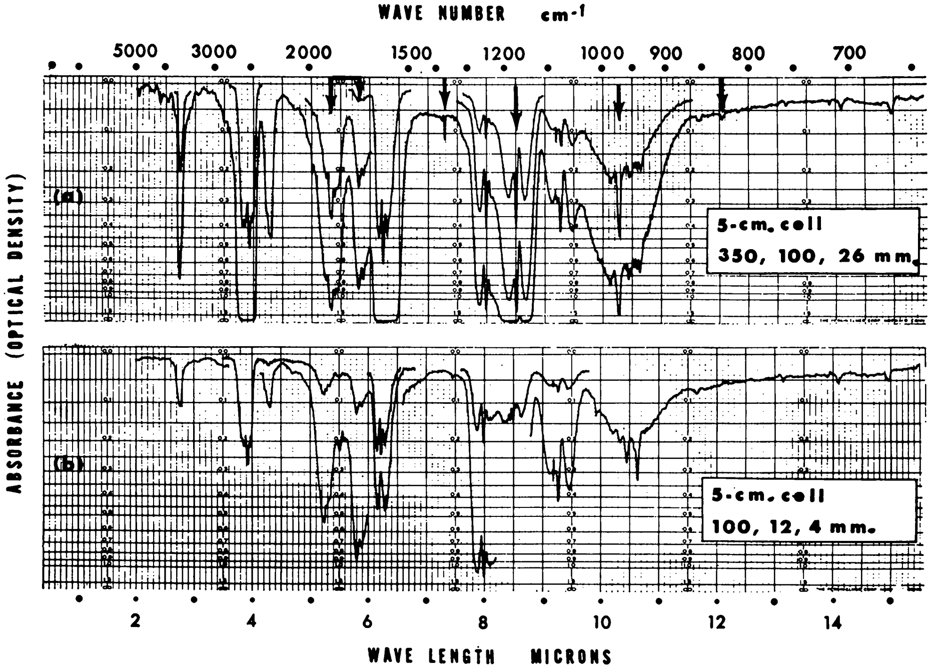

Figure 4. a. Mixture of 95% of B_2H_6 and 5% of B_2D_6 (74% of B_2H_6 + 23% of B_2H_5D)
b. Compensated B_2H_5D

Figure 4 shows a spectrum of the uncompensated mixture and the compensated spectrum of B_2H_5D (the arrows indicate B_2H_6 bands).

At this point an experimental difficulty should be mentioned. Whenever the absorption in the compensating beam exceeds about 80 or 90%, not enough energy is available to activate the pen. The pen response becomes sluggish and eventually ceases altogether. The curve traced out under this dead-pen condition has no relation to the absorption in the sample beam and thus is meaningless.

This condition is illustrated in Figure 5. The center spectrum shows the 95/5 mixture when compensated by B_2H_6. Whenever B_2H_6 (in the compensating beam) absorbs strongly, the pen is dead (see arrows). It is at these points that the principal curve in Figure 4 is interrupted. The obvious remedy is to reduce sample pressures in both cells until the pen responds again (lower chart of Figure 5).

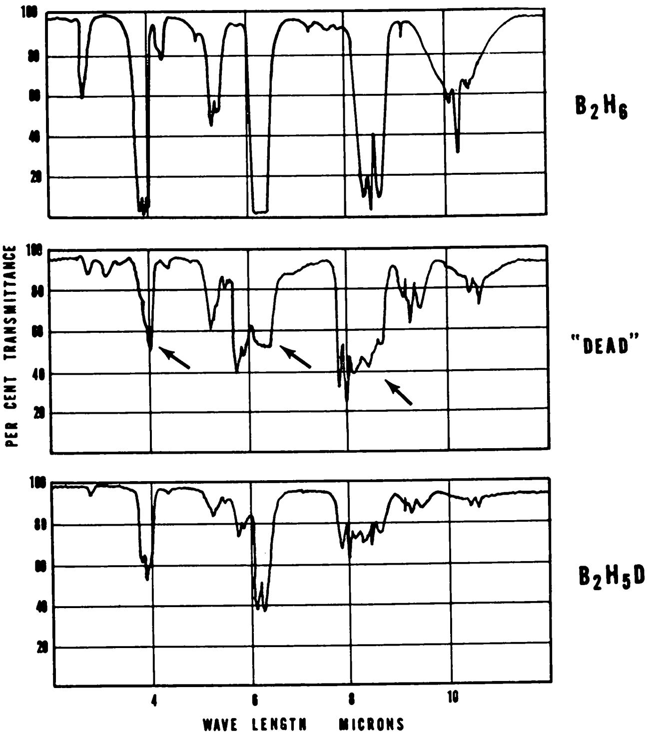

Figure 5. Dead pen

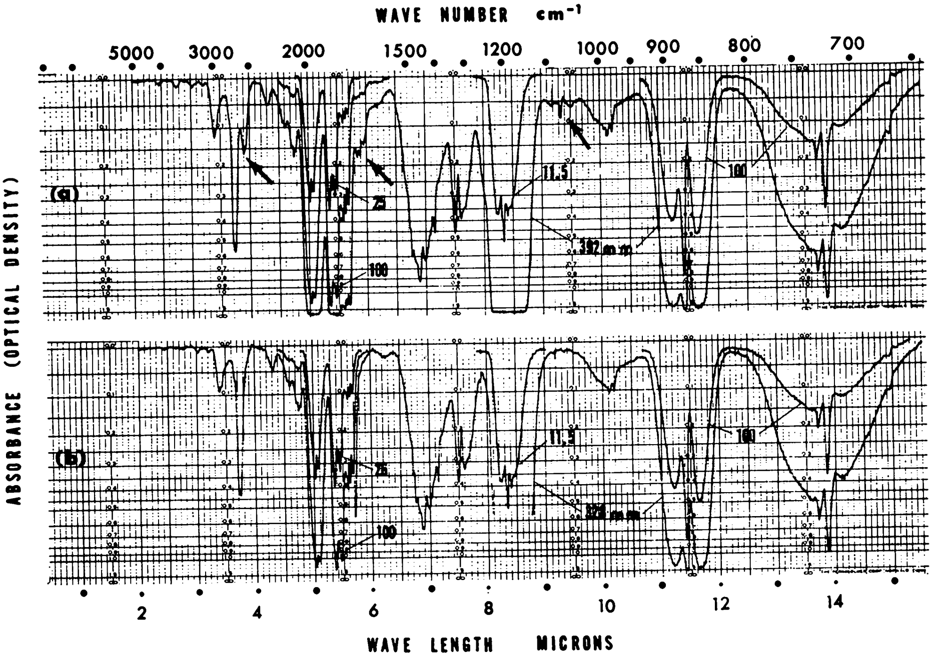

Figure 6. Contamination

a. B_2D_6 with some B_2D_5H

b. Compensated B_2D_6

To interpret the spectrum properly it must be realized that the formula "B_2H_5D" actually represents two compounds; the single substituent, deuterium, can be at the terminal or at the bridge position. Simple statistics would predict these two compounds to be present in a ratio of 2 to 1. A similar situation applies to B_2HD_5. The situation gets worse for $B_2H_4D_2$, where five compounds are possible—viz., an unsym-

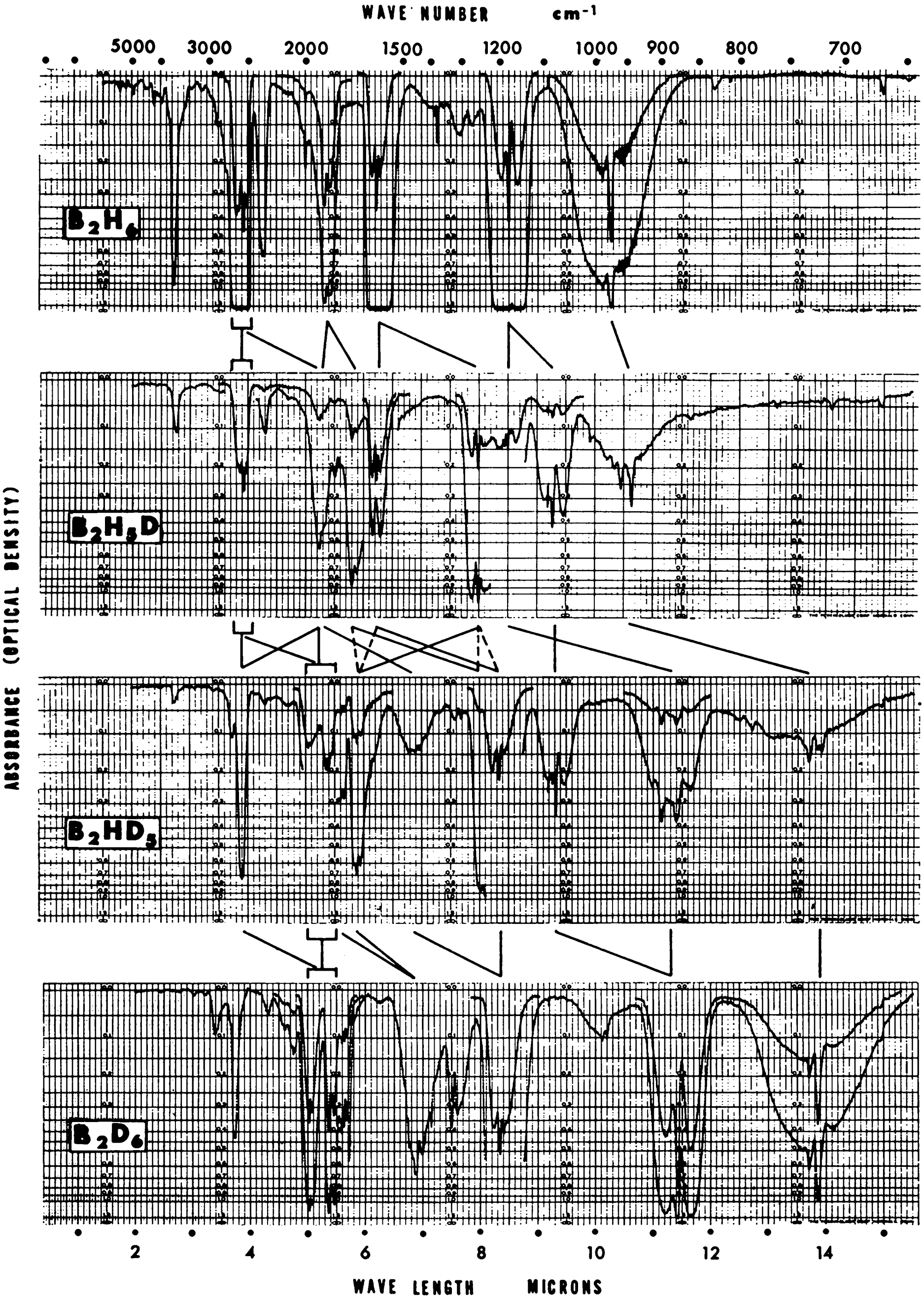

Figure 7. Diborane and its deutero derivatives

metrically substituted di-terminal, a cis- and a trans-compound, a terminal-bridge, and a double-bridge substitution. Altogether the five molecular formulas for the partially deuterated diboranes represent 19 different species, each with its own spectrum (*13*). Because of this complexity the authors were unable to obtain good results for any but the B_2H_5D and B_2D_5H groups.

Because deuterium normally is contaminated by a small amount of protium, an ordinary spectrum of deuterodiborane, B_2D_6, is contaminated by B_2HD_5. Figure 6 presents B_2D_6 contaminated with the usual amount (ca. 0.7%) of hydrogen, which produces ca. 4% of B_2HD_5; the lower chart has that contribution subtracted (indicated by arrows). By use of compensation techniques the authors were able to de-

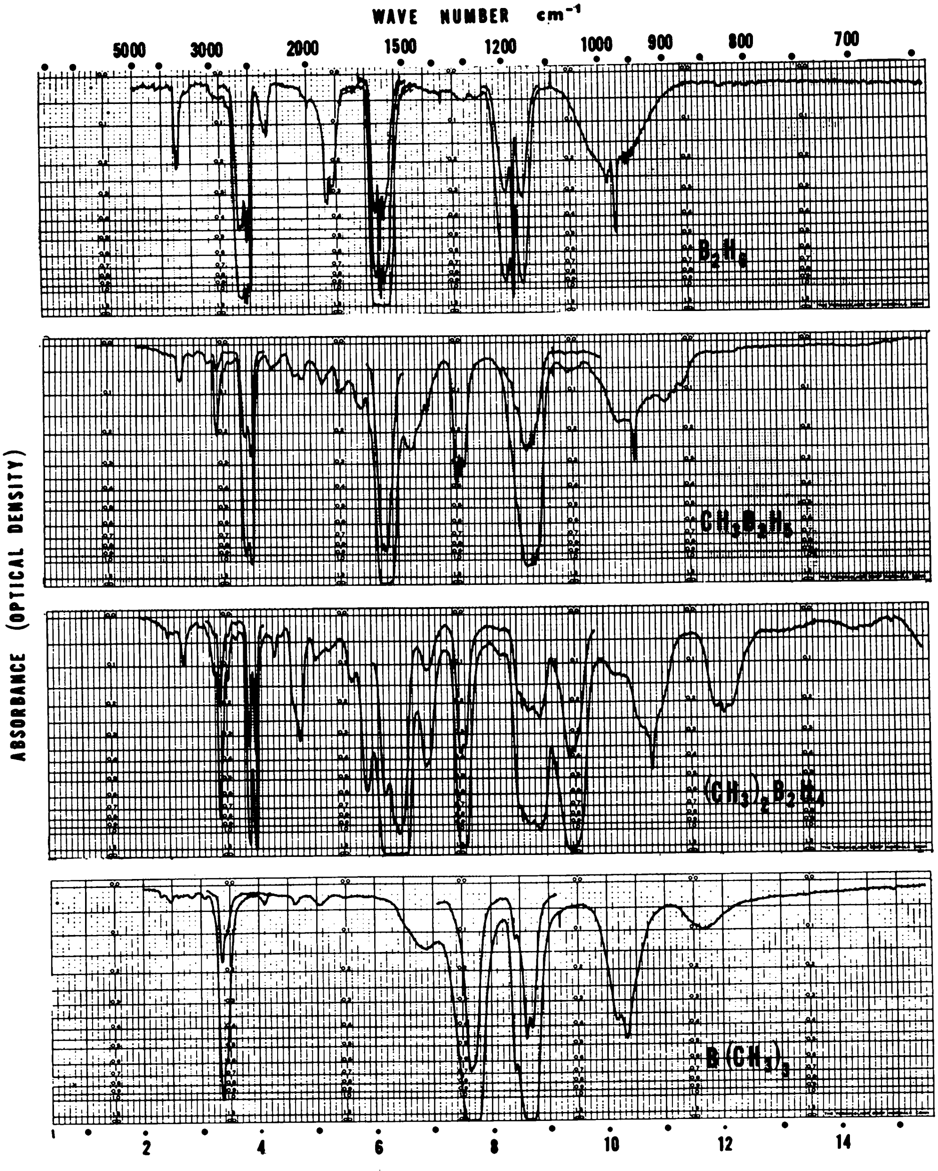

Figure 8. Two methyldiboranes and parent compounds

termine the amount of B_2HD_5 present to within about ±0.2% (out of 4%)—i.e., an accuracy of about 1 part in 20. Thus they were able to determine the protium concentration to be 0.80 ± a few hundredths per cent. Within this error they were unable to detect any deviations from the predicted statistical distribution, such as might be due to differences in bond strengths of B—H and B—D.

Figure 7 compares the spectra of B_2H_6, B_2H_5D, B_2HD_5, and B_2D_6 and indicates some of the transitions. One interesting trend is that of the strong A-type BH_2 deformation band near 1200 cm.$^{-1}$ in the upper chart. In B_2H_5D this splits into two bands—a BH_2 deformation still near 1200 cm.$^{-1}$, and a BHD deformation near 1100

Figure 9. Monomethyldiboranes

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cm.$^{-1}$. B_2HD_5 has a BHD band as well as a BD_2 band, of a frequency (880 cm.$^{-1}$) similar to that in B_2D_6.

Alkyldiboranes

The substitution of alkyl groups (methyl and ethyl) on the parent diborane molecule allows a study of the effects of terminal substitution on diborane and helps to resolve bridge *vs.* terminal assignments. One can substitute up to four alkyl groups at the terminal positions but none at the bridges. Thus, even though the alkyl groups add complexity by introducing vibrations internal to the alkyl groups, the picture as a whole is somewhat simplified by the elimination of bridge substitution. Although these alkyl compounds do disproportionate, the disproportionations are sufficiently slow to permit their spectra to be recorded.

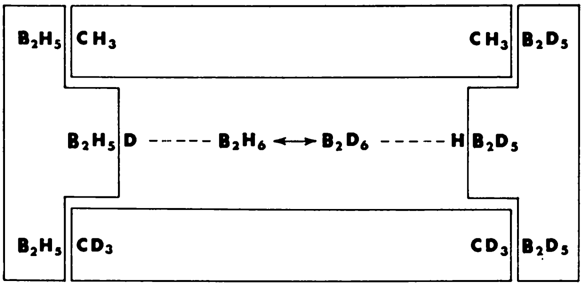

Figure 10. Schematic comparison of some monosubstituted diboranes

As expected, the spectra of the alkyldiboranes have some of the characteristics of both diborane and trialkylborane, as shown in Figure 8. All but B_2H_6 have C—H bands at 3000 cm.$^{-1}$, and all but $B(CH_3)_3$ have B—H (terminal) bands at 2500 cm.$^{-1}$ and B—H′ (bridge) bands at 1600 cm.$^{-1}$. Such comparisons aid considerably in the assignment of bands to group vibrations.

Another technique that aids in making assignments is to compare isotopic variants of a compound—for example, the monomethyldiboranes in Figure 9. Bands caused by vibrations of the —B_2H_5 part of the molecule will be common to the spectra of $CH_3B_2H_5$ and $CD_3B_2H_5$, while —CH_3 bands will be common to $CH_3B_2H_5$ and $CH_3B_2D_5$. In an analogous manner the —B_2D_5 and —CD_3 absorptions are determined. Further checks on the —B_2H_5 and —B_2D_5 assignments can be obtained from examination of the spectra of B_2H_5D and B_2D_5H (as well as other mono-substituted diboranes). These relationships are schematically shown in Figure 10.

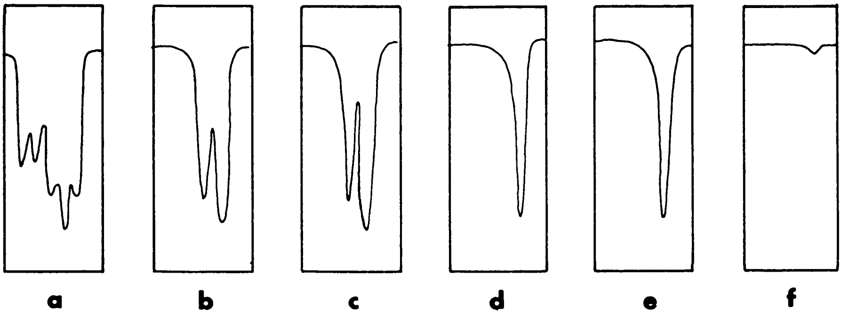

Figure 11. B—$H_{term.}$ band of some methyldiboranes

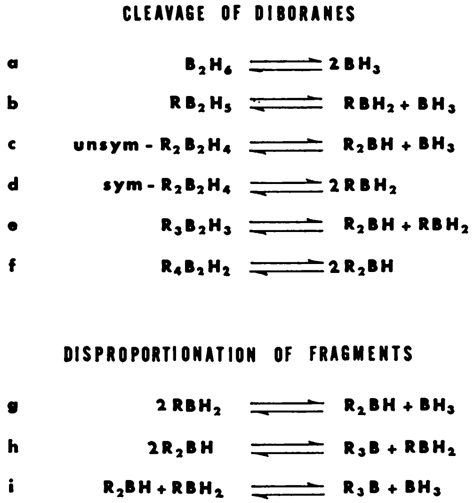

Figure 12. Reactions of alkydiboranes

The information obtainable from the B—H (terminal) stretching region illustrates a "practical" utilization of vibrational assignments (*26*). In the infrared spectrum of diborane two bands are found at 2612 and 2525 cm.$^{-1}$ corresponding to asymmetric in-phase stretching and symmetric out-of-phase stretching, respectively. As the terminal hydrogens are replaced, one can expect these bands to change. Figure 11 is a close-up of these B—H (terminal) bands in the various methyldiboranes. The first three exhibit asymmetric and symmetric B—H bands, because at least one boron atom in each is bonded to a hydrogen pair. *sym*-$Me_2B_2H_4$ and $Me_3B_2H_3$ contain only

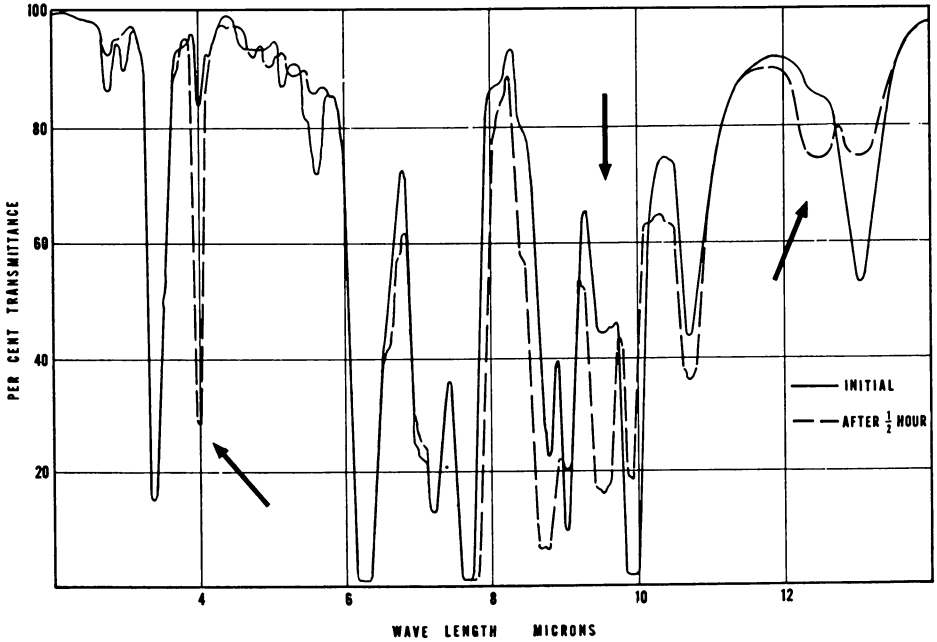

Figure 13. Decomposition of tetramethyldiborane

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single terminal hydrogens attached to the borons, thus exhibit only one frequency. $Me_4B_2H_2$ has no terminal hydrogens and thus should exhibit no such frequency; the little pip shown here is due to $Me_3B_2H_3$ impurity.

In the authors' laboratory they utilized infrared spectra to follow various disproportionation reactions of the alkyldiboranes. Analysis into the steps listed in Figure 12 would be a simple way of picturing these reactions. The reaction scheme consists of a splitting of the compound along the double-hydrogen bridge, followed by disproportionation of the fragments through a mechanism, which most probably involves formation of a single alkyl- and a hydrogen bridge. This is followed finally by simple recombination of the fragments.

Incidentally, this mechanism (as well as the preparation of alkyldiboranes from trialkylborane plus diborane) implies at least a transitory existence of alkyl bridges between boron atoms. The possibility of such a bridge in pure trimethylborane has been investigated by others (*36*), and on the basis of the observation that carbon-13 does not migrate from one trimethyl molecule to another, they concluded that such alkyl bridges are absent in that compound—i.e., no alkyl double bridges. However, in all the various alkyldiboranes one finds more or less rapid disproportionations, which indicate fairly rapid formation of single alkyl bridges—i.e., bridges that consist of one hydrogen atom and an alkyl group.

Figure 13 shows the rapid disproportionation of $Me_4B_2H_2$ into $Me_3B_3H_3$ and Me_3B, which can be pictured as:

$$Me_4B_2H_2 \rightarrow 2Me_2BH \rightarrow Me_3B + MeBH_2$$

$$MeBH_2 + Me_2BH \rightarrow Me_3B_2H_3$$

These disproportionation studies open up an interesting area of future work, primarily with regard to closer scrutiny of the rates of the various reactions and to a study of the equilibria that can be attained. Work of this nature would help to elucidate some of the mechanisms involved in the decompositions of the various alkyldiboranes.

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Interaction of Boranes

A Tracer Study of the Diborane–Pentaborane(9) Reaction

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During a study of the mechanism of the pyrolysis of diborane it became necessary to determine whether or not pentaborane(9) can be a precursor of decaborane. The reaction of diborane(93% B^{10}) and pentaborane(9)(80% B^{11}) at 77.5°C. for 24 hours gave only four products: diborane(71% B^{10}), pentaborane(9)(74.6% B^{11}), a small amount of decaborane, and much polymeric material. The isotopic distribution of the final pentaborane(9) indicated that it contained less than 2.5% of material synthesized from the diborane during the reaction, and that an exchange reaction had taken place with diborane, probably involving two boron atoms at a time. The isotopic distribution of the decaborane indicated that at least 92% arose from a combination of five boron atoms from diborane and five from pentaborane(9) and that less than 8% arose from the initial diborane alone. Thus pentaborane(9) is an intermediate in a sequence of reactions from diborane to decaborane. An experiment using enriched pentaborane(9) and natural diborane confirms these results. Low ionizing voltages (approximately 13 volts) were used on the mass spectrometer. New monoisotopic spectra for pentaborane(9) and for decaborane are given for this voltage.

Stock (*12*), in his original studies of the boranes, found that diborane could be converted to a series of higher boranes containing four, five, six, and ten boron atoms. A hepta(11)-, an octa(9)-, and a nonaborane(5) have since been added to this list by other workers in the field.

Original interest centered upon the structure of the boranes and the nature of their unique bonding. As these features became adequately understood, attention was focused on the nature of the reactions during the thermal decomposition of the boranes (*3*). All these studies were directed toward elucidating the early stages of the reaction. Bragg, McCarty, and Norton (*1*) studied the rate of pressure increase and of hydrogen formation for the pyrolysis of diborane and found both reactions to be 1.5 order with respect to diborane. From this and an accompanying study of the

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decomposition products of the various known boranes, they offered the mechanism illustrated:

$$B_2H_6 \rightleftharpoons 2BH_3 \qquad (1)$$

$$BH_3 + B_2H_6 \rightleftharpoons \text{intermediate products} \qquad (2)$$

$$\text{Intermediate products} + B_2H_6 \rightleftharpoons B_5H_{11} + 2H_2 \qquad (3)$$

$$B_5H_{11} \rightarrow B_5H_9 + H_2 \qquad (4)$$

$$B_5H_{11} \rightarrow B_2H_6, \text{ higher hydrides} \qquad (5)$$

Step 1 as the rate-determining step accounts for the 3/2 order dependency.

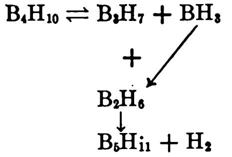
Clarke and Pease (*2*) measured the rate of disappearance of diborane and the rate of formation of hydrogen and concurred in the 3/2 order dependency of diborane. The mechanism they offered is as follows, with Reaction 6 in the forward direction the rate-determining step:

$$B_2H_6 \rightleftharpoons 2BH_3 \qquad (1)$$

$$B_2H_6 + BH_3 \overset{\text{slow}}{\rightleftharpoons} B_3H_7 + H_2 \qquad (6)$$

$$B_3H_7 + B_2H_6 \rightarrow B_4H_{10} + BH_3 \qquad (7)$$

Pearson and Edwards (*6*) have lent support to the previous work by showing that in the presence of hydrogen, tetraborane probably decomposes to B_3H_7 and BH_3, which in turn react to give pentaborane(11), diborane, and other unspecified products, thus explaining the formation of pentaborane(11) from tetraborane.



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

Schaeffer (*7*) has offered a reasonable explanation of the formation of pentaborane(9), in that tetraborane acts as a dehydrogenation agent to transform B_5H_{11} to B_5H_9.

In summary, the positive information offered by these studies is that B_3H_7 may be an important intermediate for the formation of tetraborane and pentaborane(11) and that pentaborane(9) is probably formed from pentaborane(11).

The formation of decaborane, from the intermediate hydrides, has not previously been examined. The mechanism offered by Bragg *et al.* (*1*) seems to suggest that pentaborane(9) and decaborane are both formed from pentaborane(11) by independent processes. Indeed, pentaborane(9) is a thermally very stable hydride and for this reason workers in the field have been apparently reluctant to consider it as a reactive intermediate. Shapiro and Keilin (*10*) have shown that there is no boron self-exchange in pentaborane(9) even at temperatures causing considerable decomposition.

There have been indications, however, that pentaborane(9) will react with diborane. Schlesinger (*8*) has found that diborane accelerates the decomposition of pentaborane(9) and Koski *et al.* have found a small boron exchange between diborane and pentaborane(9) (*4*).

Because of the ready availability of the reactants, the diborane-pentaborane(9) interaction presented itself as an initial prospect. Equimolar quantities of diborane (92.7% boron-10) and natural pentaborane(9) were heated in a sealed tube at 77.5°C. for 24 hours. Analysis of previous runs using only natural material showed that diborane, pentaborane(9), a small amount of decaborane, and much nonvolatile solid were the only detectable products. The three volatile products were analyzed with a mass spectrometer. In one run the normal operating conditions (ionizing voltage of 70 volts)

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were used and the monoisotopic spectra give by Norton and by Shapiro were used to determine isotopic distributions. These conditions offered some difficulties. Impurities in the decaborane pattern occluded the peaks with $m/e = 124$ and 123. The complexity of the pattern made computations equally complex.

In a second run, lower ionizing voltages were used (approximately 13 volts) and new monoisotopic spectra were derived for these conditions. The ionizing voltage apparently did not remain exceptionally stable with time, however, and changes in the patterns could be noted. Monoisotopic spectra were therefore derived not only for each determination but before and after an unknown was run, and the average value was taken. Sample monoisotopic spectra for pentaborane(9) and decaborane are given in Table I.

Table I. Sample Monoisotopic Spectra

Pentaborane(9)		Decaborane	
B_5H_9	100.0	$B_{10}H_{14}$	27.5
B_5H_8	0.9	$B_{10}H_{13}$	3.0
B_5H_7	43.2	$B_{10}H_{12}$	100.0
B_5H_6	0.0	$B_{10}H_{11}$	2.6
B_5H_5	14.8	$B_{10}H_{10}$	12.4
B_5H_4	0.0	$B_{10}H_9$	0.2
B_5H_3	0.8	$B_{10}H_8$	1.5
		$B_{10}H_7$	0.2
		$B_{10}H_6$	0.2
		$B_{10}H_5$	0.1

It can be readily seen how relatively simple these monoisotopic spectra are.

Natural boron abundance of 80% boron-11 and 20% boron-10 is used throughout the calculations, because previous workers in the field (*4*) have found that these values work more satisfactorily for the boranes. The authors carried out all calculations using 81.8% boron-11 as the natural value and found no significant difference in the results.

Theoretically, if two species of known and different isotopic distributions interact to form a compound species, the isotopic distribution of the compound species can be calculated. If the isotopic distributions of the initial species are statistical, the calculations are even simpler. For decaborane formed from five boron atoms from diborane and five boron atoms from pentaborane(9), in which the boron atoms simply combine without any complications, the expression $(P_1 + P_2)^5(P_3 + P_4)^5$, where P_1 and P_2 represent the boron-10 and boron-11 abundances, respectively, in diborane and P_3 and P_4 the same for pentaborane(9) when expanded, will give the isotopic distribution of the product. The sum of the values of all terms $C_tP_1{}^qP_2{}^rP_3{}^sP_4{}^t$ with identical values for $(q + s)$ and $(r + t)$ is the abundance of that species with $(q + s)$ boron-10 atoms and $(r + t)$ boron-11 atoms.

A bar graph illustrating the results of this expansion is given in Figure 1, including a bar graph of the isotopic distribution of the decaborane obtained from the reaction under study. Qualitatively, it can be readily seen that the decaborane was formed from five boron atoms from diborane and five boron atoms from pentaborane(9). Pentaborane(9) must now be recognized as an intermediate in the formation of decaborane.

An experiment was conducted under identical conditions using enriched pentaborane(9) (92.6% boron-10) and natural diborane. Theoretically, the isotopic distribution of the decaborane obtained from this reaction should be identical to that of the reverse reaction, if the reaction involves exactly five boron atoms from each reactant. Bar graphs of the observed isotopic distribution show that this is not precisely so. Exactly how many boron atoms from each reactant are involved in the formation of the product cannot readily be determined, but it is evidently close to five from each.

It was hoped that an estimate could be made of the amount, if any, of decaborane formed from a reaction path not involving the initial pentaborane(9). Such decaborane, if formed in considerable quantities, would appear as a separate peak at

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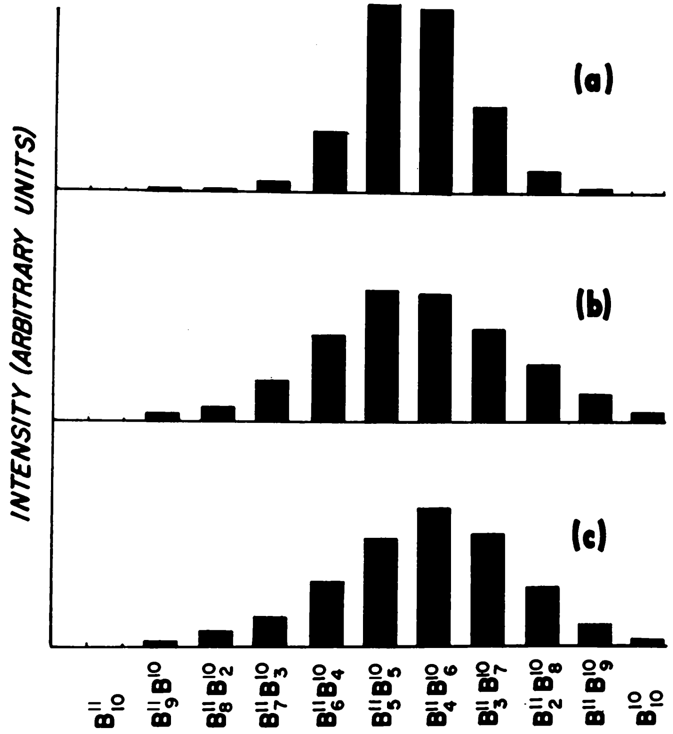

Figure 1. Isotopic distributions of decaborane

a. Theoretical reaction of five boron atoms of diborane and five of pentaborane(9) $(P_1 + P_2)^5(P_3 + P_4)^5$
b. $B_2^{10}H_6 + B_5H_9$ reaction
c. $B_2H_6 + B_5^{10}H_9$ reaction

the B_{10}^{10} end of the spectrum of the first experiment and the B_{10}^{11} end of the second (or reverse) experiment. A secondary peak was not obtained. It would be convenient to estimate an upper limit for the amount of synthesis of decaborane in this manner. The value of the B_{10}^{10} abundance in the first experiment or of the B_{10}^{11} abundance in the second experiment can be used to compute this upper limit. Because of the nature of the computations involved, confidence in the B_{10}^{10} end of the isotopic distribution cannot be too great. For this reason only the second experiment should be considered seriously. Using this distribution, an upper limit of approximately 8% is arrived at for the percentage of the decaborane synthesized by an alternate path. This is probably too high.

Three points should be noted. First, a problem arises in determining the isotopic distribution of the decaborane synthesized from diborane alone, because the boron abundances are continuously changing throughout the reaction. An average value of the boron abundances was used, but with reservations.

Second, decaborane arising from diborane alone need not suggest that an entirely different reaction path is in force. Diborane could first have been converted to pentaborane(9), followed by further reaction of that pentaborane(9) with diborane.

Third, the peak values of the isotopic distributions of the decaborane products are lower than the theoretical values. Subtracting the maximum allowable product from diborane alone does not raise the peak values sufficiently. This lowering is probably due chiefly to inadequacies in computing the theoretical distribution, as the boron abundances are not constant in both the diborane and the pentaborane(9) throughout the reaction.

Table II. Best Values for Changes on Abundance

	$B_2^{10}H_6 + B_5H_9$ Reaction		$B_2H_6 + B_5^{10}H_9$ Reaction	
	Diborane	Pentaborane(9)	Diborane	Pentaborane(9)
Initial B^{10} abundance	0.927	0.20	0.20	0.926
Final B^{10} abundance	0.712	0.26	0.47	0.858
Change: boron atoms per molecule	0.43	0.30	0.54	0.36

In Table II are given the best values for the changes in abundance in the diborane and pentaborane(9). The change in the diborane is not accounted for by the change in the pentaborane(9). As there is probably synthesis of some pentaborane(9) during the reaction which would alter the abundances in pentaborane(9) but not in the diborane, the accountability is even poorer than depicted here. The excess change in the diborane can be accounted for only by a reaction in which diborane but not pentaborane(9) is formed. Nor could this be due to an exchange between diborane and decaborane, as Shapiro (*9*) has shown that there is no boron exchange between diborane and decaborane. The authors have confirmed his results. However, as they are not absolutely certain of the magnitude of the experimental error involved in this determination, they reserve further discussion on this point.

In Table III are given the isotopic distributions of the initial and final pentaborane(9). An upper limit of pentaborane synthesized during the reaction can be estimated from the $B_5^{10}H_9$ reaction as approximately 2.5%.

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Table III. Isotopic Distributions of Pentaborane (9)

	$B_2^{10}H_6 + B_5H_9$ Reaction		$B_2H_6 + B_5^{10}H_9$ Reaction	
	Product	Starting material	Product	Starting material
B_5^{11}	0.276	0.328	0.004	0.000
$B_4^{11}B^{10}$	0.355	0.410	0.023	0.000
$B_3^{11}B_2^{10}$	0.213	0.205	0.050	0.003
$B_2^{11}B_3^{10}$	0.105	0.051	0.093	0.044
$B^{11}B_4^{10}$	0.046	0.006	0.259	0.272
B_5^{10}	0.004	0.000	0.570	0.681

Without giving experimental data, Koski *et al.* (*4*) state that boron exchange between diborane and pentaborane(9) apparently involves two boron atoms at a time. The authors' data favor a two-boron exchange over a one-boron exchange as shown in Table IV, although the fit is not as good as desirable and the magnitude of the experimental error is unknown.

Table IV. Borane Exchange

	$B_2^{10}H_6 - B_5H_9$ Reaction		$B_2H_6 - B_5^{10}H_9$ Reaction	
	Observed	Theoretical	Observed	Theoretical
B_5^{11}	0.014	0.017	0.000	0.001
$B_4^{11}B^{10}$	0.082	0.144	0.093	0.021
$B_3^{11}B_2^{10}$	0.288	0.427	0.248	0.127
$B_2^{11}B_3^{10}$	0.397	0.306	0.342	0.430
$B^{11}B_4^{10}$	0.219	0.094	0.230	0.336
B_5^{10}	0.000	0.010	0.087	0.085

The observed values are obtained by subtracting the maximum amount of synthesis from the isotopic distribution of the pentaborane(9) product. The maximum amount of unchanged pentaborane(9) was then subtracted, followed by successive approximations to determine how much B_5^{11} in the enriched diborane reaction and how much B_5^{10} in the enriched pentaborane(9) reaction was not from the original pentaborane(9). The theoretical values consider a two-boron displacement reaction and include a secondary reaction—i.e., a number of molecules that have reacted once in the reaction have also reacted a second time.

Conclusion

The following scheme is offered as a possible mechanism for the formation of decaborane.

$$B_5H_9 + B_2H_6 \rightleftharpoons B_7H_{13} + H_2 \qquad (8)$$

$$B_7H_{13} \rightarrow B_6H_{10} + BH_3 \qquad (9)$$

$$B_6H_{10} \xrightarrow{\text{Stepwise build-up}} B_{10}H_{14} \qquad (10)$$

$$B_7H_{13} \xrightarrow{\text{Stepwise build-up}} B_{10}H_{14} \qquad (11)$$

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Unstable Intermediates in the Pyrolysis of Diborane

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Pyrolysis of diborane was carried out in a borosilicate glass cell designed to freeze out products that would condense at —78.5°C. Between 100° and 130°C. pentaborane(11) was the main condensable product. The stoichiometry of such a reaction caused a decrease in total pressure, as pentaborane(11) exhibits little vapor pressure at the condensation temperature: $5\ B_2H_6 \rightarrow 2\ B_5H_{11} + 4\ H_2$. Without exception, an initial increase in pressure was observed. This pressure increase was not due to fast initial decomposition of pentaborane(11) to polymer or pentaborane(9), nor to slow attainment of temperature equilibrium in the reaction vessel. An alternative explanation appeared to be a high initial concentration of unstable intermediates in the formation of pentaborane(11). To test this hypothesis, a differential infrared technique was used.

Several studies have been made of the kinetics of diborane pyrolysis (*1–4*). In the presentation of these studies the investigators have postulated various unstable intermediates on the basis of diborane disappearance—i.e., BH_3, B_3H_7, B_3H_9, B_4H_8, etc. Several investigators have postulated borane (BH_3) to be in equilibrium with diborane; however, to the authors' knowledge, positive physical detection has not yet been made.

During the general studies of diborane pyrolysis in this laboratory, a series of experiments using a borosilicate glass cell (Figure 1) was carried out. This cell was designed to allow all condensable products to freeze out in a small mushroom-type condenser located at the top of the cell. To accomplish this the cup surrounding the condenser was cooled with dry ice and acetone. A pressure transducer (Statham Laboratories, Model P 24-2A-500-P10A) was attached to the capillary leading from the cell, allowing the total pressure to be followed continuously as a function of time at constant temperature. It had previously been found that, using the "freeze-out method," it was possible to effect large percentage conversion to pentaborane(11). This being possible up to 130°C., it appeared reasonable to attempt a kinetic study, as freezing out the first condensable product would minimize the complications arising from the formation of polymer or higher hydrides.

The total pressure *vs.* time plot for a typical "condensation" experiment is given

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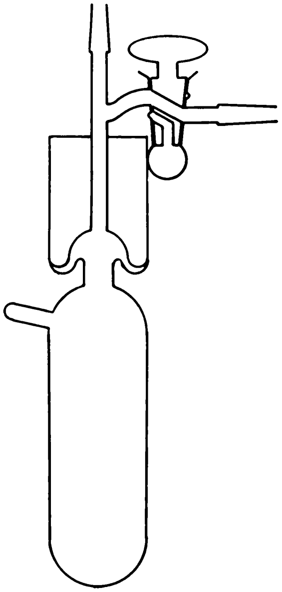

Figure 1. Borosilicate glass reaction cell

in Figure 2. Knowing that pentaborane(11) was formed in high yield, the authors were not surprised that the pressure decreased with time:

$$5B_2H_6 \rightarrow 2B_5H_{11} + 4H_2$$

Formation of tetraborane would likewise decrease the pressure, whereas pentaborane(9) would increase the pressure:

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

$$5B_2H_6 \rightarrow B_5H_9 + 6H_2$$

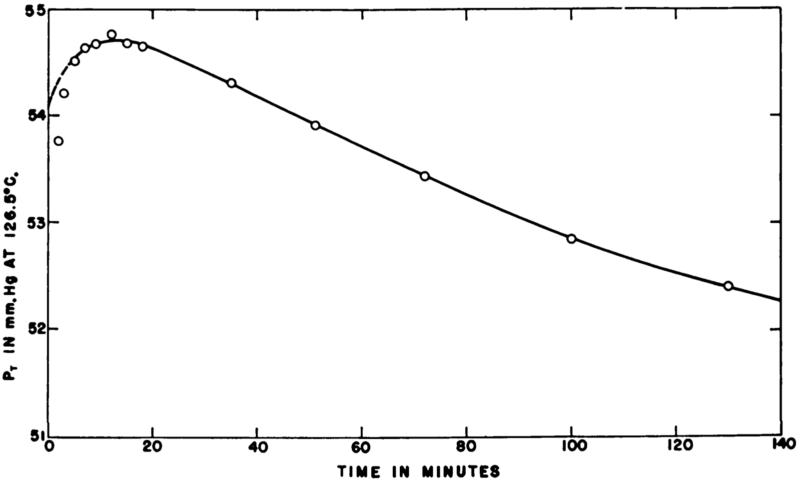

Figure 2. Pyrolysis of diborane
Total pressure vs. time

(In each case, the higher hydrides are in a condensed state.) An initial increase in pressure was not expected; nevertheless it occurred without exception when conditions were favorable for the formation of pentaborane(11) as the principal product. Initially this was explained by assuming that two competing rate processes take place: (A) diffusion of pentaborane(11) to the condensation trap and (B) further decomposition of pentaborane(11) to polymer or pentaborane(9). It was supposed that during the first minutes of the run, (B) was faster than (A); later, because of possible back reactions involving hydrogen, (A) became important.

To test the hypothesis, two duplicate experiments were carried out—i.e., all conditions were duplicated except the time allowed for reaction. One experiment was quenched upon attaining the maximum pressure, whereas the other was allowed to continue until the pressure decrease was well under way. Subsequent to the quenching, the condensable products were fractionated from hydrogen and remaining diborane, then were determined by infrared spectroscopy. Table I summarizes the results obtained.

Table I. Effect of Time on Pyrolysis of Diborane

Initial Pressure at 25°C., Atm.	Experiment Duration, Sec.	Diborane Decomposed, %	Stoichiometry[a]					
			W	X	Y	Z	Q	S
0.0549	6960	65.5	1.04	0.082	0.270	0.024	8.3 ± 0.5	0.01
0.0535	2100	37.0	1.03	0.070	0.270	0.021	Ind.[b]	0.02

[a] $B_2H_6 = WH_2 + XB_5H_9 + YB_5H_{11} + ZB_{10}H_Q + SB_4H_{10}$.
[b] Too little polymer formed to determine the B/H ratio.

In the table the polymer is arbitrarily designated as $B_{10}H_Q$. Some of the early determinations of molecular weight of polymers made by Stock indicated an average of ten boron atoms per molecule. The temperature of both runs was 411.1°K.

The analysis of products of both experiments showed no appreciable difference in stoichiometry. Unless fortuitous, the initial pressure rise could not be attributed to a high initial rate of pentaborane(11) decomposition.

Subsequently, experiments were carried out with a thermocouple suspended in the reaction cell to see whether equilibrium was reached before the pressure maximum occurred. They showed that the reaction cell reached temperature equilibrium within 4 to 5 minutes under the most adverse conditions and remained at equilibrium throughout the remainder of the run.

The above conclusions led to the postulate that the initial pressure increase was attributable to the initial formation of unstable intermediates. To test this hypothesis, the following experiment was conceived.

Two infrared cells were filled with a pressure of diborane at room temperature such that when the 10-cm. borosilicate glass cell was placed in the reference beam and the brass, heatable cell (6.59 cm.) in the sample beam of an infrared spectrometer (Perkin-Elmer Model 21), the diborane absorbance in the sample beam exactly offset that of the reference beam.

The objection has been raised that the initial pressure increase might have been due to a build-up of pentaborane(11) in the gas phase; the rate of production of pentaborane(11) might have been faster than either the rate of diffusion and condensation or the further decomposition of pentaborane(11). The authors are well aware of this possibility. However, because at least four competing rate processes are involved, all with intricate interdependence, it would be difficult to establish this point experimentally. In any case, the positive detection of unstable intermediates has been made and offers at least one substantial explanation of the initial pressure increase.

If the absorbances of the reference and sample beams are simultaneously strong enough, the detecting thermocouple will be rendered insensitive. In the experiments here reported, the pressure in the borosilicate glass cell was about 60 mm. of mercury at room temperature and that of the brass cell was about 88 mm. of mercury. The response mechanism of the spectrometer was still operative but sluggish on the

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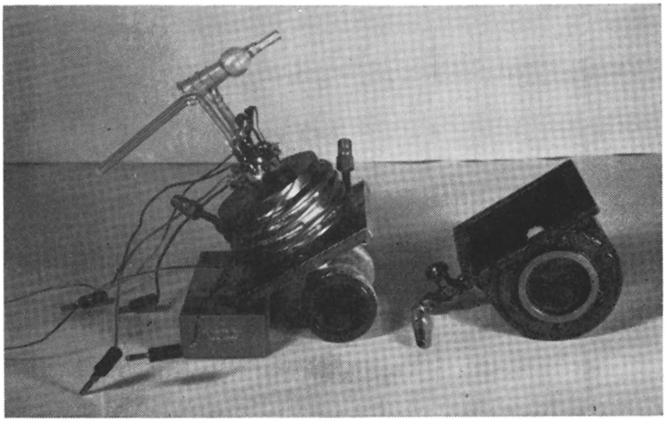

Figure 3. Dismantled brass infrared cell

strongest peak (6.23 microns). However, the fast scanning rate necessary during preliminary investigations rendered the response mechanism essentially inoperative in some wave length regions. This condition can be readily detected by momentarily closing the shutter to one of the beams and observing the pen deflection; it must be guarded against when applying this technique.

The brass cell pictured in Figure 3 consists of two cells, the inner cell being wound with a resistance thermometer for temperature control, and a Nichrome heating element. The outside cell is primarily for thermal insulation. The resistance thermometer is one of the resistance arms of a Wheatstone bridge in the temperature controller.

After compensation had been accomplished, the brass cell was rapidly heated (see Figure 4). It took about 3 minutes to attain reaction temperature. The

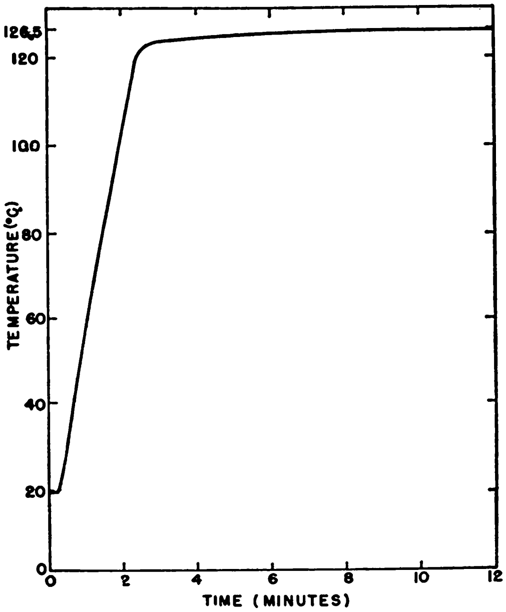

Figure 4. Heating curve for infrared cell

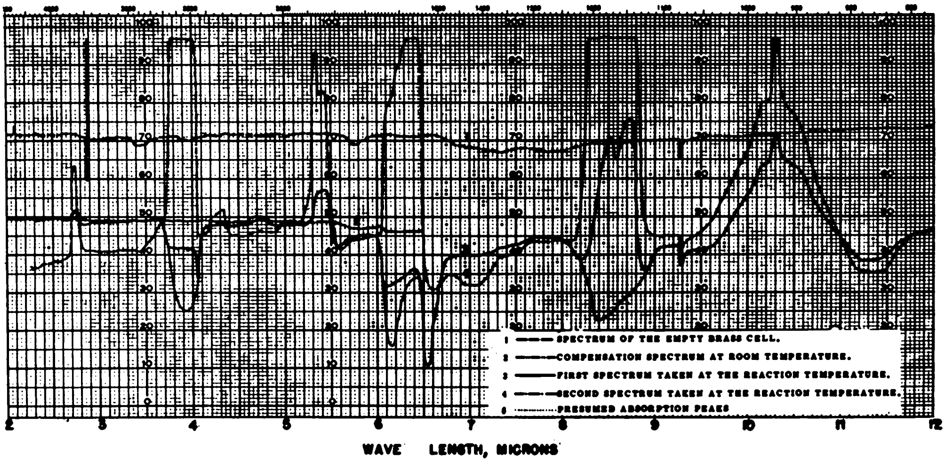

Figure 5. Infrared spectra

spectra subsequently obtained are given in Figures 5 and 6. They were taken at approximately 157° and 126.2°C., respectively. Spectra *A*, *B*, and *C* (Figure 7), and 8 are of tetraborane, pentaborane(9), and pentaborane(11) and diborane, respectively. They were included for reference.

Discussion of Infrared Peaks

After the cell had been allowed to heat for 1 to 2 minutes, a scan of the 2- to 12-micron region was made at the rate of 2 microns per minute.

It may be noticed (5–3, 4; 6–3, 4, 5) that absorption at 2.8 to 2.85, 3.73 to 4.05, 5.5 to 5.8, 6.0 to 6.75, and 8.0 to 9.0 microns was due to compounds or species found in the heated cell which were not found in the borosilicate glass cell. As would be expected, the diborane decomposed very rapidly. Decomposition produced overcompensation by the reference beam at 2.7, 3.7 to 4.05, 5.15 to 5.5, 6.05 to 6.5, 8.15 to 9, and a broad peak from 9.3 to 11.2 microns. In other words, the disappearance of reactant is given by maxima in the curves whereas the appearance of any products is given by minima.

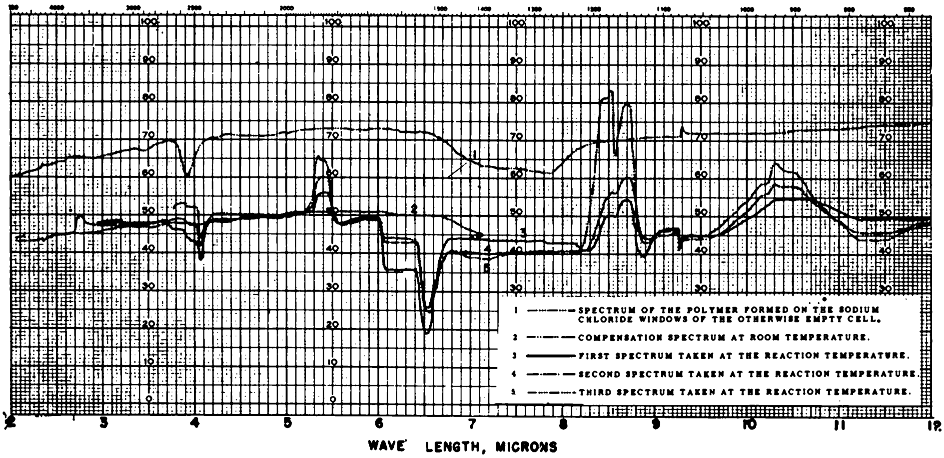

Figure 6. Infrared spectra

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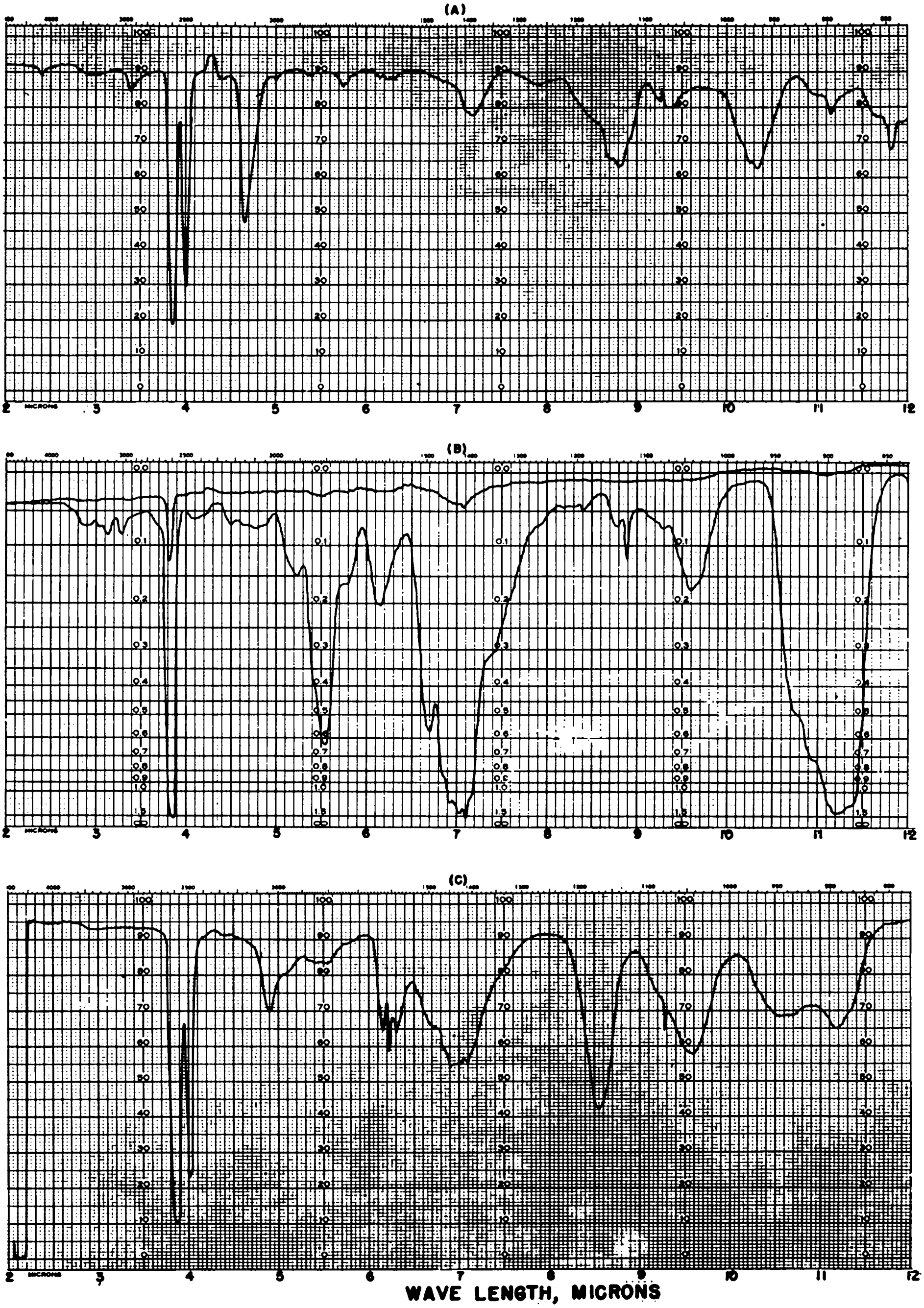

Figure 7. Infrared spectra

A. B_4H_{10} B. B_5H_9 C. B_5H_{11}

The peak at 2.82 microns has no analog in the known volatile hydrides. It might be argued that it is simply an overshoot from the maximum caused by diborane absorbing at 2.7 microns. However, spectrum 5–4 verifies that no overshoot takes place.

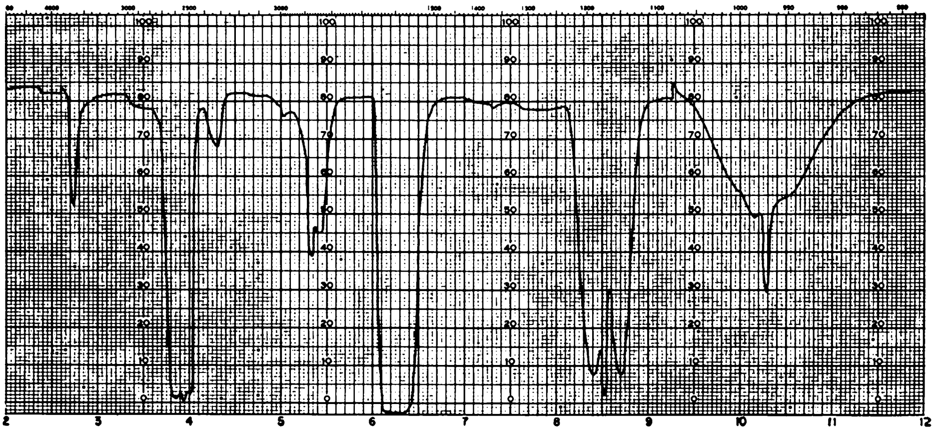

Figure 8. Infrared spectrum of B_2H_6

The region between 3.75 and 4.02 microns represents an insensitive zone; the recorder pen was simply drifting as a result of inadequate thermocouple response. However, at the edges of this region (3.70 and 4.06 microns) the pen was sensitive. Diborane, pentaborane(11), and tetraborane all absorb at 4.05 microns. They also absorb in the region from 3.75 to 3.95 microns. One might suspect therefore that the minimum at 4.05 microns (5–3, 4, and 6–3, 4, 5) is due to pentaborane(11) and/or tetraborane. However, other regions (4.65, 4.90 microns) give ample evidence that neither pentaborane(11) nor tetraborane was present in sufficient quantities to account for the minimum at 4.05 microns. For example, the absorbance at 4.05 microns predicted for B_5H_{11} would not exceed 0.02, whereas actual absorbance was 0.135. Absorbance is defined as ($D = \log_{10} I_0/I$) where I_0 is the intensity of the incident light and I is the intensity of the light leaving the cell.

The peak at 5.54 microns probably is due to pentaborane(9). Pentaborane(9) also exhibits a peak at 6.15 microns ($D_{6.15}/D_{5.54} = 0.221$). From the absorbances, however, it is easily seen that the strong 6.05-micron absorbance cannot be attributed to pentaborane(9) exclusively; neither can it be attributed to pentaborane(11) or tetraborane. The peak at 6.55 microns is unique, having no counterpart in any of the common volatile boron hydrides. It is not due to any polymeric compound. In spectrum 5–3, another insensitive zone occurs between 6.05 and 6.40 microns. However, because of the disappearance of most of the diborane in the sample cell, this same region in spectrum 5–4 is not an insensitive zone.

The region between 8 and 9 microns exhibits a peak having a minimum at approximately 8.4 microns. However, the peak due to the greater amount of diborane in the reference cell (overcompensation) has cancelled all but the edges of this peak. If one examines the pure diborane peak (Figure 8) at this point, a strong maximum appears at 8.55 microns with two rather broad heavy peaks at either side at 8.4 and 8.72 microns. Examination of the spectra (5–3, 4 and 6–3, 4) reveals complete disappearance of the 8.4-micron and a diminishing of the 8.55-micron peak. This can only be explained by a cancellation due to a peak in the opposite direction. Spectrum 6–5 shows the reappearance of the 8.4-micron and strengthening of the 8.55-micron peaks of the reference cell. This gives evidence that the peak due to intermediates disappears with time.

Examination of the spectrum (5–4) shows a tailing off of the "overcompensation" peak between 6.0 and 6.3 microns. It should, however, have approximately equal absorption at 6.15 and 6.4 microns. That it does not is explained by the continual existence of the strong minimum at approximately 6.15 microns. It is

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noticed in addition that the peak at 6.55 microns diminishes with time—see, for example, 5–4 and 6–4, 5.

In view of the fact that the observed absorption peaks (minima) for the unstable intermediates are in each case close to absorption peaks of diborane, one might question whether pressure broadening of the hot diborane could account for some of the peaks ascribed to unstable intermediates. There is evidence to believe that this effect is negligible; spectrum 5–2 should have shown the effect if not negligible since the pressure in the sample cell had to be 1.5 times that in the reference cell for balancing, even at room temperature. Furthermore, as soon as the diborane in the sample cell was heated, the diborane started to decompose into hydrogen, polymer, and a small amount of pentaborane(9). One would not expect a hydrogen molecule to perturb the rotational spectra of a diborane molecule as much as the diborane molecule it replaced.

Predicted Bond Constants for BH_3 Assuming Infrared Frequencies Experimentally Obtained

A priori one might expect borane (BH_3) to be the unstable species detected. Although no positive physical identification has been made, considerable chemical evidence of at least transitory existence is available. To examine the compatibility of the observed spectrum with that which might be expected of borane, the authors have outlined the following argument.

If one assumes that BH_3 belongs to the point group D_{3h}, there are six normal vibrational modes (see Figure 9). One is inactive in the infrared, one is active and nondegenerate, and two are doubly degenerate. Using equations developed by Herzberg (*5*) for molecules of symmetry D_{3h} and assuming the frequencies at 3.9, 6.40, and 8.4 microns as the normal fundamental frequencies of BH_3 the force constants k_1, k_δ, and k_Δ for potential energy Equation 1 were obtained. (The frequency was taken as 6.40 microns because ν_2 is expected to be a doublet and may well be represented by the two peaks at 6.15 and 6.55 microns, respectively, with a center at about 6.4 microns.)

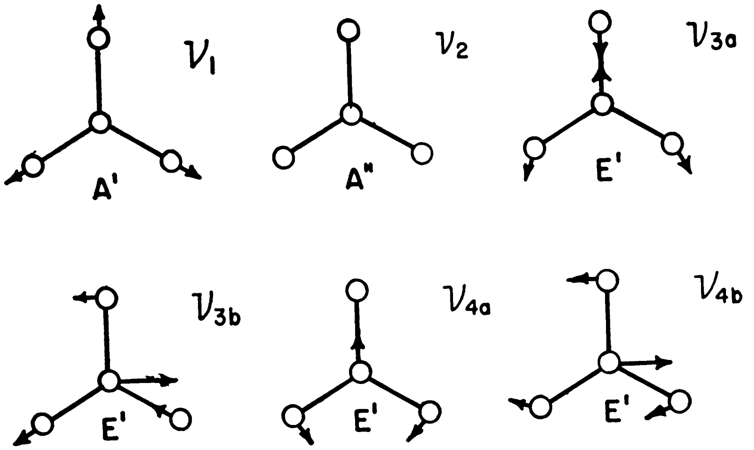

Figure 9. Normal frequencies, XY_3 planar molecule

$$2V = k_1(Q_{12}^2 + Q_{13}^2 + Q_{14}^2) + k_\delta(\delta_{23}^2 + \delta_{24}^2 + \delta_{34}^2) + k_\Delta(\Delta_{12}^2 + \Delta_{13}^2 + \Delta_{14}^2) \qquad (1)$$

Subscripts 1, 2, 3, and 4 refer to the boron and three hydrogen atoms, respectively; k_1, the stretching force constant; k_δ, bending force constant in the plane, and

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k_Δ the bending force constant out of the plane; Q_{ij} is the displacement from equilibrium of atom i from atom j; δ_{ij} represents the angular displacement from equilibrium of atom i from atom j in the plane of symmetry and Δ_{ij} represents the angular displacement of atom i from atom j from equilibrium out of the plane. The resulting secular equation leads to the following equations

$$\lambda_1 = k_1/m_y \tag{2}$$

$$\lambda_2 = (1 + 3m_y/m_x)(k_\Delta/m_y\, l^2) \tag{3}$$

$$\lambda_3 + \lambda_4 = [1 + 3/2(m_y/m_x)]\ (k_1/m_y + 3k_\delta/m_y l^2) \tag{4}$$

$$\lambda_3\lambda_4 = 3\ (1 + 3m_y/m_x)(k_1k_\delta/m_y^2l^2) \tag{5}$$

where $\lambda_i = 4\pi^2\nu_i^2$ and ν is the fundamental frequency, sec^{-1}. The masses m_y and m_x refer to hydrogen and boron, respectively, and l is the distance between the boron and hydrogen atoms. Rearranged these equations give

$$k_1 = \lambda_1 m_y \tag{6}$$

where

$$k_\delta/l^2 = \tfrac{1}{2}[B + \sqrt{B^2} - 4C] \tag{7}$$

$$B = m_y(\lambda_3 + \lambda_4)/3(1 + 3m_y + 2m_x) \tag{8}$$

and

$$C = (\lambda_3\lambda_4 m_y^2)/9(1 + 3m_y/m_x) \tag{9}$$

$$k_1 = 3C/(k_\delta/l^2) \tag{10}$$

$$k_\Delta/l^2 = (\lambda_2 m_y)/(1 + 3m_y/m_x) \tag{11}$$

Using primed symbols to represent isotopic masses or frequencies, one can combine Equations 2 and 5 to produce equations of the Teller-Redlich product rule:

$$\frac{\lambda_1'}{\lambda_1} = \frac{M_y}{M_y'} \tag{12}$$

$$\frac{\lambda_2'}{\lambda_2} = \frac{m_y(1 + 3m_y'/m_x')}{m_y'(1 + 3m_y/m_x)} \tag{13}$$

$$\frac{\lambda_3'\lambda_4'}{\lambda_3\lambda_4} = \frac{(1 + 3m_y'/m_x')m_y^2}{(1 + 3m_y/m_x)m_y'^2} \tag{14}$$

The measured frequencies were assigned to each of the λ's and the force constants k_1, k_δ, and k_Δ were obtained from these values and tabulated in Table II. Other $B^{11}X_3$ molecules having D_{3h} symmetry are also included.

Table II. Fundamental Frequencies and Force Constants of Plane Symmetrical XY_3 Molecules Assuming Valence Forces

Molecule	ν_1	ν_2	ν_3	ν_4	k_1	k_δ/l^2	k_Δ/l^2
$B^{11}H_3$	2400 ± 300	1560 ±[a] 50	2560 ±[a] 100	1190 ±[a] 10	3.41 ± 0.78	0.25 ± 0.05	1.13 ± 0.04
$B^{11}D_3$	1700 ± 200	1215 ± 36	1900 ± 300	873 ± 23	3.41 ± 0.78	0.25 ± 0.05	1.13 ± 0.04
$B^{11}F_3$	888	691	1446	480	8.83	0.37	0.87
$B^{11}Cl_3$	471	462	958	243	4.63	0.16	0.42
$B^{11}Br_3$	279	372	806	151	3.66	0.13	0.29
	cm.^{-1}				$X10^{-5}$ dyne cm.^{-1}		

[a] Experimental frequencies. Uncertainty is expressed in standard deviation.

A comparison of k_1's for the various molecules shows a decrease as mass increases for the halides. The fact that k_1 for $B^{11}H_3$ is small may seem inconsistent. However the stretching force constant for diborane is 3.42×10^5 dyne cm.^{-1} compared to 3.41×10^5 dyne cm.^{-1} calculated for BH_3. In calculating the entropy of BH_3, Bauer (*1*) used the constants $k_1 = 3.38 \times 10^5$, $k_\delta/l^2 = 0.10 \times 10^5$, and $k_\Delta/l^2 = 0.22 \times 10^5$ dyne cm^{-1}.

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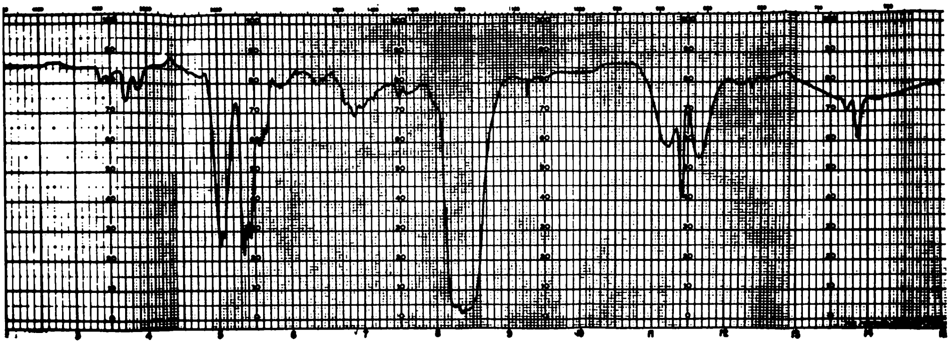

Figure 10. Infrared spectrum of B_2D_6

If one assumes the same force constants for deuterated borine, it is possible to predict the frequencies which should show up if deuterated diborane were pyrolyzed under the same conditions that normal diborane was. These are given in Table II. In order to test the prediction B_2D_6 was pyrolyzed. For comparison purposes, a spectrum of pure B_2D_6 is given in Figure 10. Figure 11, analogous to Figures 5 and 6, shows the pyrolysis spectrum of B_2D_6. Using the same arguments as outlined in the analysis of pyrolysis of diborane leads to results tabulated in Table III.

Table III. Comparative Frequencies of Isotope Molecules

Molecule	Predicted Frequency, μ	Possible Assignment	Experimental Frequency, μ	Description
BH_3	2.67 ± 0.08	$\nu_3 + \nu_4$	2.84 ± 0.03	Weak, fairly broad
BD_3	3.35 ± 0.58	$\nu_3 + \nu_4$	3.91 ± 0.03	Weak, fairly broad
BH_3		ν_3	3.9 ± 0.15	Probably strong, might have doublet structure
BD_3	5.2 ± 0.9	ν_3	5.35 ± 0.03	Probably strong, might have doublet structure
BH_3		ν_2	$\left\{\begin{matrix} 6.15 \pm 0.15 \\ 6.55 \pm 0.15 \end{matrix}\right\}$ 6.40 ± 0.20	Possibly a doublet, strong
BD_3	(8.21 ± 0.25)	ν_2	$\left\{\begin{matrix} 8.25 \pm 0.15 \\ 8.72 \pm 0.15 \end{matrix}\right\}$ 8.50 ± 0.10	Possibly a doublet, strong
BH_3		ν_4	8.40 ± 0.10	Strong, fairly wide
BD_3	11.45 ± 0.30	ν_4	11.45 ± 0.02	Weak, sharp
B_5H_9			5.54	Weak, broad
B_5D_9			7.40	Weak, broad

Aside from the combination frequencies, the results agree within experimental error. Nevertheless, one wonders why the peak at 11.45 microns for BD_3 was attenu-

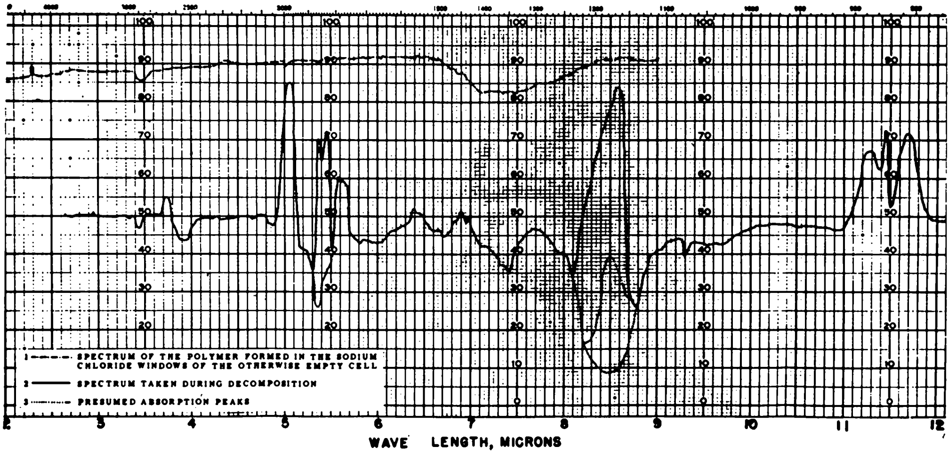

Figure 11. Infrared spectra

ated considerably in comparison with the corresponding peak of BH_3. In fact, an analysis of relative absorptions had to be made to show its existence. These are summarized in Table IV.

Table IV. Effect of Time on Absorbances at 11.27, 11.45, and 11.70 Microns (B_2D_6, Compensating Spectrum)

Approximate Time, Min.	Absorbance $D_1(11.27)$	Absorbance $D_2(11.45)$	Absorbance $D_3(11.70)$	D_2/D_1	D_3/D_1	D_2/D_3
8	0.132	0.155	0.177	1.17	0.98	1.34
15	0.203	0.278	0.260	1.37	1.05	1.29
22	0.286	0.586	0.364	2.05	1.61	1.28
Pure B_2D_6	0.163	0.310	0.181	1.91	1.72	1.11

Although results are encouraging it is obvious that more refined measurements will have to be made before the assignment to BH_3 can be considered proved.

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Conversion of Diborane to Higher Molecular Weight Boranes in the Presence of Certain Heterogeneous Catalysts

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This paper reviews some approaches taken by the research staff of Olin Mathieson Chemical Corp. on the behavior of diborane when in contact with certain catalytic materials. In such studies it is desirable to employ relatively low temperatures, because diborane is known to react with other boranes to form nonvolatile solids of variable composition at higher temperatures. Some of these solids are colorless, but with increasing temperature they lose hydrogen and progressively change in color through yellow and brown toward black. The structural and chemical characteristics of these materials, referred to as "yellow solids," are still virtually unknown.

Relatively little work has been done on the catalytic decomposition of diborane. Schlesinger (*6*), at the University of Chicago, has considered the possibility that some catalyst might be found which would promote the formation of pentaborane(9) from diborane. Schlesinger found that the conversion temperature was lowered in the presence of dehydrogenation catalysts. Relatively pure pentaborane(9) was formed in 50% yield with a 50% diborane conversion when diborane was passed over a Universal Oil Products dehydrogenation catalyst at 115° to 135°C. Pentaborane(11) however, was obtained in good yields when hydrogenation catalysts were employed at higher temperatures (about 195°C.).

Several investigators have been interested in the effects of various gases on the conversion of diborane to higher molecular weight hydrides—in particular, Schlesinger and Burg (*7*), Stock and Mathing (*9*), and McCarty and DiGiorgio (*4*).

None of the gaseous catalysts employed produced any significant change in the conversion of diborane or in the distribution of the products. During the course of early work in these laboratories it was observed that many materials resulted in very large conversions of diborane. Unfortunately, however, this apparent "catalytic activity" in the majority of cases was of an undesirable nature, resulting in the formation of large amounts of yellow solids. In many instances a reaction occurred between diborane and the catalytic surface to form undetermined products. On the other hand, many of the materials screened were found to act only as chemically inert heat transfer agents.

Experimental

The reactor shown in Figure 1 was used in these experiments. The catalyst and/or supporting material to be tested rested on the coarse sintered-glass plate. The

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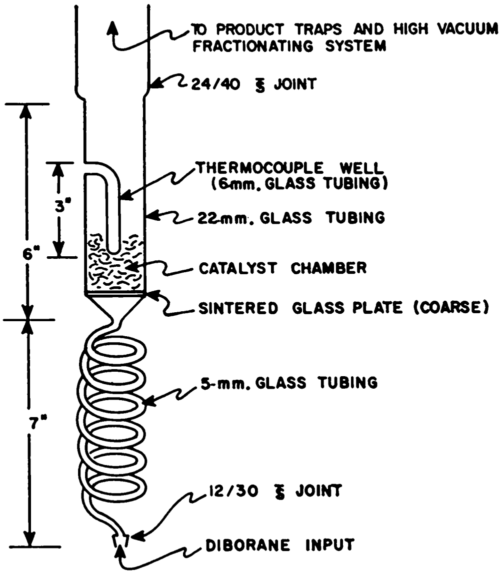

Figure 1. Catalytic reactor

thermocouple well was designed to allow the temperature of the interior of the catalyst bed to be measured. This particular arrangement for temperature measurement was important, especially where an exothermic reaction occurred between the catalyst and diborane. During the experiment, both the 22-mm. tube enclosing the catalyst bed and the entire 5-mm. spiral glass tubing immediately below the sintered-glass plate were enclosed by a furnace and heated to the same temperature. The purpose of the spiral tubing was to preheat the diborane and diluent gas to the reaction temperature before they came in contact with the catalyst bed. Care had to be taken in all experiments with this reactor that extensive pyrolysis of diborane did not take place in the spiral preheater as evidenced by the appearance of yellow solids.

In Figure 2 is shown an outline of the catalyst evaluation apparatus used in this

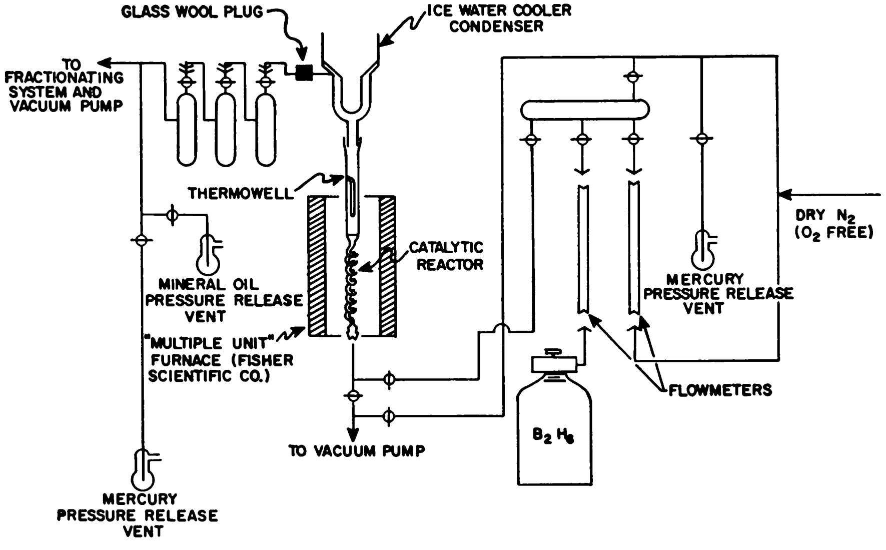

Figure 2. Catalyst evaluation apparatus

work. The ice water–cooled condenser was effective in removing decaborane from the gas stream leaving the catalyst bed. Unreacted diborane, along with other volatile boranes, was collected in three traps cooled to −196°C. After the experiment, the catalytic reactor was isolated from the system and the contents of the −196°C. traps were analyzed by fractional condensation. Infrared analysis of the fractions served to confirm the results.

Before testing, each potential catalyst was baked out for at least 12 hours at about 400° under the vacuum obtainable with a glass three-stage mercury diffusion pump. The final vacuum at room temperature was usually about 1×10^{-4} mm. of mercury.

It was soon realized in the early stages of this work that the common silica and activated alumina–supported catalysts so commonly used in the petroleum field were unsuitable for use with the boron hydrides. This may be best illustrated by consideration of Table I, in which is shown the effect of some common hydrogenation-dehydrogenation catalysts on diborane in the single-pass reactor system. The second column refers to the temperature of the catalyst bed at the beginning of the experiment, and the third column to the maximum temperature rise occurring within the catalyst bed after exposure to diborane. Although the experimental runs lasted 15 to 20 minutes each, the maximum temperature rise was always noticed within 1 or 2 minutes after exposure of the catalyst to diborane. The last three columns of the table refer to the corrected mole per cent yields of the four boron hydrides most commonly found as a result of the decomposition of diborane. For the sake of brevity, the yields of pentaborane(9) and pentaborane(11) have been combined. Infrared analysis has repeatedly shown that the amount of hexaborane formed in these experiments is very small; thus it may be assumed that the corrected yields for the four hydrides shown in the table should equal 100% unless diborane was being lost through chemical interaction with the catalyst itself. The high temperature increase observed with the molybdena on alumina catalyst could not have been due simply to oxidation of the diborane, because the catalyst was treated with hydrogen at 400° for approximately 6 hours prior to the run.

Table I. Catalytic Conversion of Diborane to Higher Hydrides

Catalyst	Temp., °C.	▲ Temp. During Run, °C.	Conversion of Diborane, %	Corrected Mole % Yields		
				B_4H_{10}	B_5H_9(11)	$B_{10}H_{14}$
Activated alumina	156	+22	54.5	0.77	6.0	0
0.5% Pt on alumina	156	+12	100	0	0	0
MoO_3 on alumina	25	+94	37.5	1.3	1.7	0
Silica gel	154	+30	51.0	Trace	Trace	0
Nickel on charcoal	148	+6	71.6	0	0	0

In an attempt to determine the nature of the interaction of diborane with catalytic surfaces, a series of experiments with activated alumina was undertaken (Table II). The first two columns refer to the way in which the activated alumina was pretreated prior to a run. The heating of the alumina samples was performed in Vycor tubes under a pressure of approximately 10^{-4} mm. of mercury. Surface

Table II. Effect of Heat Treatment of Alumina on Conversion of Diborane

(Catalyst. Activated alumina)

Pretreatment of Catalyst		Surface Area, Sq. M./Gram	Temp., °C.	▲ Temp. during Run, °C.	Diborane Conversion, %	Corrected Mole % Yields		
Temp., °C.	Time, hours					B_4H_{10}	B_5H_9(11)	$B_{10}H_{14}$
...	...	80.5	157	+36	86.0	0	1	0
750	15	132	150	+22	82.6	Trace	4.9	0
920	15	80.4	154	+20	76.1	Trace	6.6	0
920	38	69.0	148	+12	64.9	Trace	6.2	0
1000	15	70.2	148	+20	73.0	Trace	7.3	0
Anhydrous alumina (Alundum)[a]		10.1	150	+2	16.9	6.4	39.4	0

[a] Commercial material.

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area measurements of the treated aluminas were obtained employing the procedure of Brunauer, Emmett, and Teller, using nitrogen as the adsorbing gas. In most cases when the diborane flow was begun, the temperature of the alumina bed began to rise, reaching a maximum value in several minutes. This temperature rise is, no doubt, due to a reaction between diborane and the chemically bound water on the alumina surface. The observed temperature rise was greatest in those experiments which showed the greatest conversions of diborane. After reaction, the alumina in most cases had a strawlike color. The catalyst beds were analyzed for total boron, and the results were applied to the boron recovery in the material balance calculation. On the basis of only the volatile boron hydrides formed over the alumina surface, the boron recovery ranged from 15.0 to 39.4%. However, considering the boron in the form of yellow solids and/or other by-products on the catalyst bed, the total boron recovery ranged from 75.6 to 99.5%.

Results

The results of these experiments are shown graphically on Figure 3.

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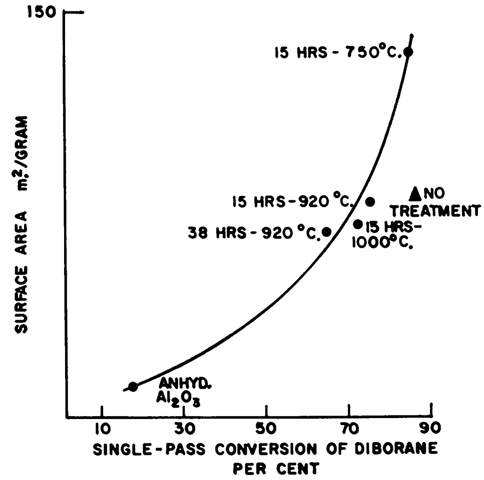

Figure 3. Heat treatment of alumina

Effect on the conversion of diborane

The thermal treatment of activated alumina under reduced pressure at 750° for 15 hours increased the surface area from 80.5 to 132 square meters per gram. This apparent increase in surface area probably is due to the removal of adsorbed water and gases from the surface of the alumina. This initial degassing apparently does not appreciably alter the reactivity of alumina toward diborane, since the diborane conversion dropped only slightly, from 86.0 to 82.6%. Treatment of the alumina at 920° for 15 hours brought about a sharp decrease in surface area, to within the original value of 80 square meters per gram. This is the temperature at which chemically bound water is removed. The extent of conversion of diborane in the presence of this material was reduced to 76.1%. Diborane was converted to the extent of 73.0% in the presence of alumina treated at 1000° for 15 hours. The surface area of this material was 70.2 square meters per gram. More extensive treatment at 920°C. for 38 hours did not reduce the surface area appreciably; the conversion of diborane in the presence of this material was reduced to 64.9%.

With commercial anhydrous alumina, 16.9% of the diborane was converted, 90.9% of the diborane being recovered in the form of identifiable products. However, the surface area of this material (10.1 square meters per gram) is deemed too small to make it valuable as a catalyst carrier.

In a qualitative way these results are in agreement with the work of Shapiro and Weiss (*8*), who studied the nature and location of the bound water in silica gel through the reaction of this water with diborane. Shapiro and Weiss concluded from their studies that the water existed in the form of hydroxyl ions, and that the bulk of the hydroxyl ions were located at the surface of the silica. Thus, as with silica gel, it is to be expected that a correlation exists between the amount of bound water and the specific surface of activated alumina. Such a trend seems to be shown by the curve in Figure 3 and is in agreement with previous work of Krieger (*2*), Owen (*5*), and others (*1*), who have shown that the heat treatment of activated alumina lowers its surface area.

Discussion

Based upon the above results, hydrogenation-dehydrogenation catalysts supported upon aluminas of moderate surface areas (approximately 10 to 40 square meters per gram) were studied. However, none of the materials investigated were satisfactory.

A fundamental postulate of heterogeneous catalysis theory is that in any catalytic reaction at least one of the reactants is first chemisorbed on the surface of the catalyst, after which further reaction can take place either between the chemisorbed species themselves or between the chemisorbed species and another reactant in the gas phase. According to Twigg and Rideal (*10*) an essential requirement for chemisorption is that the lattice distance of the reacting surface should be comparable to that of the adsorbed species. Based upon this theory, a compilation was made of the boron to boron bond length in various borides and compared to the boron bond length in diborane as given by Lipscomb (*3*). These values are summarized in Table III. In light of the above facts it was deemed worthwhile to study the effect of a series of borides on the conversion of diborane. Metallic borides, representative of various classes of molecular structures, were tested. These included the M_2B type, isolated boron atoms in a matrix of metal atoms, the MB type, zigzag chains of boron atoms, the M_3B_4 type, double boron chains or fragments of nets, the MB_2 type, hexagonal boron nets, and finally the MB_6 and MB_{12} types, three-dimensional boron framework. The borides were all used as finely ground powders and were supported on borosilicate glass wool for greater effective surface area.

Table III. B—B Bond Lengths in Diborane and Some Metallic Borides

Substance	B—B, A.
Diborane	1.77
Calcium boride	1.70
Boron carbide	1.74–1.80
Rare earth borides	1.82

In general the borides were not active catalysts as evidenced by the low conversions obtained, seldom over 15% (Table IV).

Table IV. Catalytic Conversion of Diborane to Higher Hydrides

Catalyst	Temp., °C.	▲ Temp. during Run, °C.	Conversion of Diborane, %	Mole % Yield B_4H_{10}	Mole % Yield B_5H_9(11)	Mole % Yield $B_{10}H_{14}$
Aluminum boride	175	+1	8.3	Trace	4.9	Trace
Chromium boride	169	+1	6.6	Trace	3.6	Trace
Magnesium diboride	174	+2	9.7	0.2	1.8	Trace
Magnesium tetraboride	178	+1	10.2	0.2	6.6	Trace
Manganese boride	175	0	10.2	0.9	2.3	Trace
Molybdenum boride	174	+5	23.3	Trace	3.6	Trace

Carbon has also been investigated as a possible catalyst or catalyst support for the conversion of diborane to higher hydrides. It was generally found with carbon catalysts that high diborane conversions were obtained with freshly degassed materials. Upon further treatment with diborane the activity of the carbon catalyst decreased until no activity was shown. It was not known whether this decrease was accompanied by a marked decrease in surface area. The apparent inertness of carbon after treatment with diborane might, however, make it suitable for use as a catalyst carrier, if the high surface area of the catalyst is maintained.

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Impact of Recent Developments in Boron Chemistry on Some Scientific and Engineering Problems

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In the last few years the study of the chemistry of boron compounds has been very much intensified, resulting in profound effects on both science and technology. The reasons for this increased interest include:

Boron is an excellent absorbent for thermal neutrons; therefore, boron itself and some of its compounds are important in nuclear engineering.

The incomplete electron shell of the boron atom gives rise to interesting structural and valence problems. Furthermore, boron is, because of its electronic structure, an extremely versatile element and forms a great variety of compounds which have numerous and unique applications in chemistry.

Some boron compounds are, because of their high heat of combustion, excellent fuels for jet propulsion, known under such names as high-energy or exotic fuels.

Effect of Recent Developments on Industry and Science

Boron Compounds as Fuels for Jet Propulsion. HEATING VALUE. Boron compounds are excellent propellants because of the high energy released in the combustion of boron. Evidently the first question to be answered is, "Why is heat of combustion so important?" The answer is given by the following range formulas for various jet-propelled devices:

Jet-propelled aircraft

$$R_{\max} = \eta \times \Delta H \times \frac{L}{D} \times \ln M \qquad (1)$$

where $R_{\max}$ = range
η = propulsion system efficiency
ΔH = energy released per unit mass
L/D = lift to drag ratio
M = mass ratio (ratio of structure plus fuel weights to structure weight)

Rocket on surface of earth
$R_{\max}$ = const. $\times \Delta H \times \ln^2 M$ (horizontal range) (2)

Rocket ascending vertically (maximum height)
$R_{\max} \sim$ const. $\Delta H \ln^2 M$ (vertical range after cutoff) (3)

These formulas are, of course, greatly simplified. But even from these rough approximations the importance of the energy released during combustion is apparent. Range or height in all cases is proportional to this energy.

The energy released (ΔH in the equations) is, however, not identical with the heat of combustion measured in a calorimeter. Rather, it is the energy released by the combustion gases during the working cycle. The exact determination of this quantity is rather cumbersome. Basically, it is the fraction of the heat being developed in the combustion chamber which can generate the propulsive force by being converted into directed motion of the exhaust jet.

In BORAX TO BORANES;
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For a preliminary rough estimate of the heat released by compounds containing various atomic species two sweeping assumptions are made.

First, it is assumed that the heat released is about proportional to the heat of combustion measured calorimetrically. This assumption is justified by experience.

Second, it is assumed that the heats of combustion of the elements contained in a molecule add up to give the heat of combustion of the compound. The justification for this assumption is that the heat of formation of most fuels is only a small fraction of their heats of combustion.

For more accurate computations it would be necessary to use the most recent thermochemical measurements, and lacking such values, the heats of formation must be estimated from bond energies. Evidently, fuel combinations with small bond energies to be broken are desirable and endothermic compounds are even better (*24, 30*).

Comparison of Boron with Other Elements Used in Fuels. With the limitations involved in the assumptions made, the heating values of the elements will give some idea of the performance of propellants made up from different species.

Table I shows the heat of combustion for various light weight elements at stoichiometric mixture ratios.

Table I. Heat of Combustion of Elements in the First and Second Row of the Periodic Table

Atomic No.	Element	Atomic (Molecular) Weight	Heat of Combustion, Kg. Cal./Mole	Kg. Cal./Gram Fuel	Prod.	M.W. Prod.	Kg. Cal./Gram Prod.
1	H_2	2	68.4	34.2	$H_2O(g)$	18	3.7
3	Li	6.9	141.7	10.3	$Li_2O(s)$	29.8	4.75
4	Be	9.0	154.8	17.2	BeO(s)	25.0	6.2
5	B	10.8	280.0	13.0	$B_2O_3(s)$	69.6	4.0
6	C	12.0	94.4	7.9	$CO_2(g)$	44.0	2.14
11	Na	23.0	99.1	2.2	$Na_2O(s)$	62.0	1.60
12	Mg	24.3	145.8	6.0	MgO(s)	40.3	3.6
13	Al	27.0	399.1	7.4	$Al_2O_3(s)$	102.0	3.9
14	Si	28.1	201.3	7.2	$SiO_2(g)$	60.1	3.54
15	P	31.0	365.8	5.7	$P_2O_5(s)$	142.0	2.5
16	S	32.1	91.5	2.85	$SO_3(g)$	80.1	1.14

Electronegative elements and noble gases have been omitted for obvious reasons. The table has been discontinued with the element sulfur because elements with higher atomic weight will give more and more decreasing values of heat of combustion per unit weight.

Evidently only light weight elements of the first and possibly of the second row can form compounds suitable as propellants for jet propulsion.

Two values are shown for each element: the heat released per unit weight of fuel alone and the heat released per unit weight of fuel plus oxidizer. The first value applies to the air-breathing engines, the second one to rockets. The difference in the application of fuels to these two types of engines is obvious.

This difference becomes even more clear in Table II, where the figures are arranged in decreasing order for both cases.

Table II. Comparison of Heats of Combustion per Unit Weight of Fuel and Unit Weight of Fuel plus Oxidizer

(Systems arranged in decreasing order)

	Air-Breathing Engines		Rocket Engines	
No.	Element	Kg.-cal./gram	Element	Kg.-cal./gram
1	H_2	34.2	Be	6.2
2	Be	17.2	Li	4.75
3	B	13.0	B	4.0
4	Li	10.3	Al	3.9
5	C	7.9	H_2	3.7
6	Al	7.4	Mg	3.6
7	Si	7.2	Si	3.55
8	Mg	6.0	P	2.5
9	P	5.75	C	2.2
10	S	2.85	Na	1.6
11	Na	2.2	S	1.15

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This table makes it very clear that the rank of the elements as fuel constituents changes with the application. Boron ranks in the third place in both cases.

Hydrogen is in first place for air-breathing engines by a great margin, but falls behind for rocket engines. Actually it gives the highest specific impulse in this case because the heat release per unit weight is much higher at off mixture ratios and because the actual performance of metal oxides is greatly reduced by their evaporation and dissociation. Unfortunately, hydrogen has very unsatisfactory physical properties. It is, therefore, advantageous to use hydrogen in combination with other elements which act as hydrogen carriers.

Lithium and beryllium have to be excluded for large scale applications. No liquid or suitable solid compound of these elements is known, and they carry much less hydrogen than does boron per unit weight.

For both applications carbon ranges below boron and is also undesirable because of the high energy loss resulting from the ease of dissociation of carbon dioxide.

Therefore, from these admittedly very crude considerations, it can be inferred that compounds consisting primarily of hydrogen attached to boron should give the most desirable propellants and should be superior to conventional hydrocarbon fuels.

This conclusion is borne out by the figures in Table III, which compare the heat of combustion of some boron hydrides with the energy released by hydrocarbon fuels and hydrazine.

Table III. Heating Value of Propellants and Boron Hydrides (*26*)

	Fuel Only, Kg.-Cal./Gram	Fuel Plus Oxidizer, Kg.-Cal./Gram
Hydrogen	28.8	3.21
Diborane	17.6	3.95
Pentaborane	16.6	4.12
Decaborane	15.5	4.00
Ethyldiborane	14.9	3.74
JP-4	9.5	2.10
Ethyl alcohol	6.4	2.08
Hydrazine	4.1	2.00

Remembering that the range of jet-propelled devices is approximately proportional to the heating value of the fuel, it is obvious that the use of boron compounds as fuels will increase the range by about 25 to 50% and it becomes immediately evident that the successful development of chemical boron fuels will have a tremendous impact on aviation and the technology of rockets.

On the other hand the application of these new fuels has raised many practical problems, the solution of which has required intensive fundamental research.

One of these problems is discussed here briefly.

For the first approximation, calorimetric heating values based in the case of boron on solid boron trioxide, B_2O_3, have been tabulated.

But at elevated temperatures or in the presence of other combustion products, such as steam, boron trioxide is neither the only oxygen compound of boron formed nor is it always present in the solid state. The loss by evaporation alone is nearly 25% of the tabulated heat of combustion.

For a correct evaluation of boron compounds as fuels one must, therefore, know the type of boron oxides present in the combustion chamber and in the exhaust, as well as their vapor pressures and thermodynamic functions. Also, the equilibrium constants for the interaction of the various oxides between themselves and with other combustion products must be known. The study of these fundamental properties has received a great impetus by the use of newly developed boron compounds in jet propulsion. Many of the pertinent problems have been solved by Brewer, Margrave, Inghram, and Bauer, a few of the many contributors (*1, 9, 14, 15, 21*).

One important result seems to be that the evaporation of boron oxide is promoted by the presence of steam.

These results of basic research in boron chemistry are especially important for an evaluation of rocket power plants with their very high chamber and exhaust temperatures; they affect only to a lesser degree air-breathing engines.

Superiority of Boron Compounds for Reasons Other Than Heating Value. Up to now the superiority of boron compounds as jet fuels has been related to their thermochemical properties. The contribution of the chemical characteristics of boron is probably equally great.

Boron is an excellent hydrogen carrier. Possibly just as important is its extreme versatility, which is the result of its position in the periodic system. It approaches in this respect its neighbor, carbon, although the chemistry of boron has, of course, been developed to a far lesser extent than organic chemistry.

As a result of this versatility the physical properties of boron compounds can be tailored to meet most requirements for boron fuels, and vice versa, the necessity to meet these requirements has led to the discovery of entirely new classes of boron compounds and of numerous unique and unexpected reactions.

New Boron Compounds in Industry and in Basic Chemistry. BORON HYDRIDES. Compounds containing only boron and hydrogen would be the best jet fuels.

They have also been the first unusual compounds to be studied and have, because of their reactions and structure, aroused the interest of chemists ever since A. Stock in Germany discovered them early in this century. But the real starting point for the study of boron hydrides in this country was the work by H. I. Schlesinger and his coworkers at the University of Chicago, which began in the thirties of this century.

Table IV gives the formulas and the physical properties of the more common representatives among them.

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Table IV. Physical Properties of Some Boron Hydrides

	Formula	M.W.	M.P., °C.	B.P., °C.	*d* (Liquid)
Diborane(6)	B_2H_6	27.7	−165.5	−92.5	0.447 (−112°)
Tetraborane(10)	B_4H_{10}	53.4	−120	+18	0.59 (−70°)
Pentaborane(9)	B_5H_9	63.2	−45.6	+60	0.61 (0°)
Pentaborane(11)	B_5H_{11}	65.2	−128.6	—	—
Hexaborane(10)	B_6H_{10}	75.0	−65.1	—	0.70 (0°)
Decaborane(14)	$B_{10}H_{14}$	122.3	99.7	+213	0.78 (100°)

Evidence for the existence of many other boron hydrides such as octaborane, B_8H_{12}, and nonaborane, B_9H_{15}, has been obtained (*5, 6, 17*). B_3H_7 is known in its coordination compounds with Lewis bases (*8*), and also as a product of the cleavage of B_4H_{10}. At least the transitory existence of dodecaborane has been reported (*22*).

Diborane(6), the lowest and the simplest member of the series, is most easily prepared. All other boron hydrides are obtained from this compound by controlled pyrolysis.

Methods for large scale manufacture of diborane(6) have been developed by a number of organizations. But these methods have found until now only very limited practical application.

The simplest and smoothest reaction for the laboratory preparation of diborane is still the hydrogenation of boron trifluoride etherate by lithium hydride. This reaction was, to the author's knowledge, discovered independently in the year 1944 by H. I. Schlesinger (*19*) in Chicago and Sherman Lesesne (*12*) of the since defunct Lithaloys Corp. It made diborane available for the first time in substantial amounts. At the end of the war the equivalent of one pound of diborane per day was produced at Lithaloys. The over-all reaction is shown in the first line of Table V.

Table V. Laboratory Preparation of Diborane

(1) $6LiH + 2BF_3 \rightarrow B_2H_6 + 6LiF$

(2) $3LiBH_4 + BF_3 \rightarrow 2B_2H_6 + 3LiF$

Unfortunately lithium hydride and boron trifluoride are rather expensive materials and, therefore, not suitable for the production of diborane in tonnage quantities as required by the mushrooming demand for the manufacture of high energy fuels. But attempts to replace them in the direct hydrogenation reaction by less expensive starting materials, such as BCl_3 or $B(OCH_3)_3$ and NaH met, as far as is known, only moderate success or no success at all. An indirect way proved to be more successful.

METALOBOROHYDRIDES. This indirect method is based on the use of metaloborohydrides as intermediates. Metaloborohydrides can be considered as double hydrides of a metal hydride and the radical borine, BH_3, which is the unstable monomer dimerizing to diborane. They were discovered in 1939, again by H. I. Schlesinger and coworkers.

Since their discovery they have turned out to be essential for the manufacture of boron hydrides, and consequently, also of high energy fuels and they have become indispensable for hydrogenation reactions in organic chemistry.

Aluminum borohydride, $Al(BH_4)_3$, the first of these compounds to be synthesized, was prepared in 1939 by H. I. Schlesinger, R. T. Sanderson, and A. B. Burg (*20*) by reacting aluminum trimethyl with diborane.

Since 1940 a large number of metaloborohydrides have been prepared, mostly by an interchange reaction of $NaBH_4$ and the pertinent salt in an appropriate solvent.

Sodium borohydride itself is now manufactured in tonnage quantities by the hydrogenation of the easily accessible trimethoxyborane with sodium hydride.

Table VI shows, as an example, the sequence of steps in the manufacture of potassium borohydride as it is carried out by Metal Hydrides Inc.

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Table VI. Manufacture of Potassium Borohydride (*7*)

1. $Na + H_2 \xrightarrow[\text{oil}]{\text{in}} NaH$ dispersion
2. $4NaH + B(OCH_3)_3 \xrightarrow[\text{liq. mixture}]{\text{in}} NaBH_4 + 3Na(OCH_3)_3$
3. Extraction of $NaBH_4$ with water
4. Precipitation of KBH_4 with KOH

The decisive step in Table VI is the second one leading to sodium borohydride. It proceeds, according to Brown and coworkers (*3*), exceedingly smoothly in suitable solvents such as diethylene glycol (diglyme) or tetrahydrofuran. But most important, sodium borohydride reacts in the same solvents with boron trichloride to give excellent yields of diborane (*2*).

This sequence of reactions represents, therefore, an excellent route for the large scale production of diborane.

Many derivatives of metaloborohydrides, where the hydrogen is replaced by organic groups, have also been reported.

Attempts to prepare ammonium borohydrides have, however, remained unsuccessful to date; but the author obtained quaternary ammonium borohydrides by the reaction shown in Table VII.

Table VII. Analogy Leading to First Preparation of a Quaternary Ammonium Borohydride

(1) KBF_4 from BF_3 and KOH
$4BF_3 + 3KOH \rightarrow 3KBF_4 + B(OH)_3$

(2) KBH_4 from B_2H_6 and KOH
$2B_2H_6 + 3KOH \rightarrow 3KBH_4 + B(OH)_3$ (*29*)

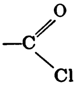
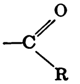
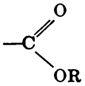
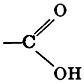
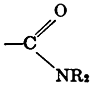
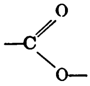
(3) $(CH_3)_4NBH_4$ from B_2H_6 and KOH (*28*)
$2B_2H_6 + 3KOH \rightarrow 3(CH_3)_4BH_4 + B(OH)_3$

The analogy between BF_3 and the borine radical, BH_3, is evident when comparing the three reactions shown, including the unpublished preparation of KBH_4. Incidentally, the author hit on this preparation of KBH_4 by accident when he tried to obtain potassium hypoborate according to A. Stock's description by the reaction of potassium hydroxide with diborane and was unable to verify Stock's findings. It appears, however, possible that the hypoborates are intermediates in this reaction.

The hydrogenation effect in general is at least as important as the use of metaloborohydrides in the production of borohydrides. In the words of Wiberg (*27*), the foremost German expert, "one can today not imagine preparative inorganic and organic chemistry without the metaloborohydrides (which he calls boranates) and the analogous aluminum compounds."

Many hundreds of papers have been published on this subject and in this brief survey not even the surface of this vast field can be touched. Table VIII is taken from a paper given by E. Wiberg.

Table VIII. Hydrogenation of Organic Groups by Metaloborohydrides

	$NaBH_4$	$LiBH_4$	$Ca(BH_4)_2$	$Al(BH_4)_3$	$NaBH_4 + AlCl_3$
	+	+	+	+	+
	+	+	+	+	+
	–	+	+	+	+
	–	–	+	+	+
	–	–	–	·	·
	–	–	–	–	–

In the first column a series of carbonyl compounds is arranged according to decreasing ease of hydrogenation and in the first row a number of metaloborohydrides are listed in increasing order of hydrogenation ability.

The table shows the high selectivity of the hydrogenating effect. This selectivity extends also to groups other than those shown in the table. As an example, conjugated double bonds are not attacked by metaloborohydrides, a fact which is widely being applied in the synthesis of pharmaceuticals and fine chemicals—for instance, in the preparation of vitamin A. Thus, the recent developments in boron chemistry have affected also seemingly remote fields.

Many organic derivatives of boron hydrides, metaloborohydrides, boric acid, and other organic boron compounds have been prepared and extensively studied in recent years.

An excellent review of their complicated chemistry by Lappert (*11*) in London, England, has been published recently in *Chemical Reviews*. Many of them exhibit properties and reactions which are highly interesting for the theoretical chemist.

Boron-Nitrogen Compounds. The simplest nitrogen-boron compounds result from the addition of an amine to borine, BH_3, the monomeric radical mentioned before.

Up to now nitrogen-boron compounds have had very little effect on industry, and

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their influence on preparative chemistry can in no way be compared with that of the two classes of compounds which have been discussed before. But some of them appear to be stepping stones in the preparation of inorganic or semiorganic polymers which may become industrially important some day. Their principal interest at present is, however, their contribution to the theoretical concepts of chemical bonds.

There are three types of these borine-amine addition products, all containing coordination bonds between boron and nitrogen. They are analogous to saturated, olefinic, and acetylenic hydrocarbons (Table IX).

Table IX. Systematic Arrangement of Hydrocarbon and Borine-Amine Addition Compounds

Alkanes	C—C	Boranes	$B \leftarrow N$
Alkenes	C═C	Borenes	$B \underline{\leftarrow} N$
Alkynes	C≡C	Borazines	$B \overset{\leftarrow}{=} N$

Boranes are pyrolyzed under the influence of heat to give boranes, which in turn are converted by further pyrolysis to borazines. The reaction scheme is illustrated in Table X.

Table X. Pyrolysis of Aminoborine Compounds

1. Boranes to borenes

$$BX_3 \leftarrow NR_3 \xrightarrow[\Delta]{-RX} BX_2 \underline{\leftarrow} NR_2$$

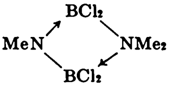
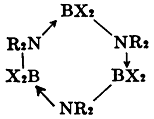
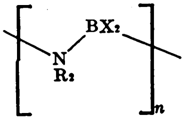
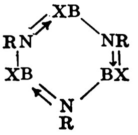
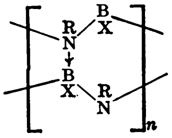
2. Borenes to borazines

$$BX_2 \underline{\leftarrow} NR_2 \xrightarrow[\Delta]{-RX} BX \overset{\leftarrow}{=} NR$$

X = halogen, H, CH_3; R = H, CH_3, etc.

The boranes exist as monomers. But the borenes, and more so the borazines, have a tendency to form dimers, trimers, and polymers. It is so pronounced with the borazines that their monomers or dimers are not known. Thus, many years ago A. Stock (*23*) obtained the practically stable trimer borazole by pyrolyzing under pressure the addition product of diborane and ammonia. Table XI, compiled from Wiberg's paper (*27*), gives a schematic survey of the known borenes and borazenes.

Table XI. Schematic Arrangement of Known Borenes and Borazenes

	Monomer	Dimer	Trimer	Polymer
Borenes	$Cl_2BN \underline{\leftarrow} Me_2$			
Borazines	....	....	 Borazole	

Evidently for the preparation of inorganic polymers containing the B—N bond, the borazines have the greatest interest. But in the past, efforts have been directed mainly towards the synthesis of the six-membered ring compound which is known as borazole and many syntheses for the preparation of this compound or its derivatives have been published.

The synthesis of alkyl- and aryl-boron substituted borazoles by the reaction of

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alkyl or aryl-boron dichlorides has been reported (*18*). All these syntheses can be interpreted by the intermediate formation of borazines supporting what has been said before of their tendency towards polymerization.

This is well illustrated by an unpublished synthesis of substituted borazoles from diborane and organic nitriles which Leo Spillane and the author carried out at Reaction Motors, Inc., a few years ago (*28*).

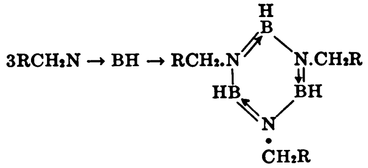
A product was obtained, for instance, from acetonitrile and diborane (*N*-triethylborazole), the formation of which can be explained only by an α-γ shift of two hydrogens attached to boron. But this shift clearly produces a borazine as shown in Table XII.

Table XII. Borazoles from the Reaction of Diborane and Nitriles

(*a*) $2R.CN + B_2H_6 \rightarrow 2R.CN \rightarrow BH_3$

(*b*) $R.CN \rightarrow BH_3 \rightarrow RCH_2N \rightarrow BH$

(*c*)



Polymers Containing Boron. One might expect to obtain higher polymeric products in all reactions leading to borazoles under proper conditions. In fact, in many cases insoluble polymeric materials have been reported in these and similar reactions. These claims have been doubted for the most part, but the borazene compound containing hydrogen on both nitrogen and boron definitely occurs in a highly polymerized form.

The existence of boron-containing polymers is also evidenced by many patents claiming plasticizing and vulcanizing effects of boron hydrides and other boron compounds.

Burg (*4*) has prepared high temperature–resistant boron phosphorus polymers, and Nielsen and McEwen (*16*) recently obtained a temperature-resistant polymer consisting of phenylene groups attached to boroxole, an oxygen analog of borazole.

Certain organic or semiorganic polymers containing boron linkages seem, therefore, to withstand high temperatures better than the usual polymeric materials, a property which is very important for aircraft applications. Such polymers may give superior solid high energy propellants.

Altogether, research on boron-containing polymers is still in its infancy, but further work in this field may have a revolutionary effect some day on the polymer industry similar to that exerted by silicon polymers in recent years.

Boron Compounds and Valence Theory. In the discussion of the small number of selected compounds, reference has been made occasionally to the types of bonds formed by boron.

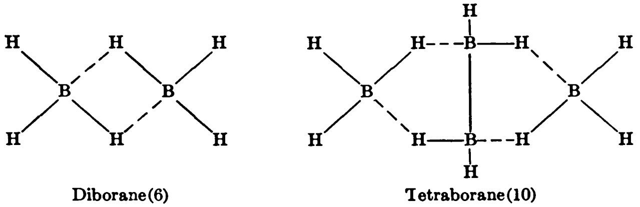
In fact, boron exhibits a greater variety of bonding than most other elements because of the deficiency of its electron shell, and the study of the structure of boron compounds had a decisive effect on our concepts of the nature of the chemical bond.

MOST IMPORTANT TYPES OF BONDS BY WHICH BORON ATTEMPTS TO COMPLETE ITS DEFICIENT ELECTRON SHELL. Besides the normal covalent bond, essentially three types of bonds are observed.

In boron hydrides the deficient electron shell is completed by means of hydrogen bridges or three-centered bonds. Two-centered and three-centered bonds are, therefore, present simultaneously in the same molecule. This is illustrated in Table XIII, which shows the well known structures of diborane-6 and tetraborane-10.

The number of three-centered and two-centered bonds present in boron hydrides can be determined formally in a very simple way, but it is very difficult to establish the complete structures of boron hydrides (*13*). With modern methods it has, however, been possible to elucidate the structure of practically all known boron hydrides,

Table XIII. Structure of Diborane(6) and Tetraborane(10)



Diborane(6) Tetraborane(10)

and from the study of isotopic exchange reactions also the reactivity of the various bonds could be determined in many cases (*10*).

Hydrogen bridges occur, of course, also in boron compounds other than boron hydrides proper. They have, for instance, been postulated, but not proved, as an explanation for the stability of boron trimethyl.

The second type of bond by which the electron shell of boron can be stabilized is the dative or coordination bond. Here, the shell is completed by the donation of a pair of electrons by a donor atom with a free pair of electrons. In the boramines, which were discussed briefly, the nitrogen furnished the pair of electrons, and in the boroxoles, oxygen is the donor. The strength of the dative bond between boron and the donor atom depends on the electronegativity of the substituents, and on steric and inductive effects. This field has been studied extensively, especially with respect to nitrogen, by H. C. Brown and coworkers.

Finally, stabilization can also occur by intramolecular resonance double bonding. This type of bond is, for instance, responsible for the stability of boron trifluoride, as has been established from the experimentally found bond length between boron and fluorine.

It occurs also in tetrachlorodiborane-4 (*25*) which was discovered again by Schlesinger and coworkers a few years ago. The peculiar reactions of this compound still pose many problems.

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Metal Boron Hydrides

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Stock described reactions of alkali metals with boron hydrides and the formation of such materials as $M_2B_2H_6$, $M_2B_4H_{10}$, and $M_2B_5H_9$. More recent investigations, particularly of the reactions of sodium amalgam and sodium hydride with boron hydrides, suggest that Stock's materials may be intermediates and that further reactions occur. The results of Stock and those of more recent investigators can be correlated by considering the possible reaction mechanisms. The reactions of sodium hydride with the boron hydrides are less complex than the reactions with sodium amalgam. However, analogies may be drawn between the sodium amalgam and sodium hydride reactions that show similarities in mechanism. Consideration of the formation and properties of NaB_3H_8, $Na_2B_{10}H_{14}$, and $NaB_{10}H_{13}$ and the relationships of these compounds to the parent boron hydrides leads to speculation for future metal boron hydride studies.

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The most familiar metal-boron-hydrogen compounds that have been described are the metal borohydrides. A great number of these borohydrides have been isolated and characterized. There is little need to review the physical and chemical nature of this series of compounds because of the widespread literature available.

A more complex series of metal-boron-hydrogen compounds are those that contain metals and boron-hydrogen groups other than borohydride, BH_4. The published experimental work dealing with these compounds is meager. A large proportion of the studies may be attributed to Stock and his coworkers (*10–15*), who have described investigations of the reactions of sodium amalgam and potassium amalgam with some of the boron hydrides. A substantial number of new metal boron hydride materials were obtained. Stock defined many of the new materials as mixtures, while others appeared to be single compounds. Although there is evidence that the metal borohydrides were present in many of Stock's products, the compositions of these products definitely show the presence of other materials. However, Stock was not aware of the existence of the now familiar borohydride salts.

Since the time of Stock's reports, little work has been published which might further define the reactions and products he described. Kasper, McCarty, and Newkirk (*7*) prepared several of the materials Stock reported and obtained x-ray data which showed the presence of the borohydrides in almost every case. Recent work at Callery Chemical Co. on Project Zip was not available for immediate publication; these studies of the reactions of the boron hydrides with sodium amalgam (*4*, *5*) in ethyl ether gave ultimate reactions quite different from those reported by Stock.

In BORAX TO BORANES;
Advances in Chemistry; American Chemical Society: Washington, DC, 1961.

At the present time there is considerable confusion arising from the scant knowledge of the reactions of metals with boron hydrides.

Reaction of Diborane with Alkali Metals

Stock investigated in great detail the reactions of diborane with sodium amalgam and potassium amalgam. In both cases the experimental evidence for the absorption of 1 mole of diborane for 2 gram-atoms of metal was excellent. No hydrogen was evolved and little decomposition of diborane was found even after many days. The compositions of the products obtained were without doubt $Na_2B_2H_6$ and $K_2B_2H_6$. Because a greater part of the experimental work was devoted to $K_2B_2H_6$, this will be reviewed first.

Potassium diborane (*15*) was prepared by shaking a glass-tube reactor of approximately 100-cc. volume containing potassium amalgam and diborane for 3 or 4 days at room temperature. Diborane was always in excess of that required for the formation of $K_2B_2H_6$, but never as great as 1 mole per gram-atom of potassium. The reaction was terminated when the mercury became mobile. Unreacted diborane was recovered by vacuum condensation and measured. In a typical experiment 38.8 cc. of diborane, 1.6 cc. of hydrogen, and a trace of pentaborane(9) were recovered from a charge of 115 cc. of potassium (calculated as gas) and 90.5 cc. of diborane. By assuming that the hydrogen evolved in the formation of pentaborane(9), a reaction ratio of potassium to diborane of 2.00 to 0.87 can be calculated from the reported data. The equation for the reaction was written

$$2KHg + B_2H_6 \rightarrow K_2B_2H_6 + 2Hg \quad (1)$$

The unreacted mercury was distilled from the reactor at 250°C. During the distillation hydrogen was evolved. (In the above experiment 13.0 cc. of hydrogen was evolved from the absorbed 49 to 50 cc. of diborane.) The $K_2B_2H_6$ residue was a fine, white powder.

Pure $K_2B_2H_6$, free of mercury, did not evolve hydrogen below 300°C. When the solid was heated to 450°C., hydrogen was evolved vigorously at first but the evolution subsided after 6 hours. Metallic potassium was distilled from the reactor, a portion of the $K_2B_2H_6$ was sublimed, and a residue was obtained which corresponded empirically to KB_2H_2. The chemical properties of the material KB_2H_2 (referred to by Stock as $K_2B_4H_4$) demonstrated that this was probably a mixture of materials. Stock proposed a mechanism for the formation of $K_2B_4H_4$ but obtained no evidence in support of it.

Analysis of the sublimed $K_2B_2H_6$ by hydrolysis and titration was in reasonable agreement with the proposed composition. However, the x-ray pattern of the material (*13*) has been demonstrated to be identical to the pattern for potassium borohydride (*7*). Stock points out that the evolution of hydrogen upon hydrolysis of the $K_2B_2H_6$ sublimed at 450°C. was always high. In fact, it is of note that all of the analytical data for sublimed $K_2B_2H_6$ would correspond to the analyses of potassium borohydride, with approximately the same deviations from theoretical as are found when the samples are assumed to be $K_2B_2H_6$.

Stock's $K_2B_2H_6$ was a white, nonvolatile solid. In dry air no reaction was observed, but in the laboratory atmosphere the material slowly increased in weight. The material was soluble in water, but insoluble in alcohol, ether, benzene, and chloroform. Explosive reaction occurred when the material was added to nitric acid. Ammonia did not react with it, and at the boiling point of ammonia the salt was insoluble.

Sublimed $K_2B_2H_6$ did not react with gaseous hydrogen bromide even after several hours of heating at 100°C. The $K_2B_2H_6$, freed of mercury by heating, reacted with hydrogen bromide to release approximately 2% of the boron as diborane, but nearly quantitative substitution occurred according to the equation

$$K_2B_2H_6 + 4HBr \rightarrow 2K_2(B_2Br_4H_2) + H_2 \quad (2)$$

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The unheated, mercury-contaminated $K_2B_2H_6$ reacted with hydrogen bromide to give approximately 30% recovery of the boron as diborane in addition to the substitution of bromine for hydrogen according to Equation 2.

The hydrolysis of $K_2B_2H_6$ in water was described rather completely by Stock. Evidence was obtained for intermediate hydrolytic products having empirical formulas such as $K_2[B_2H_4(OH)_2]$ and $K_2[B_2(OH)_6]$. Most significant was the fact that sublimed $K_2B_2H_6$ hydrolyzed more rapidly than the nonsublimed material. However, all samples of the $K_2B_2H_6$ hydrolyzed slowly, incomplete hydrolysis being obtained after 14 weeks with 29 mg. of the material in 2 ml. of water.

The data reported by Stock for the absorption of diborane by sodium amalgam (*13*, *14*) were in better agreement with the equation

$$2NaHg + B_2H_6 \rightarrow Na_2B_2H_6 + 2Hg \qquad (3)$$

than the corresponding data with potassium.

Typically, from 144 cc. of sodium and 88.7 cc. of diborane a total of 3.9 cc. of hydrogen and 11.3 cc. of diborane was recovered after 16 days. The sodium reaction proceeded more slowly than the potassium reaction. The mercury was distilled from the product sodium diborane at 180° to 190°C. From the above reaction product were evolved 9.8 cc. of hydrogen, 0.51 cc. of diborane, and 1.96 cc. of pentaborane(9) during the mercury distillation. The composition of the product after removal of mercury corresponded excellently to the formula $Na_2B_2H_6$, with the exception of hydrogen, this being low because of the hydrogen loss during heating. At 450°C. 9.9 cc. of the salt gave 8.34 cc. of hydrogen, 4.5 cc. of distilled sodium, 5.3 cc. of sublimed sodium diborane, and a yellow-brown glassy residue with an empirical formula of $Na_2B_4H_5$.

Beyond the description of several preparations and the one thermal decomposition above, there is no further report of the sodium-diborane reaction by Stock except for the x-ray patterns (*13*). The x-ray pattern of unsublimed sodium diborane was identical with that of the sublimed materials. Again it has been demonstrated that either pattern given by Stock is identical with the pattern obtained from sodium borohydride.

About the only work that was reported concerning the structure of Stock's metal-diborane reaction products was that of Klemm and Klemm (*8*). They reported that the materials $M_2B_2H_6$ were diamagnetic. Thus was pointed out the improbability of a BH_3^- anion, and the $B_2H_6^{--}$ anion was suggested.

No further studies, other than Stock's, of the reactions of diborane with metals were published before 1949, when Kasper (*7*) observed that more than 1 mole of diborane had been absorbed by each 2 gram-atoms of alkali metal in the amalgam. Further, no evidence of a change in reaction rate was noted after the absorption of diborane according to Stock's stoichiometry. In agreement with Kasper, more recent work in these laboratories (*5*) showed the absorption of diborane in excess of that demonstrated by Stock. However, the reaction of sodium amalgam with diborane was demonstrated to be more rapid in an ether medium.

The reaction of diborane with sodium amalgam in ethyl ether was complete after about 1 day, at which time 1 mole of diborane was absorbed by each gram atom of sodium. The ultimate reaction was defined by the equation

$$2Na + 2B_2H_6 \rightarrow NaBH_4 + NaB_3H_8 \qquad (4)$$

Some evidence was noted for an intermediate material, $Na_2B_2H_6$. After the completion of the reaction, a product of composition NaB_2H_6 was obtained which did not contain sodium borohydride. Rather, sodium borohydride and NaB_3H_8 formed from the solid NaB_2H_6 in a short time. Because of the solid phase formation of the two products, the empirical NaB_2H_6 would appear to be at least dimeric, NaB_2H_6. Thus, evidence for at least two intermediate steps was obtained to suggest the equations

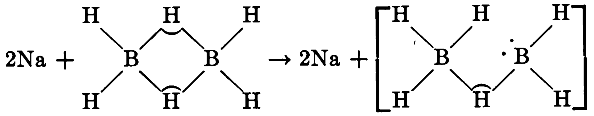
$$2NaHg + B_2H_6 \rightarrow Na_2B_2H_6 + 2Hg \qquad (3)$$

$$Na_2B_2H_6 + B_2H_6 \rightarrow Na_2B_4H_{12} \qquad (5)$$

and

$$Na_2B_4H_{12} \rightarrow NaBH_4 + NaB_3H_8 \qquad (6)$$

On the basis of Equations 3, 5, and 6, a mechanism may be proposed which agrees with the findings of Stock as well as the recent work. The most probable mechanism for Equation 3 would occur by the cleavage of one boron-hydrogen-boron bridge bond by an electron pair obtained from two sodium atoms:



However, the possibility of even an earlier intermediate, Na_2BH_3, must not be discounted. The formation of such a borane base was suggested by Burg and Campbell (*2*) as an intermediate in the reaction of sodium with H_3NBH_3 in liquid ammonia. Furthermore, the compound Na_2BH_3 would be a parent to the known salt $Na_2HB(CH_3)_2$. The intermediate $Na_2B_2H_6$ may then be analogous to the compound $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$. The electronic distribution in such a material is such that a reasonable representation of $Na_2B_2H_6$ would be $Na_2BH_2BH_4$. Further, on the basis of Stock's work, it could be concluded that $Na_2B_2H_6$ (or $Na_2BH_2BH_4$) is unstable and tends to form sodium borohydride. However, in the recent work in ether, diborane is absorbed rapidly (probably before the decomposition of $Na_2BH_2BH_4$) to yield the second observed intermediate, $Na_2B_4H_{12}$. This may occur in two steps

$$Na_2BH_2BH_4 + \tfrac{1}{2}B_2H_6 \text{ (or } BH_3) \rightarrow Na_2BH(BH_4)_2 \qquad (7)$$

$$Na_2BH(BH_4)_2 + \tfrac{1}{2}B_2H_6 \text{ (or } BH_3) \rightarrow Na_2B(BH_4)_3 \qquad (8)$$

The conversion of the product, $Na_2B(BH_4)_3$, to $NaBH_4$ and NaB_3H_8 would constitute the final step of the reaction.

Reaction of Tetraborane with Alkali Metals

The reactions of tetraborane with alkali metals reported by Stock (*11*, *13*) were not so thoroughly investigated as the analogous reactions of diborane. Tetraborane was absorbed very slowly by the alkali metal amalgams. Consequently, considerable decomposition of tetraborane to other boron hydrides occurred and the data ultimately obtained were difficult to interpret. As in the study of diborane reactions, the reaction of potassium amalgam was investigated more thoroughly than that of sodium amalgam.

In a typical reaction 115 cc. of potassium and 93.8 cc. of tetraborane were shaken in a sealed glass tube at room temperature for 48 hours. At the end of this time the mercury became mobile and the reaction was terminated. The volatile products contained 14.8 cc. of hydrogen, 11.9 cc. of diborane, 14.6 cc. of tetraborane, and 7.6 cc. of a pentaborane mixture [interpreted by hydrolysis and titration to be 6.1 cc. of pentaborane(9) and 1.5 cc. of pentaborane(11)]. The total boron and hydrogen recovery amounted to 120 cc. of boron and 318 cc. of hydrogen. It was then assumed that this boron and hydrogen represented tetraborane and that the materials recovered represented 120/4 = 30 cc. of tetraborane. Thus, approximately 64 cc. of tetraborane was consumed by the 115 cc. of potassium.

From the experiment Stock drew three conclusions:

That potassium and tetraborane gave the product potassium tetraborane ($K_2B_4H_{10}$).

That more tetraborane (about 6 cc.) than required was taken up by absorption or formation of polymeric boron hydrides.

That it could be assumed that some potassium diborane and potassium pentaborane may have formed by side reactions.

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Stock reported three experiments in addition to the one above in which tetraborane was agitated with potassium amalgam. The calculations were made in the same way as above. The reacting ratios of potassium to tetraborane consumed were (calculated): 115 cc. to 68.5 cc. in an experiment of 1.5 days; 172 cc. to 105.7 cc. in an experiment of 2 days; 230 cc. to 160.4 cc. in an experiment of 3 days. In all experiments the quantity of boron recovered represented from 20 to 30 cc. of tetraborane. Stock stated that the reaction is not clearly defined because of the side reactions occurring, but that it may be assumed that the principal reaction is the formation of potassium tetraborane.

It was not possible to separate the mercury from the potassium diborane. The temperatures required for distillation of the mercury caused decomposition of the tetraborane product. In addition, changes in the materials mixed with the potassium tetraborane during the heating rendered the decomposition reaction uncertain. The product of the first reaction above (115 cc. of potassium and 64 cc. of tetraborane) was separated from a large part of the mercury by decantation, during which approximately 5% of the potassium product was lost. When the remaining material was heated gradually, hydrogen evolution began at 120°C. This increased as the temperature was increased. When all the mercury had been removed by distillation at 170°C., the product was further heated at this temperature until hydrogen evolution was negligible. A total of 49 cc. of hydrogen was evolved. Volatile materials consisting of 6.8 cc. pentaborane(9), 0.7 cc. of tetraborane, and 5.7 cc. of diborane were recovered. When all the data were taken into consideration, the composition of the residual product was calculated to be 109 cc. of potassium, 194 cc. of boron, and 390 cc. of hydrogen. The composition corresponded approximately to the formula $K_2B_4H_8$. Stock proposed that the principal reaction might be written as

$$K_2B_4H_{10} \rightarrow K_2B_4H_8 + H_2 \qquad (9)$$

but that this reaction was obscured by side reactions.

The product of thermal decomposition, $K_2B_4H_8$, was hygroscopic. However, a sample that reacted for 1.5 days in a sealed tube containing dilute hydrochloric acid at 100°C. was not completely hydrolyzed. When 37 cc. of the $K_2B_4H_8$ material was heated to 200°C., slight hydrogen evolution occurred. The rate of hydrogen evolution increased with temperature. At 250°C. potassium distilled from the heated tube and a white sublimate was recovered. At 450°C. no further change was observed. Analysis of 10.4 mg. of the sublimate gave 16.8 cc. of hydrogen and 4.8 cc. of boron. The sublimate was identified by x-ray analysis as the same material obtained from potassium amalgam and diborane, $K_2B_2H_6$. From the quantities of potassium, potassium diborane, and hydrogen recovered from the heated product, the composition of the residue was calculated to be 28 cc. of potassium, 60 cc. of boron, and 87 cc. of hydrogen, corresponding approximately to the composition $K_2B_4H_6$.

The x-ray pattern of Stock's $K_2B_4H_8$ (*13*) was more recently demonstrated to be indentical with the pattern of potassium borohydride (*7*), but the pattern was not so intense as the borohydride pattern obtained with $K_2B_2H_6$. The presence of other materials besides potassium borohydride was evident from the appearance of additional x-ray lines.

The reaction of tetraborane with sodium amalgam was much slower than the analogous reaction with potassium amalgam. Typically, 69.5 cc. of sodium and 51.5 cc. of tetraborane had to be agitated at room temperature for 18 days before the mobility of the mercury indicated complete consumption of the sodium. When the recovery of volatile materials was taken into account [9.7 cc. of hydrogen, 8.9 cc. of diborane, 7.3 cc. of tetraborane, and 6.4 cc. of pentaborane(9)], approximately 31.5 cc. of tetraborane was calculated as having been absorbed. When the mercury was distilled off at 170°C., the evolution of 24.8 cc. of hydrogen, 1.2 cc. of diborane, 0.2 cc. of tetraborane, and 1.0 cc. of pentaborane(9) occurred. The calculated composition of the residue was 69.5 cc. of sodium, 119 cc. of boron, and 244 cc. of hydrogen, corresponding to a ratio of 2.34 to 4.00 to 8.20.

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The decomposition appeared to be similar to that of the potassium salt

$$Na_2B_4H_{10} \rightarrow Na_2B_4H_8 + H_2 \qquad (10)$$

At 450°C. further hydrogen was evolved, a white sublimate was collected, and a trace of free sodium was distilled from the heated zone. The empirical formula of the product was $Na_2B_4H_{5.5}$. The white sublimate corresponded to $Na_2B_2H_6$ (x-ray pattern identical to sodium borohydride).

Stock pointed out that the thermal decomposition of the diborane reaction products probably proceeds by way of the equation

$$2M_2B_2H_6 \rightarrow M_2B_4H_{10} + 2M + H_2 \qquad (11)$$

but that since $M_2B_4H_{10}$ was demonstrated to decompose thermally by the equation

$$M_2HB_{410} \rightarrow M_2B_4H_8 + H_2 \qquad (12)$$

the diborane salts appear to decompose by the over-all equation

$$2M_2B_2H_6 \rightarrow M_2B_4H_8 + 2M + 2H_2 \qquad (13)$$

Stock then suggested that the decomposition of $M_2B_4H_8$ ultimately would yield $M_2B_4H_4$, equivalent to the MB_2H_2 obtained from decomposition of the diborane products. This proposal is based on the observation that decompositions of either the diborane salts or the tetraborane salts result in products having 4 boron atoms for each 2 alkali metal atoms. The only evidence of the equivalence of the decomposition products obtained from the diborane and tetraborane salts, other than the empirical relationships between the boron and alkali metal content, was the solubility of these products in water and their ability to give red color to nitric acid solutions.

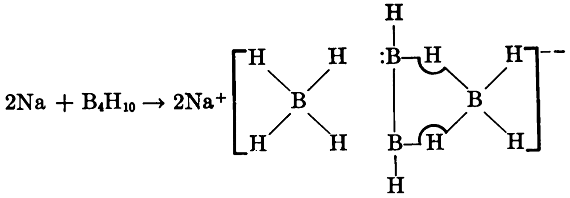
As the x-ray pattern of the tetraborane salt was nearly identical to that of the diborane salt, Stock attempted to demonstrate the formula $K_2B_4H_{10}$ by reacting the material with hydrogen chloride to recover the tetraborane. Initially, 125.2 cc. of hydrogen chloride was added to a sample of potassium tetraborane containing 172.5 cc. of potassium and 105.7 cc. of tetraborane and allowed to react for 16 hours. The volatile products were removed and investigated. Hydrogen chloride was continuously added to the residues and allowed to react further until five additions had been made. The data showed an ultimate recovery of 22.5 cc. of diborane, 28.7 cc. of tetraborane, and 3.4 cc. of pentaborane(9). The total quantity of hydrogen chloride that reacted was 317.0 cc., while 290.5 cc. of hydrogen was evolved. Most of the hydrogen chloride had reacted to substitute chlorine for hydrogen with the evolution of hydrogen gas. However, the formation of tetraborane was considered by Stock to support the identity of the starting material as $K_2B_4H_{10}$. The substitution reaction gave a product of approximate composition $K_2B_4H_5Cl_5$.

No further reports of studies of reactions of metals with tetraborane are in the open literature. Recently a study of the reaction of tetraborane with sodium amalgam was conducted at these laboratories on Project Zip. This study was made using ether as a reaction medium, paralleling the study with sodium amalgam and diborane (*5*). The reaction occurred smoothly in ether and the rate of consumption of the sodium was rapid compared to the 18 days employed by Stock. When a molar excess of tetraborane was used (at least 2 moles of tetraborane for each gram atom of sodium), the reaction was complete in as little as 5 hours. Upon removal of the volatile materials, a residue was obtained consisting of NaB_3H_8, quantitative with respect to sodium charged, and small quantities of polymeric boron hydrides. The interaction of tetraborane with the ether (*6*) was known, and the data were interpreted in terms of the two reactions—i.e., the reaction of tetraborane with ether and the reaction of tetraborane with sodium. The latter reaction was best interpreted in terms of the equation

$$2NaHg + 2B_4H_{10} \rightarrow 2NaB_3H_8 + \frac{1}{2}B_2H_6 + (BH)_x + 2Hg \qquad (14)$$

Analysis of the products demonstrated the presence of approximately 1 mole of BH for each 2 moles of NaB_3H_8.

In these recent studies there was no evidence for the intermediate $Na_2B_4H_{10}$. However, in ether the reaction was complete in such a short time compared with Stock's reaction time that the isolation of such an intermediate might be improbable. But it is conceivable that an intermediate, $Na_2B_4H_{10}$, possibly the same material observed by Stock, may have formed. If the mechansim for the tetraborane reaction were similar to that proposed for the diborane reaction, the first step could very well be



(15)

The second step of the reaction would be the addition of an electron-deficient tetraborane molecule to the $Na_2B_4H_{10}$ above, yielding an intermediate $Na_2B_8H_{20}$ (NaB_4H_{10}), which is analogous to the intermediate $Na_2B_4H_{12}$ formed from sodium and diborane. This intermediate could dissociate into 2 moles of NaB_3H_8, while the additional boron and hydrogen are evolved as diborane and polymeric boron hydride.

Further concurrent studies in the Callery laboratories (*4*) have demonstrated that NaB_3H_8 may be prepared from the reactions of tetraborane with either sodium hydride or sodium borohydride in ethyl ether. Both reactions are rapid and quantitative with respect to the sodium. The reaction stoichiometries were clearly

$$NaH + B_4H_{10} \rightarrow NaB_3H_8 + \tfrac{1}{2}B_2H_6 \tag{16}$$

and

$$NaBH_4 + B_4H_{10} \rightarrow NaB_3H_8 + B_2H_6 \tag{17}$$

Upon evaporation of volatile materials white, solid NaB_3H_8 was obtained free of impurities other than those originally present in the sodium hydride or borohydride. These reactions do not appear to be complex, as does the reaction of sodium amalgam with tetraborane. Rather, a single symmetrical cleavage of the tetraborane may occur (*6*).

Reactions of Pentaboranes with Alkali Metals

In discussions involving reaction of pentaborane(9) and alkali metals, Stock cited only two experiments with potassium amalgam. No studies of pentaborane(11) were reported. Pentaborane(11) was not only unstable and probably unsuited to a slow alkali metal reaction, but its preparation by the methods available to Stock would have been difficult.

A very small quantity of pentaborane(9), 5.3 cc., was charged to 57.5 cc. of potassium in mercury and agitated for 16 hours. At the end of this time the mobile mercury was decanted and the remaining mercury and unreacted potassium were distilled off at 265°C. in vacuo. At 200°C. a small quantity of hydrogen was evolved. This was attributed to hydrolysis by slight water contamination. Analyses of the reaction product were consistent with the formula $K_2B_5H_9$.

Although no mention is made of hydrogen evolved on heating, other than the suggestion that slight hydrolysis occurred, the x-ray pattern of this material is labeled $K_2B_5H_8$ or $K_2B_5H_9$ freed of mercury. Thus, it appears that Stock considered the hydrogen evolved to be derived from the $K_2B_5H_9$ by thermal decomposition rather than by hydrolysis. Nevertheless, once again the x-ray pattern obtained from $K_2B_5H_8$ shows the presence of sodium borohydride and other materials.

Stock reported one experiment on the reaction of hydrogen chloride with potassium pentaborane(9). To a sample of the salt containing 60.8 cc. of potassium, 155.5 cc. of boron, and 267.7 cc. of hydrogen was added 89.6 cc. of hydrogen chloride. This mixture was allowed to react at room temperature for 48 hours with agitation. The volatile reaction products obtained were 77.8 cc. of hydrogen, 3.8 cc. of diborane, 1.84 cc. of tetraborane, and 2.0 cc. of pentaborane(9). The following equations were proposed:

$$K_2B_5H_9 + 2HCl \rightarrow 2KCl + B_5H_9 + H_2 \tag{18}$$

and

$$K_2B_5H_9 + 3HCl \rightarrow K_2B_5H_6Cl_3 + 3H_2 \tag{19}$$

However, the quantity of pentaborane(9) recovered by the reaction of Equation 18 was small. The reaction of Equation 19 predominated.

The only experimental work other than Stock's in the available literature is Schlesinger's report (*9*) of an experiment with lithium hydride and pentaborane(9). These reacted in ether to give a possible addition product of composition $Li_2B_5H_{11}$.

Several experiments were recently conducted with pentaborane(9), sodium amalgam, and sodium hydride in ethyl ether (*4*). After several days' agitation of solutions of pentaborane(9) in ethyl ether over sodium amalgam, a gray solid was observed covering the surface of the mercury. Upon removal of the volatile materials the solid disappeared. The pentaborane(9) was recovered nearly quantitatively. From visual observation the formation of a possible reaction product was concluded. The product, if formed, released pentaborane(9) in vacuo. In view of the recent studies of Burg (*1*), in which an addition product, $(CH_3)_3N_2B_5H_9$, was isolated which released pentaborane(9) and trimethylamine on heating in vacuo, the formation of an analogous, but less stable, addition product, $Na_2B_5H_9$, is reasonable. However, no further evidence was obtained. In the case of sodium hydride and pentaborane(9) in ethyl ether under similar reaction conditions, no evidence of reaction was observed after weeks, other than slight decomposition of the pentaborane(9).

Studies of the interaction of pentaborane(11) with sodium amalgam were also initiated (*4*) to obtain a more complete survey of the metal-borane reaction systems. As rapid reactions were observed in ether with diborane and tetraborane, it was thought that the reaction of pentaborane(11) with sodium amalgam might supersede decomposition of the unstable boron hydride. The experimental observations, however, were not consistent with this theory. Pentaborane(11) decomposed in the presence of the ether even more rapidly than in the absence of ether. Sodium borohydride, NaB_3H_8, polymeric boron hydrides, and unidentified materials were recovered. Pentaborane(11) was consumed after only a few hours even when a molar excess was charged to the amalgam, and the quantities of volatile boron hydrides obtained were not reproducible. Unreacted sodium was always present, even after consumption of all the pentaborane(11). Thus, it was concluded that the decomposition of pentaborane(11) was more rapid than the reaction with sodium amalgam.

Reaction of Decaborane with Alkali Metals

No report of studies of the reaction of metals with decaborane may be found in the open literature (prior to the writing of this paper). A study of the reaction of sodium amalgam with decaborane carried out in this laboratory (*4*) gave rise to the isolation of some interesting new compounds.

After 5 hours' agitation of solutions of decaborane in ethyl ether over sodium amalgam (B_{10} H_{14} to Na, 1 to 1), the sodium was completely consumed. No hydrogen was evolved at this time, and the recovery of unreacted decaborane demonstrated that 1 mole of decaborane had reacted with 2 gram atoms of sodium to give the compound $Na_2B_{10}H_{14}$. When the reactions were allowed to take place in excess of 5 hours, further consumption of decaborane was observed and hydrogen was evolved. After

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approximately 3 days, 2 moles of decaborane had been consumed for each 2 gram atoms of sodium, and 1 mole of hydrogen was evolved. The data were consistent with the ultimate stoichiometry

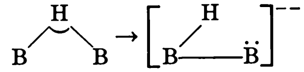
$$2NaHg + 2B_{10}H_{14} \rightarrow 2NaB_{10}H_{13} + H_2 \tag{20}$$

The product of the reaction, $NaB_{10}H_{13}$, reacted quantitatively with equimolar amounts of hydrogen chloride in ether according to the equation

$$NaB_{10}H_{13} + HCl \rightarrow B_{10}H_{14} + NaCl \tag{21}$$

There was little doubt that $NaB_{10}H_{13}$ was a simple sodium salt of decaborane.

A mechanism may be proposed for the reaction of sodium with decaborane which parallels the mechanisms proposed for the tetraborane and diborane reactions. Again, sodium would cleave one bridge bond:



Thus, the initial reaction might be written

$$2NaHg + B_{10}H_{14} \rightarrow 2Na^+ + B_{10}H_{14}^{--} \tag{22}$$

The further addition of electron-deficient decaborane could yield an unstable intermediate, $Na_2(B_{10}H_{14})_2$, which immediately cleaves off 1 molecule of hydrogen and yields 2 moles of the monosodium salt. The existence of the intermediate $Na_2(B_{10}H_{14})_2$ is reasonable because formation of $NaB_{10}H_{13}$ would require the release of 1 hydrogen atom from each of 2 molecules of decaborane, but formation of such an intermediate is not required.

Further evidence for the molecular formula of the sodium salt of decaborane, $NaB_{10}H_{13}$, was obtained in concurrent investigations (*4*). Sodium hydride reacted almost spontaneously when added to ether solutions of decaborane to yield $NaB_{10}H_{13}$:

$$NaH + B_{10}H_{14} \rightarrow NaB_{10}H_{13} + H_2 \tag{23}$$

The reaction was quantitative in all respects. The equivalence of sodium decaborane prepared from sodium hydride and that prepared from sodium amalgam was demonstrated by x-ray and infrared analyses.

The reaction of sodium hydride with decaborane was interpreted as a simple acid-base reaction to give the salt $NaB_{10}H_{13}$. The quantitative reaction of this salt with hydrogen chloride gave further support for this interpretation. Further, it was found that sodium hydroxide and sodium methoxide reacted with decaborane in ether to give $NaB_{10}H_{13}$. The identity of the product was confirmed by x-ray and infrared analyses. Recently, Guter and Schaeffer (*3*) reported that decaborane acts as a strong monoprotic acid in alcohol-water or dioxane-water solutions. The titration of decaborane with sodium hydroxide demonstrated the existence of the decaborane anion, $B_{10}H_{13}^-$, possibly better written $B_{10}H_{14}OH^-$ in these water solutions.

Decaborane also reacts in ether with lithium borohydride (*4*). The stoichiometry of the reaction is best described by the equation

$$LiBH_4 + B_{10}H_{14} \rightarrow LiB_{10}H_{13} + \tfrac{1}{2}B_2H_6 + H_2 \tag{24}$$

The reaction product, $LiB_{10}H_{13}$, prepared in ethyl ether was recovered as a monoethyl etherate, from which the removal of ethyl ether was difficult.

Conclusions

Stock's work with the boron hydrides and metal amalgams may be considered to be the key to a realm of reactions and products that have been investigated only partially. The existence of a greater number of metal-boron-hydrogen compounds is only now being realized. Had the existence of sodium and potassium borohydrides been known to Stock, the reactions which he studied would no doubt have been clarified to a greater extent.

There is no doubt that the diborane salts prepared by Stock contained sodium borohydride. However, it was probable that his original product did not contain the borohydride, as is the case with the more recent NaB_2H_6 ($Na_2B_4H_{12}$). The sublimates obtained from the reactions, however, particularly the sublimate from potassium diborane, consisted principally of the borohydrides. The analyses of potassium diborane were consistent with analyses of potassium borohydride, as the hydrogen obtained on hydrolysis was always too high for the diborane salt. In general, it would appear that Stock isolated the intermediates that were bypassed in the recent rapid reactions in ether.

It is hoped that this review of the work by Stock will contribute in some manner to rectify many current misconceptions as to the scope of his work. For instance, in many cases Stock had been quite clear as to the empirical nature of products obtained and attempted to represent the data by equations involving the empirical compositions. However, it is common today to talk of the materials and their empirical compositions as if they were pure compounds and quantitative equations. A few examples of such misconceptions that are familiar to the authors are as follows:

Many hold that sodium diborane decomposes with heat to a compound NaB_2H_2. Stock gave experiments that show that NaB_2H_2 was no more than an empirical formula representing a mixture and he pointed out this fact in the text of his paper.

It is a common misconception that hydrogen chloride released diborane, tetraborane, and pentaborane(9) quantitatively from $K_2B_2H_6$, $K_2B_4H_{10}$, and $K_2B_5H_9$, respectively. The data reported in the present papers represent the entire data reported by Stock. No experiment was reported from which more than 10 to 20% of the boron was recovered as the boron hydride sought.

Some quote Stock as saying that $K_2B_5H_9$ releases pentaborane(9) quantitatively when heated. There is no mention of this in Stock's reports.

The x-ray patterns reported by Stock remain the most confusing part of his work. However, the present authors are not the only ones confused by the x-ray data. To quote Stock, in translation: "This undertaking (the x-ray determinations) showed, on the one hand, such great agreement of the patterns from the potassium salts, and on the other hand, such agreement of the patterns of the sodium salts that we became doubtful whether we were dealing with the compounds of the salts proposed, or whether we were not dealing with some sort of mixture, which contained not only the diborane salt, but solid boron hydrides (*13*) . . . etc." To prove that the products were not mixtures, Stock ran the hydrogen halide experiments, the data for which have been reviewed herein. The last experiment is concluded by the statement: "This experiment ($HCl + K_2B_5H_9$) also disproved the assumption that the salt obtained was not $K_2B_5H_9$ but a mixture of $K_2B_2H_6$ and something else. The striking agreement of the x-ray diagrams thus requires a different explanation."

In view of the information on hand today, a clarification of the metal boron hydride work is greatly needed. It is remarkable that Stock was able to accomplish the excellent work reported in his papers in consideration of the great handicaps under which the work was done. Stock remains the originator and main source of information for the reactions of boron hydrides with metals. Further work in this field should be encouraged. Although a reasonable correlation can be made between the work of Stock and the more recent work, there is no strong evidence to support such correlation. Studies of the reaction rates and subsequent evidence of reaction mechanisms would be welcomed.

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In BORAX TO BORANES;
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The Unusual Salts Derived from the Boron Hydrides

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The existence of salts derived from the boron hydrides has been of interest since Stock reported the formation of "$Na_2B_2H_6$." With the development of boron hydride chemistry, a number of salts have been derived from these compounds which can be classified according to the elements they contain. Some of the salts have only a transitory existence or they have been assumed to be highly reactive or unstable intermediates. The chemical properties and the probable structures of these salts are discussed.

Early in the development of the chemistry of the boron hydrides Stock and his coworkers reported the preparation of some solid salts which were thought to be formed by the addition of electrons from an active metal to the electron-deficient structure of diborane, thus producing an anion with an ethane-like structure (*36*). Although the early interpretation of the product obtained now appears to have been in error, the evolution of the chemistry of the boron hydrides has shown the existence of a variety of salts with some unusual properties, and a few with surprising structures.

The largest and most important class of boron hydride salts is that of the borohydrides. However, because this subject has been treated extensively elsewhere, this paper is concerned primarily with the less common salts. At the present time, these compounds appear to be primarily of fundamental interest. In many cases the structures are still uncertain, and the chemical properties have been studied only briefly. However, the possibility of preparing new and unusual boron compounds by the use of these salts, as well as finding specific uses for them in chemical processes, should attract increasing attention.

For convenience, the salts have been separated into three classes: nitrogen-containing salts, oxygen-containing salts, and the boron hydride salts. Nearly all of the salts which contain nitrogen may be considered as derivatives of the boron hydrides and ammonia or its substituted derivatives. In general, if the boron atom is found in the anion portion of the salt, the negative charge may be thought of as coming from the amide ion, or possibly from the imide ion. In a like manner, the salts containing oxygen may be thought of as acquiring their anionic charge from the hydroxide or the oxide ions which have been coordinately bonded by the boron hydride. On the other hand, the salts in the third class appear to acquire their negative ionic charge either by the addition of electrons to the boron hydride structure directly, or by the addition of hydride ions to the otherwise neutral boron hydrides.

Salts Containing Nitrogen

The salts included in this class are those which have a direct boron to nitrogen bond, and also have one or more boron to hydrogen bonds.

Salts Derived from Ammonia and Diborane. The reaction of diborane with ammonia, at low temperatures, produces the "diammoniate," $B_2H_6 \cdot 2NH_3$ (*36*, *40*). This substance was believed to be the diammonium salt $(NH_4^+)_2\ B_2H_4^{-2}$ by Stock and Wiberg. The evidence included the observation that the electrolysis of solutions of the diammoniate in liquid ammonia produced hydrogen at the cathode before any nitrogen was liberated at the anode. However, as was pointed out by Schlesinger and Burg (*30*), these results did not provide a basis for an estimation of the amount of ammonium ion furnished by the original salt. On the other hand, the reaction of the diammoniate, $B_2H_6 \cdot 2NH_3$, with sodium in liquid ammonia was found to produce just one equivalent of hydrogen rapidly, and some additional gas was formed very slowly. The total quantity of hydrogen, however, never exceeded 1.4 equivalents per mole of diborane (*29*). On this basis, Schlesinger and Burg proposed that the diammoniate might best be represented as the monoammonium salt, $NH_4^+(BH_3NH_2BH_3^-)$. It was further reported that the stable (to 70°C. in vacuo) salt, NaB_2H_8N, was obtained by the reaction of one mole of sodium with one mole of the diammoniate in liquid ammonia, followed by the careful removal of the solvent.

To explain the slow secondary reaction, which increased above one the equivalents of hydrogen produced per mole of diborane, an equilibrium was postulated in accord with the equation

$$NH_4^+(BH_3NH_2BH_3^-) + 2NH_3 \rightleftharpoons 2NH_4^+(BH_3NH_2^-)$$

In support of this postulate, Schlesinger and Burg prepared the salt borine-dimethyletherate, $NaNH_2BH_3$, by the reaction of borine-dimethyletherate, $BH_3 \cdot O(CH_3)_2$, with ammonia and sodium, and they further showed that solid $NaNH_2BH_3$ absorbed diborane, presumably to form $NaBH_3NH_2BH_3$.

A recent study by Schaeffer and Basile (*28*), on the reaction of lithium amide with diborane, indicated that the reactive intermediate $LiNH_2BH_3$ was formed, but that it reacted further with diborane to produce lithium borohydride and polymeric aminoborine. In this work no evidence for the existence of $LiBH_3NH_2BH_3$ by the reaction of $LiNH_2BH_3$ with diborane could be found.

On the basis of x-ray diffraction studies, Schaeffer, Adams, and Koenig (*27*) have also demonstrated that when the diammoniate of diborane reacted with an alkali metal in liquid ammonia, followed by the removal of the solvent, the corresponding borohydride and polymeric aminoborine were produced. These results imply that the "NaB_2H_8N" obtained by Schlesinger and Burg (*30*) was actually a mixture of these two compounds. As a result of these observations Schaeffer *et al.* argued that the structure of the diammoniate might best be represented as $NH_4^+BH_2NH_2BH_4^-$, which would be interpreted as ammonium borohydride stabilized by association with an aminoborine group. It has also been suggested (*26*) that further production of hydrogen beyond one equivalent by the reaction of the diammoniate with sodium in liquid ammonia might well be due to the reaction of trimeric aminoborine [comparable to trimeric *N*-methylaminoborine, as described by Bissot and Parry (*3*)] with sodium to produce the hypothetical salt $Na^+B_3N_3H_{11}^-$.

On the other hand, it has been argued by Parry and his coworkers (*24*, *31–34*), that the existence of the ammonium ion in the diammoniate of diborane is inconsistent with the chemical properties which have been observed. Ammonium borohydride, NH_4BH_4, is unstable above −20°C., whereas the properly prepared diammoniate is stable up to 70°C. Ammonium salts, such as ammonium chloride and bromide, react with the diammoniate of diborane to produce hydrogen. Consequently, the structure of the diammoniate of diborane has been suggested to be $BH_2(NH_3)_2^+BH_4^-$. In further support of this suggestion, salts of the cation have been prepared and purified, including the salt $BH_2(NH_3)_2^+Cl^-$.

The diammoniate of tetramethyldiborane shows very analogous chemical properties to the diammoniate of diborane, $B_2H_6 \cdot 2NH_3$ (*6*), and hence it should have a comparable structure. However, by treating the tetramethyl derivative, $(CH_3)_4B_2H_2 \cdot$

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$2NH_3$, with successive small amounts of trimethylamine in vacuo; Martincheck (*23*) displaced up to 1.6 moles of ammonia. This observation is difficult to interpret, if the addition compound is assumed to be an ammonium salt, either

$$NH_4^+[(CH_3)_2BHNH_2HB(CH_3)_2]^- \text{ or } NH_4^+(CH_3)_2BNH_2[H_2B(CH_3)_2^-]$$

However, the displacement of more than one mole of ammonia from $(CH_3)_2B(NH_3)_2^+$-$H_2B(CH_3)_2^-$ would not be unexpected. Hence, it now appears that the interpretation proposed by Parry and his coworkers best explains the observed properties of the diammoniates of diborane and of tetramethyldiborane.

Ammoniates of Higher Boranes. The ammonia complexes of B_4H_{10} and $B_{10}H_{14}$ may also be considered as salts, in view of the electrolysis results reported by Stock (*35*). In liquid ammonia these complexes conduct electrolytically in a manner similar to the diammoniate of diborane. Stock suggested that the ammoniate of tetraborane was best represented as the tetrammonium salt, $(NH_4)_4B_4H_6$. However, a recent investigation by Kodama and Parry (*20*) has raised some question on whether the tetrammoniate exists, although the existence of the diammoniate appears to be well substantiated. Hence it appears that more work is needed before the structure of the ammoniate of tetraborane can be established. This appears to be true also of the ammoniate of decaborane, although Stock proposed the hexammonium salt formula $(NH_4)_6B_{10}H_8$ (*35*).

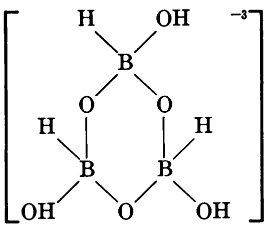
In a recent investigation, Schlesinger and Henle (*29*) have found that when pentaborane, B_5H_9, was dissolved in liquid ammonia, and allowed to stand several days at −80° to −64°C., the addition of lithium metal caused a reaction which generated two equivalents of hydrogen per mole of pentaborane. On the basis of this reaction, and the analysis of the final product obtained after the removal of the solvent, Schlesinger and Henle have tentatively proposed that the salt formed was $Li_2B_5H_9(NH_2)_2$, although it was not definitely established that this product was a single substance. The reaction of aged solutions of B_5H_9 in ethylamine with lithium apparently proceeded in a similar manner to produce a substance believed to be $Li_2B_5H_9(NRH)_2 \cdot 4NRH_2$ (where $R = C_2H_5$). When this product was warmed it decomposed to produce lithium borohydride, hydrogen, and bis-ethylaminoborine, $HB(NRH)_2$. These studies are not yet complete, and further results should be of considerable interest.

In contrast to the behavior of ammonia, the low temperature reaction of diborane with phosphine apparently forms the simple complex, borine phosphine, BH_3PH_3 (*5, 12*). It is likely that the substituted phosphines would react similarly; therefore these complexes cannot be considered to be salts or saltlike.

Salts Containing Oxygen

The salts included in this class are those which appear to have both boron to oxygen and boron to hydrogen bonds. There has been relatively little work reported on them, recently, and the structures which have been proposed for some of them are difficult to accept, in view of the present understanding of the structures of the boron hydrides.

When tetraborane or diborane is treated with concentrated solutions of alkalies, the hypoborates are produced (*35*). The empirical formula for the potassium salt so produced is $KOBH_3$. This substance is diamagnetic (*19*); hence it has been proposed that the formula should be doubled, and that it might best be written as $K_2(BH_2OH \cdot BH_2OH)$. However, the existence of a boron-boron bond has not been demonstrated. In view of the relative difficulty of forming such a bond in aqueous systems and the fact that no such bond does exist, as such, in diborane, this interpretation of the structure of the hypoborate ion appears unlikely. In speculation, it appears likely that the reaction of diborane with hydroxide in water actually produced the borohydride ion and an anion, possibly trimeric, with the structure

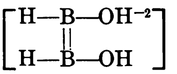


This postulate appears to be more consistent with the known behavior of the boron hydrides than the earlier proposal. However, additional studies are needed before any decision can be made.

The hypoborates are stable in dry air, and when heated strongly they decompose to produce some of the free metal, which accentuates their reducing power. In solution the hypoborates reduce salts of silver, bismuth, mercury, arsenic, and antimony to the free elements. A solution of copper sulfate will react with potassium hypoborate to produce a precipitate of what appears to be a hydride of copper. Perhaps the most characteristic reaction of the hypoborates is that with nickel sulfate to precipitate nickel boride, Ni_2B, even from a cold solution.

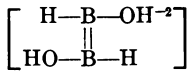
There are a number of other salts which belong in this class. They are the salts of the lower oxyacids of boron—the subborates—derived from $H_4B_2O_4$, and the borohydrates, derived from the two forms of $H_6B_2O_2$. All of these compounds, powerful reducing agents, have been supposed to have boron to boron bonds, although there have been no structural studies reported.

The acid, $H_6B_2O_2$, appears to have two forms. From one of these forms salts such as $K_2H_4B_2O_2$ may be prepared, whereas from the other both $K_2H_4B_2O_2$ and $K_4H_2B_2O_2$ have been obtained. The structures which have been proposed for the anions $H_4B_2O_2^{-2}$ are



cis
α-form

and



trans
β-form

In view of the rarity of boron to boron bonds, and the fact that boron to boron double bonds have not been found elsewhere, these structures are difficult to accept.

The acids from which all of these salts are obtained, including the hypoborates, are found in the hydrolysis products of magnesium boride. It has been suggested that they may all be considered as hydrolysis products of tetraborane. A review by Ray (*25*) treats these derivatives in detail, but little recent work has been reported.

The existence of another salt which may be included in this class has been indicated by the work of Guter and Schaeffer (*13*) in which decaborane was shown to behave as a strong monoprotic acid in water. Since this reaction occurred in a water solution, it would appear that a hydrate of decaborane was first formed and the base removed a proton from the bound water. The salt formed by the neutralization of this acid, therefore would appear to contain the anion $B_{10}H_{14}OH^-$. However, decaborane has been shown to have protonic character (*15*), so it may well be that the anion produced in this system was $B_{10}H_{13}^-$ (*14*), although if this were the case an association equilibrium would be expected, according to the equation

$$B_{10}H_{13}^- + H_2O = B_{10}H_{13}\cdot OH_2^- \quad (\text{or } B_{10}H_{14}OH^-)$$

Thus, both the $B_{10}H_{13}^-$ and the $B_{10}H_{14}OH^-$ ionic species may well be present in this system. However, the ionic species $B_{10}H_{13}\cdot OH_2^-$ and $B_{10}H_{14}OH^-$ would not necessarily be the same.

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The Boron Hydride Salts

Salts Produced by Reaction of Diborane with Alkali Metal Amalgams. The first preparation of boron hydride salts was reported by Stock and his coworkers (*35–39*). These salts, produced by the reaction of diborane with active metal amalgams, and believed to contain the $B_2H_6^{-2}$ anion, have been shown to contain the borohydride ion, BH_4^-, as a principal component (*18*). More recently Hough, Edwards, and McElroy (*17*) have discovered that the reaction of diborane with amalgamated sodium is promoted by ethers, and in these studies both simple borohydrides and salts of the triborohydride anion, $B_3H_8^{-2}$, have been identified.

This topic is considered in great detail by Hough and Edwards (*16*).

Reaction of Diborane and Its Derivatives with Ammonia Solutions of Active Metals. If diborane is carefully added, at low temperatures, to a solution of sodium in liquid ammonia, a reaction takes place in which the sodium is used up, but only an insignificant amount of hydrogen is produced (*6, 26*). However, it has not been possible to separate the products of this reaction from the solvent without decomposition. On the other hand, Burg and Campbell (*6*) found that the reaction of tetramethyldiborane with sodium-ammonia produced the compound $Na_2HB(CH_3)_2$ according to the equation:

$$(CH_3)_4B_2H_2 + 2Na + NH_3 \xrightarrow[-75°C.]{NH_3} Na_2HB(CH_3)_2 + (CH_3)_2BHNH_3 \qquad (3)$$

The salt $Na_2HB(CH_3)_2$ is a white solid which dissolves in liquid ammonia to give a pale yellow solution. In liquid dimethyl ether it seems to be highly aggregated.

The formation of $Na_2HB(CH_3)_2$ appears to take place by the reaction of the solvated electrons with the boron-hydrogen bridge structure, causing a symmetrical cleavage of tetramethyldiborane, a pair of electrons adding to one $HB(CH_3)_2$ group, the other dimethylborine forming the ammonia complex $(CH_3)_2BHNH_3$. The formation of the simple dimethylborine ammine complex rather than the diammoniate of tetramethyldiborane was indicated by the fact that at —75°C. there was no hydrogen produced from this system, even when sodium was present in great excess. This also indicated that the simple ammonia addition complex of dimethylborine was not readily converted to the diammoniate of tetramethyldiborane. More recently, Shore and Parry have prepared borine ammine, BH_3NH_3 (*32*), which was converted to the diammoniate of diborane only with difficulty, if indeed it could be converted at all.

It has been argued that the structure of the $HB(CH_3)_2^{-2}$ ion has a pair of unshared electrons on the boron atom, and, therefore, it could be considered as a Lewis base. On the other hand, the availability of the hydride ion from $Na_2HB(CH_3)_2$ should exceed that of sodium borohydride. In support of the dual character to be expected from this salt, it was found that in dimethyl ether, in which it was highly aggregated, $Na_2HB(CH_3)_2$ proved to be a ready source of hydride ion, easily converting chlorosilane to silane; while in liquid ammonia solution $Na_2HB(CH_3)_2$ was indeed a Lewis base, bonding trimethylboron to form the compound $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$ which was stable up to 100°C. in vacuo.

Other reactions which were interpreted as demonstrating the hydride potential of $Na_2HB(CH_3)_2$ were the 1 to 1 addition of trimethylboron to $Na_2HB(CH_3)_2$ in methyl ether to produce a product which released trimethylboron completely at 0° to 20°C. in vacuo and the addition of diborane to $Na_2HB(CH_3)_2$ in methyl ether yielding products, stable in vacuo at room temperature, which contained $1.4BH_3$ groups per mole of $Na_2HB(CH_3)_2$.

Attempts to prepare other alkali metal salts of the $HB(CH_3)_2^{-2}$ ion have indicated that it may be possible to prepare $Li_2HB(CH_3)_2$ (*7*), but only with unusual difficulty. Only the slightest suggestion was found that the potassium salt could exist. On the other hand, the solvated calcium salt, $CaHB(CH_3)_2 \cdot NH_3$, was prepared by the same process used for the sodium salt, and with less difficulty.

While the hydride activity of $CaHB(CH_3)_2 \cdot NH_3$ in liquid methyl ether was easily demonstrated by the ready conversion of chlorosilane to silane, the base activity of the calcium salt in liquid ammonia was greatly reduced by comparison with $Na_2HB(CH_3)_2$. Hence, trimethylboron was not observed to add to $CaHB(CH_3)_2 \cdot NH_3$ in liquid ammonia. However, it appears that the liquid ammonia reactions of both $Na_2HB(CH_3)_2$ and $CaHB(CH_3)_2 \cdot NH_3$ with tetramethyldiborane are best interpreted in terms of the base activity of the $HB(CH_3)_2^{-2}$ ion. The reaction of $CaHB(CH_3)_2$ with tetramethyldiborane, in the ratio of two moles to one, respectively, gave a clear ammonia solution, from which a solid slowly separated at −75°C. On the basis of the assumed base activity of $CaHB(CH_3)_2$, the analysis of the solid ultimately produced, and from which calcium dimethylborohydride, $Ca[H_2B(CH_3)_2]_2$, could be separated, the equations proposed for the reactions which occur in this system are

$$2CaHB(CH_3)_2 + (CH_3)_4B_2H_2 \rightarrow 2CaHB(CH_3)_2 \cdot HB(CH_3)_2 \quad (4)$$

$$2CaHB(CH_3)_2 \cdot HB(CH_3)_2 \rightarrow Ca[H_2B(CH_3)_2]_2 + Ca[B(CH_3)_2]_2 \quad (5)$$

These same final products were obtained when tetramethyldiborane reacted with calcium in liquid ammonia, provided that the mole ratio of reactants was 3 to 2, respectively. In this reaction, exactly half of the calcium was converted to the ammonia-soluble calcium dimethylborohydride. However, when the ratio of tetramethyldiborane to calcium exceeded 2 to 1, all of the calcium was converted to calcium dimethylborohydride. This has been interpreted in terms of the initial formation of $CaHB(CH_3)_2$ by a reaction comparable to that of Equation 3 followed by that of Equation 4, and finally the reaction of the diammoniate of tetramethyldiborane with the product of Equation 4 as follows:

$$2CaHB(CH_3)_2 \cdot HB(CH_3)_2 + 2NH_4{}^{+}H_2B(CH_3)_2{}^{-} \rightarrow 2Ca[H_2B(CH_3)_2]_2 + 2NH_3HB(CH_3)_2 \quad (6)$$

The behavior of lithium toward tetramethyldiborane appears to be comparable to that of calcium. Lithium dimethylborohydride has been prepared by the reaction of excess tetramethyldiborane with lithium. In contrast, however, when either sodium or potassium reacted with tetramethyldiborane (in excess) none of the dimethylborohydride could be identified, and considerable trimethylboron was produced by the hydrolysis of the product. In fact, it has been difficult to avoid contamination of sodium dimethylborohydride, $Na_2HB(CH_3)_2$, by trimethylboron in the preparation of the boron base, and it has been impossible to avoid such contamination of the potassium salt; therefore the latter has not been prepared in a pure state. Although the reasons for the differences between these systems are not yet clear, it appears that while the dimethylborohydrides of calcium and lithium are both stable, the corresponding sodium and potassium salts disproportionate easily, and may actually be incapable of a stable existence. The reactivity of the boron base anion, $HB(CH_3)_2^{-2}$, is so high toward tetramethyldiborane that it has not been possible to prepare these salts free of secondary product contamination except at very low concentrations and with great excesses of active metals. As a result, the scale of preparation has not exceeded approximately 50 mg. of product.

Very little attention has been given the dimethylborohydrides, but in one study it was found that the reaction of calcium dimethylborohydride with chlorosilane, in methyl ether, produced two moles of silane per mole of calcium salt, and tetramethyldiborane was a product of this reaction. It appears, therefore, that this reaction may be represented by the equation

$$Ca[H_2B(CH_3)_2]_2 + 2SiH_3Cl \rightarrow 2SiH_4 + CaCl_2 + B_2H_2(CH_3)_4$$

The salt $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$, produced by the reaction of sodium dimethylborohydride, $Na_2HB(CH_3)_2$, with trimethylboron in liquid ammonia, appears to be the first true case of a salt of the diborohydride type in which at least one B—H bond exists. It now seems unlikely that any of the less substituted diborohydrides will be prepared in view of the apparent formation and disproportionation of the tetramethyldiborohydrides, together with the unsuccessful attempts to prepare the simple diborohydrides by the reaction of diborane with metal amalgams.

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Not much is known about the salts of the $B(CH_3)_2^-$ anion. In fact, their existence has not been proved, although the evidence for such salts appears to be convincing. Hence, when $Na_2HB(CH_3)_2$ reacts with chlorosilane, the formation of silane implies the loss of a hydride ion from the boron base. Thus it appears that the most acceptable equation for this reaction is

$$Na_2HB(CH_3)_2 + SiH_3Cl \xrightarrow{(CH_3)_2O} NaCl + SiH_4 + NaB(CH_3)_2$$

However, the product does not hydrolyze to release all of the boron as the dimethylboric acid, suggesting that the $B(CH_3)_2^-$ is polymeric. The evidence for the existence of the calcium analog, $Ca[B(CH_3)_2]_2$, is more convincing. When $CaHB(CH_3)_2$ reacted with chlorosilane, silane was produced in agreement with the equation

$$2CaHB(CH_3)_2 + 2SiH_3Cl \rightarrow CaCl_2 + Ca[B(CH_3)_2]_2 + 2SiH_4$$

The residue, presumably $CaCl_2$ and $Ca[B(CH_3)_2]_2$, contained 33.6% calcium (calculated 34.3%). However, the treatment of this solid with aqueous hydrochloric acid produced only a small fraction of the amount of dimethylboric acid potentially available, although 80% of the expected hydrogen was produced. The nonvolatile part of the hydrolysis mixture charred when evaporated to dryness with sulfuric acid, indicating that organic carbon—apparently in the methyl groups—was held back, probably in a polymer containing CH_3—B groups.

In view of these results, further attempts to prepare and study the salts of the postulated anion $B(CH_3)_2^-$ are of interest. It should be noted, however, that salts of the dibutyl analog were reported by Auten and Kraus (*1*). According to them, dibutylboron chloride was reduced by means of a sodium-potassium alloy, in ether solution. The reduction produced, stepwise, dibutylboron and the dibutylboron salt. The salt, $MB(C_4H_9)_2$, in contrast to the salts of the $B(CH_3)_2^-$ anion, was soluble in ether. It reacted readily with methyl iodide to form methyl dibutylboron, and with dibutylboron chloride to produce tributylboron and monobutylboron, which was probably polymeric. The reasons for the remarkable differences between the salts of the dimethylboron anion and the dibutylboron anion are not yet clear, and further studies are required.

The work of Krause and Dittmar (*21*), Bent and Dorfman (*2*), and Chu and Weissman (*8–10*) on the preparation of salts containing triarylboron anions should be mentioned in this discussion, although they are not derived from the boron hydrides. In ether solutions, triphenyl boron reacts with sodium to produce the ether-soluble salts $NaB(C_6H_5)_3$ and $Na_2B(C_6H_5)_3$. The monosodium salt has been shown to be diamagnetic (*8, 9*) thus suggesting the formation of the dimer $Na_2B_2(C_6H_5)_6$, or of ion clusters, as proposed by Chu and Weissman (*9*). The disodium salt, $Na_2B(C_6H_5)_3$, would be structurally similar to the boron base, $Na_2HB(CH_3)_2$, although the chemical properties of the triaryl salt have not been studied extensively. When the phenyl group was replaced by the mesityl group, the corresponding monosodium salt $NaB(Ar)_3$ was dissociated in ether solution, thus forming the corresponding free radical ion, or better, the odd-electron salt, because there would be little true ionization in ether solution. Similar results were observed when tri-β-methylnaphthylboron was used for the preparation of the triarylboron anion.

Salt Derived from Sodium Hydride and Diborane. It has been reported recently by Brown (*4*) that, in the presence of diethylene glycol dimethyl ether (diglym), sodium hydride absorbs diborane to form first sodium borohydride and then, with sufficient diborane, the new salt NaB_2H_7. It appears likely that this salt contains one B—H—B three-center bond holding two borine groups together. However, no further information regarding this salt is now available.

Salts Produced from the Higher Boranes. The studies of Stock and his coworkers on the reactions of alkali-metal amalgams with boron hydrides included tetraborane and pentaborane (*35, 37*). It was reported that $K_2B_4H_{10}$ and $Na_2B_4H_{10}$ were prepared, and that the preparation of dipotassium pentaborine, $K_2B_5H_9$, was probable, although it was not obtained in a pure state. In each of these preparations, the system was heated to approximately 170°C. or higher to distill away the mercury. Further heating to temperatures as high as 450°C. produced some hydrogen, sublimed some salts (apparently the borohydrides), and left behind mixtures that had simple formulas such as $K_2B_4H_8$, $K_2B_4H_4$, and $K_2B_5H_3$. It was reported that when the salt produced from tetraborane, $K_2B_4H_{10}$, was treated with hydrochloric acid tetraborane was regenerated by the reaction

$$K_2B_4H_{10} + 2HCl \rightarrow 2KCl + B_4H_{10} + H_2$$

There is now some question whether these reactions actually produce the salts formulated, because of the work of Kasper, McCarty, and Newkirk (*18*), in which similar reactions involving diborane produced borohydrides.

Some interesting recent work by Schlesinger and Henle (*29*) has been concerned with the behavior of pentaborane with lithium in liquid ammonia and liquid ethylamine. The reaction of lithium with aged ammonia solutions of pentaborane, whereby hydrogen was produced, has been discussed earlier. If, however, pentaborane was added to ammonia solutions of lithium only an insignificant amount of hydrogen was produced. The removal of ammonia, first by evaporation, followed by repeated additions and removals of small quantities of dimethyl ether, yielded a substance which approached the formula $Li_2B_5H_9$. It was soluble in a 1 to 1 mixture of tetrahydrofuran and diethyl ether. However, the work is not yet completed, and there is no definite evidence that this "apparent" lithium salt was homogeneous. If this is indeed a salt with the formula $Li_2B_5H_9$, a study of its structure and chemical properties should be of great interest.

A study of the reactions of decaborane with sodium amalgams and with sodium dissolved in liquid ammonia (*41*) has shown the existence of salts corresponding to the following formulas: $NaB_{10}H_{14}$, $Na_2B_{10}H_{14}$, $NaB_{10}H_{13}$, and $Na_2B_{10}H_{12}$. There was some evidence for a salt with the formula $Na_2B_{10}H_{13}$, but the question has not been resolved whether this is a single substance or a mixture of $Na_2B_{10}H_{12}$ and $Na_2B_{10}H_{14}$.

On the basis of the topological theory of boron hydrides (*11*), Lipscomb has proposed that in addition to $B_{10}H_{12}^{-2}$, $B_{10}H_{14}^{-2}$, $B_{10}H_{13}^{-}$, and $B_3H_8^{-}$, the following boron hydride ions should also have some stability: $B_6H_{11}^{+}$, $B_4H_7^{-}$, $B_6H_6^{-2}$, $B_5H_{10}^{-}$, and $B_3H_6^{+}$ (*22*). Since both positive and negative ions are included, it has been suggested that some purely ionic hydrides might be prepared by metathetical reactions of salts containing these ions.

Conclusions

The salts containing nitrogen and those containing oxygen present a number of still unsolved structure problems. Progress is being made in resolving these problems for the salts containing nitrogen, but further investigations regarding the structures of the hypoborates and the borohydrates are needed.

The reactions of diborane with alkali metal amalgams produce borohydrides and salts such as sodium triborohydride, NaB_3H_8, rather than the "diborane salts" as proposed by Stock. However, comparable systems utilizing the higher boron hydrides should be further investigated.

The boron hydride salts hold considerable promise for the synthesis of new boron compounds. This is especially true of boron bases such as $Na_2HB(CH_3)_2$, and those salts in which the boron-containing ion can serve as either a Lewis acid or a Lewis base. The ability of $Na_2HB(CH_3)_2$ to establish a firm B—B bond by reacting with trimethylboron in liquid ammonia implies the possibility of forming previously unknown bonds by donor-acceptor bonding with appropriate acceptor molecules. The preparation of similar boron bases from the higher boranes should be of interest.

Hence, these salts derived from the boron hydrides are of importance from the standpoint of fundamental chemistry and also as reagents potentially useful in chemical synthesis.

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Structures of $NH_3B_3H_7$ and $(NH_3)_2BH_2Cl$

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A single-crystal x-ray diffraction study of $NH_3B_3H_7$ and $(NH_3)_2BH_2Cl$ was undertaken, to gain greater understanding of the reactions by which they may be prepared. The $NH_3B_3H_7$ molecule contains a triangle of boron atoms having one side slightly shorter than the others. The NH_3 group is attached to the boron atom opposite the shorter boron—boron bond and is pointed at about a 63° angle out of the boron plane. The $(NH)_3BH_3Cl_7$ structure contains chloride ions lying very nearly at the points of a simple tetragonal lattice. The true unit cell, however, is orthorhombic and contains eight formula units of the compound. The $(NH)_2BH_2^+$ ions have an angular N—B—N configuration and are stacked in layers perpendicular to the pseudotetragonal c axis, interleaving the layers of chloride ions.

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Tetraborane has been shown to form a stable diammoniate, $B_4H_{10}\cdot 2NH_3$, when allowed to react with ammonia in ether solution at −78°C. (*1*). The diammoniate undergoes the following reaction when treated with anhydrous hydrochloric acid in ether solution at low temperature (*2*):

$$B_4H_{10}\cdot 2NH_3 + HCl + Et_2O \xrightarrow[-78^\circ C.]{Et_2O} (NH_3)_2BH_2Cl + Et_2OB_3H_7 + H_2$$

The chloride salt separates as a precipitate. The etherate in turn, when treated with ammonia, undergoes the following reaction:

$$NH_3 + Et_2OB_3H_7 \xrightarrow[-78^\circ]{Et_2O} NH_3B_3H_7 + Et_2O$$

The present single crystal x-ray study of $(NH_3)_2BH_2Cl$ and $NH_3B_3H_7$ was undertaken for the purpose of clarifying the structural chemistry of these reactions, and of the compounds themselves.

$NH_3B_3H_7$

The room temperature modification of $NH_3B_3H_7$ is disordered and transforms on cooling to an ordered phase (*4*). Single crystals of the low temperature modification, suitable for x-ray study, were grown from ether solution at −45°C. and mounted for x-ray study on a cold stage. A total of 502 reflections were observed using the precession and Weissenberg methods and keeping the crystal specimen at about −80°C.

The crystals are monoclinic with $a = 10.40 \pm 0.015$ A.; $b = 4.824 \pm 0.006$ A.;

$c = 9.997 \pm 0.012$ A.; $\beta = 115.2° \pm 0.15°$ and belong to the space group $P2_1/n$. The unit cell contains four formula units.

An *h0l* Patterson projection yielded approximate x and z coordinates for the nitrogen and boron atoms and tentative y coordinates were found by trial and error. These parameters were then refined by least squares methods using an IBM 650 computer. The hydrogen atoms in the B_3H_7 group were now located by means of three-dimensional Fourier difference syntheses. Ultimately all atomic coordinates, including those of the B_3H_7 hydrogens, were refined by least squares methods using individual thermal parameters for all atoms. The three hydrogen atoms of the ammonia group were not unambiguously located, presumably due to high thermal motion or disorder about the B—N bond. The final value of the conventional R factor was 0.107 with all observed reflections included.

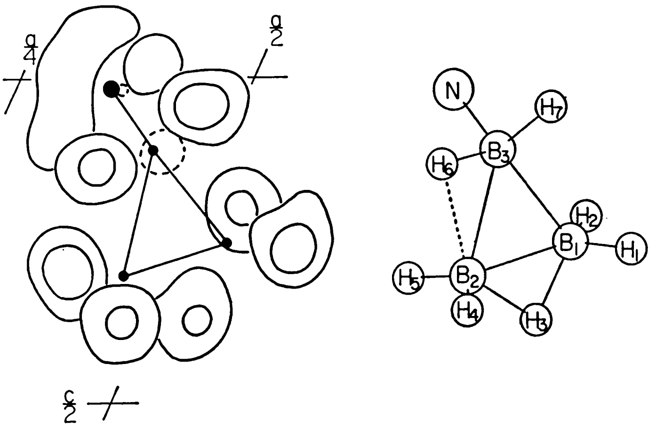

Figure 1. Final difference Fourier synthesis

Left. Electron density distribution in ammonia-triborane molecule represented by sections near centers of hydrogen atoms. Nitrogen and boron atoms are indicated schematically

Right. Schematic drawing of the same molecule

Figure 1 shows the final difference Fourier synthesis and a schematic drawing of the molecule. Intramolecular interatomic distances and angles and their estimated standard deviations are given in Table I.

Table I. Interatomic Distances and Bond Angles in $NH_3B_3H_7$

A. Bond Lengths, A.

$N—B_3$	1.581 ± 0.003
$B_1—B_2$	1.744 ± 0.005
$B_1—B_3$	1.820 ± 0.006
$B_2—B_3$	1.803 ± 0.006
$B_1—H_1$	1.09 ± 0.03
$B_1—H_2$	1.18 ± 0.04
$B_1—H_3$	1.23 ± 0.03
$B_2—H_3$	1.39 ± 0.05
$B_2—H_4$	1.12 ± 0.05
$B_2—H_5$	1.11 ± 0.04
$B_2—H_6$	1.75 ± 0.03
$B_3—H_6$	1.12 ± 0.03
$B_3—H_7$	1.14 ± 0.07

B. Nonbonded Intramolecular Distances, A.

$N \ldots B_1$	2.806 ± 0.007
$N \ldots B_2$	2.861 ± 0.005
$N \ldots H_6$	2.18 ± 0.04
$N \ldots H_7$	2.28 ± 0.07
$B_1 \ldots H_7$	2.28 ± 0.04

C. Bond Angles

NB_3B_1	111.0 ± 0.5°
NB_3B_2	115.3 ± 0.5°
NB_3 (B plane)	117.2 ± 0.5°

The topology of the B_3H_7 group apparently is that of a fragment of tetraborane (*3*), the boron triangle containing two bridge bonds, $B_1H_3B_2$ and $B_2H_6B_3$, and one nonbridged bond $B_1—B_3$. There are, however, some significant differences. The $B_1—B_3$ distance is considerably longer than the value 1.712 A. found for the nonbridged distance in tetraborane; at the same time the bridged $B_1—B_2$ distance is

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shorter than any of the bridged distances in B_4H_{10}, all of which are in the range 1.84 ± 0.01 A. Another difference is the strong asymmetry of the $B_2H_6B_3$ bridge bond. While the B_3—H_6 distance is that of a B—H single bond, the B_2—H_6 distance is about 0.4 A. longer than the B—H distance normally found in BHB bridges.

In view of these departures from the geometry of the tetraborane molecule, an alternative description involving one bridge, $B_1H_3B_2$, and a central three-center $B_1B_2B_3$ bond cannot be entirely ruled out.

$(NH_3)_2BH_2Cl$

Considerable difficulty was experienced in preparing a single crystal usable for x-ray work. Most common solvents either fail to dissolve the compound or decompose it. Crystallization from liquid ammonia yielded a powder. A small number of crystals were finally grown from a solution in diethylene glycol dimethyl ether layered with diethyl ether in which the compound is insoluble. Only one of the crystals was found to be good enough for x-ray work and repeated attempts to grow more crystals failed.

A total of 160 reflections were recorded, but no attempt was made to record all *hkl* reflections since the crystal began to deteriorate.

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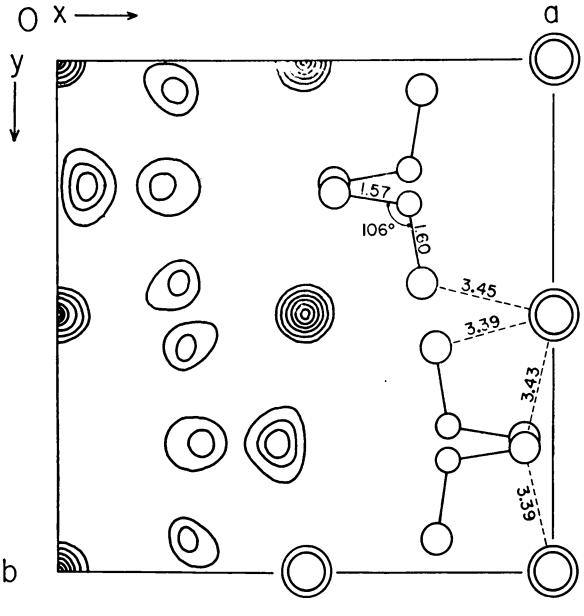

Figure 2. Projection onto (001) of the $(NH_3)_2BH_2Cl$ structure

Arrangement of boron (small circles), nitrogen (large circles), and chlorine atoms (double circles). Electron density contours are at intervals of 4 e A.$^{-2}$ for B and N; 10 e A.$^{-2}$ for Cl. Zero contour omitted

The unit cell of $(NH_3)_2BH_2Cl$ is orthorhombic with $a = 10.20$ A.; $b = 10.20$ A.; $c = 8.71$ A. A few very weak and somewhat diffuse reflections calling for a doubling of the above c axis were ignored in the structure determination. The diffraction patterns taken parallel to the $hk0$ net showed almost fourfold symmetry. The appearance of systematic absences, which were inconsistent with any space group extinction, led to the conclusion that the crystal was a twin consisting of fragments whose orientation differed by 90 degrees about the c direction. This was supported by the observation that the reflections *hkl* and "*khl*" were in a constant ratio whenever, because of space group extinctions, these spots were not overlaps of reflections from the two fragments. In this way the ratio of the sizes of the two fragments could be found and the F^2 values could be determined for all reflections, including those which were overlaps of reflections from the two fragments.

The space group is either *Bba*2 or *Bbcm;* the two are not distinguishable by diffraction methods. The space group *Bbcm* requires the atoms to lie in special positions.

The observation that the diffracted intensities were particularly high for h, k, and l all even suggested that the chlorine atoms were located roughly on a simple tetragonal lattice having the repeat distances of one half those of the orthorhombic lattice. This was confirmed by Fourier projections, which also showed that the B and N atoms lie in layers, parallel to *ab,* halfway between the chlorine layers. This arrangement is consistent with space group *Bbcm;* the boron and nitrogen atoms are at $z = 0$ and $1/2$ and the Cl atoms at $x = y = 0$; $z \approx 0.25$.

The parameters were refined by several cycles of least squares, yielding a final value of $R = 0.137$. The atomic coordinates (x,y,z) are (0, 0, 0.264) for Cl, (0.236, 0.064, 0) and (0.060, 0.237, 0) for N_1 and N_2, and (0.212, 0.219, 0) for B.

The projection onto (001) of the structure is shown in Figure 2. The arrangement of the chlorine atoms, and the N . . . Cl distances, indicate that the compound is ionic—namely, $[(NH_3)_2BH_2^+]Cl^-$. The estimated standard deviations in the interatomic distances are 0.04 A. for B—N and 0.02 A. for N . . . Cl distances. The two boron-nitrogen bonds in the cation are therefore equal within experimental error, and also equal to the B—N distance in ammonia-triborane.

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Organoboron Compounds

Aromatic Compounds

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Aromatic boron derivatives such as boronic and borinic acids can be prepared by a modified Grignard reaction between an arylmagnesium compound and an alkyl borate. The mechanism for this reaction involves a boron-substituted anion which displays tetracoordination. The reaction is influenced by electronic, steric, and solvent effects. The ease of cleaving a boron-carbon bond in boronic and borinic acids is also considered. A theoretical discussion is presented with the experimental data.

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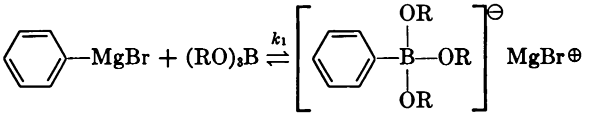
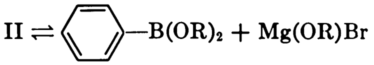
Recently a modified Grignard procedure was reported for the preparation of benzeneboronic acid in greatly improved yields (*33*). The improved procedure was based on a recognition of the importance of a tetracoordinate intermediate, II, and some of the equilibria in which it takes part (Equations 1 to 9).



I II

(1)

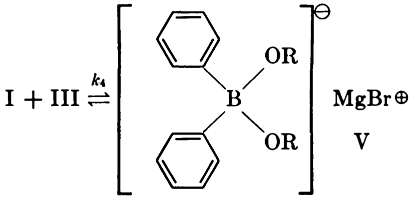


III

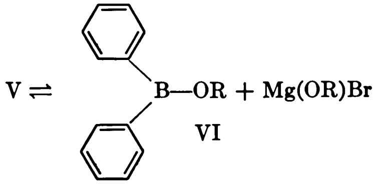
(2)

$$II + (RO)_3B \rightleftharpoons III + [(RO)_4B]^{\ominus}\, MgBr^{\oplus} \quad (3)$$

IV



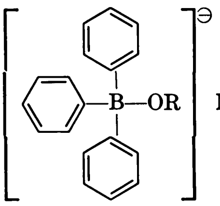
(4)



(5)

$$V + (RO)_3B \rightleftharpoons VI + IV \qquad (6)$$

$$I + VI \overset{k_7}{\rightleftharpoons}$$

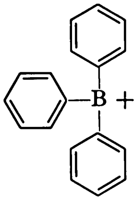


MgBr⊕

VII

(7)

VII ⇌



+ Mg(OR)Br

VIII

(8)

$$VII + (RO)_3B \rightleftharpoons VIII + IV \qquad (9)$$

The first step in the reaction of a Grignard reagent with a borate ester can be formulated as the establishment of an equilibrium between the reactants and a tetracoordinate boronate anion, II (*26, 33*). Torssell (*31*) has formulated the reaction of a Grignard reagent with a dialkyl benzeneboronate as shown in Equation 4.

It was previously postulated (*33*) that by-product borinic acid could arise only through reaction of the Grignard reagent with an ester of a boronic acid (Equation 4). It was then shown that an excess of Grignard reagent led to the formation of a large amount of borinic acid, and although the effect was not as great, an excess of borate ester permitted another mechanism for the formation of borinic acid (Equations 3 and 4). However, simultaneous addition of stoichiometric quantities of the two reactants led to greatly improved yields of boronic acid. For the simultaneous addition of reactants to be most effective, there would have to be a simultaneous reaction of the Grignard reagent and the borate ester (Equation 1). It is shown (*33*) that k_1 is much greater than the rate-determining step for the formation of the dibenzeneborinate anion, V (probably a combination of Equations 1 and 2), which in turn is greater than the rate-determining step for the formation of VIII. This is to be expected, because the formation of alkyl dibenzeneborinate, VI (by either Equation 5 or 6), is probably a slower process than the formation of the dialkyl benzeneboronate, III (by either Equation 2 or 3), because VI is a stronger Lewis acid than III (*13, 24*).

Thus it was expected that any effect, electronic or steric, which would stabilize the boronate anion, II, should provide a higher yield of boronic acid.

Electronic Effects. Branch and Calvin (*2*) and Ingold (*12*) have discussed the acidity of substituted benzeneboronic acids. The pK_a data of Branch and his co-workers (*1, 3, 7, 35*) for substituted benzeneboronic acids are plotted against the pK_a data for substituted benzoic acids (*5*) in Figure 1. Because, in general, the gross effects of various meta and para groups are the same in the boronic acids as in the benzoic acids, the tetracoordinate boronate anion, II, should be more stable if the ring were substituted with electron-withdrawing substituents. This would make the boron atom even more electrophilic and therefore more susceptible to charge transfer with nucleophiles.

Using the incremental reaction of phenylmagnesium bromide and methyl borate at 0°C. as reference, the reactions of *p*-chloro-, *p*-methoxy-, and *o*-methylphenylmagnesium bromide with methyl borate were investigated.

Figure 2, *A*, which shows the observed variation in yield of *p*-chloro-, *p*-methoxy-, *o*-methyl-, and benzeneboronic acid as a function of pK_a of the boronic acids, clearly indicates the importance of increasing the Lewis acidity of the boron atom in stabilizing the anion, II.

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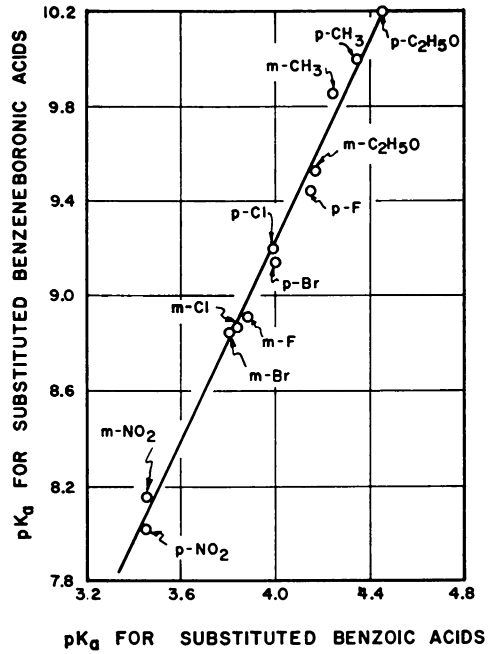
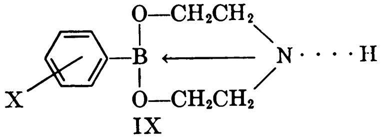


Figure 1. Relationship between pK_a of substituted benzeneboronic acids and substituted benzoic acids

A similar effect is observed in comparing the N—H infrared stretching frequencies for the diethanolamine esters of substituted benzeneboronic acids, IX, studied by Musgrave and Park (*27*). Their data, given in Table I and shown as Figure 2, *B*, show that electronegative substituents on the ring cause N—H bond lengthening.

Table I. N—H Infrared Stretching Frequencies for Diethanolamine Esters of Substituted Benzeneboronic Acids (27)

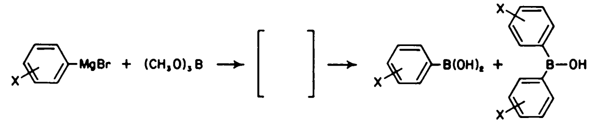
Substituent	Frequency, Cm.$^{-1}$
p-CH_3O	3135
p-CH_3	3110
H	3100
p-Br	3090
m-NO_2	3090



IX

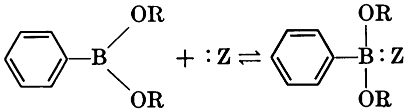
Table II gives the yields of boronic and borinic acids isolated from the reaction of substituted Grignard reagents with methyl borate. There was no borinic acid isolated from the reaction of the phenyl- or *p*-chlorophenylmagnesium bromide reactions, but considerable borinic acid was obtained from the *p*-methoxy- and *o*-methylphenylmagnesium bromide reactions in accordance with a decreased stability of the anion, II.

Table II. Reaction of Substituted Phenyl Grignard Reagents with Methyl Borate



X	Yield, %	
	Boronic acid	Borinic acid
H	75.5	...
p-Cl	82.0	...
p-CH_3O	50.5	14.1
o-CH_3	33.0	18.1

Effect of Solvent. If the formation of borinic acid depends on the formation of the dialkyl benzeneboronate, III (by Equation 2 or 3), the solvent should play an important role in determining the rate of borinic acid formation, k_4. A basic solvent will coordinate with III according to Equation 10.

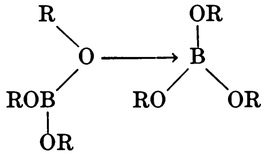


(10)

With very nucleophilic solvents there should then be decreased concentrations of dialkyl benzeneboronate for reaction according to Equation 4. This hypothesis has been tested by the incremental addition of methyl borate and a diethyl ether solution of phenylmagnesium bromide to tetrahydrofuran and pyridine. The yield of benzeneboronic acid isolated from the tetrahydrofuran run at 0°C. was at least 82.6% and may have been as high as 89.3% (see below). This can be compared with a 75.5% yield using diethyl ether alone as solvent. A similar reaction with pyridine gave a 78% yield of boronic acid. If coordination of the solvent with dimethyl benzeneboronate (Equation 10) is an important factor, the yields would be expected to vary in the order, ether < tetrahydrofuran < pyridine. However, a strongly basic solvent such as pyridine presents the problem of complex equilibria between the amine and the Grignard reagent about which very little is known. For example, Drahowzal and König (*9*) observed that pyridine solutions of Grignard reagents react about one tenth as fast as ether solutions with carbonyl compounds. The relatively low yield with pyridine may be partially due to a rate problem, or to the nucleophilic character of the solvent (see below).

Steric Effects. Various steric effects have been noted by many investigators. Brown, Mead, and Shoaf (*6*) attributed the stability of sodium triisopropoxy- and tri-*tert*-butoxyborohydrides toward disproportionation to the steric strain in the corresponding tetraalkoxyborohydride, the product of disproportionation.

Washburn *et al.* (*32*) have qualitatively assigned weak to medium infrared absorptions at 1250 and 1190 cm.$^{-1}$ as caused by base–trialkyl borate interaction. Pure methyl borate has a medium doublet which might arise from the intermolecular interaction shown in X.



X

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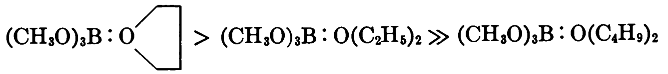
Goubeau and Stirn (*11*) concluded from a thermal study of the methanol–methyl borate system that there is no compound formation—i.e.,

$$CH_3OH + (CH_3O)_3B \rightarrow H^+[(CH_3O)_4B]^-$$

Furthermore, Goubeau and Köhler (*11*) found no evidence for a compound formed from methanol and methyl borate, by studying the Raman spectrum of mixtures of the two.

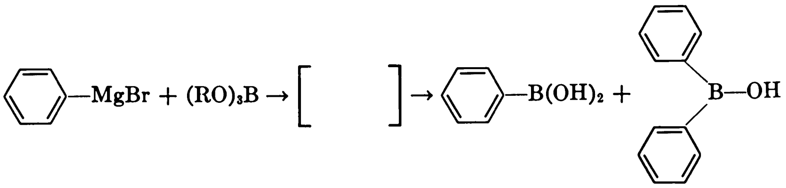
The intensities of the infrared absorptions at 1250 and 1190 cm.$^{-1}$ for various aliphatic borate esters are in the order, $(CH_3O)B > (C_2H_5O)_3B > (CH_2 = CHCH_2O)_3B > (n\text{-}C_4H_9O)_3B$, which is in accordance with the expected steric interaction in X. Furthermore, the variation in intensities of the 1250- and 1190-cm.$^{-1}$ bands of methyl borate dissolved in various ethers was found to be:



which is also in the expected order due to steric strain.

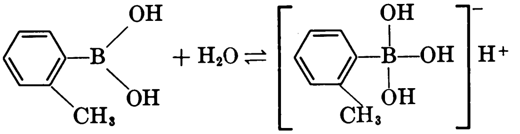
Because the formation of borinic acid results from the reaction of a Grignard reagent with the dialkyl benzeneboronate, III, according to Equation 4 the importance of a steric decrease in the stability of the anion, II, was investigated by varying the R group in II from methyl through *n*-butyl. The yields of boronic and borinic acid are shown in Table III. It is apparent that large R groups provide a sterically controlled dissociation of the anion, II, probably according to Equation 2.

Table III. Reaction of Phenylmagnesium Bromide with Various Borate Esters



R	Yield, % Boronic acid	Borinic acid
CH_3	75.8	. . .
C_2H_5	33.0	21.1
$n\text{-}C_3H_7$	14.1	76.3
$i\text{-}C_3H_7$	16.1	69.7
$n\text{-}C_4H_9$	15.5	77.6

The steric effect of an *o*-methyl group was investigated using *o*-methylphenylmagnesium bromide and methyl borate. The effect on the yield of boronic acid is shown in Figure 2. Although the curve is grossly similar to the curve obtained by a plot of the data of Musgrave and Park (*27*), the value for the *o*-methyl group is probably high, because of a steric effect. McDaniel and Brown (*25*) have explained the abnormally high pK_a for *o*-methylbenzeneboronic acid as resulting from a steric restraint of ionization, according to Equation 12.



(12)

The steric effect of *o*-methyl groups is also observed in the reaction of phenyl-, 1-naphthyl-, and mesitylmagnesium bromide with boron trifluoride-etherate. The phenyl and naphthyl Grignard reagents react readily to give the corresponding

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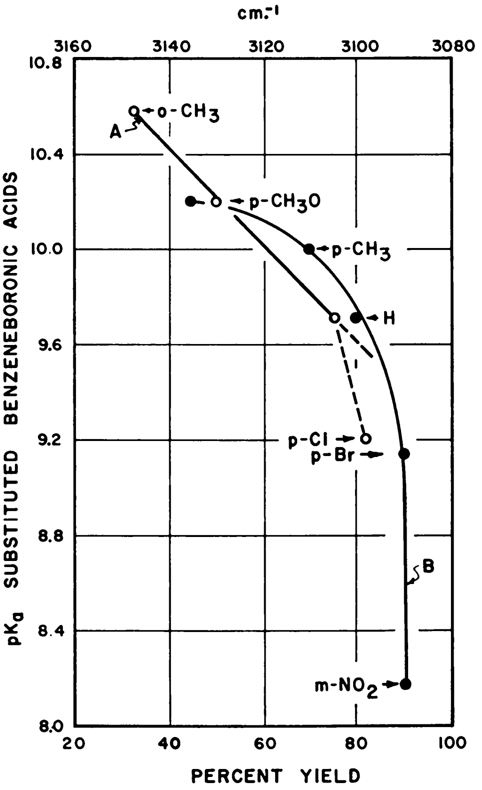
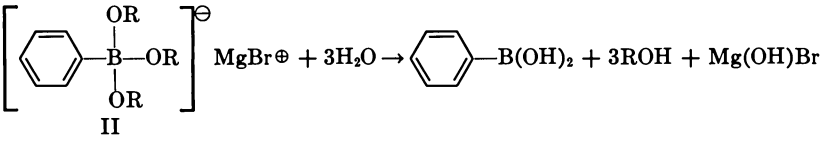


Figure 2. Substituted benzeneboronic acids

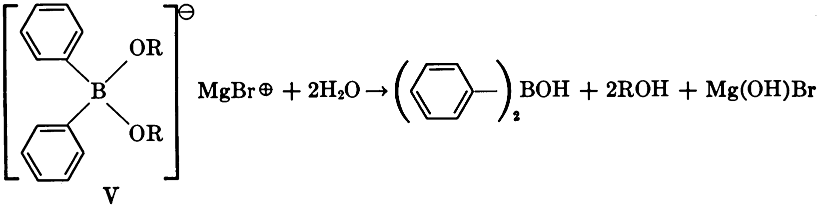
A. Variation in yield of acids with pk_a
B. Variation in infrared N—H absorption in diethanolamine esters of the acids (*13*)

boranes; however, under the same conditions dimesitylborinyl fluoride was formed; trimesitylborane was obtained only under forcing conditions (*4*).

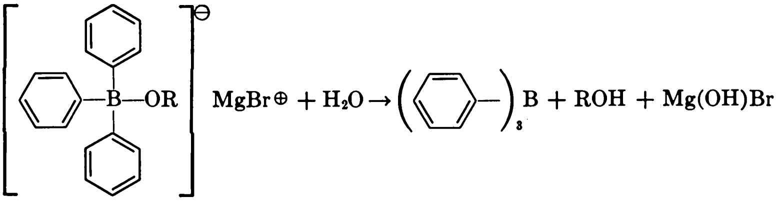
Boron-Carbon Bond Cleavage. It is possible that small amounts of some of the triaryl boranes formed (Equations 7 and 8) would not be isolated because the work-up procedure involves aqueous hydrolysis (Equations 13, 14, and 15), neutralization with acid (Equation 16), and then steam distillation to remove ether, alcohol, and small amounts of biphenyl and phenol.



(13)



(14)



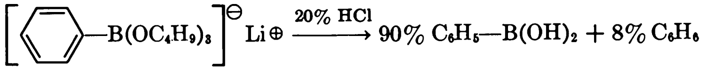
VII

(15)

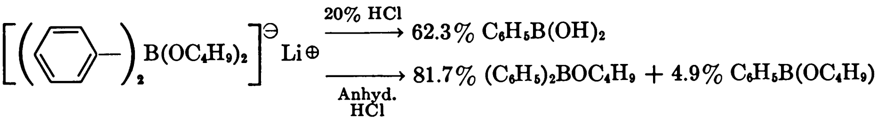
$$Mg(OH)Br + \tfrac{1}{2}H_2SO_4 \rightarrow \tfrac{1}{2}MgBr_2 + \tfrac{1}{2}MgSO_4 + H_2O \qquad (16)$$

The equations for the hydrolysis of the various tetracoordinate anions (II, V, and VII) show that there are water and alcohol present in the hydrolysis mixture and it is known that triphenylborane is cleaved by water (*4*, *34*) and alcohol (*14*, *28*).

Mikhailov and Aronovich (*26*) have shown that 20% hydrochloric acid reacts with lithium phenyltriisobutoxy- and diphenyldiisobutoxyborohydride to give considerable cleavage of the boron-carbon bond (Equations 17 and 18).



(17)



(18)

A similar phenomenon has been observed by Brown and Dodson (*4*) during the attempted hydrolysis of sodium tri-1-naphthylmethoxyborohydride; naphthalene and di-1-naphthaleneborinic acid were the major products. On the other hand, treatment of the borohydride with anhydrous hydrogen chloride gave tri-1-naphthylborane as the major product.

Kuivila and coworkers (*16–24*) have studied the electrophilic displacement of the boronate moiety by bromine, peroxide, and iodine. In general, the rate data indicate that a tetracoordinate boronate anion is involved in the reaction. The over-all rates were found to be pH-dependent. Furthermore, electronegative substituents on the phenyl ring gave slower rates than electropositive substituents.

Thus, the cleavage of substituted dibenzeneborinic acids should be more facile than that of the corresponding boronic acids, and cleavage of the boronic acids should be in the order,

$$p\text{-}CH_3O > o\text{-}CH_3 > H > p\text{-}Cl$$

The experimental evidence supporting this hypothesis is: During the reaction of phenylmagnesium bromide with various alkyl borates a large amount of borinic acid was isolated (Table III), but with the *p*-methoxy- and *o*-methylphenylmagnesium bromide reactions only a relatively small amount of borinic acid was obtained, suggesting a hydrolytic cleavage of the borinic acid (Table II). The fact that no borinic acid was isolated from the *p*-chloro reaction can be attributed mainly to two factors: stabilization of the boronate anion, II, and the incremental reaction method.

During a cursory study of the effect of different solvents on the yield of benzeneboronic acid from the phenylmagnesium bromide–methyl borate reaction, it was observed that the yield of boronic acid was far less than expected when pyridine was employed. Because the hydrolysis of a tetracoordinate boronate anion leads to some cleavage, and electrophilic displacement of boronate is pH-dependent, the presence of pyridine as solvent, although tending to prevent the formation of borinic acid, may also have promoted the hydrolytic cleavage of the boron-carbon bond. Considerable losses of benzeneboronic acid occurred when aqueous pyridine solutions containing known amounts of the boronic acid were acidified.

In an attempt to determine at what stage bond rupture occurs, a sample of very

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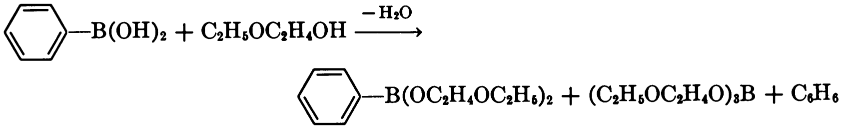
pure benzeneboronic acid was made strongly basic and extracted with ether. Vapor chromatographic analysis of the ether extract indicated that no benzene was present. When the basic solution was made acidic and again analyzed, no benzene was found. Thus, no cleavage products were found with highly purified benzeneboronic acid. On the other hand, vapor chromatographic analysis of routine reaction mixtures indicated that some cleavage always accompanied treatment with base followed by acidification. The possibility that some chelating agent present in the reaction mixtures acts as a catalyst (*22*) for the cleavage reaction is being investigated.

Rondestvedt *et al.* (*28*) reported that methanol reacted with triphenylborane to give boric acid; this implies cleavage of benzeneboronic acid. In the writers' laboratory experiments were run to check for methanolysis and acetonolysis of pure benzeneboronic acid by heating methanol and acetone solutions under reflux in a nitrogen atmosphere for 6 days. Only traces of cleavage products were found. However, during the attempted preparation of di-(β-ethoxyethyl) benzeneboronate by azeotropic distillation, a mixture was obtained after distillation which consisted of 83.3% tri-(β-ethoxyethyl) borate and 16.7% di-(β-ethoxyethyl) benzeneboronate (Equation 19).



(19)

During the preparation of di-*n*-butyl benzeneboronate by azeotropic distillation, it was found that complete cleavage of the boron-carbon bond occurred on extended heating of the reaction mixture (156 hours). However, when the heating time was short—2 to 3 hours—and very pure benzeneboronic acid was used as starting material, an 85% yield of the boronate ester was obtained.

The preparation of diphenyl benzeneboronate by azeotropic distillation led to mixtures containing up to 75 to 80% of the boronate ester and 20 to 25% of the triphenyl borate resulting from cleavage of the boron-carbon bond.

To determine the effect of basic solvents on the alcoholysis of the boron-carbon bond, experiments were run in which boronic acid and butyl alcohol were heated under reflux for 2 days, and in another comparable experiment tetrahydropyran was added to the reaction mixture. Approximately 50% more cleavage occurred in the tetrahydropyran run, confirming that nucleophilic solvents promote boron-carbon bond cleavage.

The cleavage of the boron-carbon bond during esterification reactions seems to be promoted by the presence of nucleophilic solvents, and may further be enhanced by the presence of catalytic quantities of chelating agents present as impurities. Studies of boron-carbon cleavage reactions being carried out at present will be reported in a future paper.

Experimental

Analysis of Boron Compounds. The analysis of boron compounds (*30*) by Parr bomb fusion with sodium peroxide followed by titration with 0.1*N* sodium hydroxide in the presence of mannitol gives results accurate to within 0.25% of the amount of boron present. The mercuric chloride procedure of Wittig *et al.* (*35*) was used in the analysis of small amounts of boron-carbon compound in the presence of boric acid. It was found that amines interfered with the titration. All yields are based on analysis.

Reagents. Phenylmagnesium bromide (Arapahoe Special Products, Inc.) was an approximately 3*M* solution in diethyl ether. *p*-Chloro-, *p*-methoxy-, and *o*-methylphenylmagnesium bromide were prepared in diethyl ether by the usual method. The Grignard reagents after filtration and analysis (*10*) were transferred under dry nitrogen pressure.

Methyl, ethyl, *n*-propyl, isopropyl, and *n*-butyl borates were commercial materials

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(American Potash & Chemical Corp.). The esters were distilled directly into the addition buret.

Reaction of Methyl Borate with Phenylmagnesium Bromide. The incremental procedure (*33*) is summarized for the reaction of methyl borate with phenylmagnesium bromide.

The equipment used consisted of a Morton flask, two addition burets, thermometer, and a high-speed stirrer.

The methyl borate (22.4 ml., 0.2 mole) was distilled directly into one buret. Anhydrous ether (100 ml.) was placed in the flask and an ethereal solution of phenylmagnesium bromide (62.5 ml., 0.2 mole, 3.2*N*) was transferred under pressure to the second buret. The temperature was adjusted to and maintained at 0°C.

The reactants were added in stoichiometric increments (1 ml. of ester per 3 ml. of Grignard) during 10 minutes. The reaction mixture was hydrolyzed with distilled water (13.3 ml.), neutralized with sulfuric acid (8.4 ml. in 170 ml. water), and extracted three times with ether (100-ml. portions). The combined ether extracts were reduced to half their volume by distillation; then water was added and the distillation was continued until a head temperature of 100°C. was reached. When the aqueous distilland was cooled, the benzeneboronic acid crystallized and was removed by filtration. The yield was 75%, including the product in the filtrate.

Reaction of Ethyl, *n*-Propyl, Isopropyl, and *n*-Butyl Borates with Phenylmagnesium Bromide. Ethyl, *n*-propyl, isopropyl, and *n*-butyl borates were allowed to react with phenylmagnesium bromide, using the procedure described above for methyl borate. These reactions were less exothermic than the methyl borate reaction. Only the ethyl borate reaction gave a precipitate of benzeneboronic acid, after the steam-distillation step. With the other alkyl borates, a two-phase system consisting of a dark brown oil and an aqueous layer was obtained. The mixture was extracted with petroleum ether to remove borinic acid, and the resulting aqueous layer was extracted with ether to remove boronic acid. The solubility of boronic acid in petroleum ether was assumed negligible. Evaporation of the petroleum ether extracts at temperatures from 100° to 120°C. at 3 to 4 mm. of mercury gave crude dibenzeneborinic anhydride. This was calculated as borinic acid based on the boron analysis.

Calculated for $C_{24}H_{20}OB_2$ (anhydride): 6.25% B
Found: 6.09 to 6.82% B

Evaporation of the ether extracts provided relatively pure benzeneboronic acid (Table III).

Reaction of *p*-Chloro-, *p*-Methoxy-, and *o*-Methylphenylmagnesium Bromide with Methyl Borate. The results are summarized in Table II. The incremental procedure and equipment described above were used to study the reaction of substituted phenyl Grignard reagents with methyl borate. *p*-Chlorophenylmagnesium bromide reacted very smoothly at 0°C. to give an 82% yield of the corresponding boronic acid. No borinic acid was obtained. *o*-Methylphenylmagnesium bromide gave a 33.0% yield of boronic acid and an 18.1% yield of borinic acid.

A materials balance was made for the reaction of *p*-methoxyphenylmagnesium bromide (149.6 ml., 0.25 mole, 1.67*N*) with methyl borate (28.4 ml., 0.25 mole) (Table IV). After reaction, hydrolysis, and neutralization, the reaction mixture was

Table IV. Reaction of *p*-Methoxyphenylmagnesium Bromide with Methyl Borate

		Analysis[a]						
			Millimoles				Equivalent to	
Fraction	Weight, Grams	B, %	Boric acid	Boronic acid	Borinic acid	Anisole	Methyl borate	Grignard
A	195.0	0.141	64.7	18.1	...	...	82.8	18.1
B	372.0	1.88 (anisole)	...	...	...	64.7[b]	...	64.7
C	13.1	7.13[c]	...	86.4	...	...	86.4	86.4
D	305.0	0.15	20.5	21.8	...	...	42.3	21.8
E	10.9	3.51[d]	...	...	0.0354	...	35.4	70.8
						Total moles	0.2469	0.2618

[a] Boric acid and boronic acid in aqueous mixtures determined by method of Wittig *et al.* (*30*).
[b] Vapor phase chromatographic analysis.
[c] Theoretical for *p*-methoxybenzeneboronic acid, 7.12% B.
[d] Theoretical for borinic acid, 4.47% B.

extracted with ether leaving an aqueous residue, A. The combined ether extracts were steam distilled giving a distillate, B. Crystalline solids and a waxy material were obtained from the aqueous distilland upon cooling. The crystalline solids which were decanted as a slurry and the waxy solids were washed with water, which was added to the slurry. The crystalline solids were removed by filtration and vacuum-dried for 24 hours at 1.0 mm. giving C. The aqueous filtrate is listed in Table IV as D.

The waxy material, E, was vacuum-dried for 8 hours at 64°C. at 0.5 mm. of mercury. The *p*-methoxybenzeneboronic acid found in A, C, and D represents a yield of 50.5% and the borinic acid found in E represents a yield of 14.1%.

Reaction of β-Ethoxyethyl Alcohol with Benzeneboronic Anhydride. The water of reaction was removed as the diisobutylene-water azeotrope, during 2 hours, from a mixture of benzeneboronic anhydride (155.9 grams, 0.58 mole) and β-ethoxyethanol (335.9 grams, 3.73 moles). The reaction mixture was distilled in a spinning band column yielding 149.4 grams of distillate, boiling point 93°C. at 0.3 mm. of mercury.

Calculated for (boronate) $C_{14}H_{23}O_4B$: 4.08% B.
Calculated for (borate) $C_{12}H_{27}O_6B$: 3.89% B.
Found: 3.97% B.

Analysis indicates yields of 83.3% of tri-(β-ethoxyethyl) borate and of 16.7% of di-(β-ethoxyethyl) benzeneboronate. Benzene (0.434 mole) was found, by vapor chromatographic analysis, in the forerun.

In a second experiment, benzeneboronic acid (276.5 grams, 2.27 moles), β-ethoxyethanol (409.2 grams, 4.54 moles), and diisobutylene (250 ml.) were heated, under azeotropic distillation conditions, for 2 hours. After water was removed (theoretical 81.7 ml., found 84 ml.), the reaction mixture was fractionated yielding 335.3 grams, 3.89% boron, which corresponds to tri-(β-ethoxyethyl) borate.

In a third experiment, benzeneboronic acid (138.7 grams, 1.14 moles), and β-ethoxyethanol (204.8 grams, 2.27 moles) afforded 66.7% of tri-(β-ethoxyethyl) borate and 33.3% of di-(β-ethoxyethyl) benzeneboronate.

Di-*n*-butyl Benzeneboronate. Benzeneboronic acid (7.0 grams, 0.057 mole) and butyl alcohol (18.5 grams, 0.25 mole) were heated under reflux for 32 hours. Vapor chromatographic analysis of the reaction mixture indicated approximately 0.1% of benzene. This is equivalent to a 0.56% cleavage.

In a second experiment, benzeneboronic acid (7.0 grams, 0.057 mole), butyl alcohol (18.5 grams, 0.25 mole), and tetrahydropyran were heated under reflux for 32 hours. Benzene equivalent to a 0.75% cleavage was found.

In a third experiment, benzeneboronic acid (244.0 grams, 2.0 moles), and butyl alcohol (534.3 grams, 7.34 moles) were heated under azeotropic distillation conditions for 2 hours. Water was removed as the butyl alcohol–water azeotrope (found 67 ml., theoretical 72 ml.) and then the excess butyl alcohol was removed by distillation at atmospheric pressure (recovered 247.3 grams, theoretical 247.8 grams). The product was fractionally distilled at a boiling point of 104–6°C. at 1.0 to 1.5 mm. of mercury. The yield was 396.5 grams, 84.6%.

Calculated for $C_{14}H_{23}O_2B$: 4.62% B.
Found: 4.62% B.

In a fourth experiment, benzeneboronic acid (900 grams, 7.38 moles), butyl alcohol (1094 grams, 14.76 moles), and diisobutylene (600 ml.) were heated under azeotropic distillation conditions. The time needed to remove water (250 ml., theoretical 266 ml.) amounted to 156 hours. The reaction mixture was stripped at atmospheric pressure and the product distilled at a boiling point of 78°C. at 0.5 mm. of mercury. The yield was 1621 grams, 95.5%.

Calculated for $C_{14}H_{23}O_2B$ (boronate): 4.62% B.
Calculated for $C_{12}H_{27}0_3B$ (borate): 4.70% B.
Found: 4.70% B.

The infrared spectrum was superimposable on a spectrum of authentic tri-*n*-butyl borate.

Diphenyl Benzeneboronate. Benzeneboronic acid (10.0 grams, 0.082 mole), and phenol (22.0 grams, 0.1804 mole) were heated together with diisobutylene, for 2.5 hours, to remove the water of reaction as the diisobutylene-water azeotrope. After

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the water was removed (1.6 ml., theoretical 2.95 ml.), the diisobutylene layer (12.0 grams) was found to contain 1.28% of benzene. The reaction mixture (292 grams) contained a trace of benzene (0.1%). The total benzene found corresponds to a 6.95% cleavage.

In a second experiment, benzeneboronic acid (221.9 grams, 1.82 moles), phenol (342.5 grams, 3.64 moles), and xylene (730 ml.) were heated under azeotropic distillation conditions for 7 hours. After removal of the water (51 grams, theoretical 65.5 grams), the reaction mixture was distilled yielding a center cut of 121.0 grams; boiling point 155–9°C. at 2 mm. of mercury; melting point 113–5°C.; reported (*8*) boiling point 140° to 150°C. at 0.05 mm. of mercury; melting point 98° to 100°C.

Calculated for $C_{18}H_{15}O_2B$: 78.8% C; 5.5% H; 3.95% B.
Found: 75.26% C; 5.80% H; 3.96% B.

The product was further analyzed by a modification of the method of Siggia (*29*), and found to contain 75.9% (theoretical 69.17%) of phenol. This corresponds to 23.9% of triphenyl borate as impurity. The analytical method was checked by analyzing authentic triphenyl borate: % phenol calculated = 97.31; % phenol found = 95.0.

Methanolysis and Acetonolysis Experiments. Very pure benzeneboronic acid (20.0 grams, 0.164 mole, B = 8.87%, theoretical 8.87%) was heated in an inert atmosphere under reflux for 6 days with 125 ml. of methanol. A small quantity of methanol was distilled from the mixture (boiling point 65–6°C.) to remove any boric acid as the methanol–methyl borate azeotrope (boiling point 54.5°C.). The distillate contained 0.00122 gram of boron, which amounted to a 0.069% cleavage.

A similar experiment with acetone indicated a 0.13% cleavage.

Recovery of Benzeneboronic Acid from Basic Solution. Very pure benzeneboronic acid (10.0 grams, 82.0 mmoles) was slurried in 200 ml. of water and slowly treated with a slight excess of solid sodium hydroxide. After 8 hours the basic solution was extracted with two 50-ml. portions of ether. No benzene was found by vapor chromatographic analysis. Analysis indicated less than 1.0 mmole of benzeneboronic acid.

The basic solution was slowly acidified by the dropwise addition of concentrated sulfuric acid. The acid solution was extracted with three 50-ml. portions of ether.

Analysis of the ether extracts indicated no benzene and 76.3 mmoles of benzeneboronic acid.

Analysis of the acidic solution indicated 5.71 mmoles of benzeneboronic acid. Total recovery of benzeneboronic acid was 82.1 mmoles.

Extraction of Acid Solutions, Benzeneboronic Acid, Ether, and Methanol. A simulated reaction mixture containing benzeneboronic acid (2.459 grams, 20.3 mmoles), ether (16.7 ml.), an aqueous solution (12.6 ml.) containing sulfuric acid (0.56 ml.), and methanol (1.92 ml.) was placed in a separatory funnel. After shaking, the phases were separated and analyzed. The aqueous phase contained 0.906 mmole of benzeneboronic acid and 1.50 milliatoms of boron. The ether phase contained 19.12 mmoles of benzeneboronic acid and 19.14 milliatoms of total boron. Thus 94% of the benzeneboronic acid was extracted by the ether and less than 1% of the boronic acid had been cleaved.

Benzeneboronic Acid, Pyridine, Ether, and Methanol. A solution of the following components was made up in a separatory funnel: benzeneboronic acid (2.459 grams, 20.3 mmoles), ether (6.7 ml.), pyridine (3.22 ml.), methanol (1.92 ml.), and enough (35 ml.) of a solution of sulfuric acid (5.6 ml. of concentrated sulfuric acid in 126 ml. of water) to make the mixture strongly acidic. After shaking, the phases were separated and analyzed. The aqueous phase contained 5.74 mmoles of benzeneboronic acid. The presence of pyridine in the aqueous phase interfered with the determination of the total boron content by the Wittig method (*35*). The ethereal phase contained 10.18 mmoles of boronic acid and 10.15 milliatoms of boron. These results indicate a 20% loss of benzeneboronic acid upon solution in pyridine, followed by acidification.

Loss Involved in Steam Distillation of a Solution of Benzeneboronic Acid, Ether, Pyridine, and Methanol. A mixture of benzeneboronic acid (2.45 grams, 20.3 mmoles), ether (6.7 ml.), pyridine (3.22 ml.), and water (50 ml.) was boiled until the odor of pyridine was no longer detectable. The resulting solution contained 18.60 mmoles of benzeneboronic acid indicating an 8% loss.

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Reaction of Phenylmagnesium Bromide with Methyl Borate, in Presence of Pyridine. The incremental procedure and quantities of reactants described above were used except that the ether heel was replaced by 100 ml. of pyridine. After reaction and hydrolysis, the reaction mixture was extracted with ten 75-ml. portions of ether. The combined ether extracts were distilled until most of the ether had been removed and then 250 ml. of water was added dropwise as distillation continued. Cooling the aqueous distilland gave a tan precipitate which was removed by filtration and dried (16.8 grams, 8.94% B). The filtrate (98 grams) contained 14.7 mmoles of benzeneboronic acid and 21.1 mmoles of boron.

The aqueous suspension, remaining from the ether extractions, was acidified by the addition of an acid solution (5.6 ml. of sulfuric acid in 113 ml. of water), and extracted with three 100-ml. portions of ether. The combined ether extracts were steam-distilled with 100 ml. of water. The cooled distilland provided a precipitate (0.2 gram after drying, 8.99% B) and a filtrate which contained 1.76 mmoles of benzeneboronic acid. From the above data, the yield was calculated as 78%.

In Presence of Tetrahydrofuran. The incremental procedure described was used, except that the ether heel was replaced by tetrahydrofuran (78.2 ml.). Phenylmagnesium bromide (62.5 ml., 0.2 mole) and methyl borate (22.4 ml., 0.2 mole) were added incrementally during 10 minutes, and the resulting reaction mixture was hydrolyzed, neutralized, and extracted with ether. The ether extracts were combined and made up to 500 ml. with ether. One fifth of the ether solution was analyzed and found to contain 35.7 mmoles of benzeneboronic acid and 36.1 milliatoms of boron. This indicated a yield of 89.3%. The remainder of the ether solution was distilled. The resulting solids were removed by filtration and vacuum-dried at 25°C. at 2 mm. of mercury for 15 hours, yielding 13.9 grams, 9.86% B. The filtrate (62 grams) contained 7.87 mmoles of benzeneboronic acid and 13.5 milliatoms of boron. Thus, the total yield of boronic acid (precipitate plus filtrate) was 82.6%. The difference between this figure and that found above (89.3%) represents mechanical and chemical losses incurred during steam distillation and filtration.

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Boroxines

Aryl and Alkoxy Derivatives

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The reactions of triphenylboroxine, tri-o-chlorophenylboroxine, tri-o-tolylboroxine, and trimethoxyboroxine with selected chlorides were examined. Triphenylboroxine is relatively stable somewhat above 200°C. toward hydrogen chloride and copper(I) chloride but forms benzene in considerable quantity when treated with anhydrous aluminum chloride, phosphorus pentachloride, and copper(II) chloride under reduced pressure or in sealed tubes; with copper(II) chloride, chlorobenzene is also formed along with small amounts of boron trichloride and hydrogen chloride. Tri-o-chlorophenylboroxine forms a small quantity of chlorobenzene with aluminum chloride and copper(II) chloride. These two chlorides produce the common product toluene with tri-o-tolylboroxine; copper(II) chloride also produces a considerable amount of hydrogen chloride along with a trace of boron trichloride. The reactions of these boroxine derivatives are in contrast to the results of previous work with alkylboroxines, in which cases compounds of the formula $RBCl_2$ were obtained. The major product of the reaction of trimethoxyboroxine with aluminum chloride and phosphorus pentachloride under reduced pressure is trimethoxyborane; in sealed tubes the major product is methyl chloride with what appears to be some methoxydichloroborane.

The reactions (*6*) of alkylboroxines, primarily tri-*n*-butylboroxine, prompted the investigation of other boroxine derivatives. The reactions of triphenylboroxine, $(C_6H_5BO)_3$; tri-*o*-chlorophenylboroxine, $(o\text{-}ClC_6H_4BO)_3$; tri-*o*-tolylboroxine, $(o\text{-}CH_3C_6H_4BO)_3$; and trimethoxyboroxine, $(CH_3OBO)_3$, with selected Lewis and non-Lewis acid type of chlorides have been examined.

Experimental

Apparatus and Procedures. The borosilicate glass vacuum system, methods of analysis, and molecular weight determinations were similar to those already described (*6*). Infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer.

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Preparation of Reagents. Boric oxide. Anhydrous crystalline oxide was obtained by the careful heating of boric acid under a vacuum at 300°C. for several hours.

Copper(I) chloride was prepared by the method of Keller and Wycoff (*5*).

Phenyldihydroxyborane, $C_6H_5B(OH)_2$, was prepared by the method of Bean and Johnson (*2*).

Triphenylboroxine, $(C_6H_5BO)_3$, was obtained by the dehydration of phenyldihydroxyborane. The latter compound was first dried at 75° to 80°C. at atmospheric pressure for 3 days, then placed under vacuum, and the drying was continued by heating to between 100° and 117°C. for a day and a half. Just before being used in reactions, the boroxine was heated from 200° to 210°C. under vacuum to ensure removal of water. Triphenylboroxine prepared in this way melts gradually between 191° and 193°C. The infrared spectrum of triphenylboroxine shows medium absorption peaks at 3.21, 6.63, 8.45, 9.18, 9.47, 12.50, and 12.80 microns and strong peaks at 6.17, 6.87, 7.25–7.50, 7.65, and 14.15–14.60 microns.

Analysis. Calculated for $B_3C_{18}H_{15}O_3$: boron, 10.41. Found: boron, 10.40.

Tri-*o*-tolylboroxine, $(o\text{-}CH_3C_6H_4BO)_3$, was prepared by dehydrating *o*-tolyldihydroxyborane (*2*), $o\text{-}CH_3C_6H_4B(OH)_2$, at approximately 100°C. under vacuum for 18 hours. During this process the platelets of the latter compound became powdery; the powder (tri-*o*-tolylboroxine) melted at 161°C. The infrared spectrum of this compound contains medium absorption peaks at 3.22, 3.35, 6.68, 9.35, 9.55, 12.21, and 13.85 microns and strong peaks at 6.18, 6.87, 7.25–7.40, 7.70, 13.70, and 14.57 microns.

Analysis. Calculated for $B_3C_{21}H_{21}O_3$: boron, 9.17. Found: boron, 9.38.

Tri-*o*-chlorophenylboroxine, $(o\text{-}ClC_6H_4BO)_3$, was obtained by heating *o*-chlorophenyldihydroxyborane (*2*), $o\text{-}ClC_6H_4B(OH)_2$, to 80°C. under vacuum for 12 hours and finally by heating for 4 hours under vacuum at 110° to 112°C. The product melted at 170–71°C. and its infrared spectrum showed medium absorption peaks at 3.26, 6.43, 6.80, 7.95, 8.07, 8.65, 8.90, and 9.15 microns and strong peaks at 6.30, 7.02, 7.30–7.50, 7.75, 9.65–9.75, 13.40–13.60, 14.72, and 14.87 microns.

Analysis. Calculated for $B_3C_{18}Cl_3H_{12}O_3$: boron, 7.81. Found: boron, 7.86.

Trimethoxyboroxine, $(CH_3OBO)_3$, was prepared by the interaction of equimolar quantities of anhydrous boron oxide and trimethoxyborane (*7*) according to the method of Goubeau and Keller (*4*). A molecular weight determination by freezing point depression in nitrobenzene gave an average value of 174; calculated, 173.5.

Reactions and Properties

Reactions of Triphenylboroxine with Halides. Triphenylboroxine (5.5 grams, 17.7 mmoles) and 6.5 grams (49 mmoles) of aluminum chloride were heated to 210°C. and opened to the fractionation apparatus where a volatile product was collected in a trap cooled in liquid nitrogen. The infrared spectrum of this product was identical with that of benzene. The puzzling formation of benzene was attributed to wet aluminum chloride.

The same reaction was performed with freshly sublimed aluminum chloride and triphenylboroxine which had been dried for nearly a week at 110°C. and heated to 200°C. under reduced pressure just before the reaction was carried out. Again the chief product, which distilled at 74°C. and 630 mm., was benzene with a trace of a substance which may have been phenyldichloroborane. An attempt to make a derivative of this trace compound, which distilled at 166°C. at 630 mm., resulted in an explosion. Repeated attempts to produce more of this compound always resulted in only traces along with large amounts of benzene and very small amounts of hydrogen chloride. Increasing the temperature of the reaction to 230°C. made no difference.

Very carefully dried triphenylboroxine and aluminum chloride (3.6 and 10.4 grams, respectively) were sealed in a tube and heated to 250°C. Between 0.9 and 1.0 ml. of benzene was obtained along with 30.3 mg. of a substance having 2 mm. of vapor pressure at 0°C. and 3.5 mm. at 27°C., and a percentage composition of 10.7 boron and 41.4 chlorine. Repeated efforts to produce more than traces of this compound were futile.

When anhydrous phosphorus pentachloride (10 grams, 48 mmoles) was added to triphenylboroxine (5 grams, 16 mmoles) which had been dried at 230°C., vigorous

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bubbling occurred. After the system was evacuated, a volatile material collected in a dry ice–acetone trap while the contents of the reaction flask changed to a tarry mass. The infrared spectrum of the product, which distilled at 72°C. at 630 mm., was identical with that of benzene.

Anhydrous copper(II) chloride (3.3 grams, 24.5 mmoles) and 1.75 grams (5.6 mmoles) of carefully dried $(C_6H_5BO)_3$ were sealed in a tube and heated at 275°C. After cooling, the volatile contents were fractionated. About 32 mg. of boron trichloride and 10 mg. of hydrogen chloride collected in the liquid nitrogen trap, 30.7 mg. of pure chlorobenzene collected in the ice–methanol trap, and 33.6 mg. of a mixture made up predominantly of benzene with a small amount of chlorobenzene collected in the dry ice–acetone trap. This indicates that less than half of the phenyl groups present in the boroxine were recovered as products. The residue in the tube was in layers: The bottom layer was black, the intermediate layer white, and the top layer brown. The bottom layer was evidently due to decomposed boroxine, the intermediate layer was copper(I) chloride, and the upper layer was unreacted $CuCl_2$.

Copper(I) chloride (1.6 grams, 16 mmoles as CuCl) and triphenylboroxine (2.1 grams, 6.8 mmoles) were heated to 280°C. in a sealed tube. The production of only about 5 mg. of benzene indicated that no apparent reaction had occurred.

Anhydrous hydrogen chloride was heated with several grams of triphenylboroxine to 240°C. in a sealed tube. Almost all of the hydrogen chloride was recovered and the small amount of benzene produced was no more than that obtained by heating triphenylboroxine alone.

Effect of Heat on Triphenylboroxine. In order to determine the cause of the production of benzene in the reactions with aluminum chloride, it was necessary to check the stability of triphenylboroxine with respect to heat. A 1.9-gram sample of triphenylboroxine was placed in a tube and heated under vacuum to 225°C. until the boroxine had sublimed to the cooler portions of the tube. The tube was then sealed off under an atmosphere of dry air and placed in a pipe heater, where it was heated to 320°C. The reaction tube was cooled and attached to the fractionation apparatus; about 0.01 ml. of benzene was obtained. To the contents of the above tube about 3 grams of sublimed aluminum chloride were added and the tube was sealed off under an atmosphere of dry air. The tube was then placed in the pipe heater and heated to 275°C. Analysis of the volatile products of the tube revealed that 0.1 ml. of benzene had been produced. This was about 10 times as much as had been obtained by heating the boroxine alone at 320°C.

Effect of Heat on Tri-*o*-tolylboroxine. Tri-*o*-tolylboroxine (1.1 grams) was sealed in a combustion tube under an atmosphere of dry air and heated to 195°C. The boroxine melted at 161°C. to form a clear liquid with a slight yellowish tinge. After cooling, the contents of the tube were found to be unchanged boroxine.

Reactions of Tri-*o*-tolylboroxine with Halides. The tri-*o*-tolylboroxine (1.1 grams, 3.1 mmoles) which had been heated to check its stability and 4 grams (30 mmoles) of anhydrous aluminum chloride were sealed under an atmosphere of dry air in a combustion tube and heated to 190°C. After fractionating, the product (14 mg.) in the liquid nitrogen trap was shown to have a molecular weight of 52. The infrared spectrum showed only C-H peaks. The substance appeared to be a mixture of hydrocarbons, probably propane and butanes. The products in the dry ice–acetone trap were both liquid and solid: The solid appeared in the upper part of the bulb above the layer of liquid. Molecular weight determinations indicated an average value of 87 for the mixture. Infrared analysis indicated the presence of toluene and some benzene. The total amount of the mixture was 10.9 mg., toluene being the major component. The solid residue in the reaction tube was a black tar with some crystals of aluminum chloride adhering to the sides of the tube.

Tri-*o*-tolylboroxine (1.6 grams, 4.5 mmoles) was heated in a combustion tube under vacuum to 225°C.; no apparent decomposition occurred. Then 3.3 grams (24.5 mmoles) of anhydrous copper(II) chloride were added, the tube was sealed under an atmosphere of dry air, and heated to 195°C. Fractionation of the product gave 21.3

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mg. of hydrogen chloride in the liquid nitrogen trap, and 21.8 mg. of a mixture of toluene (the major component) and boron trichloride in the dry ice–acetone trap.

Stability of Tri-*o*-chlorophenylboroxine toward Heat. A combustion tube containing 1.7 grams of tri-*o*-chlorophenylboroxine was heated to 260°C. No volatile product was obtained and the solid residue showed only a slight brownish coloration.

Reactions of Tri-*o*-chlorophenylboroxine with Halides. Tri-*o*-chlorophenylboroxine (1.25 grams; 3.0 mmoles) was heated under vacuum in a combustion tube to about 190°C. to ensure absence of water. At this temperature the boroxine was a clear transparent liquid with a slight brownish coloration. About 2 grams (15 mmoles) of freshly sublimed aluminum chloride were added to the contents of the tube after cooling to room temperature, and the tube was sealed under an atmosphere of dry air, and heated to 210°C. A very small amount of a volatile product was obtained, which proved to be boron trichloride. The tube was resealed and heated to 255°C. to determine whether further reaction would take place at a higher temperature. Fractionation of the volatile products produced 11.5 mg. of chlorobenzene in the dry ice–acetone trap and a trace of unidentified material in the liquid nitrogen trap.

After 1.5 grams (3.6 mmoles) of tri-*o*-chlorophenylboroxine had been heated to 210°C. under a vacuum to ensure its dryness, the boroxine was cooled and about 5 grams (37 mmoles) of anhydrous copper(II) chloride were added. The tube was sealed under an atmosphere of dry air and heated to 215°C. Only 1.8 mg. of hydrogen chloride were obtained in the liquid nitrogen trap and 17.7 mg. of product in the dry ice–acetone trap. The tube was then resealed and heated to 255°C. and the volatile products obtained were added to those obtained at the lower temperature. From the two reactions, a total of 4.4 mg. of hydrogen chloride and 48.6 mg. of chlorobenzene were obtained.

Reactions of Trimethoxyboroxine with Halides. A flask containing 13.4 grams (77.2 mmoles) of trimethoxyboroxine was attached to the vacuum system and evacuated. Phosphorus pentachloride (10 grams, 48 mmoles) was added slowly through a special side arm in the flask and the resulting mixture was stirred with a magnetic stirrer. A vigorous reaction occurred. The products were fractionated and collected in three different cold baths. A measurable amount of methyl chloride, along with a very small amount of hydrogen chloride, appeared in the liquid nitrogen trap. Methyl chloride was identified by a molecular weight determination, by vaporization from an ice-methanol bath at atmospheric pressure, and by its infrared spectrum. The chief product trimethoxyborane, $(CH_3O)_3B$, which collected in the dry ice–acetone trap, was identified by an average molecular weight of 100 (calculated, 103.8); the infrared spectrum with strong peaks at 3.30 to 3.38, 6.5, 7.2, and 9.5 microns; and a boron analysis of 10.3% (calculated, 10.5%). Among the products in the ice-methanol trap were phosphorus oxychloride and possibly a methoxychloroborane. By repeated fractionation of the liquid in the ice-methanol trap, a fraction was obtained which gave a molecular weight of 108. Hydrolysis of the sample showed 10.2% of boron and 33.5% of chlorine. The calculated molecular weight of dimethoxychloroborane, $(CH_3O)_2BCl$, is 108.3; the boron percentage, 10.0; and the chlorine percentage, 32.9. However, an equimolar mixture of methoxydichloroborane, CH_3OBCl_2, and trimethoxyborane, $(CH_3O)_3B$, would give the same analysis. Whenever the products from this trap were removed from the system for distillation and as soon as heat was applied, the solution turned from clear to reddish brown and trimethoxyborane was released.

The reaction with phosphorus pentachloride was repeated in a closed system by mixing the reactants (2.3 grams, 13.2 mmoles of trimethoxyboroxine; 8.7 grams, 41.7 mmoles of phosphorus pentachloride) in a combustion tube at liquid nitrogen temperature, sealing the tube, and allowing the mixture to warm up gradually. As soon as the trimethoxyboroxine began to melt, the reaction began and the contents warmed up to 56°C. The tube was immersed in liquid nitrogen, opened immediately, and attached to the vacuum system for fractionation. Methyl chloride (1.40 grams) collected in the liquid nitrogen trap; this is approximately 70% of the theoretical yield. The products in the dry ice–acetone trap showed an average molecular weight of 131.

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Further fractionation of this material gave a sample with a molecular weight of 107.5 and a boron and chlorine content of 10.6 and 69%, respectively. Theoretical analysis for methoxydichloroborane is 9.6% of boron and 63% of chlorine, with a theoretical molecular weight of 112.8. An infrared spectrum of this substance indicated peaks at 3.39, 6.08, 6.70, 6.95, 7.39, 7.55, 7.85, 8.50, 9.80, 10.05, and 10.44 microns. Trimethoxyborane under similar conditions has infrared peaks at 3.35, 6.74, 7.28, 8.35, and 9.6 microns. The peaks at 10.05 and 10.44 microns are in the region where boron-chlorine peaks appear. Since methoxydichloroborane should have infrared peaks quite similar to those of trimethoxyborane except for the boron-chlorine peaks, all the peaks in the infrared spectrum of the products in the dry ice-acetone trap can be accounted for as being due to methoxydichloroborane except the peaks which occur at 6.08, 6.95, 7.55, and 7.85 microns. These may be due to some phosphorus chloride.

Three grams of trimethoxyboroxine were added at room temperature by means of a vacuum dropping funnel to an excess of anhydrous aluminum chloride in a flask which was partially evacuated and attached to the fractionation apparatus of the vacuum system. The infrared spectrum of the product indicated it to be trimethoxyborane. This reaction was repeated (8.3 grams of trimethoxyboroxine plus excess aluminum chloride) by heating the reaction flask to 68°C. and pressurizing the system to 65 mm. with dry air. Again trimethoxyborane was the major product along with a small amount of methyl chloride and hydrogen chloride.

The reaction with aluminum chloride was repeated at room temperature in a sealed tube under an atmosphere of dry air. The product obtained was methyl chloride (about 16 mmoles from 26 mmoles of trimethoxyboroxine). The residue in the tube was a reddish brown solid.

Discussion of Results

Reactions of Triphenylboroxine. From a consideration of the results obtained, it seems that the presence of a Lewis acid is necessary for the degradation of triphenylboroxine to benzene. In the reactions in which phosphorus pentachloride, aluminum chloride, and copper(II) chloride are used it is highly probable that these compounds form weak coordination compounds with the boroxine ring; this could induce an electronic shift which results in cleavage of the boron-carbon bond at these temperatures and causes the boroxine ring to revert to boron oxide (B_2O_3). Some of the phenyl groups then must decompose to provide hydrogen atoms to form benzene from other phenyl groups. The decomposition of the organic material is evidenced by the large amount of tar obtained in these reactions. It may be that a small amount of cleavage also occurs between the boron-oxygen bonds and produces trace amounts of phenyldichloroborane, especially when aluminum chloride is used.

In the case when copper(II) chloride is used, the rupture of the boron-carbon bond allows the phenyl group either to acquire a chlorine atom by the reduction of copper(II) chloride to copper(I) chloride or to acquire a hydrogen atom from the decomposition of other phenyl groups. A small amount of cleavage of the boron-oxygen bonds would then lead to the formation of boron trichloride. That copper(II) chloride will not react with boron oxide at these temperatures was confirmed by attempting such a reaction.

When Perrine (*6*) added either phosphorus pentachloride or aluminum chloride to tri-*n*-butylboroxine, he obtained *n*-butyldichloroborane (n-$BuBCl_2$). Also pyrolysis at high temperature did not rupture the boron-carbon bonds at the boroxine ring but instead produced triethylboroxine, $(EtBO)_3$. Therefore it appears that the boron-carbon bond is weaker in triphenylboroxine than in tri-*n*-butylboroxine. Phenyldichloroborane has been obtained from triphenylboroxine and boron trichloride at −80°C. with methylene dichloride as solvent (*1*).

Reactions of Tri-*o*-tolylboroxine. The reaction of aluminum chloride with tri-*o*-tolylboroxine is analogous to its reaction with triphenylboroxine. However, not only is toluene produced as might be expected but also benzene and a small amount of hydrocarbons, presumably propane and butanes. In this case also the boron-carbon bonds seemed to be cleaved and the tolyl radicals either were decomposed to provide hydrogen atoms or accepted hydrogen atoms to form toluene. The presence of hydrocarbons and benzene further substantiates the supposition that some of the tolyl residues were decomposed to provide hydrogen atoms. No hydrogen chloride was produced in this reaction. This fact and the infrared spectrum of tri-*o*-tolylboroxine confirm the absence of water. The boroxine itself was shown to be stable to heat at the temperatures used in this reaction.

The reaction of copper(II) chloride with tri-*o*-tolylboroxine differed from its reaction with triphenylboroxine in that a mixture of chlorobenzene and benzene plus small amounts of boron trichloride and hydrogen chloride was formed in the latter reaction while only toluene, a small amount of boron trichloride, and a large amount of hydrogen chloride were produced from tri-*o*-tolylboroxine. Because copper(II) chloride does not react with boron oxide, the boron trichloride probably was produced by formation and decomposition of a little *o*-tolyldichloroborane (o-$CH_3C_6H_4BCl_2$). The toluene again in all probability was formed by the decomposition of some tolyl residues, releasing hydrogen atoms, and other tolyl residues accepting these to form toluene. The large amount of hydrogen chloride produced could hardly have been formed by the presence of water in the copper(II) chloride, since it was dried in the same manner as that used previously. Also, it hardly seems possible that if water were present boron trichloride would be produced.

Reactions of Tri-*o*-chlorophenylboroxine. The fact that the reaction between aluminum chloride and tri-*o*-chlorophenylboroxine yielded chlorobenzene, boron trichloride, hydrogen chloride, and possibly a slight amount of dichlorobenzene indicates that in this case also the boron-carbon bond was preferentially broken and the hydrogen atoms necessary to form chlorobenzene must have come from decomposition products. The boron trichloride could have been produced by the action of aluminum chloride on boron oxide. This latter reaction does occur to a slight extent at these temperatures.

The reaction of tri-*o*-chlorophenylboroxine with copper(II) chloride yielded a small amount of hydrogen chloride, and about four times as much chlorobenzene. The same batch of copper(II) chloride was used in this reaction as in the reaction with tri-*o*-tolylboroxine. The hydrogen chloride produced in this case may have been due to moisture present in the copper(II) chloride. The chlorobenzene was probably produced in the same manner as that in the reaction of aluminum chloride and tri-*o*-chlorophenylboroxine.

The observation that tri-*o*-chlorophenylboroxine yielded no volatile decomposition products when heated to 260°C. seems to imply that this boroxine is thermally more stable than tri-*o*-tolylboroxine and possibly more stable than triphenylboroxine.

Reactions of Trimethoxyboroxine. When phosphorus pentachloride is added to trimethoxyboroxine substantial amounts of trimethoxyborane and methyl chloride are produced; also a substance is formed which appears to be methoxydichloroborane (CH_3OBCl_2). In all probability the phosphorus pentachloride, since it is a Lewis acid, attacks the oxygen atoms of the boroxine ring; the resulting electronic shift then causes rupturing of the ring with the formation of boron oxide and trimethoxyborane. This would account for the large amount of trimethoxyborane obtained when the reaction is run at reduced pressures. As a second step in the reaction, the phosphorus pentachloride reacts with the trimethoxyborane to form methoxydichloroborane, methyl chloride, and phosphorus oxychloride. Inasmuch as it is difficult to separate the methoxydichloroborane from the phosphorus oxychloride, it may be that in the liquid state a weak coordination compound is formed. The existence of a coordination compound of phosphorus oxychloride and boron trichloride has been reported (*3*). The existence of such a coordination compound is further substantiated by the fact that the molecular weights obtained after fractionation of the sample remained almost constant at 131, which would correspond to an equimolar mixture of phosphorus oxychloride and methoxydichloroborane. It may be that under the conditions used, this coordination compound strengthens the remaining carbon-oxygen and boron-oxygen bonds of the

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methoxydichloroborane to such an extent as to make further reaction with phosphorus pentachloride unsuccessful.

As was the case with phosphorus pentachloride, aluminum chloride probably initiates the reaction by forming a coordination compound with the oxygen atoms in the boroxine ring of trimethoxyboroxine: The electron shift causes the ring to rupture and form boron oxide and trimethoxyborane. When the reaction is performed at reduced pressures, the main product is trimethoxyborane which is removed as fast as it is formed and thus further reaction with aluminum chloride is prevented. When the reaction is carried out in a sealed tube so that the aluminum chloride can react with the trimethoxyborane formed, the yield of methyl chloride from the reaction is much less than when phosphorus pentachloride is used. It may be that trimethoxyborane is less subject to attack by aluminum chloride than by phosphorus pentachloride under the conditions used.

Previous work with tri-*n*-butylboroxine, $(n\text{-BuBO})_3$, indicated an extremely stable boron-carbon bond. The present work seems to indicate that the boron-carbon bond in arylboroxines is considerably more susceptible to cleavage than that in tri-*n*-butylboroxine.

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BASED on a thesis presented by Eugene M. Vander Wall to the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree of doctor of philosophy, 1957. The first paper in this series was published in 1958 (*6*).

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Synthesis of Boron-Carbon Ring Compounds

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A procedure for the preparation of simple mixed trialkylborane compounds has been devised. *n*-Butyldiethylborane and di-*n*-butylethylborane have been prepared. Alkyl group exchange has been shown to occur when a Grignard reagent is allowed to react with tri-*n*-butylborane or di-*n*-butylchloroborane. In one attempt to prepare α,ω-bis(di-*n*-butylboryl)-alkanes, 1,4-bis(di-*n*-butylboryl)butane apparently was isolated. This reaction could not be repeated. Failure to isolate α,ω-bis(di-*n*-butylboryl)alkanes has been attributed to either disproportionation of this product or to exchange of alkyl groups during the reaction. As a result of this, two boron-carbon ring compounds, 1-*n*-butylboracyclopentane and 1-*n*-butylboracyclohexane, have been prepared.

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All reactions were conducted under anhydrous conditions with the maintenance of a nitrogen atmosphere at all times.

Boron analyses were determined by oxidation with hydrogen peroxide, according to the method of Erickson (*2*).

Molecular weights were determined cryoscopically by measuring the freezing point depressions of benzene solutions.

n-Butyldiethylborane from Di-*n*-butylchloroborane

To a cold (0°C.) ethereal Grignard solution prepared from 12.0 grams (0.5 gram-atom) of magnesium and 55.0 grams (0.5 mole) of ethyl bromide were added dropwise 40.0 grams (0.25 mole) of di-*n*-butylchloroborane (*1*), dissolved in an equal volume of ether. The reaction mixture, after being heated to reflux for 2 hours, was hydrolyzed at 0°C. with a 10% solution of hydrochloric acid. The ethereal layer was washed with water, 5% sodium bicarbonate solution, and again with water, and finally was dried over anhydrous magnesium sulfate. After the ether had been removed in vacuo, distillation of the residue gave 8.8 grams (28%) of *n*-butyldiethylborane, boiling point, 45° to 46°C. (15 mm.).

Analysis. Calculated for $C_8H_{19}B$: boron, 8.75; molecular weight, 126. Found: boron, 7.73; molecular weight, 125, 126.

In addition, 5.5 grams of an impure liquid, boiling point 63° to 73° C. (15 mm.), and 9.5 grams (21%) of tri-*n*-butylborane were collected.

During the course of this work, it became necessary to find a solvent for the

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butylchloroboranes. It was discovered that ethers are stable to monochloroboranes (>B—Cl) but not to dichloroboranes (—B<). These results are in agreement with those of Wiberg and Sütterlin, who studied the action of methoxychloroboranes on ethyl ether (*4*).

n-Butyldiethylborane from Tri-*n*-butylborane

A Grignard solution was prepared in the usual manner from 12.0 grams (0.5 gram-atom) of magnesium and 55.0 grams (0.5 mole) of ethyl bromide. To this were added dropwise at 0°C., 57.6 grams (0.3 mole) of tri-*n*-butylborane dissolved in an equal volume of ethyl ether. The reaction mixture was heated to reflux for 1.5 hours, allowed to stand overnight, and finally was heated to reflux for an additional 4 hours. The mixture was hydrolyzed and the products were isolated as described above. A total of 8.2 grams (20.5%) of *n*-butyldiethylborane, boiling point 42° to 43°C. (15 mm.), was collected.

Di-*n*-butylethylborane from Di-*n*-butylchloroborane

The procedure was the same as for the preparation of *n*-butyldiethylborane from di-*n*-butylchloroborane, except that the Grignard reagent was added *to* the di-*n*-butylchloroborane. From 3.0 grams (0.125 gram-atom) of magnesium, 13.6 grams (0.125 mole) of ethyl bromide, and 20.0 grams (0.125 mole) of di-*n*-butylchloroborane were recovered 5.5 grams (27%) of di-*n*-butylethylborane, boiling point, 75° to 76°C. (15 mm.).

Analysis. Calculated for $C_{10}H_{23}B$: boron, 7.15; molecular weight, 154. Found: boron, 7.45; molecular weight, 146, 160.

1-*n*-Butylboracyclopentane

The di-Grignard of 1,4-dibromobutane was prepared in an 80% yield from 48.0 grams (2.0 gram-atoms) of magnesium and 216.0 grams (1.0 mole) of 1,4-dibromobutane, in the usual manner. The Grignard solution was added dropwise, with stirring, to 361.0 grams (2.2 moles) of cold di-*n*-butylchloroborane dissolved in an equal volume of ether. The mixture was stirred for 1 hour at 0°C. and then filtered through glass wool. Distillation, after ether removal, gave 67.0 grams (67.5%) of 1-*n*-butylboracyclopentane, boiling point, 79° to 79.5°C. (75 mm.).

Analysis. Calculated for $C_8H_{17}B$: boron, 8.73; molecular weight, 124. Found: boron, 8.80, 8.80; molecular weight, 121.

In addition, 119.7 grams (82.5%) of tri-*n*-butylborane were isolated.

The above experiment was repeated, except that the di-*n*-butylchloroborane was added *to* the di-Grignard solution. From 12.0 grams (0.5 gram-atom) of magnesium, 54.0 grams (0.25 mole) of 1,4-dibromobutane, and 80.0 grams (0.50 mole) of di-*n*-butylchloroborane were isolated 21.5 grams (69.5%) of 1-*n*-butylboracyclopentane (boiling point, 37° to 39° at 10 mm.) and 34.8 grams (75.6%) of tri-*n*-butylborane (boiling point 87° to 98°C. at 12 mm.).

Isolation of 1,4-Bis(di-*n*-butylboryl)borane

To the cold di-Grignard solution prepared from 6.0 grams (0.25 gram-atom) of magnesium and 25.0 grams (0.13 mole) of 1,4-dibromobutane were added 32.0 grams (0.20 mole) of di-*n*-butylchloroborane dissolved in an equal volume of ether. The addition required 1 hour, and the mixture was stirred for one more hour at 0°. It was heated to reflux for 3 hours and then allowed to stand for 6 days. Distillation produced 10.7 grams (35%) of a material boiling at 80°C. (10 mm.). Molecular weight determinations gave values of 303 and 296 and a low value of 195 as compared to a calculated value of 306 for 1,4-bis(di-*n*-butylboryl)butane. Redistillation 15 days later yielded only 1-*n*-butylboracyclopentane and tri-*n*-butylborane.

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1-*n*-Butylboracyclohexane

This preparation is the same as for 1-*n*-butylboracyclopentane. The quantities used were 12.0 grams (0.50 gram-atom) of magnesium, 57.5 grams (0.25 mole) of 1,5-dibromopentane, and 34.0 grams (0.21 mole) of di-*n*-butylchloroborane. The yield of 1-*n*-butylboracyclohexane, boiling point, 60° to 62°C. (10 mm.), was 15.3 grams (100%) and that of tri-*n*-butylborane, boiling point, 100°C. (15 mm.), was 20.5 grams (100%).

Analysis. Calculated for $C_9H_{19}B$: boron, 7.85; molecular weight, 138. Found: boron, 7.65, 7.86; molecular weight 138, 138, 142, 144.

Reaction of 1-*n*-Butylboracyclopentane with Hydrogen Chloride

Anhydrous hydrogen chloride was bubbled through 28.0 grams (0.226 mole) of 1-*n*-butylboracyclopentane for 7.5 hours while the liquid was heated to an external temperature of 110°C. Subsequent distillation produced 28.0 grams (78%) of di-*n*-butylchloroborane, boiling point 60°C. (10 mm.). About 2.5 grams of an unidentified liquid also were collected.

Discussion

In a proposed study of α,ω-bis (di-*n*-butylboryl)alkanes (I), it first had to be shown that simple mixed trialkylborane compounds

$$\underset{\text{I}}{(C_4H_9)_2B(CH_2)_nB(C_4H_9)_2}$$

were capable of existence. An attempt was made to prepare di-*n*-butylethylborane (II) by the following equation.

$$C_2H_5MgBr + (C_4H_9)_2BCl \rightarrow \underset{\text{II}}{(C_4H_9)_2B(C_2H_5)} + MgBrCl \qquad (1)$$

With the use of a 100% excess of the Grignard reagent, the products isolated were *n*-butyldiethylborane (III) and tri-*n*-butylborane (IV). These unexpected products can be accounted for if it is assumed that an exchange of alkyl groups is possible between a Grignard reagent and a trialkylborane.

$$C_2H_5MgBr + (C_4H_9)_2BC_2H_5 \rightarrow \underset{\text{III}}{C_4H_9B(C_2H_5)_2} + C_4H_9MgBr \qquad (2)$$

$$C_4H_9MgBr + (C_4H_9)_2BCl \rightarrow \underset{\text{IV}}{(C_4H_9)_3B} + MgBrCl \qquad (3)$$

In view of the fact that two moles of the Grignard reagent actually were used, where one would have been sufficient, it is not unreasonable to propose such a sequence of reactions.

If alkyl group exchange occurs, it is to be expected that reaction between excess ethylmagnesium bromide and tri-*n*-butylborane should lead both to *n*-butyldiethylborane and di-*n*-butylethylborane.

$$C_2H_5MgBr + (C_4H_9)_3B \rightarrow (C_4H_9)_2BC_2H_5 + C_4H_9MgBr \qquad (4)$$

$$C_2H_5MgBr + (C_4H_9)_2BC_2H_5 \rightarrow C_4H_9B(C_2H_5)_2 + C_4H_9MgBr \qquad (5)$$

When a 66% excess of the Grignard reagent was used, based on Equation 4, only *n*-butyldiethylborane and unreacted tri-*n*-butylborane could be found. The failure to isolate di-*n*-butylethylborane can be explained by the fact that the system, as represented by Equations 4 and 5, is in equilibrium. The relative amounts of products most likely depend on the relative rates of reaction. Material distilling between *n*-butyldiethylborane and tri-*n*-butylborane was obtained, but it appeared to be a mixture and was not identified. Di-*n*-butylethylborane finally was prepared by adding an equimolar quantity of ethylmagnesium bromide to di-*n*-butylchloroborane. No other product was obtained. It thus became apparent that, although exchange of

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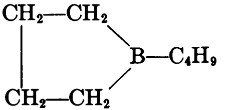
alkyl groups actually was occurring, any desired product could be achieved with the use of the proper ratio of reactants and the proper mode of addition.

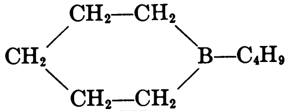
Having shown that the synthesis of mixed trialkylborane compounds presented no insurmountable difficulties, the preparation of α,ω-bis-(di-*n*-butylboryl)alkanes was attempted. The reactions of tetramethylenedimagnesium dibromide and pentamethylenedimagnesium dibromide with di-*n*-butylchloroborane were investigated in an attempt to prepare 1,4-bis(di-*n*-butylboryl)butane (V) and 1,5-bis(di-*n*-butylboryl)-pentane (VI), respectively.

$$BrMg(CH_2)_4MgBr + 2(C_4H_9)_2BCl \rightarrow \underset{V}{(C_4H_9)_2B(CH_2)_4B(C_4H_9)_2} + 2MgBrCl \qquad (6)$$

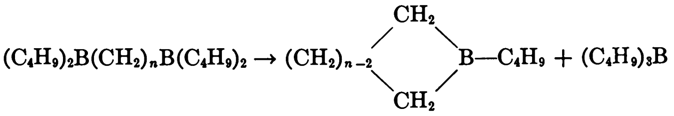
$$BrMg(CH_2)_5MgBr + 2(C_4H_9)_2BCl \rightarrow \underset{VI}{(C_4H_9)_2B(CH_2)_5B(C_4H_9)_2} + 2MgBrCl \qquad (7)$$

Instead of the desired products, Reaction 6 yielded 1-*n*-butylboracyclopentane (VII) and Reaction 7, 1-*n*-butylboracyclohexane (VIII). Tri-*n*-butylborane was also isolated in both reactions. These cyclic structures represent a new class of boron-containing compounds, none of which appear to have been reported previously. Subsequent to the writing of this article, the preparations of 1-phenylboracyclopentane and 1-phenylboracyclohexane have been reported (*3*).


VII

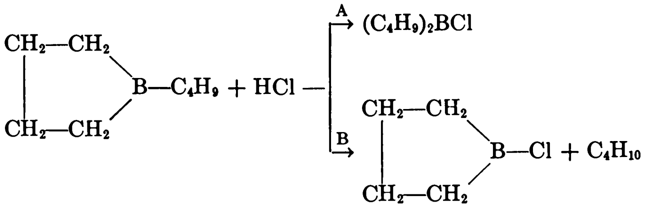

VIII

These products can be accounted for most logically by assuming a disproportionation of the 1,4-bis(di-*n*-butylboryl)alkane.


(8)

One piece of evidence was obtained that supports this hypothesis of disproportionation. In one attempt to prepare 1,4-bis(di-*n*-butylboryl)butane, a liquid was isolated which molecular weight determinations tentatively identified as the desired product. Redistillation of this liquid yielded tri-*n*-butylborane and 1-*n*-butylboracyclopentane.

The formation of di-*n*-butylchloroborane by reaction of 1-*n*-butylboracyclopentane with hydrogen chloride is in accord with this cyclic structure. Hydrogen chloride removes an alkyl group from trialkylboranes (*1*). Although two reaction paths are possible with the cyclic compound, only the product of ring cleavage was isolated.


(9)

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Borazine Chemistry

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Interest in borazine, $B_3H_3N_3H_3$, arises in part from its similarity to benzene in structure and physical properties. Relatively little is known of its chemistry, principally because of difficulties involved in the original synthetic procedures for borazine and its derivatives. The borazine ring undergoes some substitution reactions. However, unlike benzene, borazine and certain of its derivatives undergo addition reactions readily to give products like $B_3H_3N_3H_3.3HX$, where X = Cl, Br, or OH. Also borazine undergoes extensive decomposition in the liquid phase, even at room temperature. Improved syntheses recently have been developed for borazine and various types of substituted borazines. It is anticipated that these improvements will lead to a greatly expanded knowledge of borazine chemistry.

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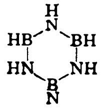
Borazine, $B_3N_3H_6$, was isolated and characterized in 1926, at which time it was suggested that it had a cyclic, benzenelike structure, with B and N atoms alternating in the ring (*34*). Both chemical and physical properties of borazine support such a structure and electron diffraction data are consistent with a planar molecule in which the B—N bond distance is 1.44 ± 0.02 A. and the ring angle is 120° (*35*).



Borazine	Benzene
B—N = 1.44 A.	C—C = 1.42 A.
N—H = 1.02 A.	C—H = 1.08 A.
B—H = 1.20 A.	
Mol. wt. = 80.5	Mol. wt. = 78.1

It is assumed that the extra electron pair on each nitrogen atom takes part in ring bonding, so that borazine is isoelectronic with benzene. The molecule therefore should be considered in terms of resonance, taking into account single-bonded and double-bonded structures.

This view is supported by a variety of spectral studies as well as the fact that the B—N distance of 1.44 A. is intermediate between that expected for a single bond (1.54 A.) and that for a double bond (1.36 A.). Though similar in structure and molecular weight, borazine differs from benzene in that it is heteroatomic, which results in charge distribution different from that in benzene, represented by a formal positive charge on nitrogen atoms and a formal negative charge on boron atoms. On the basis of spectra of substituted borazine and comparison with carbon compounds, some

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authors consider borazine to be about 50% aromatic (*7*). Despite such differences, there is a remarkable correspondence of physical properties of borazine and benzene (Table I).

Table I. Physical Properties

	Borazine	Benzene
Mol. wt.	80.5	78.1
B. P., °K.	328	353
M. P., °K.	216	279
Critical temp., °K.	525	561
Reduced b.p., °K.	0.63	0.63
Liquid density at b.p., g./cc.	0.81	0.81
H vap./mole, kcal./mole	7.0	7.4
Trouton's constant	21.4	21.1
Molecular vol. at b.p., cc.	100	96
Surface tension at m.p., dynes/cm.	31.1	31.0
Parachor	208	206
Crystal density at m.p.	1.00	1.01

While the properties of derivatives of borazine generally have not been studied as extensively as those of the parent compound, for a number of derivatives the ratio of the absolute boiling point to that of the organic analog is about 0.93, the value for borazine-benzene. Some of the available data are illustrated in Table II.

Table II. Properties of Borazines

Compound	M.P., °C.	B.P., °C.	Organic Analog	Ratio of B.P., °Absolute Borazine/Organic
	Methylborazines (*29,39*)			
Borazine	−58.0	55	Benzene	0.93
B-Monomethylborazine	−59	87	Toluene	0.94
N-Monomethylborazine		84	Toluene	0.93
B,B'-Dimethylborazine	−48	107	*m*-Xylene	0.92
B,N-Dimethylborazine		124	*o*- or *p*-Xylene	0.95 or 0.97
N,N'-Dimethylborazine		108	*m*-Xylene	0.92
B,B',B''-Trimethylborazine	31.5	129	Mesitylene	0.91
N,N',N''-Trimethylborazine	−8	134	Mesitylene	0.92
N,B,B'-Trimethylborazine		139	Hemimellitene or pseudocumene	0.92 or 0.93
N,B,B'B,''-Tetramethylborazine		158	Isodurene	0.92
Hexamethylborazine	97	233	Mellitene	0.92

Compound	M.P., °C.	B.P., °C.	Ref.
	Halogenoborazines		
$B_3F_2HN_3(CH_3)_3$	(V.p. = 5.9 mm. at 24.1°C.)		(*30*)
$B_3F_3N_3(CH_3)_3$	85	224	(*36, 42*)
$B_3F_3N_3(SiH_3)_3$	(V.p. = 2.5 mm. at 24°C.)		(*36*)
$B_3ClH_2N_3H_3$	−34.6	109.5	(*27*)
$B_3Cl_2HN_3H_3$	33.0–33.5	151.9	(*27*)
$B_3Cl_3N_3H_3$	83.9–84.5		(*4*)
$B_3Cl_3N_3(CH_3)_3$	167		
$B_3Cl_3N_3(C_2H_5)_3$	58–60		
$B_3Cl_3N_3(C_6H_{11})_3$	217–219		
$B_3Cl_3N_3(C_6H_5)_3$	273–275		
$B_3Cl_3N_3(p\text{-}C_6H_4—CH_3)_3$	304–307		
$B_3Cl_3N_3(p\text{-}C_6H_4—OCH_3)$	230–234		
$B_3BrH_2N_3H_3$	−34.8	122.3	(*27*)
$B_3Br_2HN_3H_3$	49.5–50.0	167.1	(*27*)
$B_3Br_3N_3H_3$	126–128		(*28*)
	Alkyl borazines		
B-Triethylborazine	−46.4–0.5	180	
B-Tributylborazine	(B.P. = 34° at 7 microns)		(*24,25*)
N-Triethylborazine	−49.6	184	(*14*)
N-Tri-*n*-propylborazine	Glass	225	(*14*)
N-Triisopropylborazine	−6.5	203	(*14*)
N-Tricyclohexylborazine	98–99^a		
	Aryl borazines		
B-Triphenylborazine	184–185		(*24,25*)
N-Triphenylborazine	158		
N-Tri-*p*-tolylborazine	149–150		
N-Tri-*p*-anisylborazine	127–129^b		

(Continued on page 234)

Table II (Continued)

N-Trimethyl-*B*-trialkoxyborazines, and
N-Trimethyl-*B*-triphenoxyborazines (*3*). $B_3(OR)_3N_3(CH_3)_3$

	Boiling Range		
	°C.	*P*, mm.	Melting Range, °C.
OR = methoxy	62–65	0.07	
ethoxy	79.5–80.5	0.10	
n-propoxy	101–103	0.15	
isopropoxy	85–87	0.10	
n-butoxy	130–134	0.30	
tert-butoxy	120–125	0.52	84–87
phenoxy	185–187	0.07	81–84

B-Trisubstituted *N*-Triphenylborazines,
$B_3R_3N_3(C_6H_5)_3$ (*9*)

R	M.P., °C.
CH_3	267–269
C_2H_5	169–171
n-C_3H_7	169–171
i-C_3H_7	197–198
n-C_4H_9	129–132
i-C_4H_9	185–187
C_6H_5	413–415
$CH_2{=}CHCH_2$	98– 99

[a] Difficult to purify, some uncertainty as to correct M.P.

[b] Compound apparently decomposes on standing. M.P. goes to lower values on any except freshly recrystallized samples.

The melting point variation in trimethylborazines is interesting.

The relation of borazine and its derivatives to the corresponding benzene compounds has stimulated a number of spectral studies and there has been considerable interest in utilizing borazine chemicals in a variety of applications which are suggested by consideration of benzene chemistry, as well as by the nature of borazine itself.

Stock found that borazine does not react with oxygen at room temperatures, though it will explode with oxygen in an arc to give B_2O_3, N_2, and H_2O. It dissolves in water with slow evolution of H_2 and NH_3, and fresh aqueous solutions of borazine reduce $KMnO_4$, Cu^{++} to Cu, and Ni^{++} to Ni. Heating the vapor to 500°C. for 6 hours showed only incomplete decomposition with evolution of hydrogen and formation of a white, nonvolatile solid, $(BNH)_x$. To date, relatively little more is known of the chemistry of borazine and much of what is known has been elucidated incidentally to the development of synthetic procedures.

The reason for this relative paucity of information is not hard to identify. The synthetic procedure first developed involved the use of hazardous, difficultly obtained materials, which required vacuum line techniques for their manipulation and only small quantities of borazine were obtained even by workers with the requisite equipment and experience.

Stock and his coworkers prepared borazine by heating boron hydride ammoniates in a bomb tube. After years of experience, the best yields, only about 50%, were obtained by heating B_2H_6 and NH_3 in a carefully adjusted mole ratio of 1 to 2 (*39*, *40*).

$$B_2H_6\cdot 2NH_3 \xrightarrow[\text{2–3 hours}]{200^\circ} B_3N_3H_6 + H_2$$

$$B_4H_{10}\cdot 4NH_3 \xrightarrow{180^\circ} B_3N_3H_6 + H_2 \quad \text{40\% yield}$$

$$B_2H_6\cdot 2NH_3 \xrightarrow[\text{3/4 hour, 1 atm.}]{200\text{–}220^\circ} B_3N_3H_6 + H_2 \quad \text{50\% yield}$$

Schlesinger and his group at the University of Chicago prepared various *B*-methylborazines by analogous reactions in which a diammoniate of a methyldiborane, or the corresponding mixture, was heated. *N*-Methylated derivatives were prepared by heating together diborane and methylamine or diborane and methylamine-ammonia mixtures (*31*, *32*). The relative amounts of products depended on relative proportions of reagents used. Yields better than 50%, in some cases approaching 100%, were obtained.

$$B_2R_1H_5 + 2NH_3 \xrightarrow[\text{2–6 atm.}]{180\text{–}200^\circ} B_3RH_2N_3H_3, B_3R_2HN_3H_3 + H_2, \text{ etc.,}$$
$$+ B_3R_3N_3H_3$$

$$B_2H_6 + 2RNH_2 \longrightarrow B_3H_3N_3R_3$$

$$\text{(ammonia also present)} \rightarrow B_3H_3N_3R_3 + B_3H_3N_3RH_2 + B_3H_3N_3R_2H$$

$$R = CH_3$$

Wiberg prepared *B*-trimethylborazine and hexamethylborazine by use of trimethylboron (*41*).

$$3BR_3 + 3NH_3 \xrightarrow[\text{20 atm.}]{330^\circ} B_3R_3N_3H_3 + 6CH_4$$

$$3BR_3 + 3NR_3 \xrightarrow[\text{20 atm.}]{450^\circ} B_3R_3N_3R_3 + 6CH_4$$
$$R = CH_3$$

However, within the past decade several new synthetic approaches for preparation of borazine compounds have been developed which do not require the prior preparation of boron hydrides or trimethylborane.

The first new approach was that of G. W. Schaeffer, in which *N*-trisubstituted borazines are produced by the reaction of alkylammonium chloride and lithium borohydride in an ether slurry. Addition of ether to the mixed reagents, with the borohydride in slight excess of 1 to 1 mole ratio, leads to the evolution of approximately 1 mole of hydrogen per mole of alkylammonium chloride. The hydrogen is then removed along with the solvent by evacuation at reduced pressure. The remaining solid is pyrolyzed. The volatile products of the pyrolysis reaction are then passed through a heated zone and the desired borazine is separated from gases issuing from the heated zone (*14*).

$$LiBH_4 + RNH_3Cl \xrightarrow{\text{ether}} LiCl + BNH_5R + H_2$$

$$BNH_5R \xrightarrow[\text{pyrolysis}]{} \tfrac{1}{3}\,B_3H_3N_3R_3 + 2H_2$$

R = methyl, ethyl, *n*-propyl, isopropyl

These reactions presumably proceed by the formation of an amine-borane, which on pyrolysis decomposes, perhaps in the same stepwise fashion as that established by Wiberg for the bomb tube reactions he has studied.

$$(H_3NR)Cl + LiBH_4 \rightarrow LiCl + (H_3NR)(BH_4) \rightarrow H_2 + H_2RN{:}BH_3$$

$$H_2RN{:}BH_3 \xrightarrow{-H_2} HRNBH_2 \xrightarrow{-H_2} (RNBH) \longrightarrow \tfrac{1}{3}\,B_3H_3N_3R_3$$

Preparation of borazine itself by reaction of $LiBH_4$ and ammonium chloride in similar fashion proved to require rather specific conditions to obtain any borazine at all. More recent efforts using carefully regulated conditions have succeeded, and yields as high as 42% were had in some runs. However, it was found that borazine could be produced in useful quantities by the reaction of $LiBH_4$ and NH_4Cl in the absence of solvents, using a technique generally similar to that employed for the alkylborazines. Yields of 30 to 35% could be obtained routinely (*22*, *27*).

$$3LiBH_4 + 3NH_4Cl \xrightarrow[t\text{ around }300^\circ\text{C.}]{p\,=\,1\text{ atm.}} B_3N_3H_6 + 9H_2 + 3LiCl$$

Another line of approach suggested itself after Laubengayer and Brown reported the synthesis of *B*-trichloroborazine by the reaction of BCl_3 and ammonium chloride

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in refluxing chlorobenzene (*4, 6*). While attempts to reduce $B_3Cl_3N_3H_3$ with $LiAlH_4$ did not lead to the isolation of the desired $B_3N_3H_6$, Schlesinger's group established that the reduction of $B_3Cl_3N_3H_3$ with $LiBH_4$ in butyl ether could give satisfactory yields of borazine. Smith, Eddy, and Miller at the Naval Research Laboratory extended the method to produce relatively sizable quantities of $B_3N_3H_6$ (13 grams after several runs) (*5, 28*).

$$3BCl_3 + 3NH_4Cl \xrightarrow[\text{chlorobenzene}]{\text{refluxing}} B_3Cl_3N_3H_3 + 9HCl$$

$$B_3Cl_3N_3H_3 + 3LiBH_4 \xrightarrow[\text{ether}]{\text{butyl}} B_3H_3N_3H_3 + \tfrac{3}{2}\,B_2H_6 + 3LiCl$$

B_2H_6 is a by-product, but it can be handled in a number of ways, such as by absorption in a column of $NaBH(OCH_3)_3$ to generate $NaBH_4$. This is attractive, in that $NaBH_4$ itself reduces $B_3Cl_3N_3H_3$ smoothly when polyethylene glycol dimethyl ethers are used as solvent, and yields in excess of 90% have been obtained (*11, 13*).

$$\tfrac{1}{2}\,B_2H_6 + NaBH(OCH_3)_3 \rightarrow NaBH_4 + B(OCH_3)_3$$

$$B_3Cl_3N_3H_3 + 3NaBH_4 \xrightarrow{\text{Ansul 141}} B_3H_3N_3H_3 + 3NaCl + \tfrac{3}{2}\,B_2H_6$$

This latter preparative scheme, reduction of *B*-trichloroborazine with $NaBH_4$ in polyethylene glycol ether solvents, has been used to prepare a number of *N*-substituted borazines from the corresponding *B*-trichloro *N*-trisubstituted borazines. The methyl intermediate was had by the reaction of methylammonium chloride and BCl_3 in chlorobenzene, and the others were prepared by using the appropriate amine rather than amine hydrochloride. We were guided in this work by the earlier efforts of Kinney and coworkers, who first prepared *B*-trichloroborazines by interaction of BCl_3 with amines (*15–17*).

$$B_3Cl_3N_3R_3 + 3NaBH_4 \rightarrow B_3H_3N_3R_3 + \tfrac{3}{2}\,B_2H_6 + 3NaCl$$

R = methyl, ethyl, cyclohexyl, phenyl, *p*-tolyl, *p*-anisyl

The reactive B—Cl bond in $B_3Cl_3N_3H_3$ suggested a convenient method for the preparation of *B*-substituted borazines by reaction with metallo-organic reagents. *B*-Trimethyl, *B*-triethyl, and *B*-triphenylborazines have been prepared from $B_3Cl_3N_3H_3$ and the corresponding Grignard reagent. Several research groups have been active in the synthesis of borazines substituted on nitrogen as well as on boron, by analogous reactions. The second equation indicates some of the work reported by Groszos and Stafiej (*9*).

$$B_3Cl_3N_3H_3 + 3RMgX \rightarrow B_3R_3N_3H_3 + 3MgXCl$$

R = methyl, ethyl, phenyl

$$B_3Cl_3N_3(C_6H_5)_3 + 3RMgX \rightarrow B_3R_3N_3(C_6H_5)_3 + 3MgXCl$$

R = phenyl, methyl, ethyl, *n*-butyl, isobutyl, allyl

Ryschkewitsch has reported on reactions of *B*-trichloro-*N*-trimethylborazine. The reaction proceeds stepwise to replace one chlorine at a time, and the intermediate compounds have been isolated in several cases (*10, 26*). Aminoborazines have been prepared by Gould (*8*).

$$B_3Cl_3N_3(CH_3)_3 + RMgX \rightarrow B_3Cl_2RN_3(CH_3)_3 \xrightarrow[\text{RMgX}]{} B_3ClR_2N_3(CH_3)_3 \xrightarrow[\text{RMgX}]{} B_3R_3N_3(CH_3)_3$$

Still another synthetic route has been developed by Ruigh, who has prepared *B*-trisubstituted borazines from the reaction of excess ammonia with dichloroboranes (*24, 25*).

$$3RBCl_2 + 9NH_3 \rightarrow B_3R_3N_3H_3 + 6NH_4Cl$$

R = butyl, phenyl, *β*-chlorovinyl

This method of synthesis has been limited in application because of the lack of satisfactory syntheses for dichloroboranes. A series of papers by McCusker describes the synthesis of a variety of alkyldichloroboranes by the reaction of BCl_3 with alkylboroxines. Procedures for several aryl dichloroboranes are given also (*19*).

We have outlined general synthetic approaches currently available and have not listed all the applications that have been made or suggested. The earlier synthetic method, in which ammonia and borane are heated, has been adapted to produce as much as 33 grams of pure *B*-triethylborazine in one run by carrying out the heating in an autoclave (*43*). For synthesis of *N*-substituted borazine, *N*-trialkylaminoboranes can be prepared by the method described by Koster (*18*).

$$3H_3NB(C_2H_5)_3 \xrightarrow{450^\circ} B_3(C_2H_5)_3N_3H_3 + 6C_2H_5$$

120 grams	48.6 grams crude	theoretical amount	(*43*)
	33 grams purified	48.6 grams	

$$R_3N + BEt_3 + 3H_2 \rightarrow R_3N{:}BH_3 + 3C_2H_6 \qquad (18)$$

The chemical properties of borazine, and its tri- and hexamethyl derivatives are discussed by Wiberg (*39*). However, he makes a frequently quoted statement that borazine and its methyl derivatives are thermally stable. While borazine decomposes only slightly after months of storage as a gas in borosilicate glass containers at room temperature, it undergoes extensive decomposition when stored as a liquid at room temperature. In such liquid samples, after several days, a glassy solid begins to form and slowly grows in extent. Later a white solid appears, to which eventually nearly the entire sample is converted. Simultaneously there develops in the container a considerable amount of gas, which is mostly hydrogen plus a small quantity of diborane. In one case two volatile liquids containing boron, nitrogen, and hydrogen were detected among the decomposition products (*28*).

$$B_3N_3H_6 \xrightarrow[\text{temperature}]{\text{room}} \underset{(BNH_x)}{\text{solids}},\ H_2, B_2H_6,\ \text{volatile liquids}$$

While we have only limited data as yet concerning the decomposition of liquid borazine at other conditions (*11*), one must consider the possibility that this complex decomposition proceeds at an increasing rate as borazine is heated above room temperature. Thus some of the reported chemistry of borazine probably is obscured by phenomena accompanying decomposition.

The methylborazines studied by Wiberg evidently gave no evidence of decomposition during distillation, but detailed information concerning their behavior on prolonged standing or heating is lacking. However, Russian workers (*43*) report that *B*-triethylborazine begins to decompose at 100°C. at normal pressure, and the material we have prepared begins to decompose at around 70° when subject to its own vapor pressure.

B-Trichloroborazine is reported by Brown to undergo slight decomposition even when carefully stored at room temperature, and to evolve HCl when heated to 100°C. (*4*). On long periods of standing at room temperature, $B_3Cl_3N_3H_3$ appears to undergo polymerization to give less volatile compounds, so that appreciably less volatile material is produced. Experience indicates that a similar change occurs at a faster rate when $B_3Cl_3N_3H_3$ is warmed.

Thus, in interpreting available data and in planning new experiments, one should keep in mind the potential complications connected with the possibility of decomposition of the reagent borazine.

In addition to the substitution reactions undergone by trichloroborazines, several such reactions have been reported for borazine itself (*31*). Methyl-substituted borazine undergoes similar reactions (*32*).

$$B_3N_3H_6 + B(CH_3)_3 \xrightarrow[24\text{ hours}]{100°} B_3(CH_3)H_2N_3H_3 + B_3(CH_3)_2HN_3H_3 + B_3(CH_3)_3N_3H_3 + H_2, \text{ etc.}$$

$$B_3N_3H_6 + H_2NB(CH_3)_2 \xrightarrow[\frac{1}{2}\text{ hour}]{190\text{–}200°} \text{similar products}$$

B-Mono- and dihalogenoborazines have been prepared by substitution using BCl_3 or BBr_3. No trihalo- compounds were observed (*27*). BCl_3 and *B*-trimethylborazine

$$B_3N_3H_6 + BCl_3 \xrightarrow[\text{room temperature}]{116\text{ hours}} B_3Cl_2HN_3H_3 + B_3ClH_2N_3H_3$$

$$B_3N_3H_6 + BBr_3 \xrightarrow{\hspace{3cm}} B_3Br_2H_2N_3H_3 + B_3BrH_2N_3H_3$$

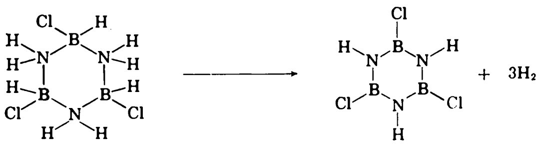
undergo extensive reaction at room temperature to give a variety of products, but this has not been investigated in detail.

Wiberg has reported the preparation of a number of borazines by way of intermediate compounds prepared by addition reactions of borazines (*39*). The types of reactions involved may be exemplified by the addition of gaseous HCl and HBr to borazine, to give white, nonvolatile, readily hydrolyzable solids.

$$B_3N_3H_6 + 3HCl \xrightarrow[\text{temperature}]{\text{room}} B_3N_3H_3\cdot 3HCl \xrightarrow[50° \text{ to } 100°]{} B_3Cl_3N_3H_3 + 3H_2$$

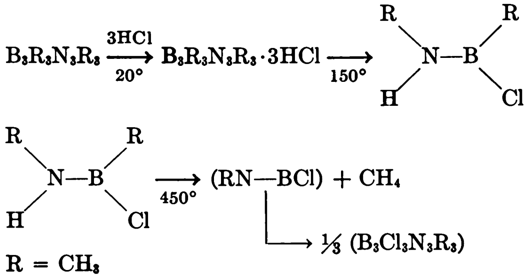
$$B_3N_3H_6 + 3HBr \xrightarrow[\text{temperature}]{\text{room}} B_3N_3H_3\cdot 3HBr \xrightarrow{\hspace{2cm}} B_3Br_3N_3H_3 + 3H_2$$

These solids on heating in vacuum split out hydrogen to give *B*-trichloro- and *B*-tribromoborazine, and so are postulated by Wiberg to have the structure analogous to a cyclohexane derivative.



$$B_3H_3N_3H_3 + 3HBr \xrightarrow{100°} H_3Br_3N_3H_3 + 3H_2$$

At higher temperatures the halogenoborazines can be produced without isolating the intermediate adducts. In the case of *B*-methylborazines similar products are obtained, but in these cases Wiberg finds that the ring splits on heating to give an aminoborane, which on further heating loses methane, as illustrated by hexamethylborazine.

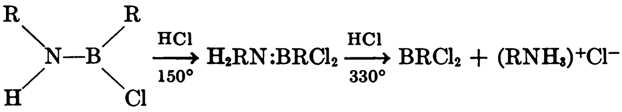


$$B_3R_3N_3R_3 \xrightarrow[20°]{3HCl} B_3R_3N_3R_3\cdot 3HCl \xrightarrow[150°]{} RHN\text{—}B(R)Cl$$

$$RHN\text{—}B(R)Cl \xrightarrow[450°]{} (RN\text{—}BCl) + CH_4 \longrightarrow \tfrac{1}{3}(B_3Cl_3N_3R_3)$$

$R = CH_3$

While excess HCl has no effect at room temperature, at higher temperature the intermediate aminoborane adds HCl to give a dichloroborane and an amine hydrochloride.



$$RHN\text{—}B(R)Cl \xrightarrow[150°]{HCl} H_2RN{:}BRCl_2 \xrightarrow[330°]{HCl} BRCl_2 + (RNH_3)^+Cl^-$$

For borazine and *N*-methylborazine reaction with water is analogous to that with HCl—that is, at low temperature a trihydrate is formed; at intermediate temperature *B*-trihydroxyborazines are formed from a stoichiometric amount of water, and with excess water at higher temperatures, the compounds are hydrolyzed completely.

$$B_3H_3N_3R_3 + 3H_2O \xrightarrow{0°} B_3H_3N_3R_3 \cdot 3H_2O$$

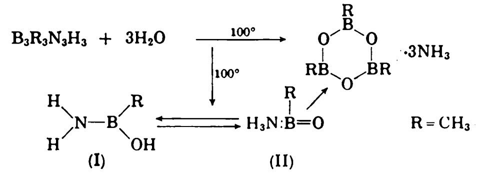
$$B_3H_3N_3R_3 + 3H_2O \xrightarrow{100°} B_3(OH)_3N_3R_3$$

$$B_3H_3N_3R_3 + 6H_2O \xrightarrow{150°} 3B(OH)_3 + 3NRH_2 + 3H_2$$

$$R = CH_3$$

(*B*-Trihydroxyborazines can be had from the action of water on chloroborazines, at least in some cases.)

In the case of *B*-methylborazine, Wiberg found that at conditions which would be expected to give hydroxyborazines, a boroxine ring is formed. Wiberg explains this on the basis of splitting of the adduct to give an analog of vinyl alcohol (I) which establishes equilibrium with its tautomeric acetaldehyde analog (II), which then trimerizes to a boroxine ring.



Wiberg reports some further observations on reactions of borazine, such as those with ammonia, methanol, amines, alkyl halides, and elementary halogens. However, few experimental data are presented and in some cases the reactions may have to be reconsidered on the basis of additional information as it becomes available. For example, Haworth and Hohnstedt (*12*) discuss the reaction of borazine with methanol.

More and more data concerning the chemistry of borazine are being made known as various workers report their results in this field. The synthesis of *N*-trimethyl-*B*-trialkoxy- and -triphenoxyborazines has been reported by Bradley, Ryschkewitsch, and Sisler (*3*). Niedenzu and Dawson (*23*) have described the preparation of *B*-triaminoborazines through the interaction of a tertiary amine with the addition product of BCl_3 and a primary amine. They have also prepared *B*-triaminoborazines by reacting an amine with an aminodichloroborane. Their application of the Friedel-Crafts reaction to *B*-trichloroborazine in benzene-chlorobenzene leads to good yields of *B*-triphenylborazine.

Other individuals and groups throughout the world are disclosing their results in the widening field of borazine chemistry (*1, 2, 6, 8, 20–22, 33, 37, 38*), so that the tabulated data and list of references do not represent a complete compilation of available information.

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Research on Boron Polymers

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Research was undertaken to explore the possibility of developing inorganic or semi-inorganic polymers stable at high temperatures. The film-forming polymer resulting from the reaction of a bifunctional isocyanate and a boronic acid is a polyurea containing physically bound boron rather than a polymeric boronamide. This program led to the development of a new borazole synthesis based on the reaction of alkyl or aryl boron dichlorides and amines. The present effort is directed at forming linear polymers from boron-substituted borazoles. In recent work on B-tri-β-chlorovinylborazole, the compound on refluxing with polar solvents gave a glassy product. This material, in addition to β-dichlorovinyl boronic acid and possibly other substances, gives an insoluble fraction which may be the desired linear polymer. Although the program has not developed heat-stable polymers, its by-products are of interest in the field of boron polymers and more generally in the synthesis and reactions of a number of unusual organoboron compounds.

The work reported here was initiated in 1953, aimed at a study of possible inorganic polymers for high temperature applications. The initial concept was to prepare condensation polymers from the 2,4-dihydroxyborazene stated to have been prepared from dibromoborazene (*26*).

Before any experimental work was undertaken, an extensive literature survey was made and the original borazene approach was abandoned because previous work seemed to indicate that the borazenes as a class were hydrolytically unstable. This literature survey covered the general field of inorganic polymers (*17*, *19–21*). It was decided to concentrate the experimental work on possible polymers based on boron.

The polyester type of polymer formed from boric acid, glycols, and glycerol dates

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In BORAX TO BORANES;
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back at least to 1866 (*22*). Polymeric glycol borates and esters of boronic acids have been investigated (*24*). A remarkably careful study in this field of condensation reactions of orthoboric acid with diols was reported recently (*12*). The area, including polyamide-type polymers, was also surveyed in 1952 (*9*).

Upson (*25*) described very stable polymers, white film-forming solids, believed to be boronamides derived from the reaction of boronic acids with bifunctional isocyanates. The polymers had softening points up to 300°C., and a relatively high degree of hydrolytic stability and were soluble in phenol and formic acid.

The Upson boronamide synthesis was patterned on the reaction discovered in 1906, where an isocyanate reacts with a carboxylic acid to form the amide and carbon dioxide (*7*, *15*, *16*). The reaction is markedly catalyzed by tertiary amines.

Upson's reaction was repeated using toluene-2, 4-diisocyanate and also hexamethylene diisocyanate in benzene solution. The former gave insoluble powdery polymers, but the latter gave a mixture of powder and a tough film which could be peeled off the side of the reaction flask.

As Upson also found, the reaction products contained somewhat less than the theoretical percentage of boron. For example, the polymer from hexamethylene diisocyanate contained 4.06 boron (theoretical 5.36%).

These materials, including the tough film-forming material, lost little boron when extracted with benzene. When methanol was used, almost all the boron was extracted (analysis 0.22% B) after 70 hours but the film was left unimpaired.

It thus appeared that the product, instead of being a polyboronamide, was polyhexamethyleneurea, which was formed from water and the hexamethylene diisocyanate. The water would readily be formed from the cyclization of benzeneboronic acid to give water and the triphenylboroxine.

The product was probably polyhexamethyleneurea prepared in 1942 (*10*) and later studied for its infrared absorption (*8*). Infrared studies on the material as interpreted by C. E. Erickson were in accord with the polyhexamethyleneurea formulation.

Preparation of Boronic Acids

The hydrolytic instability of polyesters from glycols and polyamides from diammines led next to an attempt to prepare a boronic acid in which an odd 2- or 3-carbon chain was terminated with a strong donor group such as dimethylamine. If such a compound could be prepared, one would have an internally quasi-chelate group and a quadricovalent boron atom with two hydroxyls as functional groups. These compounds, for which the trivial name of "scorpion" boronic acids was coined, would be related to hydrolytically stable cage-structured triethanolamine borate ester (*4*, *11*).

The first attempts, using a preferential Grignard reaction on 1-bromo-3-chloropropane (*1*) followed by treatment with methyl borate, failed to give any trace of the desired γ-chloropropylboronic acid. The Grignard on γ-dimethylaminopropyl chloride, following the general technique of Miesher and Marxer, also met with failure (*13*, *14*, *20*).

Finally allylboronic acid was prepared by the Grignard procedure (*19*, *21*). Early attempts to isolate this acid met with failure, but by working up the reaction mixture at low temperature under nitrogen and in the presence of 0.1% inhibitor such as hydroquinine, success was attained and the acid melting at 75°C. was isolated. Light or traces of peroxide decomposed the acid into propylene (with a trace of hexadiene) and a mixed boric acid–boric anhydride mixture (*18*, *20*). All attempts to add hydrobromic acid to allyl boronic acid to form the desired γ-bromopropylboronic acid met with failure due to its instability to both heat and peroxides. Interest then turned to repeating the work of Booth and Kraus (*3*), who reported the formation of an oily polymer stable to boiling alkali and peroxide. They prepared the polymer from butyldichloroborane and liquid ammonia in the presence of sodium and reported a

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boiling point of 100° to 110° at 5 microns. The authors' results gave a mobile liquid boiling at 34°C. at 5 microns, which was immediately identified as *B*-tributylborazene. Both this work and the preparation of the intermediate butylboron dichloride paralleled the effort of Buls (*5*). At the time this work was done we were not aware of Buls' (*5*) classified reports, which are now declassified and available from ASTIA. An improved synthesis of the alkyl halides was later described by Buls (*6*). When sodium was omitted, the reaction of alkylboron dichlorides and ammonia gave yields of up to 90% of substituted borazenes.

Borazenes

Efforts were next directed toward the formation of borazoles with α-unsaturated alkylene groups on the boron, which might be transformed to long-chain polymers through reduction of the borazene resonance. Any tendency to fill the vacant orbitals of the boron from the π electrons or the α double bond should enhance the possibility of linear *vs.* cyclic polymer formation.

The most readily available intermediate was β-chlorovinylborane dichloride, most readily prepared by passing a metered flow of acetylene and boron trichloride over a mercurous chloride–charcoal catalyst (*2*).

An apparatus was designed and put into operation, whereby acetylene was passed into a continuously recirculating flow of boron trichloride (*21*).

When ammonia gas was passed into a solution of β-chlorovinylborane dichloride in ether, a 70% yield of crude tri-β-chlorovinylborazene was obtained.

Earlier the reaction was tried in benzene solution, but the product was difficult to purify and gave insoluble materials, presumably polymers, when refluxed in benzene. The ether-prepared material appeared stable when refluxed in the polar solvents dioxane and acetone and the solvent when evaporated gave a colorless glass. This was presumed at first to be the desired polymer, in spite of one negative viscosity determination in dimethylformamide. The work was later repeated with acetone; only 10% of the material was an ether-insoluble cream-colored solid. This solid may be a polymer but a Rast camphor molecular weight determination gave results open to question. It was shown, however, that tri-β-chlorovinylborazene in refluxing acetone rapidly picked up moisture, and a hydrolysis product, β-chlorovinylboronic acid, was identified in the ether-extractable portion of the dried product. The dryness of the acetone (dried over Drierite) was also an uncontrolled factor.

Conclusions

B-tri-β-chlorovinylborazole under certain conditions gave products that appeared to be polymers. This conclusion is primarily due to their insolubility in all solvents except dimethylformamide. There is no direct structural evidence, however, of either ring or chain polymer formation. Further work on more stable borazoles lacking the β-halogen group will have to be undertaken before the problem can be solved. Furthermore, the possibility of cross-linked polymers being formed through the vinyl function of the side chain must also be borne in mind.

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The cooperation and encouragement of Peter A. Van der Meulen and Charles E. Erickson, as faculty consultants, during the part of this work carried out at Rutgers University, are gratefully acknowledged, as is the active participation of the latter in the interpretation of infrared spectra, and the editing of reports.

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