THE PRODUCTION OF
REDUCED BORON COMPOUNDS
AND BORON HYDRIDES

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THE PRODUCTION OF REDUCED BORON COMPOUNDS AND BORON HYDRIDES

By

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ABSTRACT

The electrolytic reduction of n-butyl and n-amyl difluoroboranes in acetonitrile, triethylamine, and tetrahydrofuran was attempted. These solvents were not satisfactory for electrolytic studies of the alkyldifluoroboranes. Acetonitrile decomposed when electrolyzed, triethylamine would not conduct a current, and tetrahydrofuran reacted with the alkyldifluoroboranes. The alkyldifluoroboranes which were studied were not reduced electrolytically. Since the materials with which this research was concerned were air- and moisture-sensitive, the work was carried out in a high-vacuum system. The melting point, the vapor pressure curve, the infrared spectrum, and the mass spectrum were obtained for n-butyldifluoroborane. The vapor pressure data were used to calculate the boiling point, the heat of vaporization, and Trouton's constant.

Reactions of trimethoxyboroxine with sodium and calcium hydrides, sodium and lithium borohydrides, and boron trichloride were studied. The reactions of trimethoxyboroxine with the various hydrides or borohydrides, produced hydrogen, diborane, trimethoxyborane, and a white solid residue. To explain the products of the reactions, various possible reaction patterns are given. The following physical data were determined for the trimethoxyboroxine: vapor pressure values, infrared spectrum, and density. The boiling point, the heat of vaporization, and Trouton's constant were calculated from the vapor pressure data. It was determined that the trimethoxyboroxine is miscible with benzene, ethyl ether, acetone, carbon tetrachloride, chlorobenzene, and chloroform.

Tributoxyboroxine, a new compound, was prepared by reacting diboron trioxide with tri-n-butoxyborane. It was shown by molecular weight determination that this compound is a trimer. The compound freezes into a glasslike solid at approximately -75°C, and decomposes when heated. The infrared spectrum of the tributoxyboroxine is very similar to the infrared spectra of the trimethoxyboroxine. The density and some vapor pressure values were determined for this new compound. It was found to be miscible with benzene, chlorobenzene, acetone, carbon tetrachloride, and chloroform.

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INTRODUCTION

The purpose of this research has been the investigation of probable methods of obtaining reduced boron compounds and boron hydrides. Two different procedures were studied. The first procedure was to attempt the electrolytic reduction of alkyldifluoroboranes in nonaqueous solvents. The second method was the reacting of various hydrides, borohydrides, boron trichloride, or combinations of these with trimethoxyboroxine. The trimethoxyboroxine and its various solutions of hydrides or borohydrides were tested for electrolytic conductivity.

In the progress of this research information was collected which was not the primary objective of the problem. Tributoxyboroxine, a new compound was prepared and characterized. Physical and chemical properties of trimethoxyboroxine, tributoxyboroxine, and n-butyldifluoroborane were determined. Qualitative solubilities of these three compounds were determined in various organic solvents.

The alkyldifluoroboranes studied were n-butyldifluoroborane and n-amyldifluoroborane. At room temperature these compounds are liquid, whereas the corresponding methyl, ethyl, and propyl compounds are gases. The methyl, ethyl, and propyl haloboranes disproportionate easily into boron trihalides and the corresponding boron trialkyls (11, 30). The n-butyl and n-amyldifluoroboranes do not disproportionate (15). Since the alkyl difluoroboranes are air-sensitive, the reactions were carried out in a high-vacuum system. There had been no previous electrochemical studies on the alkyldifluoroboranes recorded in the literature.

Electrochemical studies of boron trifluoride have been reported. In their review on boron trifluoride coordination compounds, Greenwood and Martin (22) discuss the electrolysis and method of ionization of various boron trifluoride coordination compounds. When the methyl etherate of boron trifluoride is electrolyzed, the gases formed at the electrode are the result of boiling the compound (4). A study by Greenwood et al. (19) revealed that, when boron trifluoride ethyl etherate was electrolyzed, it gave hydrogen, ethane, and ether at the cathode but the boron trifluoride was unchanged. Boron trifluoride in acetic acid gave hydrogen and boron trifluoride at the cathode, and oxygen, ethane, carbon dioxide, and boron trifluoride at the anode (20). These same workers found that boron trifluoride methyl alcoholate conducted and gave hydrogen at the cathode (21).

Electrolytic reduction of boron tribromide in nitrobenzene, pyridine, and quinoline was not successful (31). The same authors attempted the reduction of boron tribromide in nitrobenzene, pyridine, and quinoline by electrodepositing alkali metals from these solutions (31). Lithium and potassium were deposited but the boron tribromide was not reduced (31). The literature survey showed that electrolytic reduction of boron halides was not successful.

There is some evidence that a decrease in the boron to halogen bond energy results when an alkyl group is substituted for a halogen in boron halides. Becher (3) concluded from Raman spectra that the boron-chlorine bond in boron trichloride and methyldichloroborane is stronger than in dimethylchloroborane. It would seem that, if the energy of the boron halogen bond is lowered, the molecule might be more susceptible to electrolytic reduction. With this thought in mind, compounds were studied that had an alkyl group substituted for one of the fluorines of boron trifluoride.

If the alkyldifluoroboranes were reduced electrolytically to produce boron at the cathode, the boron would probably be in an active form. This active boron might possibly react with cathodic hydrogen to produce boron hydrides. Another reduction product possibility was the formation of a compound which had a boron-to-boron bond. These compounds might occur if either one of the boron-carbon bonds or the boron-fluorine bonds broke and two of the fragments combined. From this speculation, one would expect compounds of the type $B_2R_2F_2$, where R is an alkyl group, or B_2F_4. Diboron tetrachloride, a known similar compound, reacts with hydrogen to give decaborane (32).

At first, trimethoxyboroxine was investigated as a solvent for electrochemical studies. It was found that it would not conduct a current. During the investigation of a solution of sodium borohydride in trimethoxyboroxine to determine whether or not it would conduct a current, it was observed that, while there was no current passed, there was a reaction. The trimethoxyboroxine is a six-membered ring containing alternate boron and oxygen atoms with one methoxy group attached to each boron atom. These cyclic structures were originally called boroxoles by Wiberg (47, 48) in analogy to borazoles. However, Schaeffer and Wartig (35) have recently suggested the name boroxine for the boroxole, and borazine for the borazole. Since Schaeffer and Wartig have devised a systematic nomenclature for the boron compounds based on the hypothetical borane (BH_3), their system will be followed in this thesis.

The cyclic structure is rather common in boron chemistry. A borosulfole ($B_3S_3H_3$) has been prepared (50). Investigation of Raman spectra and X-ray diffraction data indicates that boron trioxide and metaboric acid have B_3O_3 rings (18, 41, 43). Kinney and Pontz (24) prepared phenyl or substituted phenyl boroxoles by heating the corresponding boronic acid at 110°C. The molecular weights were determined cryoscopically in nitrobenzene. Johnson et al. obtained the tributyl or trihexyl boroxole by dehydrating the corresponding boronic acid with phosphorus pentoxide, concentrated sulfuric acid, or thionyl chloride (25). The trimethylboroxole was prepared by Burg (8) from methylboronic acid by dehydration over calcium sulfate. Attempts to prepare the parent $B_3O_3H_3$ by reacting the trimethylboroxole with B_2H_6 or borazole ($N_3B_3H_6$) were not successful. From their electron-diffraction work, Bauer and Beach (1) concluded that trimethylboroxole existed as a cyclic structure. The trimethylboroxole has been prepared by hydrolysis of hexamethyl borazole (46, 49). The trifluoroboroxole is formed by passing boron trifluoride over boron trioxide at 250°C (2). Using the above method, Goubeau and Keller prepared the trifluoro, trichloro, and tribromo boroxoles (16, 17). These compounds are stable only above 250°C. The same workers used the reaction between boron trioxide and trimethylboron, trimethylborate, or tri-dimethylaminoboron at higher pressures to prepare the corresponding boroxoles. The trimethoxyboroxole was also prepared by these same authors by reacting boron trioxide and trimethylborate in a one-to-one mole ratio, at 70°C, under atmospheric pressure (17). The trimethoxyboroxine used in this research was prepared by the latter method.

EXPERIMENTAL

Apparatus

High-Vacuum System

A high-vacuum system was necessary for reactions and electrolyses of the boron compounds. Two systems were used. The first system (Figure 1) was designed for the carrying out of chemical reactions, the purification of compounds, and the storage of reagents. The second system (Figure 2) was designed primarily for electrolyses, but it could be used for reaction, separations, purifications, or storage of reagents. In future discussions the latter system will be designated the electrolysis manifold. A photograph of this system is included (Figure 3). The volumes of the various parts of the system were determined by allowing helium gas of known volume and pressure to expand into the evacuated unknown volume and measuring the new pressure. From the relationship $P_1V_1 = P_2V_2$, where V_1 is the known volume of helium at known pressure P_1, and P_2 is the pressure of the helium gas in the new volume, and V_2 is equal to that volume, the total volume can be calculated. The volume V_2 minus V_1 equals the new volume. Table I gives

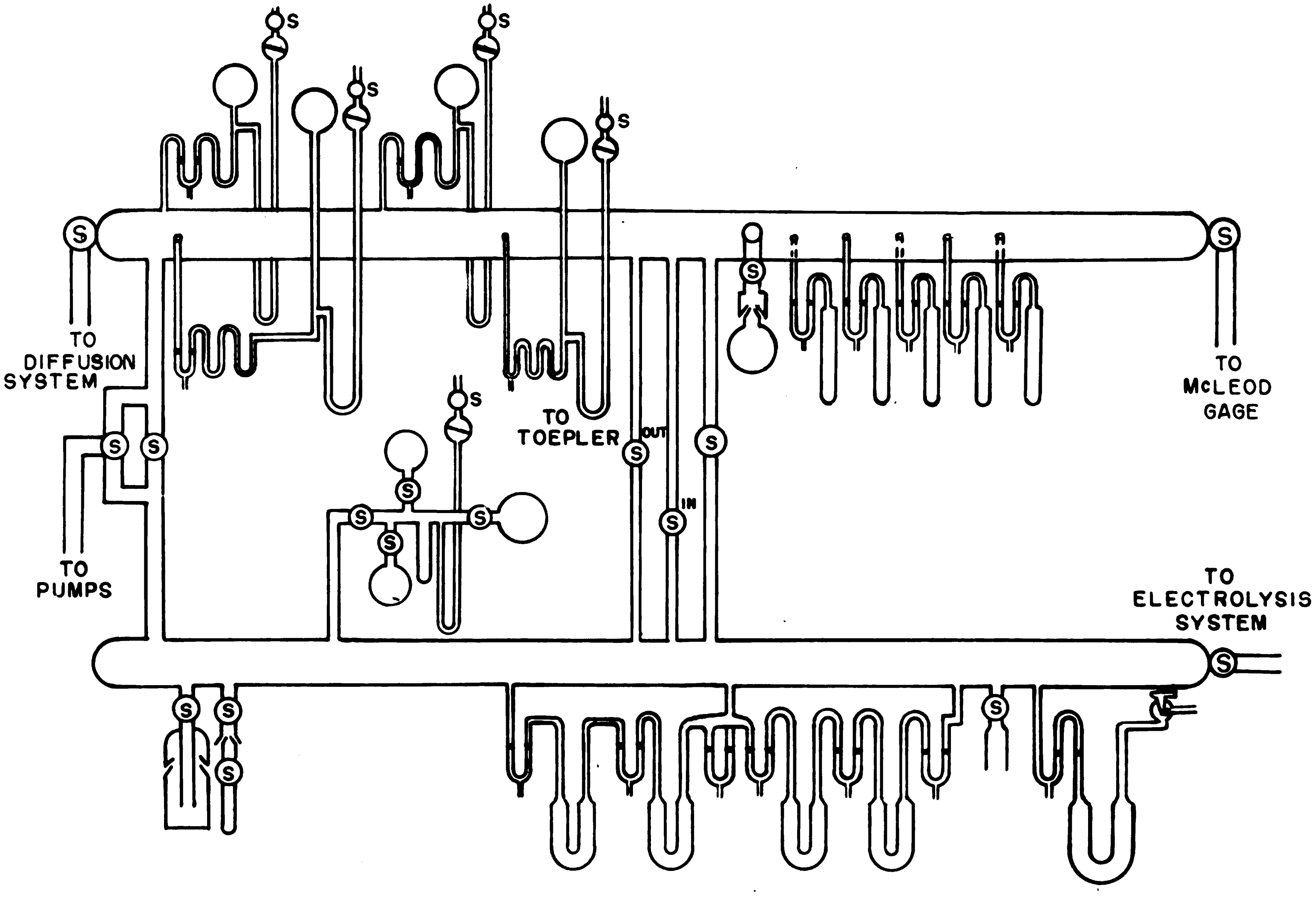

Fig. I PURIFICATION AND STORAGE VACUUM SYSTEM

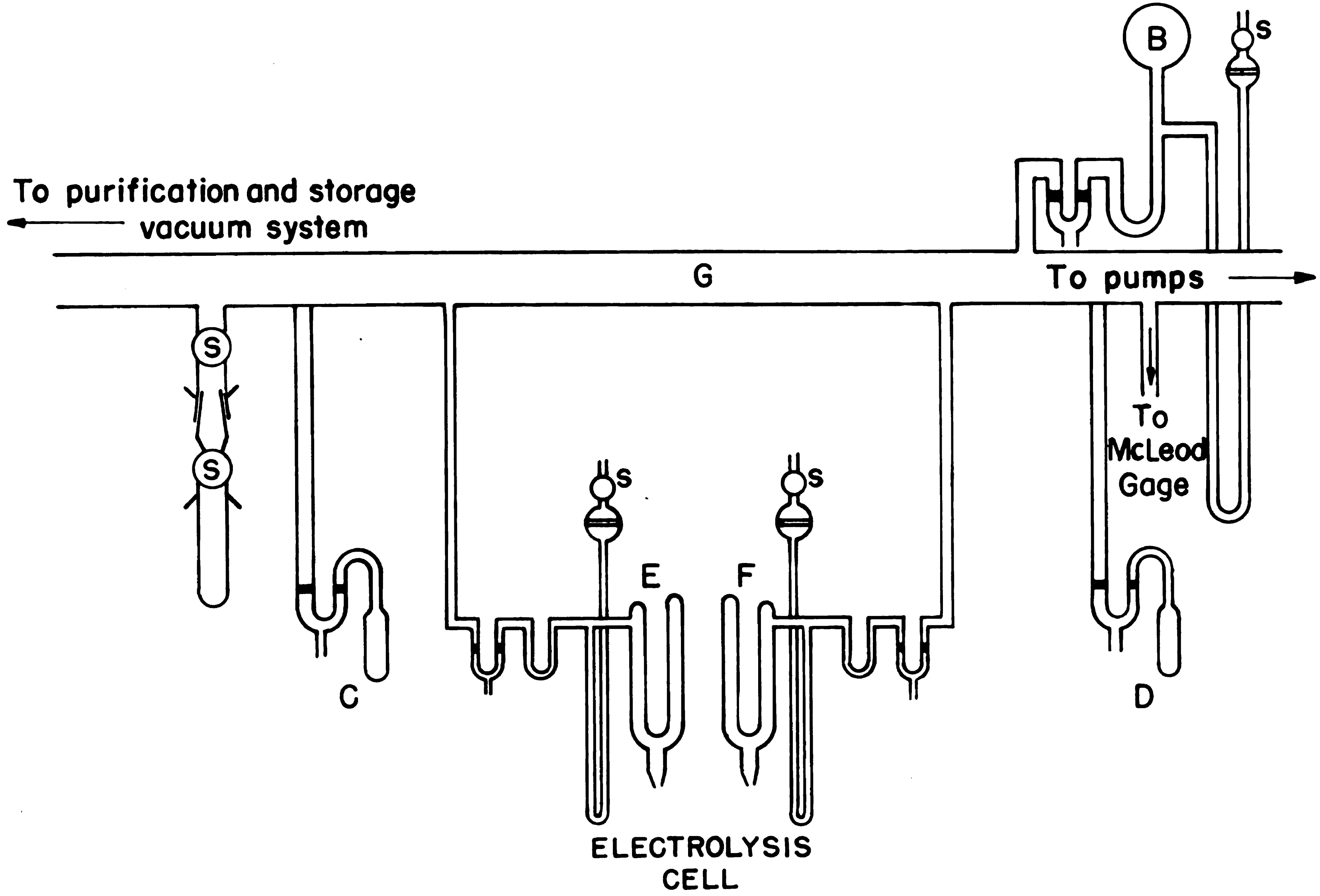

Fig. 2 ELECTROLYSIS MANIFOLD

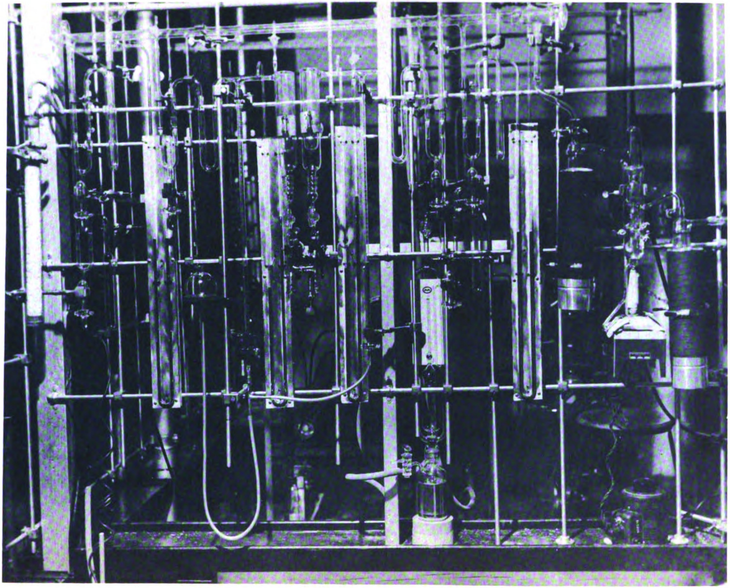

Figure 3
Electrolysis Manifold

TABLE I

VOLUMES OF THE VARIOUS COMPARTMENTS OF THE ELECTROLYSIS MANIFOLD

	Compartment	Volume (cc)
B	gas storage	741
C	liquid storage	114
D	liquid storage	118
E	electrolysis	338
F	electrolysis	319
G	manifold	863

the volumes of the various compartments of the electrolysis manifold.

In the area designated electrolysis cell (Figure 2), various electrolysis cells could be inserted into the system using 24/40 ₮ ground-glass joints. Three electrolysis cells were used during the investigation. Cell "X" was a large H-shaped electrolysis cell (Figure 4) with a glass frit in the center. The electrodes were two square centimeters in area. This cell, which needed a 60 ml. volume to cover the electrodes, was used only with solutions of which there was a large quantity available. Also, the sintered glass frit, used to separate anode and cathode compartments, made the cell highly resistive to current passage. Eventually a small hole was made in the frit to allow better transfer of solution.

Cell "Y" was a small H-shaped electrolysis cell (Figure 5). This cell required only eight cubic centimeters to cover the electrodes and did not have as great a resistance as that of cell "X." A sintered glass frit was in the center of the H to separate anode and cathode compartments. Cell "Y" was difficult to work with because it had rigid glass joints which allowed no flexibility and caused strains in the glass system.

Cell "Z" (Figure 6) was designed to eliminate strains and was eventually used for most of the electrolysis work. In this cell two

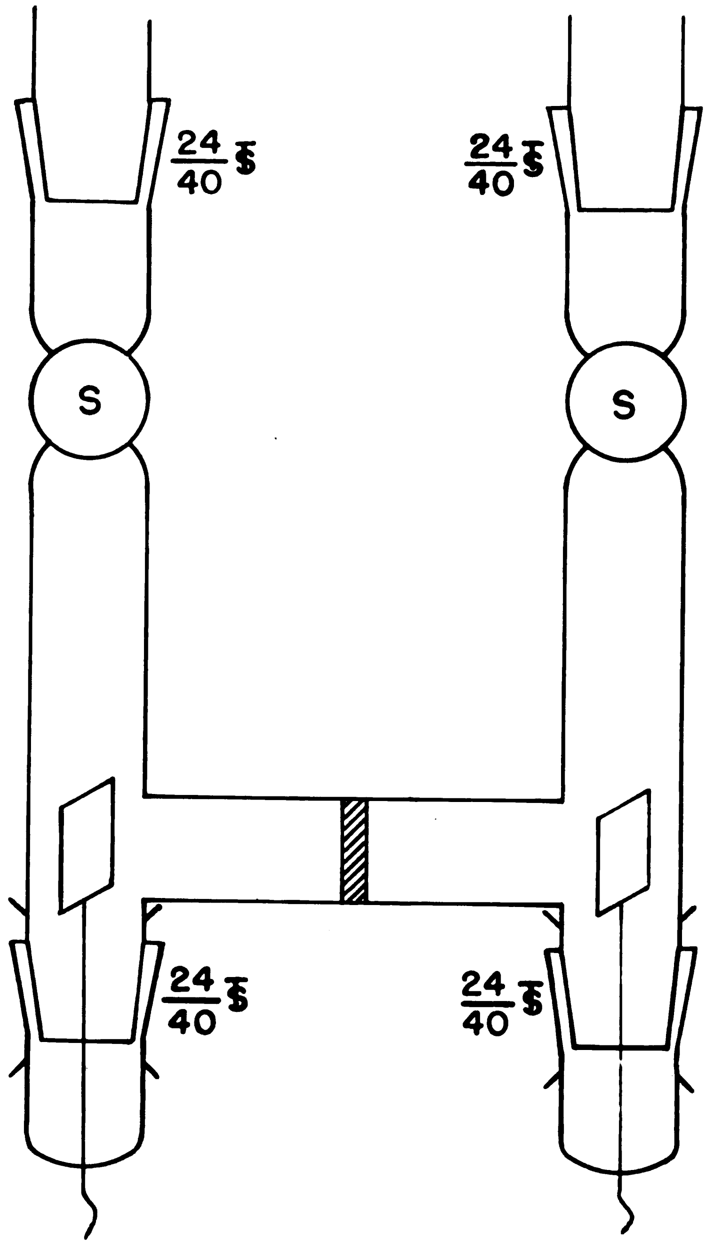

Fig. 4 ELECTROLYSIS CELL "X"

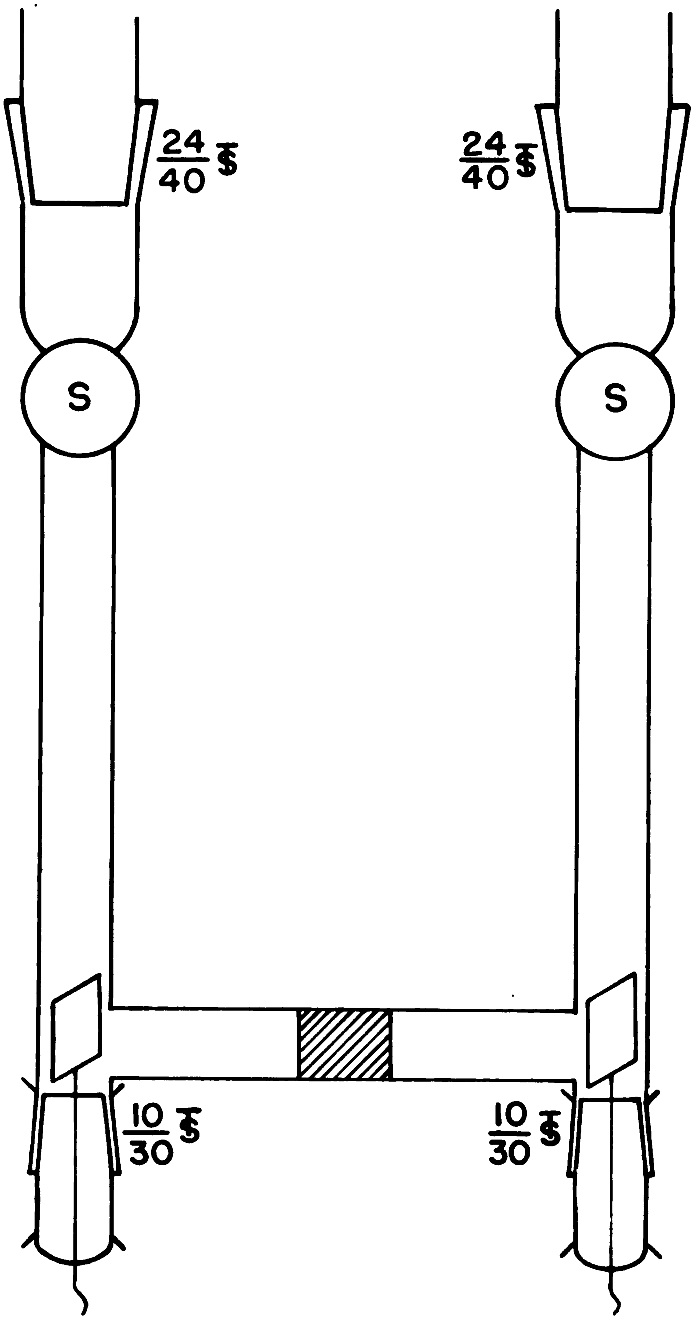

Fig. 5 ELECTROLYSIS CELL "Y"

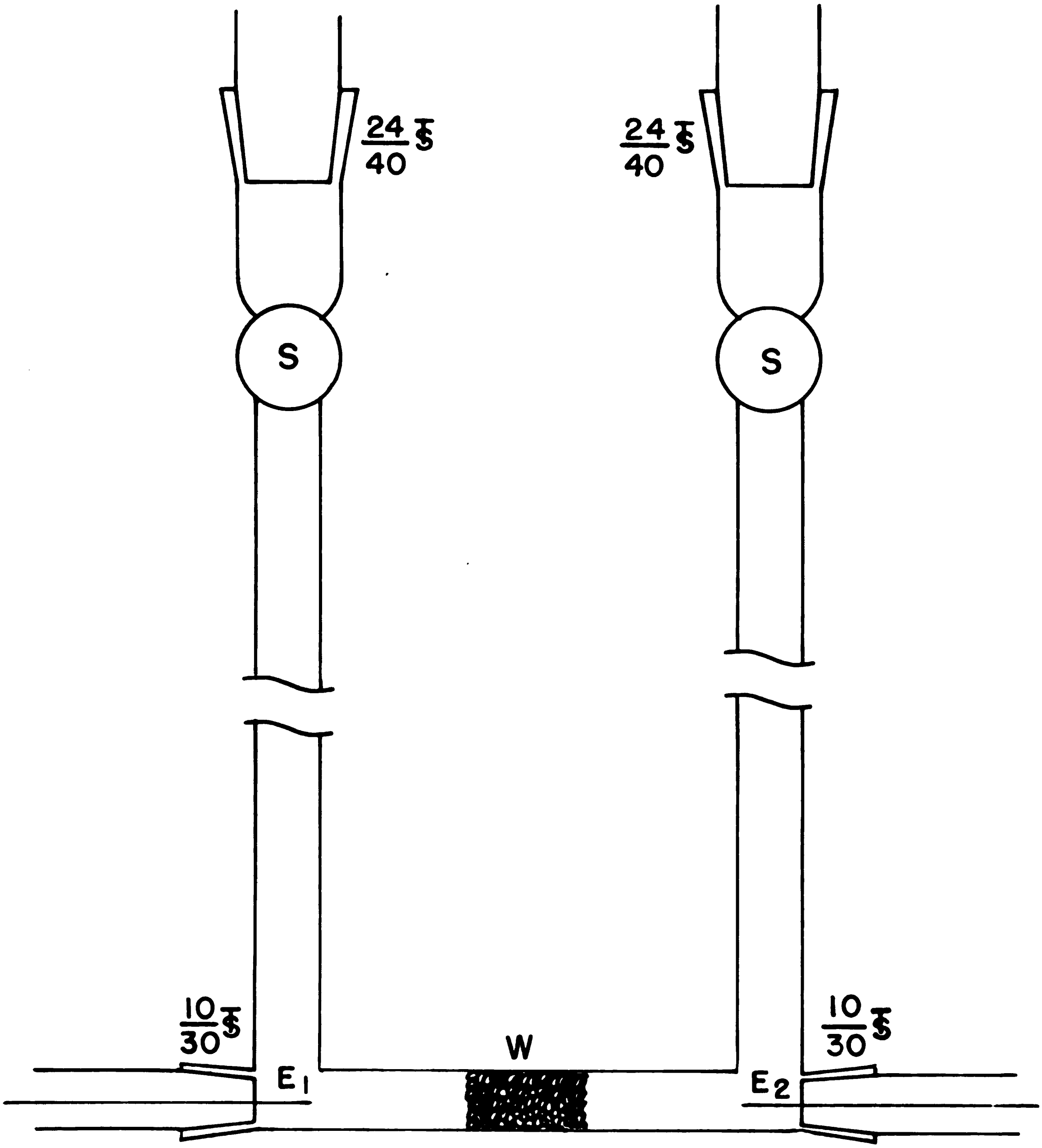

Fig. 6 ELECTROLYSIS CELL "Z"

pieces of polythene tubing joined the lower section to the 24/40 $\overline{S}$ glass joints which in turn connected the cell to the vacuum system. The polythene tubing was sealed in with Apiezon W wax and the whole joint was covered with Glyptal. The volume of the cell was eight to ten milliliters. The area of the electrode E_1 was 0.04 square inch (2.72×10^{-4} sq. ft.), and that of E_2 was 0.035 square inch (2.43×10^{-4} sq. ft.). The anode and the cathode compartments were separated by a wad of glass wool (W). The electrodes E_1 and E_2 were platinum wire, sealed in 10/30 $\overline{S}$ ground-glass joints which in turn were sealed in with Apiezon W wax.

Melting-Point Apparatus

Both the aluminum cooling block and the drop-weight melting-point apparatus were constructed according to Stock (40). The aluminum cooling block, in which there were three holes, was two inches in diameter and seven inches long. The hole which was filled with liquid nitrogen to cool the block was one inch in diameter and two and one-half inches deep. The hole used for the insertion of the drop-weight melting-point apparatus was nine-sixteenths of an inch in diameter and two inches deep. The hole for the thermometer was one-fourth inch in diameter and six inches deep. A toluene thermometer (-100°C) was used to determine temperatures. The aluminum cooling block was wrapped in glass wool and placed on Fromaglass in a Dewar flask.

The Stock drop-weight melting-point apparatus, shown in Figure 7, was attached through the 24/40 $\$$ joint to the vacuum system and evacuated. Then, using a magnet, the pointer was raised to its highest position. The material whose melting point was to be determined was frozen into a solid ring at M (Figure 7). The pointer was then dropped until it rested on the ring of frozen material. The melting-point apparatus would then be placed in the aluminum cooling block which was of the approximate temperature of the solid material. The temperature observed on the thermometer when the pointer dropped was the melting point of the material.

Isoteniscope

An isoteniscope (Figure 8) was used to measure vapor pressure above room temperature. The material whose vapor pressure was to be measured was placed in the bulb, frozen solid, and the system evacuated. Then the isoteniscope was immersed in the heated bath so that stopcock S_1 was partially covered. After the desired heating bath was put on the system, enough air was allowed in the manometer system to keep the assisting manometer balanced.

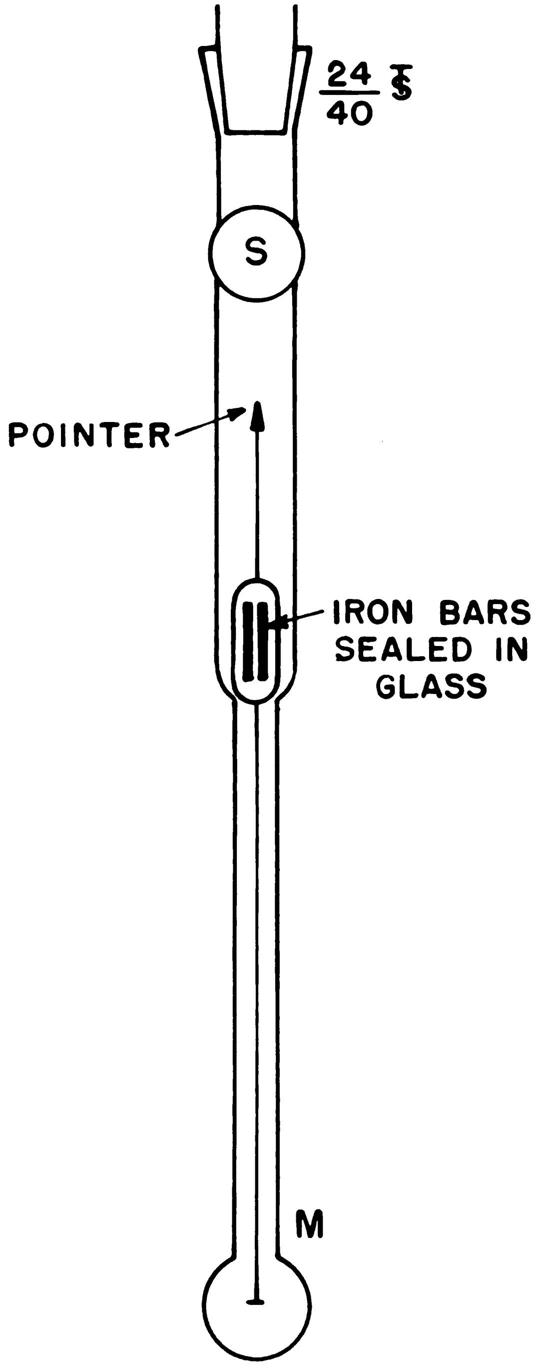

Fig. 7 STOCK DROP-WEIGHT MELTING-POINT APPARATUS

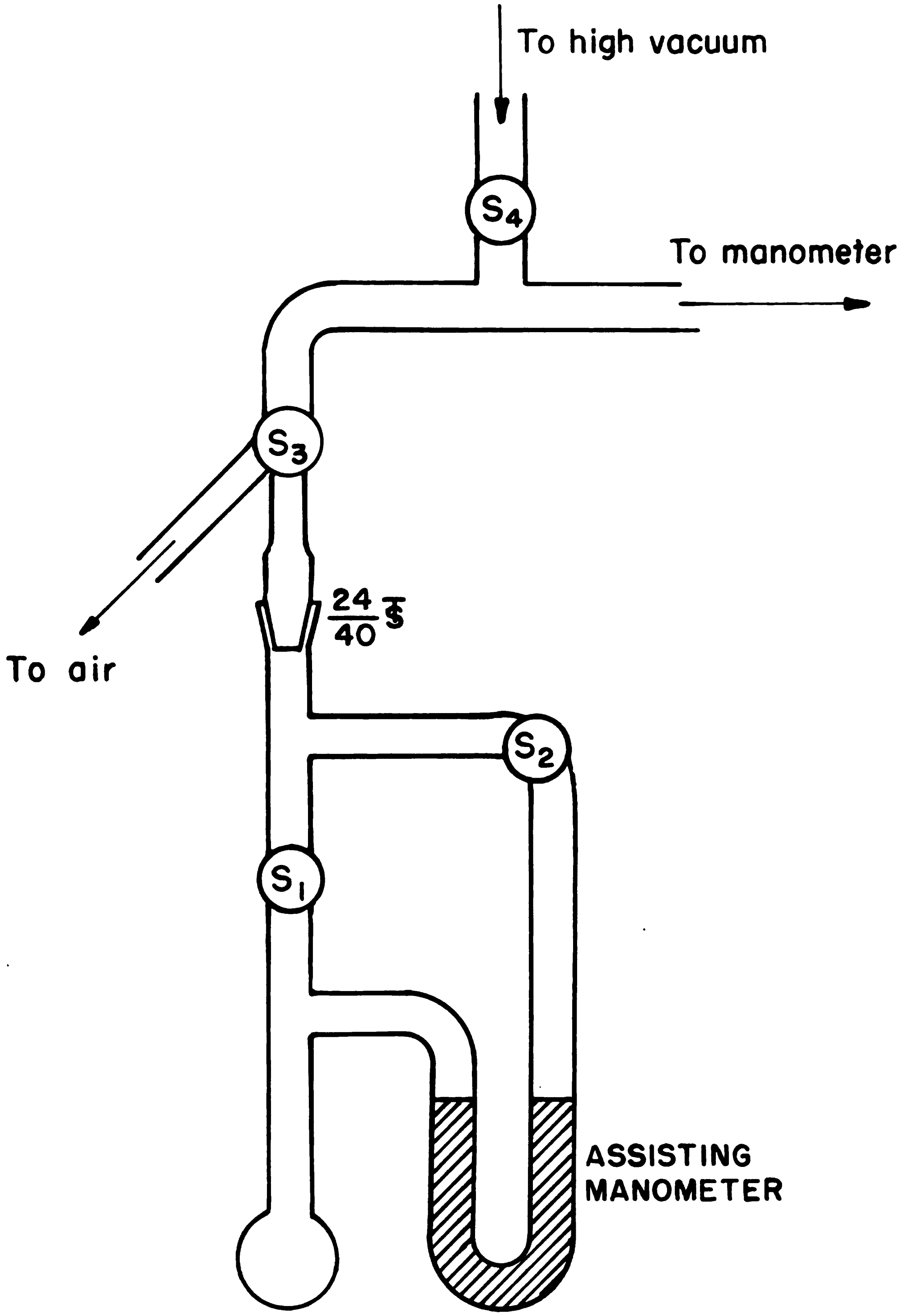

Fig. 8 ISOTENISCOPE

When the assisting manometer was level, the vapor pressure could then be read.

Dilatometer

The dilatometer was used to determine densities at various temperatures. Two dilatometers were prepared, each having bulbs with approximately ten-milliliter volumes. A one-milliliter pipette, graduated in 0.01 ml., was sealed to the bulb of the first dilatometer; to the bulb of the second was sealed a two-milliliter pipette, graduated in 0.1 ml. In future discussions they will be represented as the one-milliliter dilatometer and the two-milliliter dilatometer. The volumes of the bulbs, up to the zero line, were determined by filling them with mercury and weighing and then by weighing the bulbs empty. The volume, up to the zero line, of the bulb on the one-milliliter dilatometer was 11.041±0.001 ml. The volume, up to the zero line, for the two-milliliter dilatometer bulb was 13.66±0.01 ml.

Mass Spectrometer

This instrument was a Type 21-103B Consolidated Engineering Corporation model. The mass spectra data were obtained by Mr.

David Brown, of the Chemical Engineering Department, University of Michigan.

Infrared Spectrophotometer

The infrared spectra used in this work were obtained on a model 21 Perkin-Elmer Recording Infrared Spectrophotometer.

Fractionating Column

A 1.5 x 60 cm. glass helix packed, total reflux-partial take-off, Whitemore-Fenske Column, electrolytically heated, was used in purifying solvents and liquid reagents.

Reagents

Boron trifluoride and boron trichloride were obtained in cylinders from the Matheson Company, Joliet, Illinois.

Anhydrous C.P. ethyl ether was purified by distilling over Baker reagent-grade potassium hydroxide and anhydrous sodium sulfate and was stored over sodium ribbon.

DuPont tetrahydrofuran was fractionally distilled from Baker reagent-grade potassium hydroxide.

Commercial-grade Matheson acetonitrile was stored over Mallinckrodt analytical reagent-grade anhydrous potassium carbonate for seventy-two hours. The acetonitrile was fractionated and the fraction boiling between 80°C and 82°C was collected. The 80°-82°C fraction was treated with ten grams of phosphorus pentoxide per liter and then refractionated. The fraction boiling at 81°-82°C was used.

Trimethylborate (trimethoxyborane) and n-butylmagnesium chloride were obtained from Anderson Laboratories, Weston, Michigan. These chemicals were used without further purification. Sodium hydride, calcium hydride, sodium borohydride (sodium tetrahydridoborate), and lithium borohydride (lithium tetrahydridoborate) were obtained from Metal Hydrides. They, too, were used without further purification. Triethylamine was purified by fractionally distilling over anhydrous calcium sulfate. The fraction boiling between 88°C and 90°C was collected.

Matheson dimethylformamide was allowed to stand over potassium hydroxide for twelve hours and then over calcium oxide for twenty-four hours. It was fractionated and the fraction boiling at 150°C was collected.

The boron trioxide (diboron trioxide) was Baker's Boric Anhydride, Purified. This contained impurities of iron which could not be removed.

The tri-n-butylborate (tri-n-butoxyborane) was obtained from the American Potash and Chemical Corporation. Their analysis gave

4.70 percent boron; this is the theoretical percentage of boron in tri-n-butylborate (tri-n-butoxyborane).

Acids, solvents, and other common reagents used were those from the stockroom.

Procedure

Electrolytic Studies of n-Amyldifluoroborane

A commercial sample of n-amyldifluoroborane was used in this investigation. The n-amyldifluoroborane is a colorless liquid that fumes in air and has a boiling point of 65.0°C to 65.3°C. Solutions of n-amyldifluoroborane in various solvents were prepared for later use in electrolytic studies. These solutions were subjected to electrolysis to determine whether or not they conduct a current and to see what reactions would take place.

Preparation of solutions

Preparation of solutions of n-amyldifluoroborane with acetonitrile, tetrahydrofuran, and dimethylformamide was carried out in a dry box in a nitrogen atmosphere. Two milliliters of n-amyldifluoroborane was dissolved in 30 milliliters of acetonitrile. White fumes were evolved, but the solution did not seem to become warm. This lack of heat would indicate that there was no complex formation. The solution, which was clear and colorless, was transferred to the electrolysis manifold for use in electrolytic studies.

When two milliliters of n-amyldifluoroborane was dissolved in 30 milliliters of tetrahydrofuran only a small amount of fuming was observed, but a considerable amount of heat was liberated. The heat evolved indicated that either complex formation or a reaction had taken place. The solution, also clear and colorless, was stored for later electrolytic use.

Dense white fumes were evolved but there was no heating when two milliliters of n-amyldifluoroborane was dissolved in 30 milliliters of dimethylformamide. This clear, colorless solution was also stored for later electrolytic use.

Electrochemical observations

Cell "Y" was used for the electrolytic studies. The n-amyldifluoroborane-acetonitrile solution described in the above section had a total volume of 32 ml. Since the cell "Y" needed only eight milliliters to fill, there were four electrolyses run from the above solution. The voltage was obtained from a 110 volt D.C. generator and the current was measured on a milliammeter. A leak in the vacuum system developed during electrolysis of the first eight milliliters of

the solution and that portion had to be discarded. Since the other three electrolyses were run under similar conditions, only one of these will be described in detail.

Eight milliliters of the n-amyldifluoroborane-acetonitrile solution was transferred from the storage cell to the electrolysis cell by placing an isopropyl-dry ice mixture in the condensers above the anode and cathode compartments (E and F, Figure 2), and letting the liquid transfer by vapor diffusion. The liquid in the electrolysis cell was allowed to adjust to room temperature (25°C to 27°C) so that the liquid level and the vapor pressure were equal in each arm of the cell. Pressure in both anode and cathode compartments was 100 mm. A potential of 98 volts was applied; this gave a current of seven to eight milliamperes. The electrolysis was continued for 40 minutes. A gas was evolved immediately at the cathode but there was no noticeable change at the anode. The cathode compartment became a distinct yellow color. The pressure increase of the cathode compartment over the anode compartment was 12 mm. The electrolysis cell was closed off from the gas in the cathode compartment and a -196°C bath was put on the trap in the cathode compartment. The pressure was reduced to five milliliters. Thus there were five milliliters of gas which had to be either hydrogen or methane. In this particular electrolysis, the condensed gas was transferred into an infrared cell and its spectrum was determined. Pressure in the infrared cell was approximately 168 mm. Acetonitrile was used in the reference cell. The resulting spectrum showed only bands of acetonitrile and n-amyldifluoroborane. The spectrum of acetonitrile at 95 mm. pressure was determined in this laboratory (see Figure 11, Curve A), while that of n-amyldifluoroborane was in the literature (15).

The gas produced in the third electrolysis was tested for boron and fluorine. The gas sample was transferred into a bulb which contained ten milliliters of water and the hydrolyzed solution was titrated, using mannitol, for boric acid (28). A percentage of 7.49 boron was found but the gas sample undoubtedly contained some acetonitrile impurity. The percentage of boron in n-amyldifluoroborane is 9.03. However, the acetonitrile present in the sample would cause a lower percentage of boron than would be expected in the pure compound. By using two spot tests (12, pp. 202-3), the solution was tested for fluorine. The first test was the addition of a small amount of calcium chloride solution to the sample to see if insoluble calcium fluoride would precipitate. The second test was with a zirconium-alizarin solution which turns from red to yellow in the presence of fluoride, even if the fluorine is in such compounds as boron trifluoride or fluoroborate. No fluorine was detected by either test.

The gas from the fourth electrolysis was left in the vacuum system and disappeared overnight. Since there was mercury in a trap of the system, it was thought that the gas had dissolved in it. (The author had observed many times before that gases and vapors will dissolve in mercury.) The mercury was heated and a yellow solid was driven off which condensed on the cooler glass tubing. This yellow solid was not noticed in any subsequent electrolytic runs.

An infrared spectrum run on the solution left in the cell after electrolysis indicated that acetonitrile, n-amyldifluoroborane, and possibly other products were present in the solution.

Observations of solutions of n-amyldifluoroborane in tetrahydrofuran and dimethylformamide

The solution of n-amyldifluoroborane in tetrahydrofuran, described previously on page 23, was found to have changed, upon standing, to a viscous liquid. When the author attempted to transfer the liquid to the electrolysis cell by vapor diffusion, a clear liquid distilled off, leaving behind a jellylike mass. The clear liquid had a boiling point of 70°-71°C at 760 mm., whereas the boiling point of tetrahydrofuran is 64°-66°C. The reaction between tetrahydrofuran an n-amyldifluoroborane excluded further investigation of tetrahydrofuran as a solvent for electrolysis.

The solution of n-amyldifluoroborane in dimethylformamide was rather difficult to transfer by vapor diffusion because it would condense on the glass throughout the system. However, the solution was left in the electrolysis system overnight and the dimethylformamide dissolved away the Apiezon W wax and the Glyptal which had been used to seal a leak in the system. An atmosphere of air had contaminated the solution and it had to be discarded.

Electrolytic Studies of n-Butyldifluoroborane

n-Butyldifluoroborane was prepared for use in electrolytic studies. Solutions of this compound dissolved in various solvents were investigated to determine whether or not they would conduct a current and to see what reactions would take place when the solutions were electrolyzed.

Preparation

The n-butyldifluoroborane was prepared according to Glunz (15) except that n-butyl magnesium chloride was used instead of n-butyl magnesium bromide. Two steps were involved in its preparation. The first was preparation of n-butyldihydroxyborane; the second was the reaction of this material with boron trifluoride to give the desired product. These reactions are represented by the equations:

(1) $(CH_3O)_3B + C_4H_9MgCl \longrightarrow C_4H_9B(OCH_3)_2 + CH_3OMgCl$

(2) $C_4H_9B(OCH_3)_2 + 2H_2O \longrightarrow C_4H_9B(OH)_2 + 2CH_3OH$

(3) $3C_4H_9B(OH)_2 + 3BF_3 \longrightarrow (C_4H_9BO)_3 + 3BF_3H_2O$

(4) $(C_4H_9BO)_3 + 2BF_3 \longrightarrow 3C_4H_9BF_2 + B_2O_3$

The procedure for the preparation of n-butyldihydroxyborane was as follows. A sealed stirrer, an inlet tube for nitrogen, and a Y tube were fitted to a one-liter, three-neck, round-bottomed flask. One neck of the Y tube was fitted with a 500-ml. separatory funnel, and the other neck was the outlet for the nitrogen, which was also connected to the separatory funnel by a Y tube. The nitrogen passed through the outlet tube to a sulfuric acid bubbler. Anhydrous ethyl ether (200 ml.) and trimethoxyborane (75 g., 0.72 mole, 82 ml.) were placed in the reaction flask. The n-butyl magnesium chloride (170 ml. of 3N.; 0.51 mole) and 130 ml. of anhydrous ethyl ether were placed in the separatory funnel. For about 30 minutes prior to the addition of the n-butyl magnesium chloride, a slow stream of dry nitrogen gas was allowed to flow through the reaction flask. A Dewar flask containing isopropyl alcohol and dry ice was placed around the reaction flask. Efficient cooling was essential. The stirrer was started and the n-butyl magnesium chloride was added over a period of three hours. After this, the reaction flask was left in the dry ice-isopropyl alcohol bath, and overnight a solid, white precipitate appeared. Three hundred milliliters of 10 percent sulfuric acid, by volume, was then used to hydrolyze the reaction mixture. The flask was cooled with a -78°C bath and the reaction mixture was stirred while the sulfuric acid was being added. While the stirring continued, the cooling bath was removed and the mixture was allowed to warm to room temperature. The small amount of solid remaining in the water layer was dissolved by the addition of 200 ml. of water. A separatory funnel was used to separate the water and the ether layers. The water layer was then extracted with two 50 ml. portions of ether.

The ether solutions obtained by the above procedure were placed in a distilling apparatus and distilled until the temperature reached 60°C. Then ten milliliters of water was added to the flask and the distillation was continued slowly until the temperature reached about 80°C. The hot liquid residue was poured into a 250 ml. beaker and cooled in crushed ice. White crystals separated and were filtered on a Buchner funnel and were either dried in a nitrogen-filled desiccator over 65 percent sulfuric acid, or used immediately to prepare n-butyldifluoroborane.

The n-butyldifluoroborane was prepared by reacting boron trifluoride with n-butyldihydroxyborane as follows. A simple distillation head was attached to a 24/40 ₮ single-necked, round-bottomed, 250 ml. flask. The 10/30 ₮ thermometer on the distilling head was replaced by a 10/30 ₮ seal-through addition tube. A water-cooled condenser, connected to a vacuum adapter and a 100 ml. receiver, was attached to the distilling head. The addition tube (which extended to the bottom of the flask) was used for the addition of boron trifluoride. A heating mantel was placed around the flask. Boron trifluoride was passed through concentrated sulfuric acid, a mercury safety valve, the addition tube, and into the apparatus. The gases leaving the reaction flask passed through the receiver (which rested in an isopropyl alcohol-dry ice bath), into the vacuum adapter, into an isopropyl alcohol-dry ice trap, and was finally bubbled through concentrated sulfuric acid. The system was flushed out with boron trifluoride. The previously prepared n-butyldihydroxyborane was added to the reaction flask and boron trifluoride was passed into the system. The flask warmed and the acid began to liquify. The reaction mixture separated into two liquid layers and after the absorption of boron trifluoride had decreased the reaction flask was heated at a low heat with a heating mantle to distill out the upper layer. The upper layer was tri-n-butylboroxine and the lower layer was boron trifluoride hydrate. The heating caused the volatile reaction product, n-butyldifluoroborane, to distill over into the receiver. The n-butyldifluoroborane was easily separated since its boiling point is low (37.3°C/760 mm.) and the diboron trioxide formed goes into the lower liquid layer. The product in the receiver was fractionated through the column described on page 20. The fraction boiling at 36°-37°C was collected.

Physical properties

The n-butyldifluoroborane is a colorless liquid that fumes in air. It was not spontaneously ignited in air. It has been reported (15) that it has a boiling point of 36.3° to 36.5°C, and a density of 0.8510 g./cc. at 25°C. The same worker found that n-butyldifluoroborane did not disproportionate on distillation (15). The melting point (-74°C), infrared spectrum, cracking pattern in the mass spectrometer, and the vapor pressure curve were determined in this laboratory. The melting point was determined by the method described on page 15. The infrared spectrum (Figure 9) was determined for the n-butyldifluoroborane in the gas phase at 170 mm. pressure.

The cracking pattern of the n-butyldifluoroborane in the mass spectrometer was useful in interpreting the mass spectrum charts

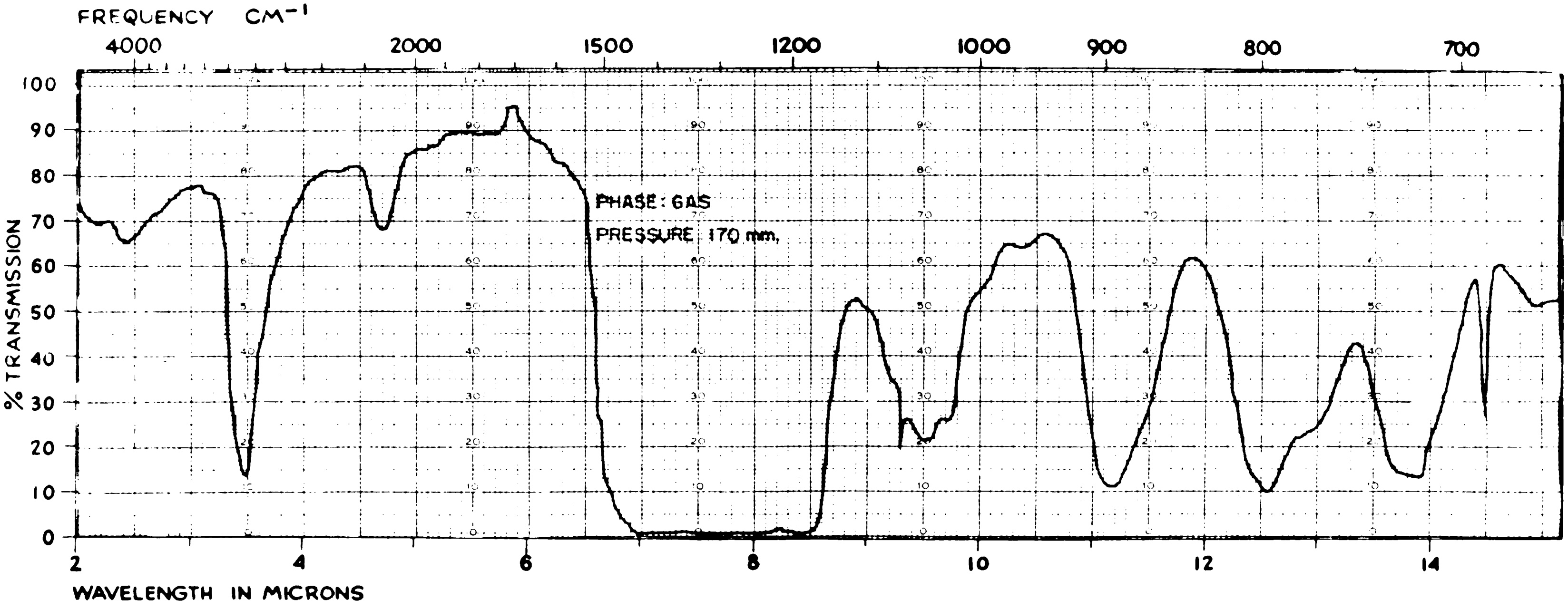

Figure 9

Infrared Spectrum of n-Butyldifluoroborane which were obtained for the cathode gases evolved in electrolytic studies. The mass spectrum of n-butyldifluoroborane, at a 125 volt emission potential, gave all the possible fragments of the molecule. Since the cracking pattern was available, it was thought that a determination of the relative amounts of fluorine and n-butyl lost from the molecule when it cracked might be of value in predicting which bonds would be broken by electrolysis. The data indicated that 60 percent of the n-butyldifluoroborane molecules that decomposed in the mass spectrometer lost a butyl group, and 40 percent lost a fluorine group.

The vapor pressure curve was determined by condensing a portion of the n-butyldifluoroborane in the U trap of the gas storage bulb "B" of the electrolysis manifold (Figure 2). A Dewar flask filled with solvents which gave the desired temperatures was placed around the U trap. The solvents used in the Dewar flask were: water (for temperatures between 0° and 25°C), carbon tetrachloride cooled with liquid nitrogen (for temperatures between 0° and -22.9°C), and chlorobenzene cooled with liquid nitrogen (for temperatures between -22.9° and -45.2°C). The Dewar flask held the temperature fairly constant. The variance in temperature for readings from 0° to 25°C was ±0.3°C; this was much less than at temperatures below 0°C where the variance ranged from ±0.4° to ±0.8°C. A National

Bureau of Standards thermometer was used for temperatures from 0° to 25°C and a toluene thermometer was used for those temperatures below 0°C. The toluene thermometer was calibrated using the ice point, carbon tetrachloride solid in equilibrium with carbon tetrachloride liquid (-22.9°C), chlorobenzene solid in equilbrium with chlorobenzene liquid (-45.2°C), and chloroform solid in equilibrium with chloroform liquid (-63.5°C). The corrected values of temperature are given in Table II. The pressure was read on a meter stick attached to the manometer. Values were estimated to a tenth of a millimeter and then rounded off to the nearest millimeter. The extrapolated boiling point from the vapor pressure curve (Figure 10) was 37.4°C/760 mm. The vapor pressure for temperatures between 0° and 25°C is given by the equation

$$\text{Log P mm.} = -1449/T + 7.548$$

where T is in °K. The boiling point (37.4°C/760 mm.), heat of vaporization (6.6±0.2 kcal./mole), and Trouton's constant (21.3) were calculated from this equation. The equation was calculated by the least squares method (10). The calculated values gave a maximum deviation of 2 percent from the observed values.

TABLE II

VAPOR PRESSURE DATA FOR n-BUTYLDIFLUOROBORANE

Temperature (°C)	Pressure (mm.±1)
24.5	480
19.2	399
15.7	345
12.5	301
6.4	227
0.0	174
- 5.3	132
- 9.8	101
-15.8	76
-22.6	45
-30.1	29
-35.3	22
-43.5	12

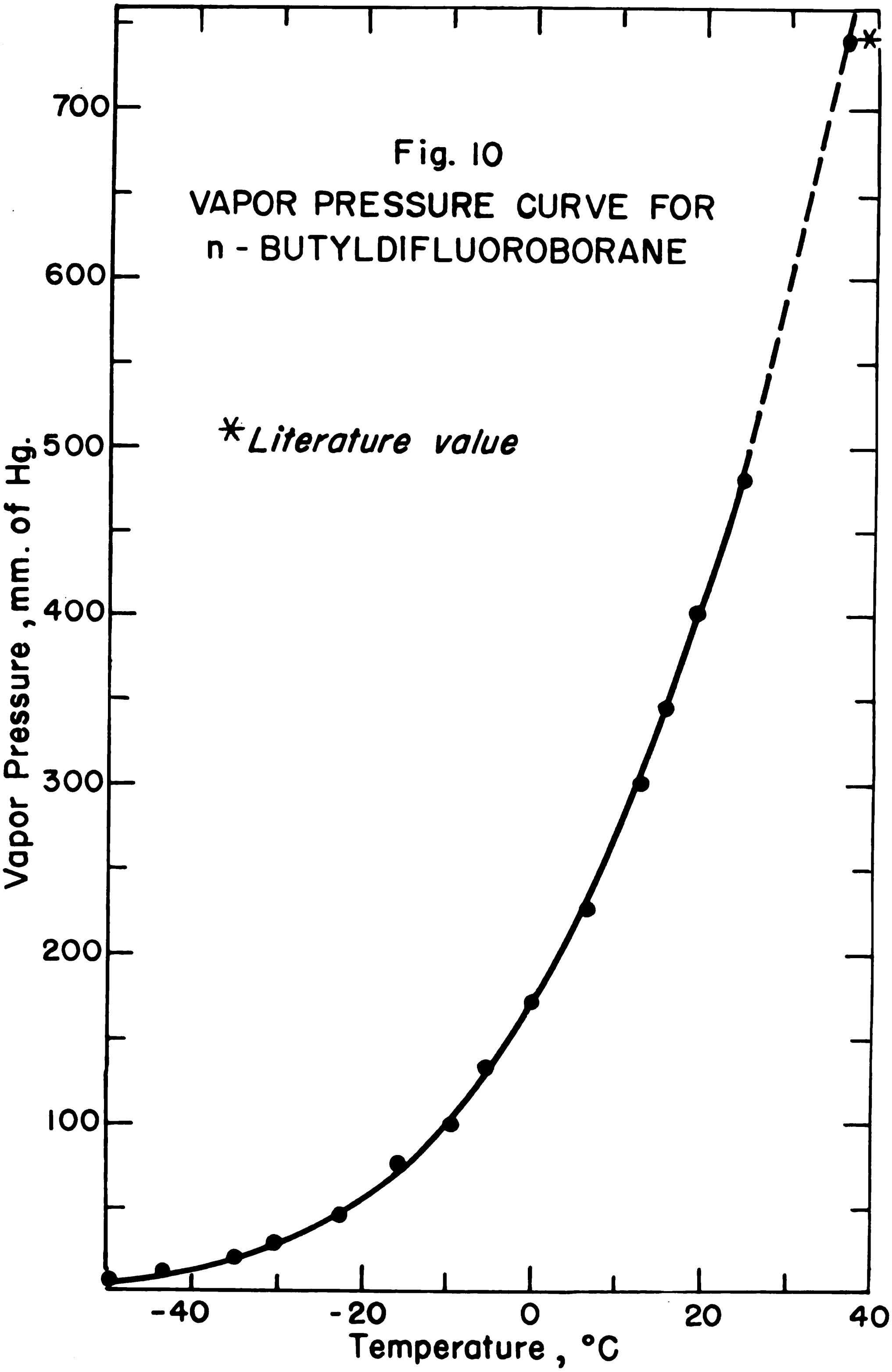
Fig. 10
VAPOR PRESSURE CURVE FOR
n - BUTYLDIFLUOROBORANE
*Literature value
Vapor Pressure, mm. of Hg.
700
600
500
400
300
200
100
-40
-20
0
20
40
Temperature, °C

Investigation of complexes with n-butyldifluoroborane

One of the purposes of this work was to attempt electrolytic reduction of n-butyldifluoroborane. Since it did not conduct a current, n-butyldifluoroborane is presumably nonionizing. (This experiment will be described under electrochemical studies.) Literature studies indicated that complex compounds of boron trifluoride form ionized solutions which conduct readily. The mode of ionization of several boron trifluoride complexes has been given (22). Since a solution of n-amyldifluoroborane in acetonitrile conducted, it was decided to determine whether or not the n-butyldifluoroborane formed a complex with acetonitrile (which might be ionizable) facilitating electrolysis.

Acetonitrile (3.2 millimole, 79 mm. in 741 cc. volume) was condensed on n-butyldifluoroborane (3.2 millimole, 79 mm. in 741 cc. volume) in the U trap of gas storage bulb "B" of the electrolysis manifold (Figure 2) at -78°C. From this, one would have expected both the acetonitrile and the n-butydifluoroborane to exist as gases in the 741 cc. volume and give a total pressure of 158 mm. (79 mm. + 79 mm.). However, the trap was allowed to warm to room temperature (23°C) and the mixture gave a clear, colorless liquid with a vapor pressure of 133 mm. A melting point for this liquid

was determined by the method described on page 15. Melting point values for three trials were -34.0°C, -34.5°C, and -34.3°C, or an average of -34.3°C.

The infrared spectrum of the vapor over a one-to-one mole ratio of acetonitrile and n-butyldifluoroborane (133 mm. pressure in the infrared gas cell) was obtained. This spectrum is shown in Figure 11 (Curve C), along with the infrared spectrum of acetonitrile (Curve A) at 95 mm. pressure, and of n-butyldifluoroborane (Curve B) also at 95 mm. pressure. The infrared spectrum of the vapor of the one-to-one mixture appeared to be merely an addition of the bands of acetonitrile and n-butyldifluoroborane, except for the 4.7 and 14.46 bands of n-butyldifluoroborane, which had disappeared completely in Curve C. The 4.7 and 14.46 micron bands are found in the infrared spectra of the bands of the n-butyl, n-amyl, and n-hexyl difluoroboranes examined by the author. The infrared spectrum of boron trifluoride has a 14.46 micron band but not a 4.7 band. Hertzberg (23) has assigned the 14.46 micron band in boron trifluoride as a frequency caused by a bending of the molecule out of the plane. If the 14.46 micron band in n-butyldifluoroborane resulted from a frequency caused by a bending of the molecule out of the plane, the formation of an addition compound may be indicated. Therefore, one would expect this 14.46 band to be changed if the

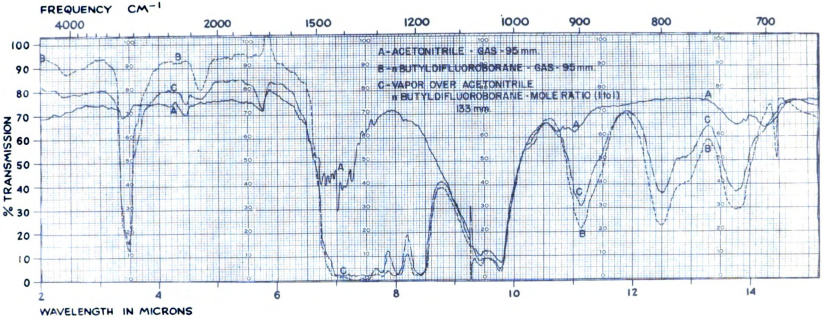

Figure 11

Infrared Spectra Study

planar n-butyldifluoroborane formed a tetrahedral addition compound with acetonitrile. If acetonitrile and n-butyldifluoroborane do form an addition compound, one would expect it to be tetrahedral since the addition compound between boron trifluoride and acetonitrile is tetrahedral (29). Since the 4.7 and 14.46 micron bands have disappeared in the one-to-one mixture of acetonitrile and n-butyldifluoroborane, it is possible that a tetrahedral addition compound is formed between these two.

There is some evidence that an addition compound between triethylamine and n-butyldifluoroborane may exist. Triethylamine (1.3 millimoles) was condensed on n-butyldifluoroborane (1.3 millimoles) at -78°C. One would have expected these compounds (when warmed to room temperature) to exist as gases at the pressure and volume under which this experiment was performed. However, a brown liquid was formed which had a vapor pressure of 57 mm. Since triethylamine and n-butyldifluoroborane are colorless liquids, the brown color and the liquid formation made it plausible that adduct formation had occurred. Since it was found that triethylamine was not a good solvent for electrolytic studies, no further work was done with this compound.

Electrochemical observations

The n-butyldifluoroborane was tested to see if it would conduct a current. The electrolysis cell "Z" was filled with n-butyldifluoroborane which had been stored in bulb "D" (Figure 2). The compound was transferred from the bulb "D" by vapor diffusion by freezing it into electrolytic cell "Z" with a -78°C bath. The n-butyldifluoroborane was allowed to warm to room temperature and potentials of 55, 110, and 400 volts were applied. No current registered on a milliammeter and there was no noticeable reaction at either electrode.

A preliminary electrolysis of a solution of n-butyldifluoroborane and acetonitrile was run to determine if the solution would conduct a current. In this electrolysis only a very small amount of n-butyldifluoroborane was added to the acetonitrile. Under a 100 volt potential, a gas evolved at the cathode, and approximately two milliamps of current was observed. Also, the negative electrode became black. No gassing or reaction was observed at the anode.

Several electrolyses were carried out using acetonitrile as a solvent. These will be described. The electrolysis cell "Z" was used in all of the electrolyses. The acetonitrile used had been stored in bulb "C" (Figure 2). The first solution was composed of five volumes of acetonitrile to one volume of n-butyldifluoroborane

(approximately 12 to 1 mole ratio). This colorless solution had a vapor pressure of 159 mm. at 24°C. A current of ten milliamps, and a 100 volt drop across the cell, resulted when the 110 volt potential was applied. A gas was immediately evolved at the cathode. The solution did not heat up and there was no noticeable change at the anode After 13 minutes the current increased to 18 ma., and the voltage drop was 98 volts. The electrolysis was stopped after two hours and twenty-four minutes. The solution had become yellow and pressure in the cathode compartment had risen to 220 mm.; there was no pressure rise in the anode compartment. The electrolysis cell had become slightly warm during the electrolysis. The volume of gas evolved at the cathode was 24.9 cc. (S.T.P.). While standing in the vacuum system, this cathode gas decomposed into a portion which could and a portion which could not be condensed at -196°C. The noncondensable gas was probably methane or hydrogen. An infrared spectrum was run on the portion condensable at -196°C. This spectrum gave only bands for n-butyldifluoroborane. A mass spectrum, which was also run on the condensable gas, indicated the presence of n-butyldifluoroborane, acetonitrile, and mass 81. The mass 81 was probably from the diacetonitrile molecule which was found to form on electrolysis of acetonitrile (37).

The second acetonitrile-n-butyldifluoroborane solution was combined in a four-to-one (approximate) mole ratio. The vapor pressure of this solution was 189 mm. at 25°C. This solution was electrolyzed for two hours and during this time the voltage drop across the cell decreased from 96 to 94 volts and the current increased from 10 to 28 ma. A gas was evolved at the cathode and there was a final pressure of 445 mm. This was equal to 98.4 cc. (S.T.P.) of evolved gas. There was no reaction observed at the anode. A sample of the cathode gas was run on the mass spectrometer within 16 hours after electrolysis The mass spectrum indicated the presence of n-butyldifluoroborane, acetonitrile, and diacetonitrile. The cathode gas was tested with bromine water and the gas decolorized it. Neither acetonitrile nor n-butyldifluoroborane decolorizes bromine water.

The third acetonitrile-n-butyldifluoroborane solution was composed of 0.29 mole of acetonitrile and 8.3 millimoles of n-butyldifluoroborane. The vapor pressure of the solution was 134 mm. at 23°C. Various voltages were applied to the solution to see if there would be any gassing at the anode. Potentials from 100 to 230 volts were applied and currents from 10 to 22 ma. resulted. Gassing occurred at the cathode but not at the anode. The solution was electrolyzed at 145 volts and 15 ma. for two hours. The cell did not warm during this time. The solution was electrolyzed for 12 more

hours at 100 volts. During this time the current varied between 50 and 100 ma. The pressure stayed at approximately 190 mm. for the last 12 hours but a liquid condensed out in the trap in the cathode compartment. Since the solution in the cell warmed considerably during the electrolysis, the gassing at the cathode may have been caused by the solution boiling. At the end of the electrolysis the solution in the cell had a dark red color. Not all of the gas condensed when a -196°C bath was put on a U trap of the cathode compartment. A pressure increase of 56 mm. resulted from the gas evolved at the cathode and 55 mm. pressure remained in the cathode compartment at -196°C. Thus it would seem that all of the gas evolved at the cathode was noncondensable at -196°C. Infrared spectra were run on the vapors left at -196°C, -78°C, -44°C, -22°C, 0°C, and 23°C. The -196°C fraction contained only a hydrocarbon group and showed no double bond. The gas was probably methane or ethane. The -78°C portion contained an unsaturated hydrocarbon. The -44°C gas seemed to be the same as the -78°C gas. The -22°C fraction was composed largely of bands of n-butyldifluoroborane. The 0°C and 23°C portions showed bands of acetonitrile and n-butyldifluoroborane.

Acetonitrile was tested for conductivity in the electrolysis cell "Z." From a 94 volt potential across the cell there was a

10 ma. current; gassing occurred at both the anode and the cathode. These gases decolorized bromine water and were condensable at -196°C. Previously, another worker in this laboratory had attempted to pass a current through acetonitrile at 110 volts, using electrolysis cell "X"; he found that no current passed (42). The difference in results may have stemmed from the fact that the current density was smaller, on this attempt, and the distance between the electrodes was greater in electrolysis cell "X" than in electrolysis cell "Z." Since a breakdown of acetonitrile evidently occurred, this solvent was discarded for further electrolytic work.

Triethylamine was tested for use as a solvent. Approximately 80 ml. of triethylamine was added to electrolysis cell "X" and potentials of 55 and 110 volts were applied. There was no current observed on a milliammeter. When 10 ml. of n-butyldifluoroborane was added, the solution warmed considerably. The heat was probably indicative of complex formation. Potentials of 55, 110, and 400 volts were applied to this solution but there was no current, except at 400 volts, where there was approximately one milliamp. At 400 volts, a very slight gassing occurred at both electrodes. However, at 400 volts, when 10 ml. of acetonitrile was added to the solution of triethylamine (80 ml.) and n-butyldifluoroborane (10 ml.), there was a 32 to 40 ma. current and very rapid gassing at both electrodes.

At 96 volts the same solution gave 10 to 12 ma. and gassing at both electrodes. The latter potential was applied for six hours. The gas evolved at both the anode and the cathode was condensable and decolorized bromine water. However, this test is not significant because triethylamine decolorizes bromine water, too. This solution was not investigated further since it was probable that the gassing resulted from decomposition of the acetonitrile.

Trimethoxyboroxine

Preparation

The trimethoxyboroxine was prepared by the method of Goubeau and Keller (17). The equation for this reaction is:

$$B_2O_3 + B(OCH_3)_3 \longrightarrow (CH_3OBO)_3.$$

Diboron trioxide (50 g., 0.718 mole) and trimethoxyborane (81 cc., 0.716 mole) were placed in a 250 ml. round-bottomed flask with a glass or Teflon covered stirring bar. The flask was connected to a reflux condenser and placed in a heating mantle on top of a magnetic stirrer. The top of the reflux condenser was fitted with a drying tube filled with Drierite. The heating mantle was set at such a temperature that the trimethoxyborane would drip slowly back into the flask. Water was circulated rapidly through the condenser and the solution was stirred as swiftly as possible. The heating was continued until the diboron trioxide had dissolved. The trimethoxyboroxine compound was then allowed to cool and the excess diboron trioxide was filtered off. (Since this compound was water-sensitive, all of the equipment used was dried in a 110°C oven.) The filtered trimethoxyboroxine was placed in a closed flask and cooled in a -78°C bath for several hours. The compound was then permitted to warm to room temperature and was stored in a one-liter, ground-glass stoppered bottle.

Physical properties

The trimethoxyboroxine is a colorless, viscous liquid that melts at approximately 10°C and decomposes before boiling by splitting out trimethoxyborane. The molecular weight, which was determined cryoscopically in benzene, was found to be 167.4 (theoretical weight, 173.56). The compound was found to contain 18.61 percent boron (theoretical percentage, 18.70). The titration procedure, with mannitol, outlined in Kolthoff and Sandell (28) was used for boron analysis. A sample, which was sent for carbon and hydrogen analysis, gave 18.01 percent carbon (theoretical percentage, 20.75) and 5.28 percent hydrogen (theoretical percentage, 5.22). No explanation can be given for the low carbon percentage. The infrared spectrum of the trimethoxyboroxine dissolved in carbon tetrachloride was obtained (Figure 12). The density of the trimethoxyboroxine, from 10.0°C to 72.0°C, was determined by using a one-milliliter dilatometer (see page 19). The dilatometer was weighed empty and then filled with trimethoxyboroxine and reweighed. The volume was obtained by reading the liquid level on the graduated stem. The dilatometer was immersed in a Dewar flask until the liquid level was covered. The Dewar flask was then filled with water of the desired temperature. The temperature was measured, using a National Bureau of Standards thermometer, to within ±0.1°C. The following equation gives the density of the trimethoxyboroxine from 10.0°C to 72.0°C:

$$D \text{ g./cc.} = 1.242 - 0.0012\, t,$$

where t equals degrees centigrade. The data for density determination are given in Table III.

The vapor pressure curve (Figure 13) for trimethoxyboroxine was determined by the method described on page 16. The data obtained are given in Table IV. Plotting log P versus the reciprocal of the temperature in °K, it was found, by the slope intercept method, that the equation

$$\text{Log } P \text{ mm.} = -2734/T + 10.140$$

fits the data. The boiling point (104°C), heat of vaporization (12.5

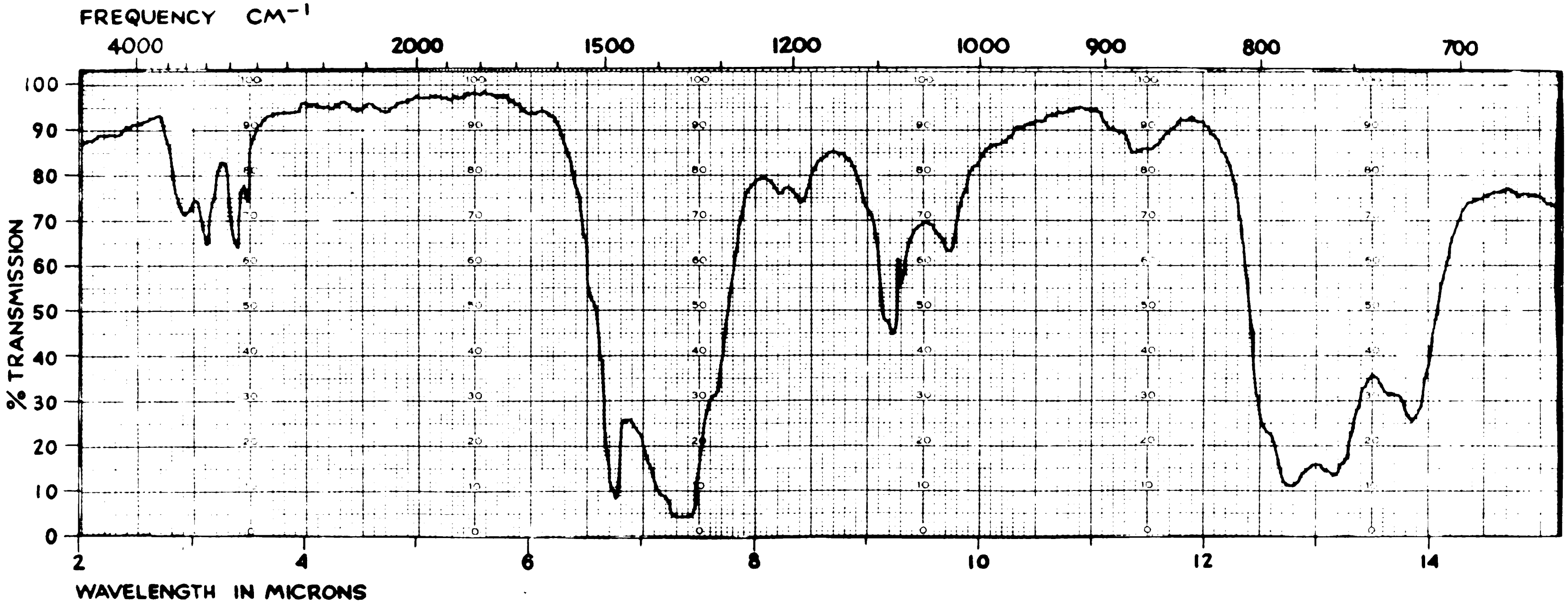

Figure 12

Infrared Spectrum of Trimethoxyboroxine Dissolved in Carbon Tetrachloride

TABLE III

DENSITY OF TRIMETHOXYBOROXINE*

Temperature (°C, ± 0.1)	Volume (cc., ± 0.001)	Density (g./cc., ± 0.001)
10.0	11.061	1.230
15.0	11.117	1.224
20.0	11.169	1.218
25.0	11.222	1.212
30.0	11.281	1.206
35.0	11.341	1.200
47.0	11.474	1.186
49.0	11.507	1.182
54.0	11.565	1.176
64.0	11.697	1.163
72.0	11.777	1.155

* Weight of sample was 13.6505 g.

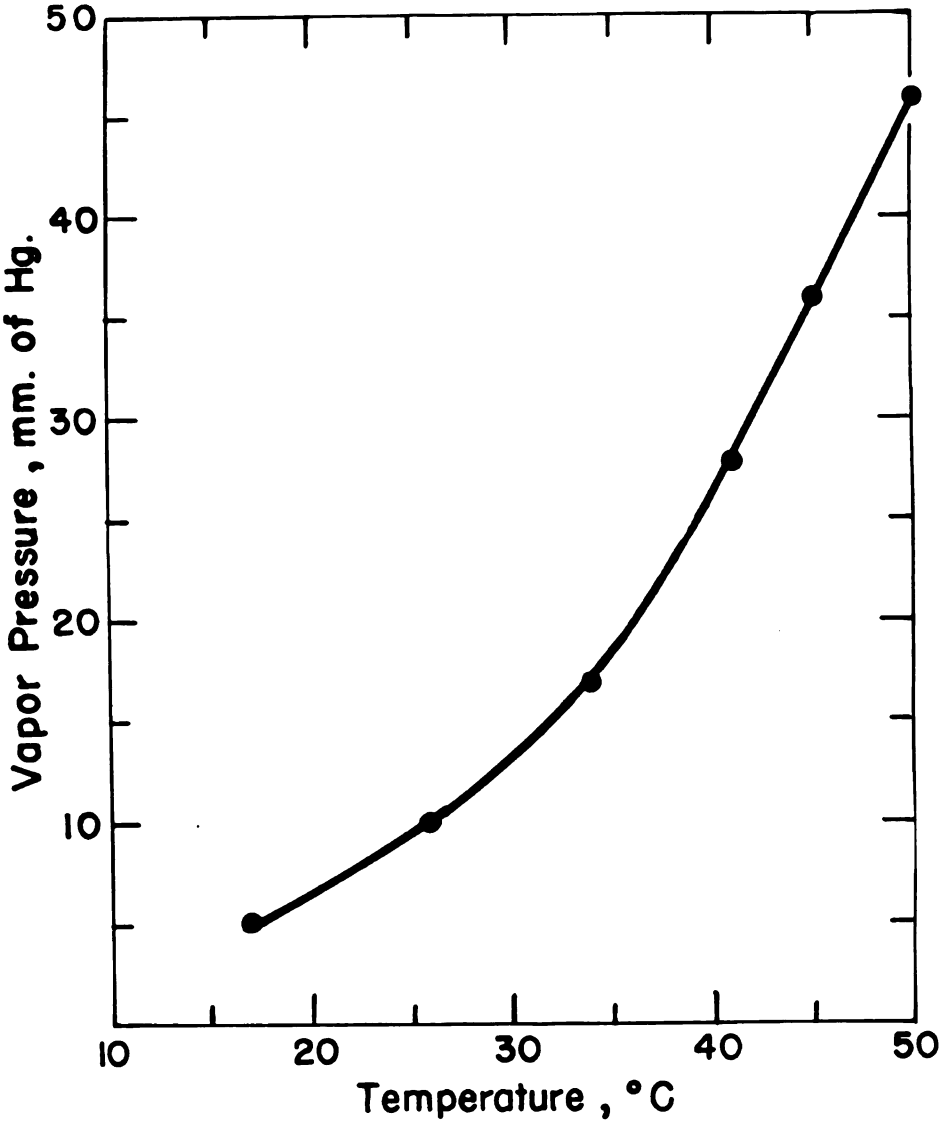

Fig. 13 VAPOR PRESSURE CURVE FOR TRIMETHOXYBOROXINE

TABLE IV

VAPOR PRESSURE DATA FOR TRIMETHOXYBOROXINE

Temperature (°C, ± 0.2)	Pressure (mm., ± 1)	Pressure Calculated from Equation
17.0	5	5
26.0	10	10
34.0	17	17
41.0	28	27
45.0	36	35
50.0	46	46

± 0.5 kcal/mole), and Trouton's constant (33.2) were calculated from this equation.

The trimethoxyboroxine is miscible with benzene, ethyl ether, acetone, carbon tetrachloride, chlorobenzene, and chloroform. In preparing the solutions, two milliliters each of trimethoxyboroxine and the appropriate solvents were mixed. Instead of dissolving, the alcohols (methyl, ethyl, propyl, and isopropyl) reacted with the trimethoxyboroxine, liberating heat and forming a white solid. The white solid gave, on analysis, varying percentages of boron which changed with the drying temperature of the sample. Two samples dried at 110°C, or higher, gave 23.6 and 28.94 percent boron. Three samples dried at 60° to 70°C gave 12.6, 13.4, and 15.8 percent boron. A sample, that was evacuated continuously as it was dried at temperatures between 60° and 70°C, gave 18.1 percent boron. Two samples dried at 45°C gave 16.6 and 16.3 percent boron. The white solid decomposes at temperatures between 180° and 200°C. When the white solid was heated it gave a liquid which, presumably, was water. A sample of the white solid was tested to see if it contained any carbon; it did not char when it was heated in concentrated sulfuric acid, nor did it give a precipitate when the gas obtained from heating it was bubbled into barium hydroxide solution. A sample sent for analysis gave 4.96 percent hydrogen. Most of these facts point to boric acid

(17.5 percent boron and 4.89 percent hydrogen) as having been the white solid. However, the boron percentages were low in some cases and high in others.

Triethylamine did not dissolve in trimethoxyboroxine, but the mixture reacted, liberating heat and forming two liquid layers. The top layer was white and the bottom layer was brown. An addition compound, of the type Burg found between trimethylamine and trimethylboroxine (8), may have been formed.

Electrochemical observations

The trimethoxyboroxine was tested to determine whether or not it would conduct a current. Potentials of 7.5 and 15 volts were applied with electrodes that were very close together, but no current registered on a milliammeter. Sodium borohydride was added to this solution and potentials of 7.5, 15, 55, and 110 volts were applied. Again no current was observed. However, since gassing was noticed when the sodium borohydride was added to the trimethoxyboroxine, a reaction must have taken place.

Sodium hydride (approximately 0.5 g.) was added to some trimethoxyboroxine that was in a beaker. The beaker was covered and allowed to stand for two hours. A slight reaction seemed to occur when sodium hydride was added. Platinum electrodes that were very close together were inserted into the beaker and potentials of 7.5, 15, 55, and 110 volts were applied to the system. The milliammeter did not show a current.

Reactions of trimethoxyboroxine with:

Sodium borohydride (sodium tetrahydridoborate).[1] The reaction between sodium borohydride and trimethoxyboroxine was investigated. Since the same general procedure as given below was followed in each of the reactions of the trimethoxyboroxine, the procedure will be given only once; the minor modifications will be included in the account of each reaction.

Trimethoxyboroxine (46.2 g., 0.266 mole) was added to a 125 ml. round-bottomed 24/40 \$ flask and frozen solid at -78°C. Then sodium borohydride (4.75 g., 0.125 mole) was poured on top of the solid trimethoxyboroxine and the flask was attached to the electrolysis manifold (Figure 2) through the 24/40 \$ joint of condenser D. While the flask was kept at -78°C, the flask and the electrolysis manifold were evacuated. After evacuation the system was closed off from the pump and the flask was immersed in a 60°C water bath.

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[1] Since the name sodium borohydride is more generally known and used than the term sodium tetrahydridoborate, it will be used in this thesis.

For the first 30 to 45 minutes the pressure in the vacuum system rose slowly; then it began to rise rapidly until it reached 790 mm. This pressure was great enough to dislodge the flask from the joint. The pressure inside the system adjusted to atmospheric pressure and the system was immediately stoppered with a 24/40 $\overset{\top}{\$}$ closed cap. The characteristic odor of diborane came from the flask. Pressure in the system was 740 mm. At -196°C the pressure was 700 mm.; at -78°C it was 732 mm. The 700 mm. pressure left at -196°C was undoubtedly caused by the freezing out of trimethoxyborane (F.P., -29°C). The other 32 mm. of pressure was probably caused by diborane (F.P., -165.5°C).

The experiment was repeated using a smaller amount of sodium borohydride so that the pressure of the reaction would not be so large. Trimethoxyboroxine (16.2 g., 0.0933 mole) and sodium borohydride (3.56 g., 0.0933 mole) were added to a flask equipped, as before, with an iron stirring bar. While this reaction was being run, at room temperature (23°C), the solution was stirred by a magnetic stirrer. The flask warmed during the reaction, and for the first hour and a half the pressure rose slowly. However, as the flask became warmer, the pressure increased more rapidly and the material in the flask began to foam. This reaction ran for 18 hours. Hydrogen (0.0908 mole), diborane (0.0072 mole), trimethoxyborane, and a white solid residue were produced. The residue contained hydrogen, carbon, sodium, and boron. When added to a nickel chloride solution, the residue gave a black precipitate (probably nickel boride); it also reduced a silver nitrate solution. This residue evolved hydrogen when heated, or when added to a water (either acid, alkaline, or neutral) solution. Since these reactions are characteristic of sodium borohydride, there was either some of it unreacted, remaining in the residue, or another substance was formed which caused these reactions. On the assumption that the hydrogen, evolved by hydrolysis or by heating, came from the sodium borohydride, the amount of unreacted sodium borohydride was calculated. It was found that, of the 0.0933 mole of sodium borohydride added, only 0.046 (approximate) mole reacted.

The procedure used for hydrogen determination follows. A 1.5908 g. sample (of the residue that resulted from the reaction between trimethoxyboroxine and sodium borohydride) was placed in a 50 ml. flask attached to the electrolysis manifold below point "F" (Figure 2). This sample was then heated over a Bunsen burner until a manometer showed there was no more pressure increase. Next the system was allowed to cool to room temperature and the pressure was measured. The volume "F" (Figure 2) had been previously determined (see Table I). By using the gas law, the number of moles and the number of grams of hydrogen was calculated. The calculation gave 0.0388 g. of hydrogen--which would be equivalent to the amount of hydrogen in 0.02360 g. of sodium borohydride. Thus, the white solid residue contained 18.6 percent of unreacted sodium borohydride. The 9.7 g. residue multiplied by 18.6 percent gives 1.8 g. (0.047 mole) of unreacted sodium borohydride. The portion (0.046 mole) of the sodium borohydride which reacted was converted mostly into hydrogen (approximate ratio of 2 moles of H_2 to 1 mole of $NaBH_4$), but some was converted into diborane (approximate ratio of six moles of $NaBH_4$ to one mole of B_2H_6). The approximate ratio of hydrogen to diborane was 12.6 to 1; this yield of diborane was quite low.

Once again, using the same general procedure, a reaction was realized between trimethoxyboroxine (29.1 g., 0.1676 mole) and sodium borohydride (3.464 g., 0.0915 mole). The reaction, which took place at temperatures between 60° and 65°C, was stopped after running for 20 hours. Hydrogen (0.0396 mole), diborane (0.0037 mole), trimethoxyborane (approximately 2.8 ml.), a liquid, and a solid residue were produced in the reaction. The trimethylborate and the diborane were separated from each other by fractional condensation. Identification of trimethoxyborane was accomplished by vapor pressure measurements (44 mm./0°C) and mass spectrometer analysis. The diborane was identified by four facts: (1) its odor; (2) its inability to be frozen out at -112°C and its solidity at -196°C, indicating that it was neither hydrogen nor the higher boranes; (3) its vapor pressure, which was 223 mm. at -112°C, compared to 221 mm. and 225 mm. reported in the literature (9, 40); and (4) confirmation of its presence by mass spectrometer analysis.

From observations of the reaction between trimethoxyboroxine and sodium borohydride, it seemed that the reaction proceeded better when there was an excess of trimethoxyboroxine. This may have resulted from the fact that sodium borohydride was not very soluble in the trimethoxyboroxine.

Lithium borohydride (lithium tetrahydridoborate).[1] The same general procedure was followed in carrying out this reaction as was followed in the reaction between trimethoxyboroxine and sodium borohydride. Trimethoxyboroxine (60.72 g., 0.349 mole) was reacted with lithium borohydride (0.5886 g., 0.0269 mole). The mixture, which was at room temperature, was stirred with a glass stirring bar. The flask became quite warm and the reaction was stopped at one

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[1] Since the name lithium borohydride is more generally known and used than the name lithium tetrahydridoborate, it will be used in this thesis.

and a half hours. A total pressure of 340 mm. at 27°C was produced in a 2336 cc. volume. A -196°C bath, which was put on a U trap of the system to remove condensable material, reduced the pressure to 318 mm. The 318 mm. pressure (0.0395 mole) was probably caused by hydrogen. The condensable material which had been frozen into the U trap of the gas storage bulb B (Figure 2) gave an 80 mm. pressure at 27°C in a 741 cc. volume. A -78°C bath was placed on the U trap to freeze out all material except diborane. During the time the -78°C bath was on the U trap the pressure was 8 mm. This was equivalent to 0.00039 mole of diborane.

One more reaction was run between trimethoxyboroxine (60.7 g., 0.349 mole) and lithium borohydride (2.131 g., 0.098 mole). This reaction was run for approximately 40 hours. Hydrogen (0.081 mole), diborane (0.012 mole), and trimethoxyborane resulted. The diborane and the trimethoxyborane were identified by their vapor pressures. Comparison of an infrared spectrum of the diborane and a diborane standard chart confirmed the presence of diborane.

Sodium hydride. While investigating whether or not sodium hydride would conduct a current in trimethoxyboroxine, it was found that, as sodium hydride was added to the trimethoxyboroxine, a gas was evolved. This was investigated further. Again the same general procedure was followed as in the reaction between sodium borohydride and trimethoxyboroxine. First a preliminary run was made. Trimethoxyboroxine (50 ml., 60.7 g.) was mixed with a large amount of hydride. The solution was reacted for eight hours and gave a total pressure of 157 mm. in a 2336 cc. volume at 27°C. The resultants were hydrogen (16.5 millimole), trimethoxyborane (0.9 millimole), and a fraction (2.25 millimole) which froze at a temperature between -78° and -196°C.

The reaction was repeated, and this time a magnetic stirrer was used. After trimethoxyboroxine (70 ml., 0.488 mole) had been reacted with sodium hydride (6.0702 g., 0.252 mole) for 11 hours, a sample of the gas was removed and analyzed on the mass spectrometer. The pressure was 252 mm. in a 2316 cc. volume. The sample contained a large percentage of hydrogen and small amounts of trimethoxyborane and diborane. When the reaction was stopped at 45-1/2 hours, there was a total pressure of 502 mm. The resultants were hydrogen (0.058 mole), diborane (0.028 millimole), trimethoxyborane, and a glassy solid which had swelled to twice its original volume. (This glassy solid had an odor different from the odors of either trimethoxyboroxine or diborane.) The gas evolved in the reaction contained approximately 0.04 percent diborane, if calculated from gas pressure, or approximately 0.05 percent if calculated from the mass spectrum data.

Calcium hydride. To determine whether or not a different hydride would increase the yield of diborane, calcium hydride was reacted with trimethoxyboroxine. The procedure used in the previous trimethoxyboroxine reaction was followed here. Trimethoxyboroxine (62 ml., 0.43 mole) was reacted with calcium hydride (8.64 g., 0.205 mole). The reaction was run, with stirring and at room temperature, for 43 hours. The gases produced had a total pressure of 172 mm. in a 2316 cc. volume at 24°C. A large portion of the gases was hydrogen but there was some trimethoxyborane and a very small amount of a gas which froze at a temperature between -78° and -196°C. This may have been diborane.

Boron trichloride and sodium hydride. Since diborane can be obtained by reducing gaseous boron trihalides with sodium or calcium hydride (24), it was thought that possibly the same results could be obtained in the trimethoxyboroxine medium. About 10 ml. of boron trichloride was frozen in a 125 ml. flask which was kept immersed in a -196°C bath. Trimethoxyboroxine (50 ml., 60.7 g.) was added and allowed to freeze. Then 1.2 g. of sodium hydride was added and the flask was transferred to the electrolysis manifold and evacuated.

The flask was allowed to warm and at -78°C the pressure was 12 mm.; at 0°C the pressure was 40 mm. When the flask had warmed to room temperature the magnetic stirrer was started. The reaction went slowly and after ten hours there was a final pressure of 199 mm. The reaction evolved hydrogen and trimethoxyborane and another product which was probably boron trichloride. There was no evidence of diborane.

Tri-n-butoxyboroxine

Preparation and identification

Since trimethoxyboroxine can be formed by dissolving diboron trioxide in trimethoxyborane, it was thought that possibly other trialkoxyboroxines might be formed in this same manner. Diboron trioxide was found to dissolve readily in tri-n-butoxyborane.[1] The following procedure was used. Diboron trioxide (52 g., 0.747 mole) and tri-n-butoxyborane (200 ml., 0.740 mole) were added to a 300 ml. round-bottomed flask equipped with a Teflon-covered magnetic stirring bar. The flask was attached to a reflux condenser which had a drying tube filled with Drierite. It was then placed on a heating mantle

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[1] A sample was donated by the American Potash and Chemical Company.

which was over a magnetic stirrer. The heater was set for low heating and the stirrer was started. Water was circulated rapidly through the reflux condenser and the heating continued until almost all of the diboron trioxide was dissolved. The solution was next cooled and then filtered to remove excess diboron trioxide.

The solution was poured into a flask (which could be stoppered) and immersed in a -78°C bath for several hours. The molecular weight of the compound was determined cryoscopically, using benzene. The average molecular weight was found to be 352 (theoretical, 299.8 for the trimer $[(C_4H_9OBO)_3]$). From this value it can be seen that, instead of a monomer (99.9), or a dimer (199.8), a trimer was formed. The percentages of boron, carbon, and hydrogen were determined and found to be 11.70 for boron (theoretically 10.83 percent), 45.85 for carbon (theoretically 48.40 percent), and 8.85 for hydrogen (theoretically 9.08 percent). These results indicated that the ratio of diborane trioxide to tri-n-butoxyborane was slightly greater than the one in this compound. Since there was a slight excess of diboron trioxide, some of it may have dissolved in the tri-n-butoxyboroxine.

Physical properties

The tri-n-butoxyboroxine was found to freeze, at temperatures around -75°C, into a glassy substance. No definite melting point could be obtained. It was also found that the compound decomposed when distilled. A clear liquid began distilling off between 70° and 80°C and continued until 186°C. The temperature then dropped and distillation was discontinued. The solid residue left in the flask was a dark brown tarlike substance interspersed with a white solid which was probably diboron trioxide. Since trimethoxyborane splits off when trimethoxyboroxine is distilled, the clear liquid probably was, in this case, tri-n-butoxyborane. The infrared spectrum of the tributoxyboroxine dissolved in carbon tetrachloride was obtained (Figure 13). The density of tributoxyboroxine, at temperatures between 0.0° and 74.0°C, was determined by the use of the two milliliter dilatometer (see page 19). First the dilatometer was weighed empty and then it was filled with tributoxyboroxine and reweighed. The same method was followed here that was used for the trimethoxyboroxine. The density of the tributoxyboroxine between 0.0° and 74.0°C is given by the following equation:

$$D \text{ g./cc.} = 1.030 - 0.0009\, t,$$

where t equals degree Centigrade. The data for density determination are given in Table V.

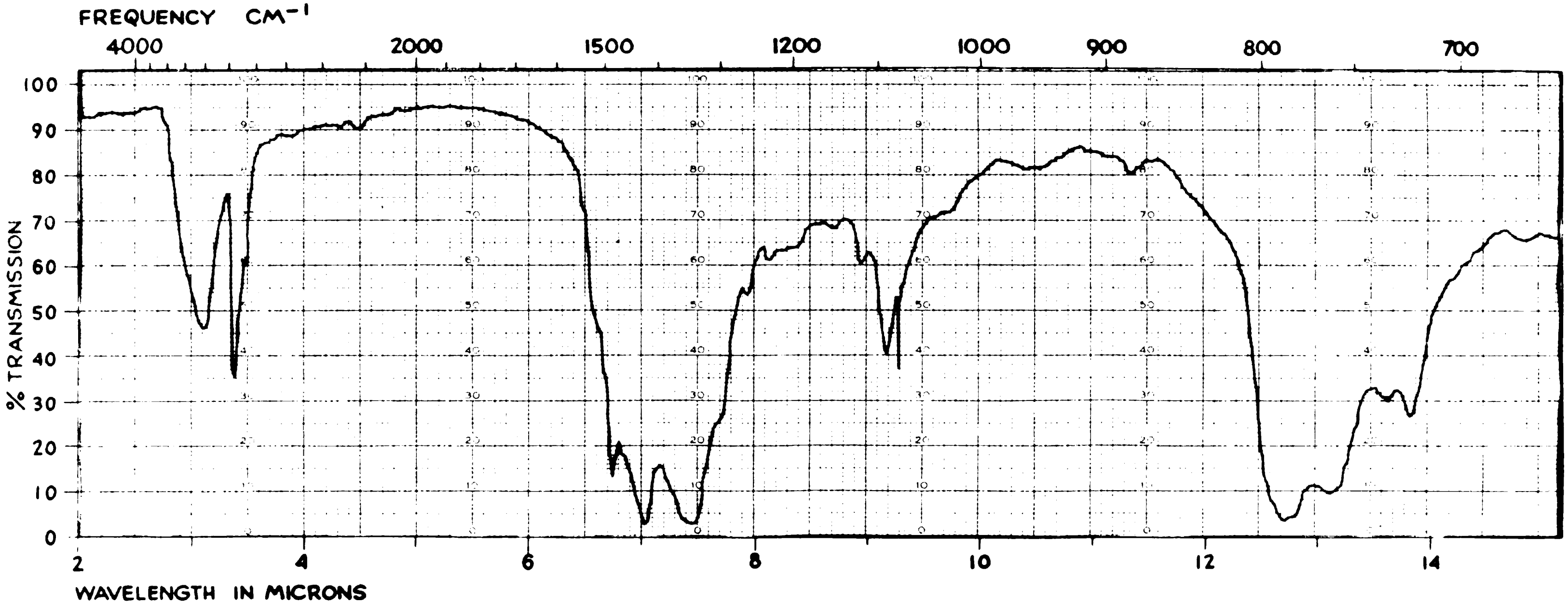


Figure 14

Infrared Spectrum of Tri-n-butoxyboroxine Dissolved in Carbon Tetrachloride

TABLE V

DENSITY OF TRIBUTOXYBOROXINE*

Temperature (°C, ± 0.1)	Volume (cc., ± 0.01)	Density (g./cc., ± 0.01)
0.0	13.68	1.030
9.0	13.79	1.022
15.0	13.85	1.018
23.0	13.94	1.011
32.2	14.07	1.002
40.9	14.17	0.995
51.9	14.33	0.984
60.0	14.42	0.978
74.0	14.58	0.967

* Weight of sample was 14.0976 g.

A few vapor pressure values for tributoxyboroxine were determined by the method described on page 16. The data that were obtained are given in Table VI.

Tri-n-butoxyboroxine was found to be miscible with benzene, chlorobenzene, acetone, carbon tetrachloride, and chloroform.

TABLE VI

VAPOR PRESSURE DATA FOR TRIBUTOXYBOROXINE

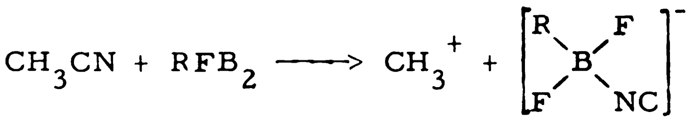
Temperature (°C, ± 1)	Pressure (mm., ± 1)
65	1
75	4
84	6
94	9

DISCUSSION

Electrolytic Work on the Alkyldifluoroboranes

It was found that the electrolysis of the alkyldifluoroboranes in acetonitrile does not produce reduced boron materials. However, the alkyldifluoroboranes do appear to induce considerable ionic character in the acetonitrile. This is evidenced in the acetonitrile solutions where the increase in the amount of current is in direct relation to the increase in the n-alkyldifluoroborane concentration. This ionic character then facilitates the decomposition of acetonitrile. Greenwood et al. found this to be the case of boron trifluoride ethyl etherate (19). The ethyl ether decomposed but the boron trifluoride remained, in the solution, coordinated to acetaldehyde, and ethyl alcohol formed at the anode.

Since a hydrocarbon was formed at the cathode and there was no evidence found to indicate any reduction of the n-butyldifluoroborane, the mode of ionization may be:



$$CH_3CN + RFB_2 \longrightarrow CH_3^+ + \left[\begin{array}{ccc} R & & F \\ & B & \\ F & & NC \end{array}\right]^-$$

where R is a n-butyl or an n-amyl group. This ionization would predict the formation of a hydrocarbon at the cathode, whereas at the anode the CN^- may have given up an electron and then reacted with the excess acetonitrile to form a polymer. The n-alkyldifluoroborane freed at the anode could then easily recombine with the excess acetonitrile in the solution. Schmidt found that alkali halides electrolyzed in acetonitrile give methane, hydrogen, sodium cyanide, diacetonitrile, and kyanmethin (an acetonitrile polymer) at the cathode (37). The red color of the solution of n-alkyldifluoroboranes in acetonitrile was probably caused by a polymer of acetonitrile since it is known that acetonitrile gives a red polymer when distilled over phosphorus pentoxide. It was also found that the gases that are liberated when acetonitrile is electrolyzed by itself will decolorize bromine water; this probably means that the double bond substance found in the cathode gas came from an acetonitrile electrolysis product and not from a breakdown of the n-alkyldifluoroborane molecule.

Boroxine Reactions

Burg (8) attempted to prepare the parent boroxine ($H_3B_3O_3$) by reacting either diborane or borazole ($H_6N_3B_3$) with trimethylboroxine ($CH_3B_3O_3$). Neither of these methods was successful, but the reaction with borazole gave a product which was unstable at the reaction temperature (140°C). It was thought that the trimethoxyboroxine, $(CH_3OBO)_3$, used in this work might possibly react with sodium hydride to give the parent boroxine $(H_3B_3O_3)$. Since sodium hydride reacts with trimethoxyborane to give sodium borohydride and sodium methoxide (36), there is a good possibility that the boron-to-oxygen bond in the methoxy group would break and give sodium methoxide and a boron-to-hydrogen bond. This reaction can be pictured as follows:

(1) $(CH_3OBO)_3 + 3NaH \longrightarrow 3NaOCH_3 + (HBO)_3$.

However, the $(HBO)_3$ is probably unstable and may decompose (like the trihaloboroxines) into diborane and boron trioxide. This reaction would be written:

(2) $2(HBO)_3 \longrightarrow B_2H_6 + 2B_2O_3$.

Since sodium methoxide reacts readily with diborane at room temperatures, the sodium methoxide (equation 1) may react with diborane (equation 2) accordingly:

(3) $3NaOCH_3 + 2B_2H_6 \longrightarrow 3NaBH_4 + B(OCH_3)_3$.

This series of equations could explain the trimethoxyborane produced in the reaction and the low yield of diborane.

Similar results could be obtained by the following reasoning. The trimethoxyboroxine has a second boron-to-oxygen bond which could be broken by sodium hydride. This is illustrated in the following equations:

$$(4)\quad (CH_3OBO)_3 + 6NaH \longrightarrow 3(CH_3O)H_2B + 3Na_2O$$

the monomethoxyborane would disproportionate readily to give:

$$(5)\quad 3(CH_3O)H_2B \longrightarrow B_2H_6 + B(OCH_3)_3$$

while the sodium oxide could react with the excess trimethoxyboroxine in this way:

$$(6)\quad (CH_3OBO)_3 + 3Na_2O \longrightarrow 3NaBO_2 + 3NaOCH_3.$$

If this happened the diborane and sodium methoxide would react as in equation 3.

The first series of reactions would produce trimethoxyborane, sodium borohydride, diboron trioxide, and possibly small amounts of diborane, boroxine ($H_3B_3O_3$), and sodium methoxide. The second series of reactions would produce sodium borate, sodium borohydride, trimethoxyborane, and possibly small amounts of diborane.

However, these two series of reactions do not explain the large amounts of hydrogen produced in the reaction between sodium hydride and trimethoxyboroxine. This might be explained in either of two ways. First, it is known (36) that the decomposition of sodium borohydride to give hydrogen is catalyzed by certain metals, or their salts, such as cobalt, copper, manganese, iron, and nickel. Since the trimethoxyboroxine used in this work contained iron salts as an impurity, it is very possible that sodium borohydride was formed and then decomposed to give hydrogen.

Second, the sodium hydride may react with trimethoxyboroxine in a manner different from that given in equations 1 and 4. This reaction might possibly be represented by the following equations:

$$(7)\quad (CH_3OBO)_3 + 9NaH \longrightarrow 9(CH_3O)HBONa$$

$$(8)\quad 2(CH_3O)HBONa \longrightarrow (CH_3O)_2B_2(ONa) + H_2$$

One of the products indicated in equation 8 is the half methyl ester and half sodium salt of subboric acid, $B_2(OH)_4$, which may decompose in the following manner:

$$(9)\quad 2(CH_3O)_2B_2(ONa)_2 \longrightarrow B_2(OCH_3)_4 + B_2(ONa)_4.$$

The $B_2(OCH_3)_4$ has a peculiar odor (38). An odor different from either diborane or trimethoxyboroxine was noticed in the residue left from the sodium hydride and trimethoxyboroxine reaction

The reaction of sodium hydride with trimethoxyboroxine probably occurs by one or a combination of the reaction series described above. The reaction of either sodium or lithium borohydride with trimethoxyborine is probably similar to those described before. It is possible that the only reaction occurring is the decomposition of sodium or lithium borohydride. This decomposition might be catalyzed by the iron impurity in the trimethoxyboroxine.

Since Glunz (15) had postulated that an internal displacement reaction occurs when tributylboroxine reacts with either boron trifluoride or boron trichloride to give n-butyldihaloboranes, it is possible that a similar reaction between boron trichloride and trimethoxyboroxine might produce methoxydichloroborane. The methoxydichloroborane might then react with sodium hydride and give either dichloroborane and sodium methoxide, or monomethoxyborane and sodium chloride. These reactions are represented by the equations:

(10) $(CH_3OBO)_3 + 3BCl_3 \longrightarrow CH_3OBCl_2 + (B_3O_3Cl_3)_3$

(11) $CH_3OBCl_2 + 2NaH \longrightarrow CH_3OBH_2 + 2NaCl$

or

(12) $CH_3OBCl_2 + NaH \longrightarrow HBCl_2 + NaOCH_3$.

The $B_3O_3Cl_3$, CH_3OBH_2, and $HBCl_2$ formed in the above reactions are unstable and disproportionate in the following way.

(13) $B_3O_3Cl_3 \longrightarrow B_2O_3 + BCl_3$

(14) $3CH_3OBH_2 \longrightarrow B_2H_6 + B(OCH_3)_3$

(15) $6HBCl_2 \longrightarrow 4BCl_3 + B_2H_6$

This method might then be convenient for preparation of diborane. Experimentally, it was found that the reaction of trimethoxyboroxine with boron trichloride and sodium hydride produced hydrogen and a solution so viscous it could almost be termed solid. There was no evidence of diborane found in this reaction.

SUMMARY

1. Electrolytic studies of alkyldifluoroboranes in acetonitrile were made. The electrolytic reduction of alkyldifluoroboranes in nonaqueous solvents was attempted but not accomplished. When solutions of alkyldifluoroboranes in acetonitrile were electrolyzed, the acetonitrile decomposed. Alkyldifluoroborane-triethylamine solutions would not conduct a current. It was found that the solvent tetrahydrofuran reacted with the alkyldifluoroboranes. Therefore, it was concluded that acetonitrile, triethylamine, and tetrahydrofuran are unacceptable for electrolytic studies. The melting point, the vapor pressure curve, the infrared spectrum, and the cracking patter on the mass spectrometer were ascertained for n-butyldifluoroborane. The boiling point, the heat of vaporization, and Trouton's constant were calculated from the vapor pressure data. It was also found that n-butyldifluoroborane does not conduct a current.

2. The infrared spectrum, the density, and the vapor pressure of trimethoxyboroxine were determined and the boiling point, the heat of vaporization, and Trouton's constant were calculated from the vapor pressure data. The trimethoxyboroxine was found to be miscible with benzene, ethyl ether, acetone, carbon tetrachloride,

chlorobenzene, and chloroform. It was also found that trimethoxyboroxine does not conduct a current. Trimethoxyboroxine reacted with sodium borohydride, lithium borohydride, and sodium hydride to give various amounts of the following: hydrogen, trimethoxyborane, and diborane.

3. The compound tri-n-butoxyboroxine was prepared by reacting diboron trioxide with tri-n-butoxyborane. It was shown, by molecular weight determination, that this compound is a trimer. The tri-n-butoxyboroxine decomposed when distilled and froze into a glasslike solid at approximately -75°C. The density at various temperatures, along with a few vapor pressure values, was determined for tri-n-butoxyboroxine. The infrared spectrum was also ascertained. Tributoxyborane was found to be miscible with the following: benzene, acetone, chlorobenzene, carbon tetrachloride, and chloroform.

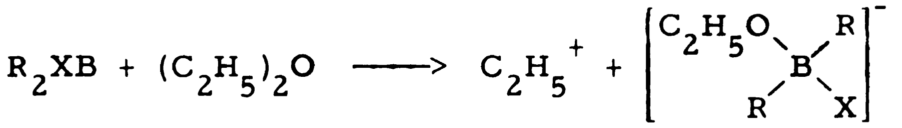
EXPERIMENTAL POSSIBILITIES

This research has suggested various experimental problems which were not investigated further because of time limitations, but which might prove to be of considerable interest. These problems will be described briefly.

Electrolytic

Since Becher's (3) work has shown that the boron-to-halogen bond strength in dialkylhaloboranes is less than it is in either the monoalkyldihaloboranes or the boron halides, work on compounds of the type R_2XB (where R is a short-chained alkyl group and X is Cl, Br, or I) might produce reduced boron compounds electrolytically. Specifically, the compounds $(C_2H_5)_2ClB$ (13), $(C_3H_7)_2IB$ (30), and $(C_4H_9)_2ClB$ (7) might be valuable in electrolytic studies. (The methods for their preparation are given in their respective references.) Ulmer (42) has found that hydrogen is one of the products formed at the anode when sodium trimethoxyborohydride, $NaBH(OCH_3)_3$, or sodium borohydride, $NaBH_4$, are electrolyzed in either ethers or dimethylformamide.

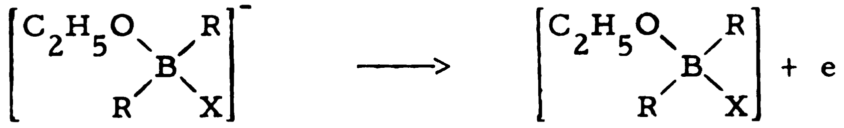
If these same solvents would dissolve sodium hydride and, when electrolyzed, give hydrogen at the anode, they might prove useful as sources of hydrogen for the reduction of the R_2ClB compounds. If ethyl ether were used as the solvent, these reactions might be pictured as:

(1) 

$$R_2XB + (C_2H_5)_2O \longrightarrow C_2H_5^{+} + \left[\begin{array}{ccc} C_2H_5O & & R \\ & B & \\ R & & X \end{array}\right]^{-}$$

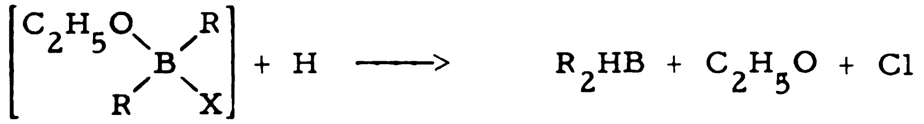
$$(2) \qquad NaH \longrightarrow Na^{+} + H^{-}$$

The anode process may be:

(3) 

$$\left[\begin{array}{ccc} C_2H_5O & & R \\ & B & \\ R & & X \end{array}\right]^{-} \longrightarrow \left[\begin{array}{ccc} C_2H_5O & & R \\ & B & \\ R & & X \end{array}\right] + e$$

$$(4) \qquad H^{-} \longrightarrow H + e$$

(5) 

$$\left[\begin{array}{ccc} C_2H_5O & & R \\ & B & \\ R & & X \end{array}\right] + H \longrightarrow R_2HB + C_2H_5O + Cl$$

$$(6) \qquad 2(C_2H_5O) \longrightarrow CH_3CHO + CH_3CH_2OH.$$

Disproportionation of the R_2HB would very likely follow:

$$(7) \qquad 6(R_2HB) \longrightarrow 4(BR_3) + B_2H_6.$$

The energy in the tetrahedral complex ion $(R_2XBOC_2H_5)^{-}$ is greater than the energy in the R_2XB molecule. However, the energy per each bond in the tetrahedral molecule is less than the energy in each bond of the planar R_2XB molecule. It is not certain whether or not the boron-to-halogen bond strength would be decreased enough that it, positively, would be broken in preference to other bonds in the tetrahedral molecule, but there is a good possibility that this would occur.

Compounds of the type $(RO)_2XB$ (where R is a short-chained alkyl group and X is chlorine, bromine, or iodine) might profitably be used for electrolytic studies. In particular, the compound $(CH_3O)_2ClB$ (45) might give $(CH_3O)_2HB$ when either electrolyzed or reacted with sodium hydride. This $(CH_3O)_2HB$ would disproportionate immediately into diborane and trimethoxyborane.

Addition Compounds

n-Butyldifluoroborane probably forms addition compounds with various oxygen- and nitrogen-containing substances such as ethers, tetrahydrofuran, diethylamine, triethylamine, trimethylamine, and dimethylformamide. The method used by Greenwood *et al.* (19) would be useful in determining whether or not an addition compound was formed.

Boroxines

Work done on the boroxines has brought up these questions:

(1) Can trimethoxyboroxine be prepared by reacting trimethoxyborane with glassy diboron trioxide?

(2) Is it necessary to freeze the product of the reaction between trimethoxyborane and crystalline diboron trioxide to obtain trimethoxyboroxine? This could probably be answered by molecular weight determination of the reaction product before and after freezing.

(3) Could either sodium tetraborate or boric acid be dissolved in trimethoxyborane or trimethoxyboroxine?

(4) It was observed that when sodium trimethoxyborohydride is added to the trimethoxyboroxine a viscous, glassy solution, blue-green in color, was produced. What occurs here?

(5) Could the triethoxy and tripropoxy boroxines be prepared by reacting crystalline diboron trioxide with triethoxyborane or tripropoxyborane?

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