THE ELECTROLYSIS OF OXYGENATED BORON-CONTAINING MATERIALS

THESIS FOR THE DEGREE OF PH. D.
MICHIGAN STATE UNIVERSITY
HARRY E. ULMER
1955

This is to certify that the

thesis entitled

The Electrolysis of Oxygenated
Boron-Containing Materials

presented by

Harry Edwards Ulmer

has been accepted towards fulfillment
of the requirements for

Ph.D. **degree in** Chemistry

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Major professor

Date August 17, 1955

O-169

THE ELECTROLYSIS OF OXYGENATED BORON-CONTAINING MATERIALS

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A THESIS

Submitted to the School of Advanced Graduate Studies of
Michigan State University of Agriculture and Applied
Science in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1955

11-26-58
G 7260

ABSTRACT

The electrolysis of oxygenated boron-containing materials in anhydrous nonaqueous solvents was investigated. Primary emphasis was placed on the electrolysis of sodium trimethoxyborohydride. Some study was made of the electrolysis of sodium borohydride and of the systems boric oxide-sulfur trioxide-water, boric oxide-sulfur trioxide, and boric oxide-phosphorus pentoxide-water. Other parts of the study were the reaction between diborane and dimethylformamide, the trimethylborate-dimethylformamide phase study, and the determination of some physical properties of trimethylborate.

Of the twenty-two solvents tried, only ethylene glycol dimethyl ether proved suitable for the electrolysis of sodium trimethoxyborohydride. The use of other solvents, which allowed the passage of a current, led to various side reactions. In ethylene glycol dimethyl ether, sodium trimethoxyborohydride electrolyzed to give metallic sodium at the cathode and hydrogen and trimethylborate at the anode as indicated by the equation,

$$NaH \cdot B(OCH_3)_3 \longrightarrow Na + 1/2\ H_2 + B(OCH_3)_3.$$

It is thought that the same processes occur in dimethylformamide but further side reactions occur because of the metallic sodium produced in the reaction.

By analogy to the above equation, it was reasoned that if the trimethylborate group, $B(OCH_3)_3$, in the sodium trimethoxyborohydride were replaced by the borine group, BH_3, electrolysis might occur according to the equation,

$$NaH{\cdot}BH_3 \longrightarrow Na + 1/2\ H_2 + BH_3.$$

In order to verify this conclusion, the electrolysis of sodium borohydride in dimethylformamide was attempted and the results could be interpreted in accordance with the proposed equation.

During the course of the electrolysis of sodium borohydride in dimethylformamide, a white solid was observed to form. Since diborane was a suspected product, the reaction of diborane and dimethylformamide was studied. It was found that the observations made of this reaction could be explained by assuming the initial formation of the compound $B[OCH_2N(CH_3)_2]_3$, and then the reversible chemisorption of diborane to form the compound $B[OCH_2N(CH_3)_2BH_3]_3$.

In a phase study of dimethylformamide and trimethylborate it was found that these two materials formed a simple eutectic phase system, and that no compound formation occurred between these two materials.

The above phase study emphasized the fact that some inconsistencies existed in the literature about some of the physical properties of trimethylborate. Accordingly, the melting point, boiling point,

and vapor pressure of trimethylborate were determined. Values for the heat of vaporization and Trouton's constant were obtained from these data.

In an attempt to produce elemental boron, the electrolyses of the systems boric oxide-sulfur trioxide-water, boric oxide-sulfur trioxide, and boric oxide-phosphorus pentoxide-water were studied. The aqueous systems, boric oxide-sulfur trioxide-water, and boric oxide-phosphorus pentoxide-water, conducted electricity well; but elemental boron was not produced under the experimental conditions. The anhydrous system, boric oxide-sulfur trioxide, did not conduct electricity.

ACKNOWLEDGMENTS

The author expresses his sincere appreciation for the guidance and understanding of Dr. L. L. Quill, under whose direction this research was conducted; and to Dr. R. K. Birdwhistell, who gave many valuable suggestions during the course of this work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Statement of the Problem

This problem has been concerned with a study of the electrolytic properties of oxygenated boron compounds with the idea of producing the boranes, particularly diborane, or substituted boron compounds which could be easily converted into the latter. Compounds of the type, $NaBH_n(OCH_3)_{4-n}$, where n may be varied from zero to four, have been considered. Most of the emphasis was placed on the electrolysis of sodium trimethoxyborohydride, $NaBH(OCH_3)_3$, in several nonaqueous solvents such as dimethylformamide and ethylene glycol dimethyl ether. Some observations are reported on the systems boric oxide-sulfur trioxide, boric oxide-sulfur trioxide-water, and boric oxide-phosphorus pentoxide-water.

Historical

Prior to 1912, very little reliable information on the boron hydrides and their derivatives was available. In that year Stock began his monumental studies on this class of compounds; and by 1933 he had prepared, isolated, and characterized most of the hydrides of boron as we know them today (48). These hydrides with some of their known physical properties are listed in Table I.

In many respects the chemical properties of the higher boranes are similar to those of diborane. The differences observed are a matter of degree, and a better understanding of diborane has led to a more complete picture of the higher boranes.

When considering the chemistry of the boranes, several points should be remembered. Through the years the transitory existence of the borine group, BH_3, has been definitely established (12). The boron atom has one "s" and three "p" orbitals available for bond formation with only three orbitals being used in the normal three-covalency state of boron. The availability of this fourth orbital for bonding allows diborane and many boron compounds to behave like Lewis acids, so that a tremendous number of coordination complexes exist in the field of boron chemistry. In addition to these complexes, another characteristic property of acids is the displacement of weaker acids from acid-base complexes by stronger acids. Schlesinger *et al.* (38) established that the acid strength of the following boron compounds decreased as indicated.

$$BF_3 > (BH_3)_2 > (CH_3)_3B > (CH_3O)_3B$$

Two of the many examples which could be cited in support of the above acidity ratings are the displacement of diborane from sodium

TABLE I

PHYSICAL PROPERTIES OF THE BORON HYDRIDES

Name	Formula	Boiling Point (°C)	Melting Point (°C)	Density (g/ml)	State	Thermal Stability
Diborane	B_2H_6	-92.5	-165.5	0.438 (bp)	Colorless gas	Relatively stable
Tetraborane	B_4H_{10}	16	-120	0.56 (-35°C)	Colorless gas	Unstable
Pentaborane	B_5H_9	58	-46.8		Colorless liquid	Relatively stable
Unstable pentaborane	B_5H_{11}	65	-123		Colorless liquid	Unstable
Hexaborane	B_6H_{10}		-65		Colorless liquid	Relatively stable
Unstable hexaborane	B_6H_{12}		-90		Colorless liquid	Unstable
Decaborane	$B_{10}H_{14}$	213	99.5	0.94 (25°C)	Crystalline white solid	Stable

borohydride by boron trifluoride, and of trimethylborate from sodium trimethoxyborohydride by diborane.

In many cases, the formation of a coordinate covalent bond by boron produces electrical and spatial strains in the acid-base complex formed. It is often observed that the boron-hydrogen bond is weaker than the coordinate covalent bond formed, and it appears that the hydrogen attached to the boron atoms in such complexes may easily migrate in the molecule to minimize the distortion. In some cases, other groups might enter into this migration. Sometimes the strain produced is so excessive that it can be relieved only by a splitting of the molecule. In the higher boranes the boron-boron bond seems to become more metallic and inert, and the boron-bonded hydrogen less reactive.

It is well to remember that, since the electronegativity of boron is approximately 2, a high heat of reaction should be observed with such electronegative elements as oxygen. All the boranes react vigorously with oxygen, once ignited, giving boric oxide and water as products.

The boranes can be divided into two groups with the formulae of B_nH_{n+4} and B_nH_{n+6}. In general, the members of the latter group are spontaneously flammable in air and are thermally less stable than the members of the former group.

A violent reaction occurs between diborane and chlorine, giving boron trichloride and hydrogen chloride. With bromine and iodine the reaction is much slower, and the intermediate diborane monohalides can be isolated. None of these monohalides, however, are stable; all disproportionate to the corresponding hydrogen and boron halides. The higher boranes react must less readily with the free halogens with some even requiring high temperatures. Various bromides and iodides of the higher boranes have been isolated. In contrast, the reaction of the boranes with hydrogen halides is very slow, and much less vigorous.

The rates of hydrolysis of the boranes to boric acid and hydrogen vary tremendously with diborane hydrolyzing the fastest. In all cases, the presence of hydrogen ions accelerates this hydrolysis, while in alkaline medium diborane and tetraborane hydrolyze, giving rise to hypoborates in contrast to the normal products of boric acid and hydrogen.

As noted, all of the boranes undergo Lewis acid-base reactions to some extent with such electron-donating molecules as ammonia to form coordination complexes. Pyrolysis of these addition complexes leads to various other boron derivatives. One such example is the pyrolysis of the diborane-ammonia complex which produces borazole.

The borine group may also complex with ions, since with hydride ions the borohydride ion is formed

The reaction of diborane with hydrocarbons produces a variety of compounds. In general, trialkylborons are formed. Hydrolysis of these compounds produces dialkyl and monoalkyl boric acids.

In addition to the boranes listed in Table I, polymeric, nonvolatile boranes have been observed. The stoichiometry of these materials ranges from $(BH_{1.5})_x$ to lower hydrogen-boron ratios. Little is known about these materials. No definite compounds have been isolated, but the chemical properties of these polymeric hydrides and the lower boranes show many striking similarities.

The classical preparation of the boron hydrides is the acid hydrolysis of magnesium boride. Since diborane is readily hydrolyzed in aqueous solution, the major product of this preparation is tetraborane with traces of the higher members of the family. Diborane and the higher boranes are produced by the controlled pyrolysis of the tetraborane thus formed.

Obviously, the above procedure is very inefficient. Since the work of Stock (48), many investigators have devised preparative methods which are more convenient and efficient for these hydrides. Schlesinger and Burg (41) found that diborane could be produced by subjecting a mixture of boron trichloride and hydrogen to a high voltage discharge. Later, Schlesinger and Brown (39) found that boron trifluoride could be reduced by lithium hydride or lithium aluminum hydride in an ether solution giving very pure diborane. Hurd (27) passed boron halide vapors over alkali or alkaline earth metal hydrides at elevated temperatures and produced diborane. Hurd (27) altered this method and successfully synthesized diborane by passing the boron halide vapors and hydrogen over heated beds of finely divided electropositive metal. Recently, Newkirk and Hurd (35) obtained evidence which indicates that the hydrides of boron are produced when hydrogen is passed through a heated tube of finely divided metal boride or commercial boron. Schaeffer and Toeniskoetter (37) have shown that diborane is formed by the reaction of cuprous chloride and lithium borohydride in ether solution.

With the advent of the "rocket age," much emphasis has been placed on high calorific materials. Relatively simple thermochemical calculations reveal that, pound for pound, the boron hydrides produce approximately twice as much energy as corresponding hydrocarbon fuels, since both boron and hydrogen have high heats of oxidation. Obviously, no survey of high-energy fuels would be complete without consideration of the boron hydrides. This is especially true since, as pointed out by Hurd (28), the spontaneous reaction of

some of the boron hydrides with water make them desirable as underwater rocket propellants.

The first problem one faces when a potential use is found for a material is that of finding a commercially feasible process whereby this material may be produced in quantity. It is easy to see that none of the processes previously mentioned are very suitable from this standpoint.

It is interesting to note that, whereas many materials are produced by electrolytic means, no attempts to produce the boranes in this fashion have been reported in the literature. In fact, the electrochemical portion of the field of boron chemistry has been sadly neglected. Consideration of the above observations led to the instigation of this research.

Although it was believed at the start that sodium borohydride would be an excellent starting material for the electrolytic production of diborane, the material chosen was sodium trimethoxyborohydride. This compound, along with sodium tetramethoxyborohydride, $NaB(OCH_3)_4$, and sodium borohydride, $NaBH_4$, constitute the only stable members of the series represented by the general formula, $NaBH_n(OCH_3)_{4-n}$, where n may vary from zero to four.

The reason for choosing sodium trimethoxyborohydride was threefold. First, as has been stated, it is stable and may be prepared easily in 99 plus percent purity by refluxing trimethylborate with sodium hydride (11). Secondly, it appears to be ionic in nature, ionizing into sodium ions and trimethoxyborohydride ions. Thus, it is possible that electrolytic reaction of these latter ions might produce diborane or some intermediate such as dimethoxyborine, $BH(OCH_3)_2$, (14) which readily disproportionates into diborane and trimethylborate. Thirdly, sodium trimethoxyborohydride may be considered as an intermediate in the preparation of sodium borohydride. Commercially, the latter is prepared by the reaction of trimethylborate with sodium hydride at elevated temperatures (51). Thus, if sodium borohydride were suitable for the electrolytic production of diborane, sodium trimethoxyborohydride might be even more suitable from a commercial point of view.

Two lines of approach to this problem were open. The first involved suspending the material to be electrolyzed in an inert medium, adding a current carrier, and electrolyzing. An example of this method is the reduction of a nitrobenzene suspension where the nitrobenzene molecule is brought into contact with the electrode by physical agitation and then reduced. The second approach was the classical one in which an ionizing solvent is found for the solute. The ions act as current carriers, and ionic oxidation and reduction occur at the electrodes.

The introduction of a current carrier obviously introduces complications; and since more interpretable results are obtained from simpler systems, the second approach was used almost exclusively.

PREPARATION OF TRIMETHYLBORATE AND SODIUM TRIMETHOXYBOROHYDRIDE

Preparation of Trimethylborate

The preparation of trimethylborate was undertaken as the first step in this investigation since it was not commercially available at the time. The method of Brown and Schlesinger (40) was used and six preparations were carried out; four using boric acid and two using boric oxide.

In a typical preparation using boric acid, 372 g (U.S.P. Pacific Coast Borax Co.) of boric acid was added slowly to 1950 ml (1036 g) of methanol (anhydrous technical grade) over a period of 3 to 4 hours. The mixture was refluxed for one hour after complete addition of the alcohol. The reflux condenser was then converted to a downward condenser and the mixture distilled using an ordinary distilling head. A distillate appeared at 55°C and was collected up to 70°C. No azeotrope was obtained at 54°C since an efficient distilling column was not used and no attempt was made to fractionate the mixture at this point.

Using boric oxide, 70 g of boric oxide (anhydrous, J. T. Baker Chemical Co.) was added to 260 ml of methanol over a period of 1 to 2 hours. The reaction mixture was refluxed for 2 hours upon completion of the addition. The reflux condenser was replaced by a downward condenser and distillation begun. Here again, no attempt was made to fractionate the mixture and a distillate appeared from 59°C to 70°C at which point collection was discontinued.

The apparatus consisted of a three-necked flask fitted with a stirring mechanism, addition tube, reflux condenser, and a heating mantle.

The azeotropic mixture obtained in the above two preparations was treated by two methods (40). The distillate obtained from one run was treated with anhydrous lithium chloride. The mixture immediately separated into two layers. Approximately 13 g of anhydrous lithium chloride was used for every 135 g of azeotropic mixture. The upper layer consisted of trimethylborate. It was removed and distilled, the fraction between 67.5°C and 68.5°C being collected.

The use of concentrated sulfuric acid to separate the azeotropic mixture was also tried. The concentrated acid was added in 5 ml portions until two layers appeared. The upper layer was trimethylborate and was removed and distilled. As before, the fraction distilling between 67.5°C and 68.5°C was collected.

Some difficulty was experienced in the extraction process. It was found that this difficulty could be overcome by fractionating the mixture as obtained in the reaction flask and obtaining the azeotrope at 54°C. Anhydrous lithium chloride was found to give the best results for extraction. The yield of trimethylborate was gradually increased to 82 percent of relatively pure trimethylborate calculated on the basis of the boron material used.

For future use it was found that a very good grade of trimethylborate could be obtained from the Anderson Laboratories, Weston, Michigan. Prior to use, this trimethylborate was treated with anhydrous lithium chloride, the clear liquid decanted, a small amount of sodium hydride added, and the mixture fractionally distilled. All of the liquid distilled between 67°C and 69°C. The fraction distilling between 67.8°C and 68.5°C was collected for use. The physical properties of trimethylborate are given in the section concerning some physical properties of trimethylborate.

Preparation of Sodium Trimethoxyborohydride

The preparation of sodium trimethoxyborohydride was carried out according to the method of Brown and Schlesinger (11). Ten preparations were made.

The apparatus consisted of a round-bottom flask equipped with a large-capacity reflux condenser and a heating mantle. In a typical preparation, 115 ml of trimethylborate was slowly added to 12 g of sodium hydride (Metal Hydrides, Inc.). A 100 percent excess of trimethylborate was used as recommended by Brown and Schlesinger (11). Upon contact of the trimethylborate and sodium hydride, the reaction mixture became extremely warm and ebullition occurred. The volume of the solid began to increase and turned slowly from a gray to a snow white color. The flask was heated upon completion of the addition of trimethylborate and the mixture refluxed until the volume increase ceased and the solid was white. The time required was 9 to 20 hours, depending on the particle size of the sodium hydride. The reflux condenser was then converted into a downward condenser and the excess trimethylborate was distilled off. The last traces of trimethylborate were removed under reduced pressure (70-80 mm of mercury). In this preparation the yield was 63.5 grams or 99 percent yield computed on the sodium hydride used and according to equation (I).

$$NaH + B(OCH_3)_3 \longrightarrow NaBH(OCH_3)_3 \qquad (I)$$

In all preparations the yield was better than 98 percent.

Some attempts were made to purify the sodium trimethoxyborohydride formed by recrystallization from isopropylamine. The sodium trimethoxyborohydride dissolved easily in isopropylamine at 34°C. However, upon filtering and cooling the solution a very fine, powdery precipitate was obtained which defied filtration. Both rapid and slow rates of cooling were tried with identical results. This difficulty was not, however, serious, since the sodium trimethoxyborohydride could be prepared in 99 plus percent purity by carefully grinding the sodium hydride to a fine powder, and extending the time of reflux to 20 to 25 hours.

The sodium trimethoxyborohydride was analyzed for sodium and boron by hydrolyzing a known weight of sample in water, titrating to a methyl red end point using standard hydrochloric acid solution, adding mannitol, and then titrating to a phenolphthalein end point using standard sodium hydroxide solution (11).

The first determinations gave erratic results since the end points were difficult to observe. Later analyses gave 17.70 percent sodium and 8.65 percent boron which agreed well with the theoretical 17.97 percent sodium and 8.59 percent boron in sodium trimethoxyborohydride.

Sodium trimethoxyborohydride is a fluffy, white solid. It is stable in dry air, but is slowly attacked by moist air. Schlesinger et al. (11) found that it decomposed at its melting point (230°C) according to equation (II).

$$4NaBH(OCH_3)_3 \longrightarrow NaBH_4 + 3NaB(OCH_3)_4 \qquad (II)$$

Some of the chemical properties of this material which were determined by Schlesinger et al. (11) are best summarized by the following equations.

$$NaBH(OCH_3)_3 + 4HOH \longrightarrow 3CH_3OH + H_2 + NaOH + H_3BO_3 \tag{III}$$

$$NaBH(OCH_3)_3 + 3NaH \longrightarrow 3NaOCH_3 + NaBH_4 \tag{IV}$$

$$NaBH(OCH_3)_3 + BF_3 \longrightarrow NaBHF_3 + B(OCH_3)_3 \tag{V}$$

$$NaBH(OCH_3)_3 + CH_3OH \longrightarrow NaB(OCH_3)_4 + H_2 \tag{VI}$$

$$NaBH(OCH_3)_3 + CO_2 \longrightarrow HCOONa + B(OCH_3)_3 \tag{VII}$$

$$NaBH(OCH_3)_3 + HCl \longrightarrow NaCl + CH_3OH + (CH_3O)_2BH \tag{VIII}$$

$$2NaBH(OCH_3)_3 + B_2H_6 \longrightarrow 2NaBH_4 + 2B(OCH_3)_3 \tag{IX}$$

$$6NaBH(OCH_3)_3 + 8(C_2H_5)_2O{:}BF_3 \longrightarrow B_2H_6 + 6NaBF_4 + 6B(OCH_3)_3 + 8(C_2H_5)_2O \tag{X}$$

Close observations of these equations will show that the reactions of sodium trimethoxyborohydride are best considered in view of the Lewis acid-base concept.

An infrared spectrum of sodium trimethoxyborohydride is given in Figure 1.

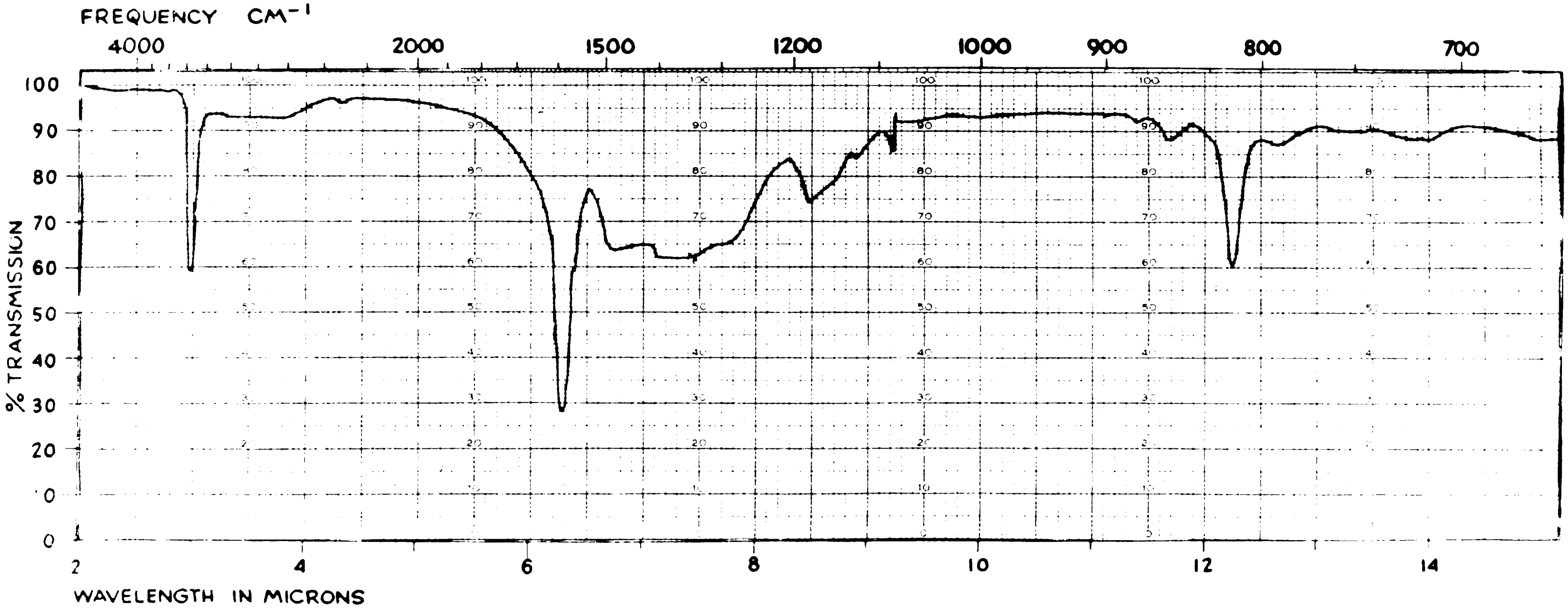


Figure 1

Infrared Spectrum of Sodium Trimethoxyborohydride
(phase, nujol mull; purity, ca. 100 percent; prism, sodium chloride)

SOLVENTS TESTED FOR ELECTROLYTIC STUDIES

As previously stated, the electrolysis of sodium trimethoxyborohydride could be approached by either of two methods. One approach involved suspending the sodium trimethoxyborohydride in an inert medium, adding a suitable current carrier, and electrolyzing. The other approach was seemingly simple and straightforward, requiring a solvent which dissolved sodium trimethoxyborohydride by ionic dissociation and allowing it to act as its own current carrier.

Since it was desired to pin down the electrolytic process occurring with the sodium trimethoxyborohydride only, the simplest system obtainable was desired. It was felt that the introduction of a current carrier would surely complicate and mask the reaction, and consequently, most emphasis was placed on finding a solvent which would dissolve sodium trimethoxyborohydride by a process of ionic dissociation. This turned out to be a much more difficult task than anticipated, and some attention was turned in the direction of current carriers.

Several requirements that the solvent had to meet are that sodium trimethoxyborohydride must:

(1) dissolve in the solvent by ionic dissociation;

(2) be totally unreactive toward the solvent; and

(3) the solvent itself should be unchanged by electrolysis.

Since it is believed that sodium trimethoxyborohydride ionizes according to the equation,

$$NaBH(OCH_3)_3 \rightleftharpoons Na^+ + BH(OCH_3)_3^-, \qquad (XI)$$

the first requirement is apparently satisfied. Accordingly, it would be logical to choose a highly polar solvent to foster this ionization. Consequently, solvents with high dielectric constants were sought.

The reductive power of the sodium trimethoxyborohydride greatly limited the solvents which could be used. In general, solvents with high dielectric constants are composed of unsymmetrical molecules which contain various reactive groups such as the hydroxyl group, et cetera. Sodium trimethoxyborohydride has very pronounced reductive properties. Brown and Mead (9) found that this compound readily reduced aldehyde, ketone, acid chloride, and anhydride groups while ester and nitrile groups were only slowly attacked at elevated temperatures. The carboxylate group did not appear to react, but the nitro group was reduced at temperatures above 140°C. Double bonds were apparently stable even when conjugated with a carbonyl group. However, the report did not indicate the effect of the alkyl groups on the reduction of the types of compounds mentioned, and some hope was held that the nitriles, substituted formamides, and similar materials might meet the second requirement if the appropriate alkyl groups could be found. Sodium trimethoxyborohydride reacts readily with hydroxyl groups and with water. Thus, any material containing hydroxyl groups had to be eliminated.

Table II lists the solvents purified and tested as to solubility, relative conductivity, and reactivity with reference to sodium trimethoxyborohydride. The estimated solubility is given as grams of sodium trimethoxyborohydride per 100 ml of solvent. The relative conductivity is the increase in current passed by the solution of the solvent saturated with sodium trimethoxyborohydride over the current passed by the pure solvent. Reactivity indicates any visual signs of reaction, such as gassing, et cetera, of sodium trimethoxyborohydride with the solvent.

Estimated solubilities were made by equilibrating the solvent with sodium trimethoxyborohydride in a closed tube placed in a 25°C bath. After five hours the tubes were removed from the bath, centrifuged, and a 5 ml aliquot of liquid, extracted by using a filter stick, was transferred to a tared weighing tube. The weighing tube and contents were transferred to a vacuum desiccator charged with barium oxide, and continuously evacuated until all liquid had disappeared, and the weighing tubes had achieved constant weight. After

TABLE II

REACTIVITY, SOLUBILITY, AND RELATIVE CONDUCTIVITY OF SODIUM TRIMETHOXYBOROHYDRIDE IN VARIOUS SOLVENTS

Solvent	Reactivity	Solubility (g/100 ml)	Relative Conductivity (ma)
n-hexane	none	<0.1	0
n-heptane	none	<0.1	0
ethyl ether	none	0.4	0
n-butyl ether	none	0.4	0
benzyl ether	none	<0.4	0
diethyl carbitol	none	<0.4	0
trimethylborate	none	<0.2	0
pyridine	none	0.4	1*
dimethylformamide	none	8.3	8
benzene	none	<0.1	0
p-fluorotoluene	none	<0.1	0
chloroform	none	0.6	0
ethyl silicate	none	<0.1	0
trimethoxyboroxine	blue gel	-	-
acetonitrile	yellowing of solution	3.3	2
dioxane	slight gassing	1.7	-
tetrahydrofuran	slight gassing	-	-
ethylene glycol dimethyl ether	none	1.4	8*
diethylene glycol dimethyl ether	none	0.5	2*
triethylene glycol dimethyl ether	none	<0.4	0*
monomethyl cellosolve	gassing, heat	-	-
methyl n-propyl ketone	white gel	-	-

the dry weights were determined, the solubility was calculated as grams per 100 ml of solvent. In cases where reactions took place no solubility or relative conductivity data were obtained.

Relative conductivity tests were carried out in the cell described in Figure 2. A milliammeter with a 0-10 milliampere range was used to detect the passing of a current. Tests were made first with the pure solvent, then with the solvent saturated with sodium trimethoxyborohydride, and the relative increase in current noted. All measurements were made using a 100 volt direct current source. The relative conductivity values with an asterisk were obtained in the electrolysis cell (Figure 5) with a source potential of approximately 175 volts. The electrodes of the cell were about 1 cm apart.

Of the solvents tested, it appears that sodium trimethoxyborohydride tends to be soluble in cyclic ethers and ethylene glycol dimethyl ethers, and N-substituted formamides without reaction.

Acetonitrile, ethylene glycol dimethyl ether, and dimethylformamide were finally chosen as solvents for electrolytic study. The amines were not selected since they themselves give rise to a series of nitrogen reduction products upon electrolysis and needlessly complicate the reaction.

Dimethylformamide (Matheson Chemical Co.) was purified by treatment with sodium hydroxide pellets, after which the liquid was

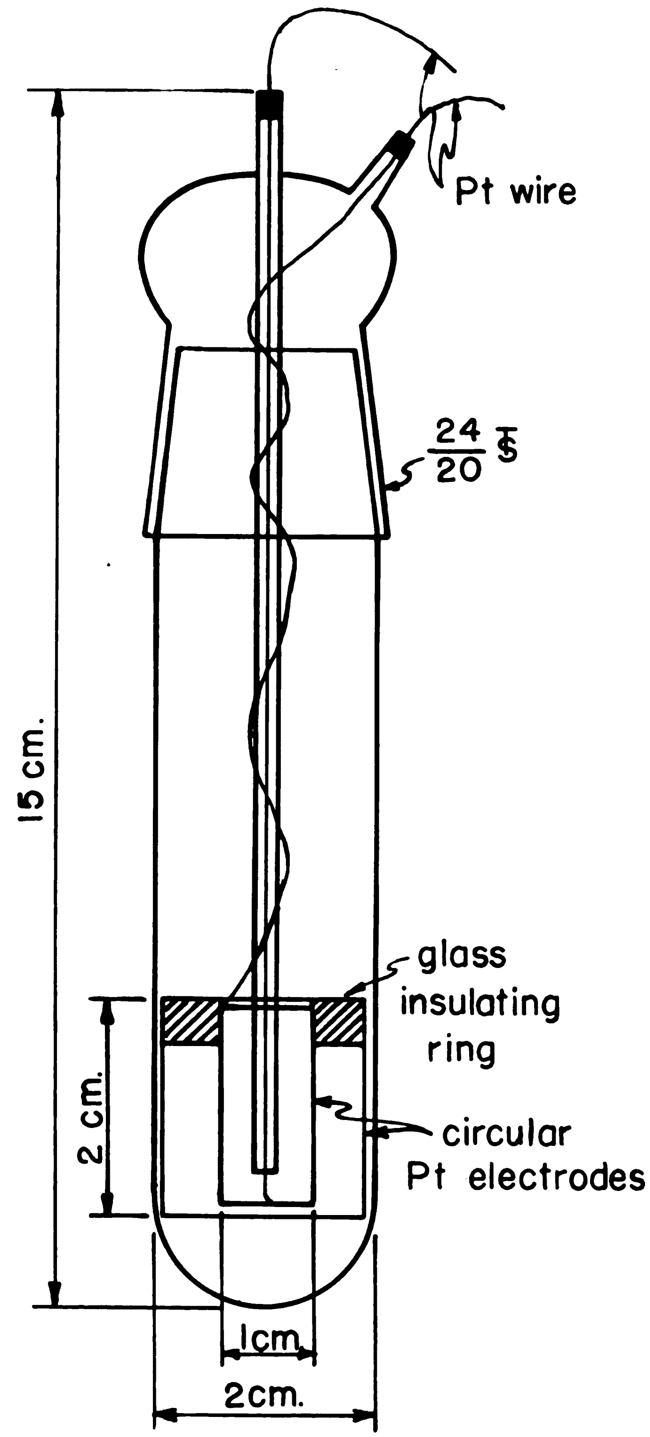


Figure 2

Relative Conductivity Cell Diagram

decanted from the pellets onto calcium oxide and distilled from the latter. The fraction distilling between 151°C and 152°C at 740 mm pressure was collected for use.

The ethylene glycol dimethyl ethers (Ansul Chemical Co.) along with diethyl carbitol (Carbide and Carbon Chemicals Co.) were treated with barium oxide and then distilled from sodium hydride.

Diethyl, di-n-butyl, and dibenzyl ethers were purified by distillation from a mixture of potassium hydroxide pellets and anhydrous sodium sulfite.

The preparation and purification of trimethylborate has been given on page 13.

Acetonitrile (Matheson Chemical Co.) was purified by treatment with anhydrous sodium carbonate after which the liquid was decanted onto phosphorus pentoxide from which it was distilled.

Tetrahydrofuran (Matheson Chemical Co.) was treated with potassium hydroxide pellets and distilled from lithium aluminum hydride.

Dioxane (Eastman Kodak Co.) was refluxed with aqueous hydrochloric acid during which dry nitrogen was bubbled through the solution. Then the mixture was treated with potassium hydroxide pellets, the dioxane layer separated and distilled from metallic sodium.

Benzene, n-hexane, and n-heptane were distilled from sodium.

All other solvents were used in the highest purity available as obtained directly from the chemistry department stockroom. For instance, Fischer reagent pyridine was used.

It should be mentioned that when sodium trimethoxyborohydride was introduced into tetrahydrofuran and dioxane a slight gassing occurred. This, at first, was believed to be caused by impurities and the materials were carefully repurified. However, repurification of these two solvents did not prevent a slight gassing upon the introduction of sodium trimethoxyborohydride. No explanation for this gassing has been found.

Since the current observed in all cases was small, lithium and sodium fluorides and tetra n-butylammonium iodide were tried as possible current carriers in pyridine, dimethylformamide, acetonitrile, and tetrahydrofuran. Upon addition of tetra n-butylammonium iodide to acetonitrile, the current increased over 150 ma and to the tetrahydrofuran over 12 ma. However, the solutions took on a yellowish color which gradually deepened as more current passed. Since iodine might have been freed in the electrolysis, iodine crystals were placed in acetonitrile and tetrahydrofuran to learn if the color of the electrolytic solutions could be reproduced. These two solutions became colored after the addition of the iodine crystals in the same manner as the electrolytic solutions. However, when sodium trimethoxyborohydride was added to these two solutions the color gradually disappeared, as would be expected, since sodium trimethoxyborohydride should reduce iodine to the iodide as indicated by the equation,

$$2NaBH(OCH_3)_3 + I_2 \longrightarrow 2NaI + H_2 + B(OCH_3)_3. \qquad (XII)$$

Sodium and lithium fluorides did not increase the conductivity of pyridine, acetonitrile, dimethylformamide, and tetrahydrofuran. Apparently, when tetra n-butylammonium iodide was used as a current carrier in acetonitrile and tetrahydrofuran it was electrolyzed, producing iodine at the cathode. This iodine was then reduced to the iodide by the sodium trimethoxyborohydride as indicated by equation (XII). Thus, it was concluded that sodium fluoride, lithium fluoride, and tetra n-butylammonium iodide could not be used as current carriers in the electrolysis of sodium trimethoxyborohydride.

VACUUM APPARATUS

Electrolysis Apparatus

Since the boranes and many of their derivatives are sensitive to oxygen and moisture, a vacuum apparatus was required for this research. Figure 3 is a diagram of the apparatus found suitable for the electrolytic studies under consideration. A picture of this apparatus is shown in Figure 4.

The manifold was of 25 mm glass tubing and approximately five feet in length. It was connected to a mercury diffusion pump, which was isolated by cold traps, and an exhaust pump by a large stopcock at the left end. The manifold was divided into three sections indicated as V_1, V_2, and V_3. Section V_1 was connected to section V_3 through a by-pass tube (B) with a stopcock in order that V_1 would be isolated without disturbing V_2. Sections V_1 and V_2 were equipped with entrance or exit tubes (E) with stopcocks and 12/30 ground glass joints, condensation tubes (C), mercury manometers (M), and electrolysis cell leads (CL) which attached to the electrolysis cell by ball joints. These two sections were designed for isolating and measuring the cathode and anode gases of electrolysis.

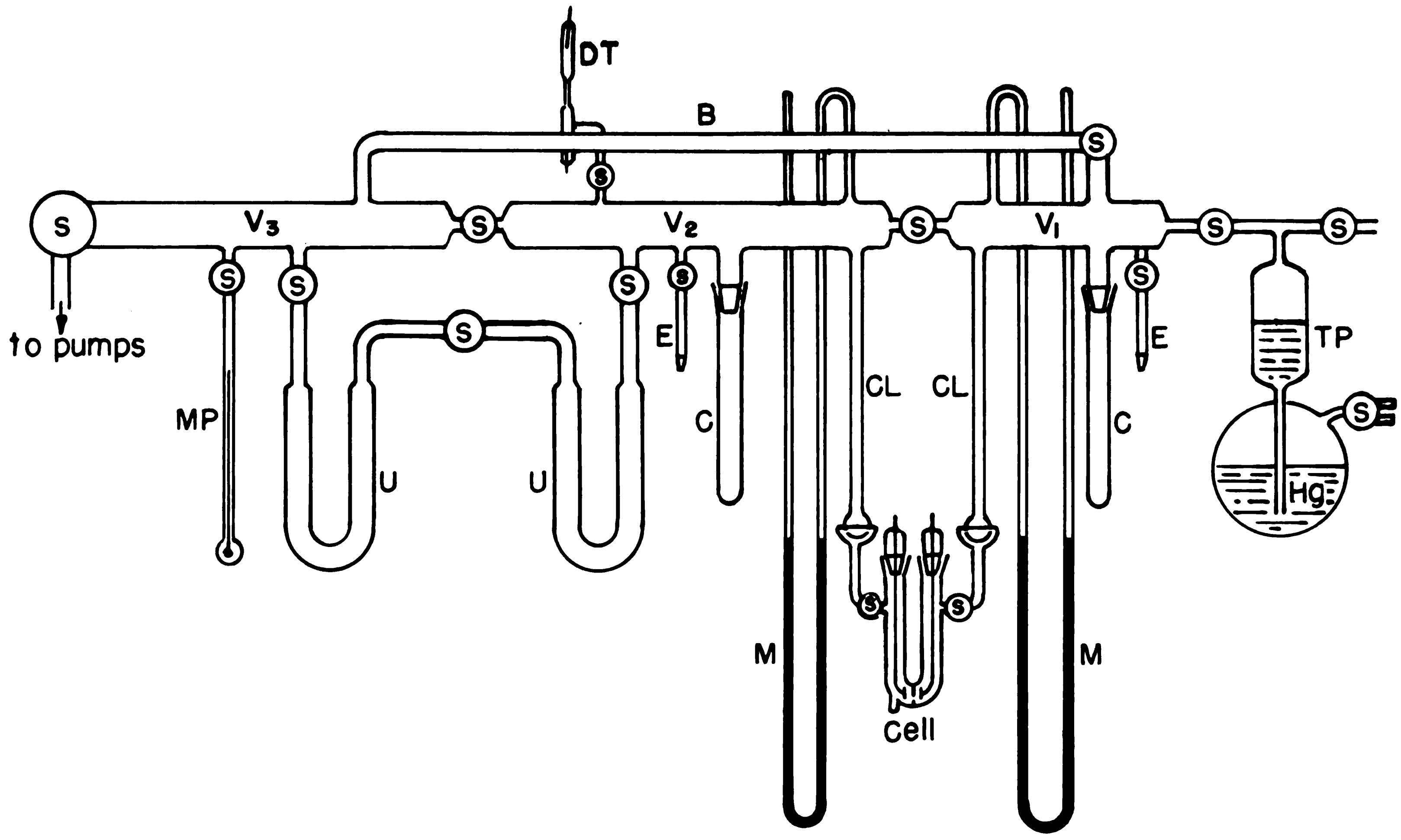


Figure 3

Electrolysis Apparatus

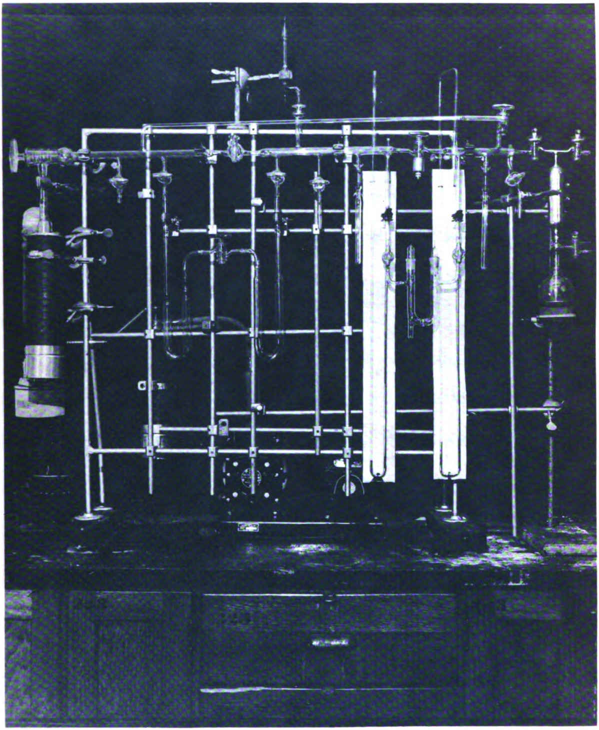


Figure 4

Electrolysis Apparatus

A hand-operated Toepler pump (TP) was connected to section V_1 for the removal of gas samples. V_2 was equipped with a gas discharge tube (DT) for identifying gases by spectroscopic methods. For simple fractionations and storage, two U-tubes (U), which were separated by stopcocks, connected sections V_2 and V_3. A melting point apparatus (MP) (48) was sealed into section V_3.

All stopcocks and ground glass joints were lubricated with Apieson "T" stopcock grease and the ball joints between the cell and the main manifold were sealed with Apieson "W" wax.

Initially, several electrolytic cells were designed with coarse glass frits separating the cathode and anode compartments. However, it was found that this frit offered too much resistance to the passage of current and some other arrangement had to be made. A diagram of the cell found to be most suited for this work is shown in Figure 5, and a picture in Figure 6. It consists of a U-tube with side arms (A) which connect to sections V_1 and V_2 of the main manifold through the electrolysis cell leads (CL) by ball joints (B). This cell could be isolated from the remainder of the system by stopcocks located in the side arms.

Electrode leads were introduced into the cell at the top of the U-tubes by 24/40 ground glass joints. This permitted removal of the electrodes and easy variation not only of the distance between

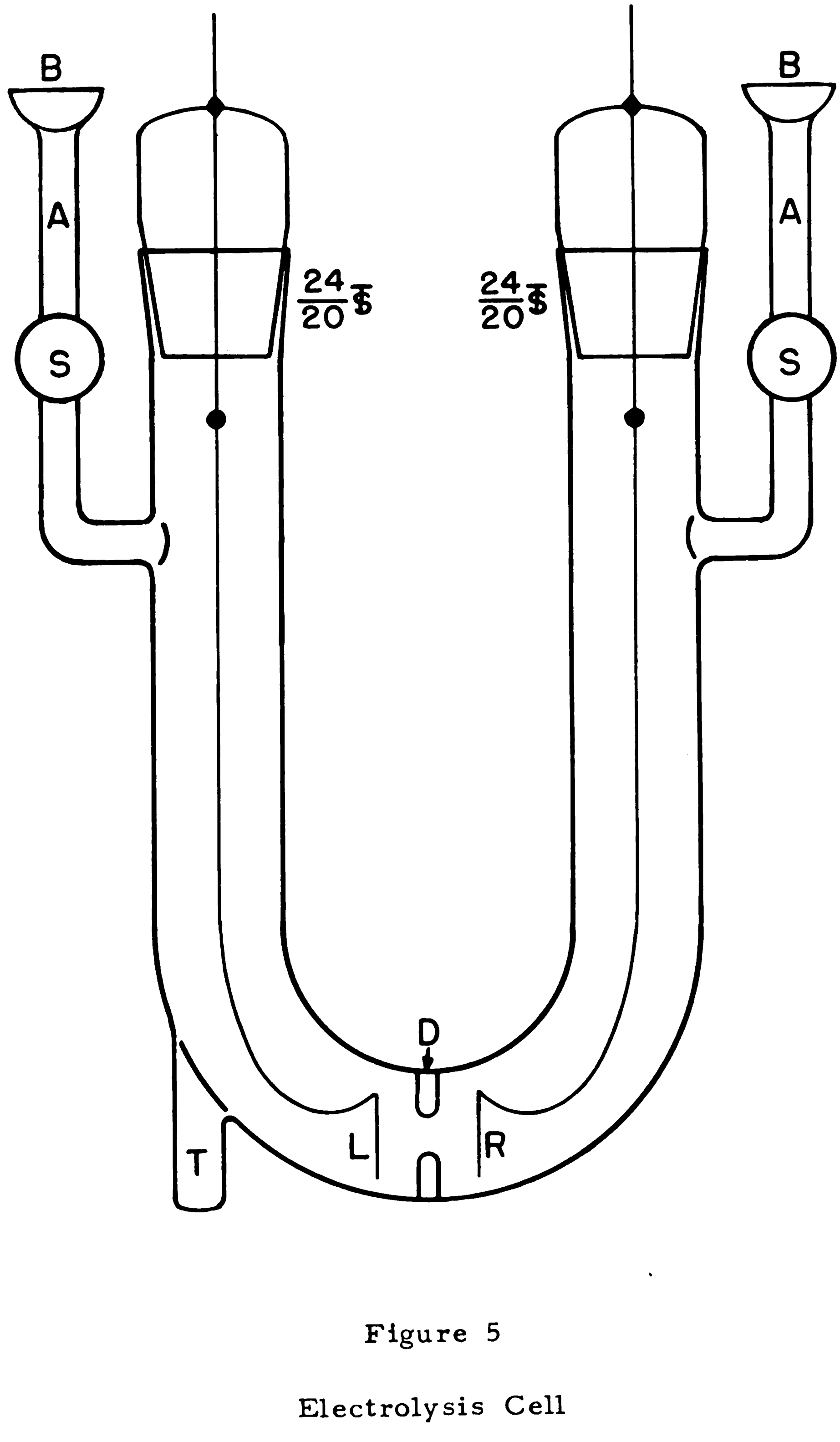


Figure 5

Electrolysis Cell

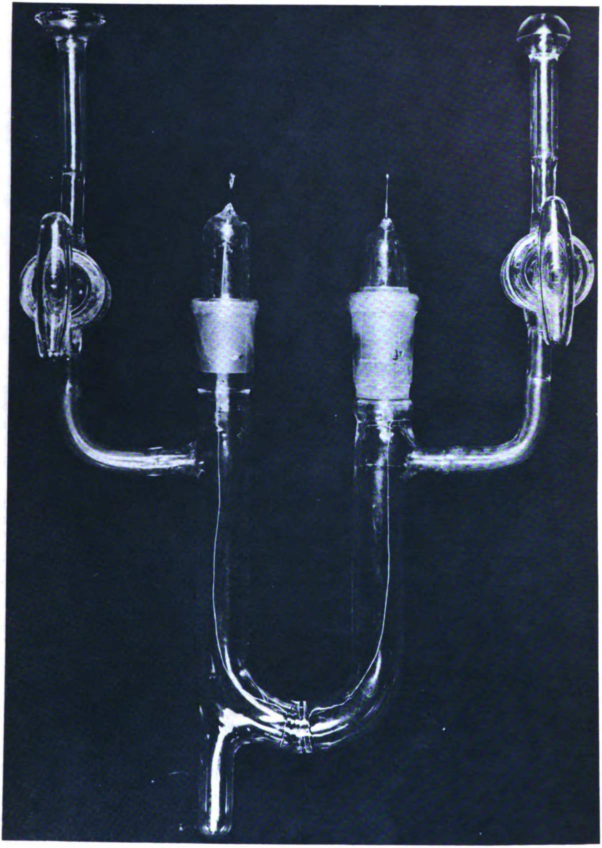


Figure 6

Electrolysis Cell

electrodes but also of the electrode material itself. The electrodes (L and R) consisted of two 1-square-centimeter platinum foils connected to the electrode leads by platinum wire.

Platinum electrodes were chosen because it was reasonably certain that this metal would be inert toward any solvent, solute, or product of electrolysis. As work progressed and hydrogen evolution was noted, some thought was given to the suppression of this hydrogen evolution by using an electrode material with a higher hydrogen overvoltage than platinum. However, the large source potentials employed for electrolysis were sufficient to evolve hydrogen from any metal. If a suitable current carrier had been found, a much lower voltage could have been employed and a change of electrode material may have served the purpose. Caution is used in the above statement because the hydrogen overvoltages as reported in the literature are for positive hydrogen rather than for hydrogen production at the positive electrode. Thus, one is confronted with two different situations, and a change in electrode material may or may not have produced the desired results. Consequently, all electrolyses were studied using platinum electrodes.

The two cell compartments were separated by a glass ''doughnut'' (D). This partition performed the duty of separating the electrode gases well, and was not subject to the resistance of the glass frit.

A small tube (T) was sealed into the left-hand side at the bottom of the electrolysis cell. This tube was used to contain the solid solute. Since the solvent and solute were in constant contact, the solvent was always saturated with solute. Furthermore, by keeping solute isolated in (T) from the electrodes (L and R), any solid formed at these electrodes during electrolysis could be isolated.

The volumes V_1 and V_2, both extending to the stopcocks of the electrolysis cell, were determined by attaching a 79 ml bulb containing a known pressure of helium onto the entrance tube (E) of V_1. The system was evacuated, the electrolysis cell isolated from the system, and the stopcocks between V_1, V_2, and V_3 closed. Then the helium was expanded first into V_1 and then into V_2. Pressure measurements were taken after each expansion and four sets of pressure data were obtained.

The volume calculations were made on the basis of the perfect gas law. A 20 cm length of the 8 mm tubing used for the manometers was filled with mercury and its volume measured to give the average volume per cm length of tubing. Using this information the volume obtained for V_1 and V_2 were corrected for zero pressure in the system.

The volume of the cell was determined by filling it with water and measuring the volume of water required.

The volume of V_1 was 101.5 ml, that of V_2 was 144.0 ml, and the cell volume was 75.0 ml.

For electrolyses a potential was impressed across the electrodes with a current regulator designed by Thompson (50).

Storage and Purification Apparatus

The storage and purification apparatus is shown in Figure 7. This apparatus consisted of connected upper and lower manifolds. The right side of the upper manifold (A) was equipped with a series of pure liquid storage bulbs while the left side of this manifold (B) contained four storage bulbs, equipped with manometers, for gases. The lower manifold was equipped with a series of U-tubes (D) for fractionations and the apparatus (C) used for the study of the diborane-dimethylformamide reaction.

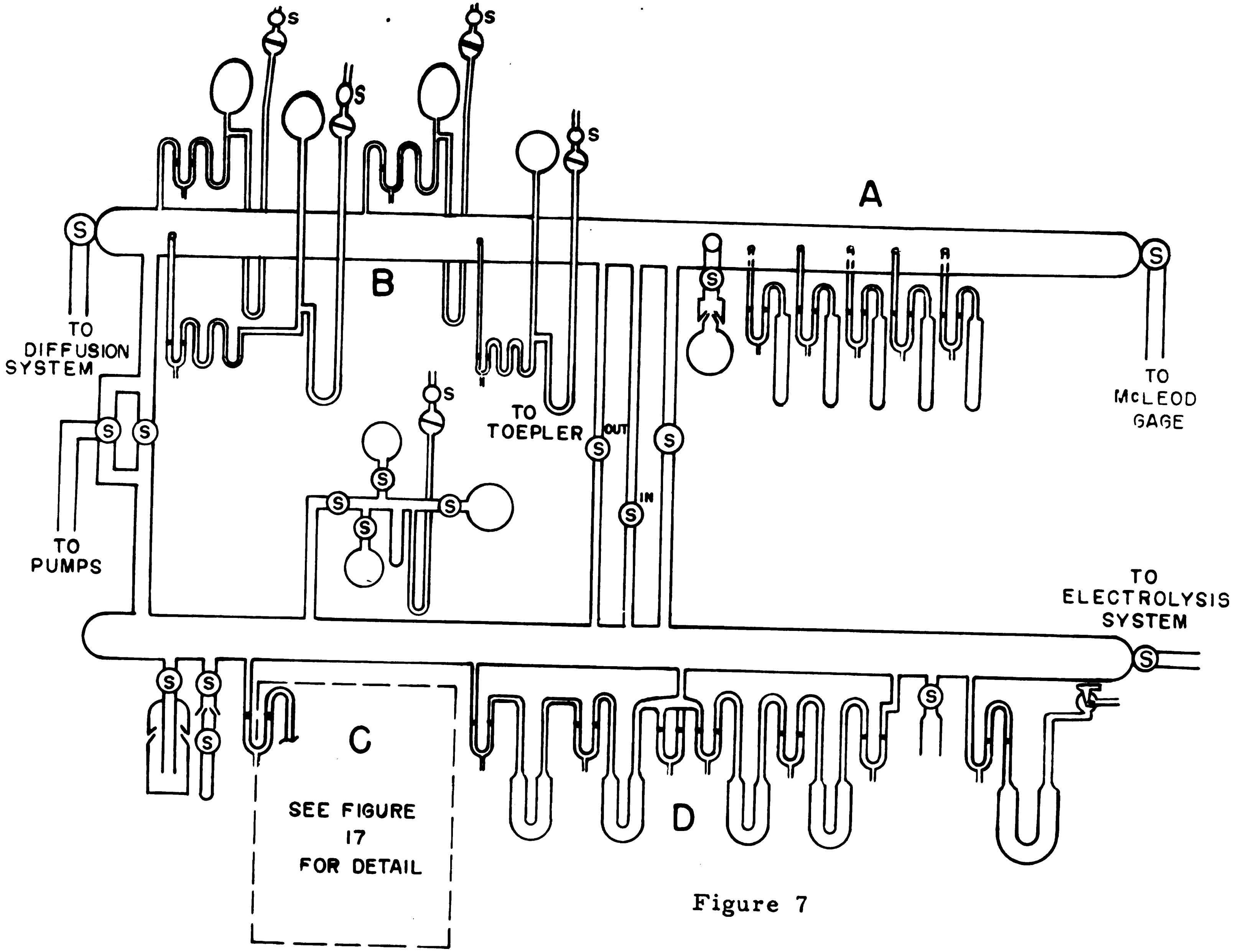


Figure 7

Storage and Purification Apparatus

ELECTROLYTIC STUDIES

Theory

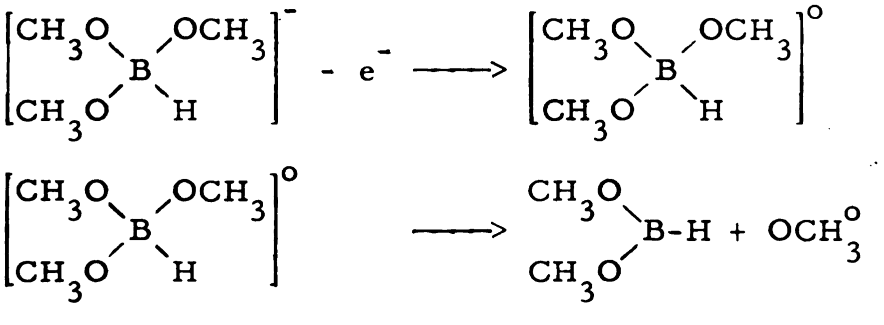
When one considers what would be the products of and the mechanism for the reaction which takes place during the electrolysis of sodium trimethoxyborohydride, one could assume, if an inert solvent were used and ionization of the solute occurred, that the anode products could be produced according to either of two mechanisms.

If one assumes ionization of sodium trimethoxyborohydride according to equation (XI), then the over-all mechanism of the reactions

$$NaBH(OCH_3)_3 \rightleftharpoons Na^+ + BH(OCH_3)_3^- \qquad (XI)$$

would involve the reduction of the sodium ion at the cathode and the oxidation of the trimethoxyborohydride ion at the anode. The two different mechanisms arise as a result of the two possible reactions involving the latter ion at the anode. The two anode reaction mechanisms would involve breaking the B-O bond on the one hand and the B-H on the other, as shown below.

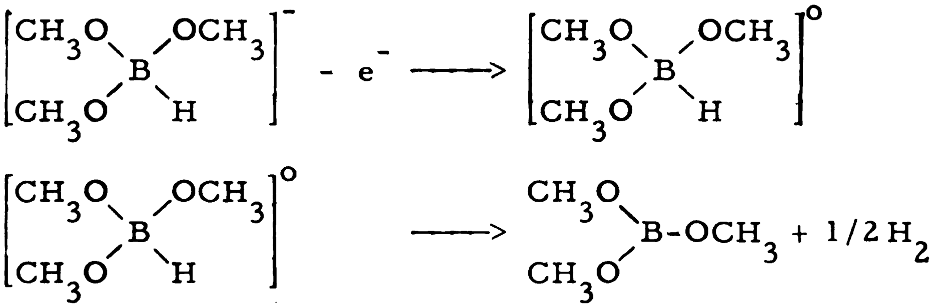
Anode Mechanism I:



(XII)

(XIII)

Anode Mechanism II:



(XIV)

(XV)

In either case the cathode product would be metallic sodium which in the case of anode mechanism I would undergo further reaction with the methoxide radical, giving the over-all reaction as shown in equation (XVI),

$$NaBH(OCH_3)_3 \longrightarrow NaOCH_3 + HB(OCH_3)_2 \qquad (XVI)$$

while in the case of anode mechanism II, the over-all reaction would be as shown in equation (XVII).

$$NaBH(OCH_3)_3 \longrightarrow Na + 1/2\ H_2 + B(OCH_3)_3 \qquad (XVII)$$

For mechanism I, involving the rupture of the B-O bond, one considers the trimethoxyborohydride ion as having a tetrahedral configuration, since an sp^3 hybridization of the boron orbitals occurs.

This tetrahedral arrangement is particularly stable. Even though the B-O bond is stronger than the B-H bond in planar configurations involving boron (sp^2 bonding), it is entirely possible that the sp^3 hybridization might equalize the B-O and B-H bond strengths to such an extent that the B-O bond of the neutral entity represented in equations (XII) and (XIV) might be broken preferentially to the B-H bond of this neutral entity. If this happens, then the reaction depicted by equation (XIII) would follow and dimethoxyborine would be formed.

One line of evidence to support this proposal is the study of dimethoxyborine made by Burg and Schlesinger (14), who found that dimethoxyborine had a boiling point of 25.9°C, a melting point of -130.6°C, and that it existed in equilibrium with diborane and trimethylborate as shown in equation (XVIII).

$$6HB(OCH_3)_2 \rightleftharpoons B_2H_6 + 4B(OCH_3)_3 \qquad \text{(XVIII)}$$

By employing suitable conditions they found that dimethoxyborine could be completely decomposed to diborane and trimethylborate. Thus, if anode mechanism I occurred, diborane would be a product of electrolysis.

Consequently, if the reaction occurred by the first mechanism, the products would be sodium methoxide, diborane, and trimethylborate; whereas if the second mechanism occurred, the products would be metallic sodium, hydrogen, and trimethylborate.

With these ideas in mind, the electrolysis of sodium trimethoxyborohydride was attempted using the solvents ethylene glycol dimethyl ether, dimethylformamide, and acetonitrile.

Electrolysis of Sodium Trimethoxyborohydride in Ethylene Glycol Dimethyl Ether

Although ethylene glycol dimethyl ether was the last solvent employed in the electrolytic studies, the electrolysis of sodium trimethoxyborohydride in this ether will be discussed first. Electrolyses in acetonitrile and dimethylformamide were complicated by numerous side reactions, and it was through the use of ethylene glycol dimethyl ether that the electrolytic process occurring was finally elucidated. In the final analysis it was found that the observations made upon the electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether might satisfactorily explain the results using dimethylformamide and acetonitrile.

The three compounds, namely the mono-, di-, and triethylene glycol dimethyl ethers, were purified and tested as indicated in the section beginning on page 18. It was found that the solubility of sodium trimethoxyborohydride in this series of ethers decreased as the length of the ether chain increased. This result was not too unexpected in view of the fact that sodium trimethoxyborohydride had been found to be insoluble in paraffinlike hydrocarbons, and it is obvious that the paraffinlike nature of these ethers would increase as the length of the ether chain increased. Thus, ethylene glycol dimethyl ether was chosen for electrolytic study, since this ether gave the greatest promise of success.

Some physical properties (1) of ethylene glycol dimethyl ether are given in Table III. Vapor pressure data for this material are plotted in Figure 8.

The ethylene glycol dimethyl ether as received from Ansul Chemical Company was tested for peroxides. This test consisted of shaking a 10 ml sample of the ether with 1 ml of freshly prepared potassium iodide solution for several minutes. Since this ether is completely soluble in water, a pale yellow color of liberated iodine will develop rapidly if peroxides are present. The intensity of this color indicates the amount of peroxide present. Purification was necessary since the test was positive. During the period of use of this ether, tests for peroxides were made and repurification accomplished when necessary.

Initially, the ether was distilled from barium oxide and potassium iodide crystals, and the fraction of distillate in the range of 82.5°C to 83°C collected. However, sodium trimethoxyborohydride reacted, with slight gassing, with this purified ether. Reaction of

TABLE III

PHYSICAL PROPERTIES OF ETHYLENE GLYCOL DIMETHYL ETHER

Molecular weight	90.078
Specific gravity 20/20°	0.8674
Melting point	-60°C
Boiling point	83°C
Flash point	34°F
Absolute viscosity 20°C	1.1 cp
Refractive index 20°C	1.3792
Color	water white
Odor	etheral
Solubility 20°C	
in water	complete
water in	complete
in hydrocarbons	complete
hydrocarbons in	complete

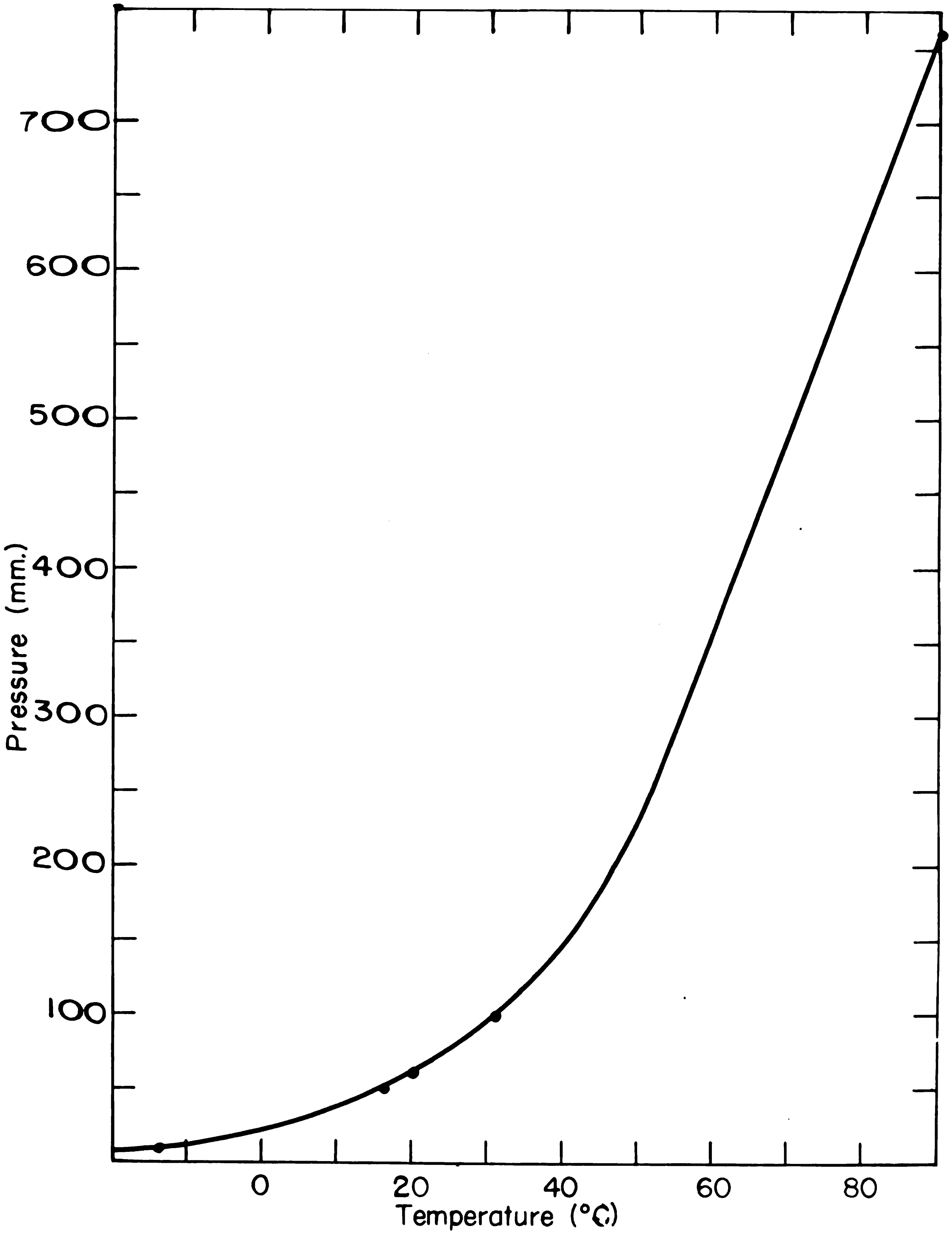


Figure 8

Vapor Pressure Curve for Ethylene Glycol Dimethyl Ether this ether with sodium hydride was also noticed. These reactions were thought to be the removal of active hydrogen in the ether.

The repurification of the ether was accomplished by allowing it to stand for 24 hours over sodium hydride at which time all gassing had ceased. Then it was distilled from sodium hydride and the fraction of the distillate between 82.5°C and 82.9°C at 734 mm pressure was collected. The boiling point of this ether at 734 mm pressure is 82.7°C. The ether, thus purified, did not show any evidence of reaction with sodium trimethoxyborohydride, and was stored in a dark bottle over sodium hydride. This method of purification of ethylene glycol dimethyl ether is highly recommended. An infrared spectrum of the ether purified by this method is given in Figure 9.

Although fifteen electrolyses were conducted with ethylene glycol dimethyl ether, all observations and results were the same with a few exceptions. It was found that these exceptions were due to the presence of small amounts of water or peroxides. A typical electrolysis is outlined below.

The electrolytic cell, as previously described, was evacuated and dried on the electrolysis apparatus. Then it was closed by shutting the stopcocks in its side arms, removed from the electrolysis apparatus into a dry box. Under an atmosphere of dry nitrogen

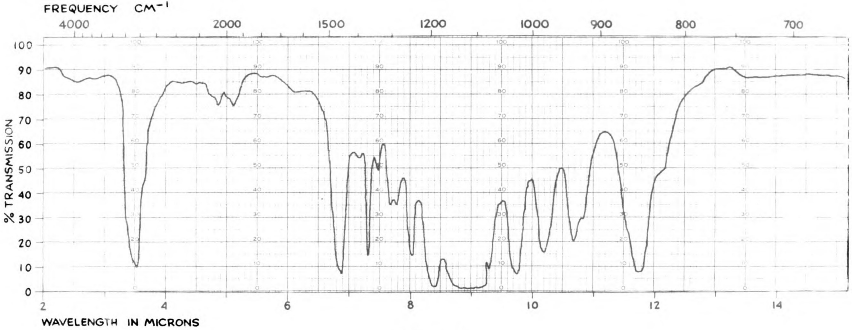


Figure 9

Infrared Spectrum of Ethylene Glycol Dimethyl Ether
(phase, liquid; purity, ca. 100 percent; thickness, 0.025 mm; prism, sodium chloride)

the left electrode (L) was removed and by using a small, long-stemmed funnel, about 1 gram of sodium trimethoxyborohydride was placed in the tube (T) at the bottom of the cell. Then the electrodes were adjusted until they were approximately 1 cm apart, the cell closed, and replaced on the electrolysis apparatus. The container of ethylene glycol dimethyl ether was attached to the left entrance tube (E) and the total apparatus evacuated for 3 to 5 hours. It was found that at least 2 hours of evacuation were necessary to remove all traces of moisture.

After evacuation, the cathode and anode sections of the electrolysis apparatus were closed off from the pumps. A -78°C bath was placed on the electrolysis cell and the ethylene glycol dimethyl ether container was opened to the apparatus. After distilling 30 ml of this ether into the electrolysis cell, the ether container was closed and removed from the apparatus. Then, the -78°C bath on the electrolysis cell was replaced by a 0°C bath, and the system was allowed to stand until the vapor pressure of the ether became constant, and it was adjudged that the sodium trimethoxyborohydride had saturated the ether. Generally, 2 to 3 hours were required for this purpose.

Most electrolyses were carried out at a temperature of 0°C. However, some were conducted at room temperature (25°C) to find if a variation in temperature caused any difference in the electrolysis.

The only difference noted was the increase in conductivity of the solution at the higher temperature. With this exception, the products and observations remained the same.

When the ether pressure had become constant and the sodium trimethoxyborohydride had saturated the ether, the electrode compartments were separated by closing the stopcock between them. Then the current regulator was switched on, the current adjusted to 8-10 ma and the electrolysis begun. It was found that a potential of approximately 150 volts was necessary for a flow of current. This was assumed to be the breakdown potential of the trimethoxyborohydride ion. This current could be increased by increasing the source potential, but most electrolyses were conducted at currents below 10 ma since arcing between the electrodes became excessive at potentials necessary for currents above this amount.

Initially, a small amount of gassing was observed at the cathode while vigorous gassing occurred at the anode. However, in 1 to 2 minutes gassing ceased at the cathode while the gassing at the anode continued. Gradually a silvery, white solid appeared on the cathode and the solution in the immediate vicinity of this electrode took on a bluish color. This solid had the appearance of an alkali metal and grew in a treelike form through the solution toward the anode; and when close to the anode, arcing occurred

between the solid and anode and the silvery solid seemed to explode. In a few cases, the solid streamers made contact between the cathode and the anode. When this occurred, the gassing at the anode ceased, but the current passing through the solution remained constant.

The electrolytic solution gradually acquired a pinkish tint and finally became a murky white, as if containing suspended particles. This actually turned out to be the case, since, upon allowing the solution to stand for several hours after electrolysis, it cleared, and the silvery, white solid collected on the bottom of the cell.

Since there was no gassing at the cathode after a short time, the pressure in the anode compartment built up rapidly and it was impossible to prevent the anode gas from bubbling through the "doughnut" in the electrolysis cell into the cathode compartment. However, when it was noticed that all gassing occurred at the anode, the two compartments were connected.

After each of the electrolyses, the gas evolved, the solid produced at the cathode, and the solution resulting from electrolysis were subjected to various tests and analyses as discussed below.

The gas evolved was tested for condensability by placing -196°C baths on the condensing tubes (C) of the electrolysis apparatus. In all cases the fraction of the gas which condensed could

be attributed to the ethylene glycol dimethyl ether present. For example, in one electrolysis the initial pressure of the ether in the apparatus was 19.5 mm. After electrolysis the pressure of the ether plus the gas evolved during electrolysis was 39 mm. Upon treating the gas with a -196°C bath the pressure dropped to 19 mm. Thus, a drop of 20 mm was observed. This pressure drop is only 0.5 mm more than the pressure of the ether present. Since this difference is well within experimental error, it was assumed that all of the gas produced was noncondensable. As will be shown later, this 0.5 mm pressure difference was probably due to the trimethylborate in the gas phase.

The gas formed during electrolysis was tested for reducing properties by noting its effect on potassium permanganate solution and on a strip of filter paper saturated with an amylamine solution of silver nitrate (18). The permanganate solution was not decolorized by the gas which indicated that this gas had little if any reducing power. The latter test is a very sensitive spot test for detecting boron hydride vapors in air. It is conducted by placing a filter paper wet with one drop of amylamine solution of silver nitrate (5 percent by weight) in contact with the gas or air suspected of containing boron hydride vapors. If these vapors are present, a yellow to brown color will develop. It is claimed that this test will detect boron hydride vapors in air in concentrations of one part per million. The indicated color change did not occur when the gases resulting from electrolysis were subjected to the test. On the basis of these two observations it was concluded that neither the boron hydrides nor any reducing boron compounds were present in the electrolysis gas.

Knowing the original composition of the electrolytic solution, and the fact that this gas was noncondensable limited the possibilities to hydrogen and methane, oxygen, and oxides of carbon which might form if the ether itself was decomposing during electrolysis. It was strongly suspected that the gas was hydrogen, and in order to verify this suspicion, the solvent was frozen out of the gas by using a − 196°C bath, and about 6 mm of the remaining gas transferred into the gaseous discharge tube (DT) on the electrolysis apparatus. A potential was impressed across the electrodes of this tube and a Zeiss spectrograph was used to record the spectrum of the discharge which occurred. The Zeiss spectrograph is a prism instrument with a range of 4000 to 6500 A, and gives very distinct lines on the spectrum plate. The distance from the source to the slit of the instrument was approximately 30 cm. Exposure times of 1, 3, and 5 minutes were used. The spectrum of the unknown gas was compared to that of hydrogen and found to be the same. Lines appeared on

the spectrum plate at wavelengths of 6562.79, 4861.33, and 4340.4 A (8). These are three of the hydrogen lines in the Balmer series of hydrogen. No other lines or bands appeared on the plate. Thus, the presence of hydrogen was established and the exclusion of hydrocarbons, oxygen, and oxides of carbon was assured by the absence of bands or other lines.

Qualitative mass spectrographic analyses of the gas of electrolysis after treatment with a -78°C bath indicated the presence of hydrogen and small amounts of the ether solvent.

The quinalizarin qualitative test for boron (33) gave erratic results when applied to the condensable portion of the gas produced during electrolysis. At times this test indicated the presence of boron and at other times the absence. Later considerations of these results after the presence of trimethylborate in the vapor phase had been established led to the following conclusions. It was noted that positive tests for boron were obtained on this condensable portion of the gas of electrolysis when the period of electrolysis had been 4 or more hours and the condensed portion of the gas, which was a white solid, was treated with water prior to the melting and warming of the resulting liquid to room temperature. When this condensed portion was allowed to come to room temperature before treatment with water, no boron test was obtained. Thus, it seems reasonable that the small amount of trimethylborate produced during electrolysis escaped as the condensed portion of the gas warmed to room temperature in the cases where warming of this condensate was followed by treatment with water, and consequently, no boron test was obtained. Where treatment with water preceded the melting of this condensed portion of the gas the trimethylborate was trapped and hydrolyzed by the water before it could escape.

The quinalizarin test for boron was conducted in the following manner. The material to be tested was dissolved in water. About 1 ml of this solution was placed in a test tube and 9 ml of 93 percent sulfuric acid added. Then 0.5 ml of a 10 percent solution of quinalizarin in 90 percent sulfuric acid was added. If boron were present, a color change of wine to deep blue would be observed. Mellan (33) reported that 0.001 mg of boric acid in a concentration of 1:1,000,000 could be detected by a procedure similar to the one above.

The production of the white solid at the cathode during electrolysis was accompanied by all the "earmarks" of what is known in electrochemistry as "sodium treeing." Naturally, elemental sodium was suspected and the following tests were conducted to confirm this suspicion. The silvery, white solid was removed from the electrolysis cell and washed several times with anhydrous ether.

Upon coming into contact with water, this solid reacted so violently with the evolution of gas that ignition occurred. The resulting aqueous solution had a pH in the neighborhood of 11, whereas the distilled water used had a pH of about 7. When subjected to a flame, this solution gave a very brilliant sodium flame. Boron was absent as indicated by a negative quinalizarin test for this element. Thus, this solid material was determined to be sodium.

The identification of the two products, sodium and hydrogen, indicated that the electrolysis proceeded according to the over-all reaction given by equation (XVII) on page 38. The detection of the trimethylborate which should be present if this equation were correct was somewhat more difficult. At this point, the only indications of the presence of trimethylborate were the fact that a pressure of about 0.5 mm in excess of the vapor pressure of ethylene glycol dimethyl ether could be frozen out of the gases resulting from electrolysis, and the erratic test for boron in this condensed portion of this gas.

In order to prove the existence of trimethylborate, the liquid remaining in the cell after electrolysis was distilled into one of the U-tubes on the electrolysis apparatus. Then this liquid was fractionated into 3 ml fractions and each fraction tested for boron by the quinalizarin test for that element. The first test gave a positive test for boron while the succeeding fractions gave negative tests for boron. This indicated that boron might have been present, but it could not indicate in what form.

It was thought that trimethylborate might be detected in the electrolytic solution by means of infrared spectra. Consequently, infrared spectra of the solvent prior to electrolysis (Figure 10A), and after electrolysis (Figure 10B), and a spectrum of an approximately 1:1 mixture of ethylene glycol dimethyl ether and trimethylborate (Figure 11) were made. Since the concentration of trimethylborate in the solvent as a result of electrolysis was very small, a relatively large thickness of sample was used. Unfortunately, this thickness of sample caused total absorption in the region 3.25-3.70 microns and 6.50-12.35 microns. However, the spectra were used solely on a comparison basis and in this capacity served the intended purpose well.

In Figure 10, the upper curve designated by A, represents the solvent prior to electrolysis, while the lower curve B is the solution resulting from electrolysis. It is to be noted that these two curves coincide with the exception of five places in which the solution resulting from electrolysis absorbs to a greater extent than the pure solvent. These points of difference are the range 2-2.15 microns, 2.84 microns, 5.76 microns, 6.10 microns, and the

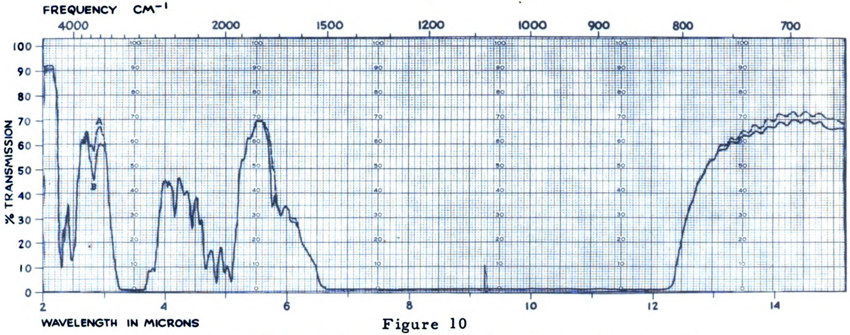


Figure 10

Comparison of Infrared Spectrum of Ethylene Glycol Dimethyl Ether Before and After Electrolysis

Curve A: Infrared Spectrum of Ethylene Glycol Dimethyl Ether Prior to Electrolysis

Curve B: Infrared Spectrum of the Electrolytic Solution

(phase, liquid; thickness, 0.5 mm; prism, sodium chloride)

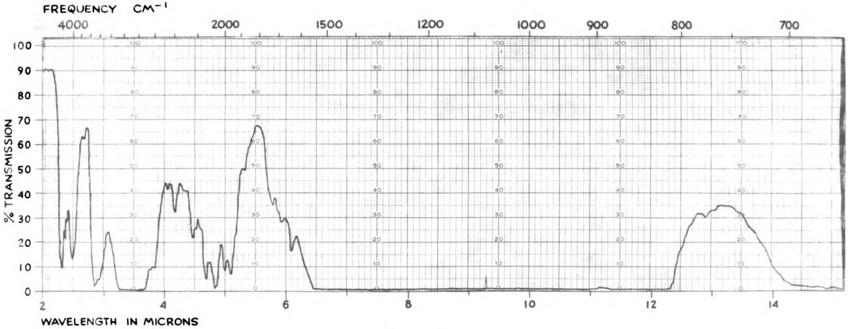


Figure 11

Infrared Spectrum of a 1:1 Mixture of Ethylene Glycol Dimethyl Ether and Trimethylborate
(phase, liquid; thickness, 0.5 mm; prism, sodium chloride)

range 13-15 microns. The most pronounced differences occurred at 2.84 and 5.76 microns. Comparing curve B of Figure 10 with Figure 11 where trimethylborate had been added to ethylene glycol dimethyl ether, it can be seen that in addition to the slight lowering of the percent transmittance over the whole curve, the most pronounced difference noted is the growth of the bands at 2.85 microns and 5.77 microns which coincide with the most pronounced variation between curves A and B in Figure 10. The absorption in the 13-15 micron range is also sharply increased in Figure 11. Thus, it appeared that identical infrared spectra could be obtained by either electrolyzing sodium trimethoxyborohydride in ethylene glycol dimethyl ether or by adding trimethylborate to this ether. From this it was concluded that trimethylborate was probably present in the solution resulting from electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether.

Further verification of the existence of trimethylborate in the electrolytic solution was observed in the form of a mass spectrographic analysis. The molecular weight of ethylene glycol dimethyl ether is about 90, whereas that of trimethylborate is in the neighborhood of 104. If a mass of 104 appeared on mass spectrographic analysis of the electrolytic solution, this would be most positive proof that trimethylborate was present. Upon obtaining the "cracking pattern'' of the vapor above the electrolytic solution, masses around 104 were obtained with no other masses above this up to approximately 200. A comparison of this ''cracking pattern'' with those of ethylene glycol dimethyl ether and trimethylborate showed that the former ''cracking pattern'' could be considered as a summation of the latter two ''cracking patterns.'' The presence of trimethylborate was definitely confirmed.

Therefore, it appeared that the electrolysis occurred according to the over-all reaction represented by equation (XVII) below.

$$NaBH(OCH_3)_3 \longrightarrow Na + 1/2\ H_2 + B(OCH_3)_3 \qquad \text{(XVII)}$$

If this equation is correct, the reaction should be quantitative and one Faraday of electricity should produce one-half mole of hydrogen as indicated.

It was desired to correlate the current used with the amount of hydrogen produced, and a gas coulometer (22) was placed in the electrical circuit. This coulometer provided an accuracy of about 3 to 5 percent, which was sufficient. Though the current regulator controlled the current to within 2 ma, variations of this magnitude could cause errors as large as 20 percent in computing the current used when currents as small as 10 ma were being used.

Previous calculations of the current-hydrogen relation had given values for the volume of hydrogen evolved below that expected.

This was attributed in part to a variation in current, since a coulometer was not used, but mainly to the arcing between electrodes. Thus, this arcing had to be suppressed before any accurate correlation between hydrogen produced and current used could be made.

Several methods of preventing this arcing were tried without notable success. The introduction of a coarse glass frit between the electrodes failed because the solid grew to the frit and then the frit acted as the electrode with arcing as usual. A glass wool plug was used with the same results. Finally, a mechanical agitation of the cathode served to dislocate the silvery solid so that it fell to the bottom of the cell, and by using a current of 8-10 ma, electrolysis could be conducted with little or no arcing. Two electrolyses were conducted in this manner; one with the electrolytic cell at 0°C and the other with the cell at 25°C. Using the current as calculated from the gas coulometer, it was found that the ratio between the hydrogen evolved and that theoretically expected from equation (XVII) was 0.99 and 1.10; which is in good agreement with the postulated reaction.

The possibility of a breakdown of the solvent was considered even though no evidence to that effect had so far been observed. As previously shown, the infrared spectrum of the solution after electrolysis could be considered as a spectrum of the two-component

system ethylene glycol dimethyl ether and trimethylborate. This indicated that no change in the solvent occurred during electrolysis.

However, it was felt that there was a possibility of cleavage of the ether in the presence of metallic sodium at high temperatures which would produce sodium alkyls. Even though the cell temperature was maintained at either 0°C or 25°C during electrolysis, it was realized that the temperature in the immediate vicinity of any arcing between the electrodes could greatly exceed these values. When the test of Gilman and Schulze (21) for organometallic linkages was applied to the solutions resulting from electrolysis, the absence of sodium-carbon linkages was indicated.

This test is a sensitive, qualitative color test directly associated with a compound having a carbon-metal linkage and not with compounds having a metal attached to an element other than carbon. It is conducted by means of Michler's ketone (p, p'-tetramethyldiaminobenzophenone) following the procedure below. One-half to one ml of the organometallic solution is added to an equal volume of a 1 percent solution of Michler's ketone in dry benzene; the reaction product is then hydrolyzed by the slow addition of 1 ml of water; and finally the addition of several drops of a 0.2 percent solution of iodine in glacial acetic acid develops a characteristic greenish-blue color if carbon-metal linkages are present.

Conclusions. From this work it was concluded that:

1. Sodium trimethoxyborohydride is electrolyzed in ethylene glycol dimethyl ether at a current density of 10 ma to give anode products of hydrogen and trimethylborate, and a cathode product of metallic sodium.

2. One-half mole of hydrogen is produced at the anode for every Faraday of electricity used.

3. The ethylene glycol dimethyl ether is not altered by the electrolysis.

4. The potential required for electrolysis is approximately 150 volts.

5. The electrolysis occurs according to the equation,

$$NaBH(OCH_3)_3 \longrightarrow Na + 1/2\ H_2 + B(OCH_3)_3. \qquad (XVII)$$

6. The electrolysis might proceed according to anode mechanism II, page 38.

Electrolysis of Sodium Trimethoxyborohydride in Acetonitrile

Prior to the construction of the electrolysis apparatus, it was found that the system sodium trimethoxyborohydride-acetonitrile conducted electricity, and hence some studies were carried out with this mixture.

A freshly prepared solution of sodium trimethoxyborohydride in acetonitrile conducted a current of 0.15 ampere at room temperature under an applied potential of 55 volts. The electrodes were approximately one square centimeter in area and two centimeters apart. This passage of current was accompanied by gas evolution at both electrodes, the formation of a white crystalline deposit at the cathode, and a yellowing of the electrolysis solution.

The white deposit at the cathode was found to be sodium cyanide as a result of a positive flame test for sodium, a positive spot test for the cyanide ion (19), and a negative quinalizarin test for boron. The gas liberated at the cathode was found to be a hydrocarbon, probably methane, as a result of emission spectroscopy using the Bausch and Lomb medium-quartz spectrograph. Although this method of analysis was not suitable for the simultaneous detection of hydrocarbons and hydrogen, it was believed that hydrogen was present. The composition of the anode gas was not determined, but it was found to be noncondensable.

After the construction of the electrolysis apparatus, the electrolysis of sodium trimethoxyborohydride in acetonitrile was restudied. It was then found that under strictly anhydrous conditions this mixture did not conduct electricity well. In fact, a potential of 110 volts caused a flow of current of less than one milliampere when

the electrodes were approximately two centimeters apart. It should be noted that these studies were carried out in cells with glass frits separating the electrodes and that the cells probably had high resistances. However, the electrolytic cells used were comparable since they both had glass frits and similar electrode distances.

As a result of the lack of conductivity of acetonitrile-sodium trimethoxyborohydride mixtures, some consideration was given to possible modes by which the conductivity of this mixture could be enhanced. In the reaction of cuprous chloride with lithium borohydride to produce diborane, it has been shown that the reaction occurs only in the presence of ether (37). The explanation offered for this was that the reacting specie was the etherate of lithium borohydride. It was reasoned that the etherate formation reduced the bond strength between the lithium and borohydride ions. By analogy, it was thought that perhaps if ether were introduced into the acetonitrile-trimethoxyborohydride mixture, the same effect might be produced on the sodium trimethoxyborohydride and the mixture rendered conducting. Thus, various amounts of diethyl ether were introduced into the mixture, but no increase was noted in the current.

Since voltages in excess of 110 volts were apparently necessary to produce a notable electrolysis, and since the addition of diethyl ether had no apparent effect on the system, it was decided to discontinue study of this particular mixture. This decision was further promoted by a reference to the work of Schmidt (43), who found that the electrolysis of such salts as sodium iodide in acetonitrile gave cathode products of methane, hydrogen, sodium cyanide, diacetonitrile, and an acetonitrile polymer, while the anode product in the case of sodium iodide was iodine.

Conclusions. From this work it was concluded that:

1. A vacuum system had to be constructed in order to study electrolyses under anhydrous conditions.

2. The electrolysis of sodium trimethoxyborohydride in acetonitrile was "catalyzed" by moisture.

3. The cathode products identified upon the electrolysis of a mixture of sodium trimethoxyborohydride and acetonitrile in the presence of moisture were sodium cyanide and a hydrocarbon, probably methane, and the gas liberated at the anode was noncondensable and probably hydrogen.

4. If this anode gas were hydrogen, it could not be determined whether it came from the trimethoxyborohydride ion directly or from the hydroxyl ion which is the reaction product of the sodium trimethoxyborohydride ion and water.

5. Electrolysis of a mixture of sodium trimethoxyborohydride and acetonitrile under anhydrous conditions would not occur at potentials of 110 volts or less with the electrolytic cells used.

6. Etherate formation of sodium trimethoxyborohydride would not aid electrolysis.

7. If the electrolysis of sodium trimethoxyborohydride in acetonitrile did occur under anhydrous conditions, the cathode products as noted by Schmidt (43) would be obtained.

8. Acetonitrile was not a suitable solvent for the electrolysis of sodium trimethoxyborohydride.

Electrolysis of Sodium Trimethoxyborohydride in Dimethylformamide

The same general procedure of introducing the solvent and solute into the electrolysis cell and the same methods were employed in these electrolyses as those described for the electrolyses of sodium trimethoxyborohydride in ethylene glycol dimethyl ether.

The initial electrolyses were conducted at 25°C at a constant potential of about 110 volts. Consequently, the current density varied from approximately 8 to 38 ma per square centimeter. This variation was presumably produced by the heating of the electrolysis cell which was observed during electrolysis. Under these conditions gassing occurred at both electrodes and a reddish solid was deposited at the cathode. As the electrolysis proceeded the solution in the cell became slightly yellow in color.

By treating the gases at both electrodes with a -196°C bath it was found that the condensable portion of the gas could be attributed to the solvent, and both of these gases were presumed to be noncondensable.

The reddish solid produced at the cathode was washed repeatedly with dimethylformamide and finally several times with anhydrous ether and dried. Samples of this solid were then analyzed by the use of a Bausch and Lomb medium-quartz spectrograph. The sodium lines at 2858, 3302, and 5889 A were observed on the spectrum plate. The presence of boron was equally certain since the most persistent line of boron at 2497 A showed up very clearly on the plate. During the above analyses it was noted that this red solid changed into a white material upon contact with the atmosphere.

When electrolyses of sodium trimethoxyborohydride in dimethylformamide were conducted at a constant current density of 10 ma per square centimeter, and the electrolysis cell immersed in a 0°C bath, the same observations were made with respect to gassing, but a red oily material was produced at the cathode. There was some indication of a solid forming on the cathode during electrolysis, but after electrolysis was discontinued this solid gradually disappeared with the evolution of a gas and only the red oily substance remained.

This oily substance gave an intense sodium flame test, but a negative quinalizarin boron test. It appeared to be unaffected by contact with the atmosphere, dissolved in water without any apparent reaction to give a yellowish, alkaline solution, and dissolved in acetone to give a reddish solution.

In these electrolyses the gases produced were found to be noncondensable as in the first electrolyses of this system. An infrared spectrum made of the gas produced at the anode during the controlled current density electrolysis is given in Figure 12. The curve designated by A is the spectrum of gaseous dimethylformamide, while the one lettered B is the spectrum of the gas formed at the anode during electrolysis. These spectra were taken using 10 cm gas cells. The pressure of the gas in the sample cell was 47 mm while the pressure of dimethylformamide in the reference cell was 4-6 mm. Curve A was obtained by running the reference cell versus an evacuated cell, while curve B was obtained by running the sample cell versus the reference cell. These spectra are included as a matter of record since their comparison with the spectra of materials, such as trimethylborate, which could possibly be present led to inconclusive results. The only conclusion drawn from the

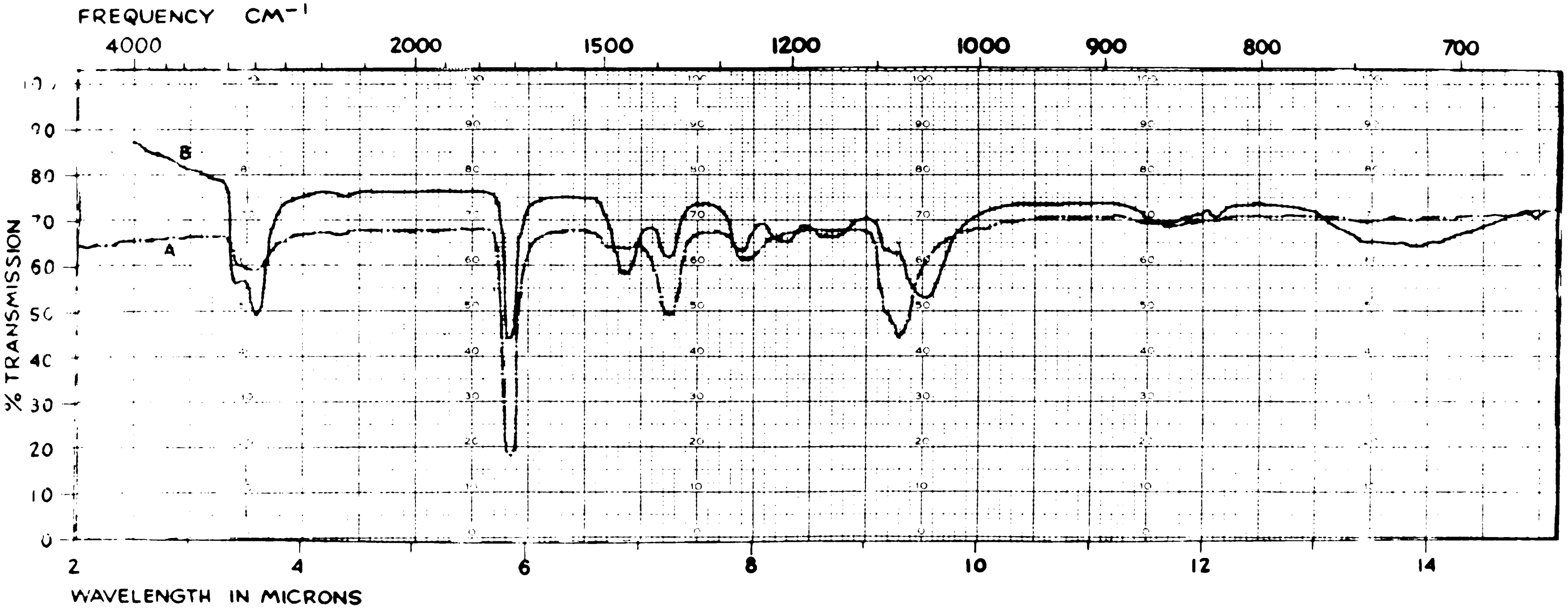


Figure 12

Comparison of the Infrared Spectrum of the Electrolytic Gas and Gaseous Dimethylformamide

A: Infrared Spectrum of Gaseous Dimethylformamide

B: Infrared Spectrum of Anode Gas

spectra in Figure 12 was that some material, in addition to the noncondensable gas, which had an appreciable vapor pressure was present at the anode.

Two further tests were made on this gas. The condensable fraction was tested for boron by the quinalizarin boron test. This test was negative, but here again the condensed material was allowed to warm to room temperature before treatment with water, and it is possible that any trimethylborate which might have been present escaped into the atmosphere.

An emission spectrum of the noncondensable gas from the anode indicated the presence of hydrogen only. This spectrum was obtained in the same manner as described in the section on the electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether.

Conclusions. From this work it was concluded that:

1. When sodium trimethoxyborohydride was electrolyzed in dimethylformamide at 25°C and a constant potential of 110 volts, gassing was observed at both electrodes, and a reddish solid observed at the cathode, and the electrolytic solution became yellowish.

2. Under the above conditions the gases at both electrodes were noncondensable.

3. The reddish solid changed to a white solid upon exposure to the atmosphere and contained both sodium and boron.

4. Electrolysis of sodium trimethoxyborohydride in dimethylformamide at a constant current density of 10 ma per square centimeter and a cell temperature of 0°C gave gases at both electrodes and a reddish oil at the cathode.

5. This reddish oil seems to result from the reaction of a solid formed on the cathode and some constituent of the electrolysis mixture.

6. This reddish oil analyzed for sodium but not for boron, dissolved in water without apparent reaction to give a yellowish, alkaline solution, and in acetone to give a reddish solution.

7. An infrared spectrum of the gas at the anode indicated that the condensable portion of this gas contained some material in addition to dimethylformamide.

8. The condensable portion of the anode gas probably did not contain boron.

9. An emission spectrum of the noncondensable fraction of the anode gas indicated the presence of hydrogen.

10. Dimethylformamide was not a suitable solvent for the electrolysis of sodium trimethoxyborohydride since apparently several side reactions occurred.

Electrolysis of Sodium Borohydride in Dimethylformamide

In an attempt to verify some conclusions to be reached as a result of the electrolyses of sodium trimethoxyborohydride in ethylene glycol dimethyl ether, a preliminary study of this system was conducted.

Some sodium borohydride was purified by dissolving the crude material in water at 15°C. Little reaction was noted; the solution took on a dark color, but after filtration it was colorless. Then, upon cooling to -25°C white crystals separated from the solution. These crystals of sodium borohydride were filtered and washed with three 100 ml portions of anhydrous ether. A fine, snow-white powder remained upon drying these crystals in a vacuum for 24 hours.

The purified sodium borohydride was dissolved in dimethylformamide by placing the solid in the electrolysis cell, evacuating the apparatus, and then distilling dimethylformamide onto the solid sodium borohydride. No reaction was noted when the two materials came in contact.

Electrolysis was begun at room temperature and the current could be regulated from 3 ma with a 15 volt source to 0.6 a with a 210 volt source. Vigorous gassing occurred at both electrodes. In addition, the negative electrode was covered with a light yellow solid

and the solution took on a yellow tint. No change was observed in the appearance of the positive electrode.

When the solid sodium borohydride in the bottom of the cell disappeared, the current abruptly dropped to practically zero and gassing at both electrodes ceased. At this time the temperature of the cell had risen considerably.

This same procedure was followed using the sodium borohydride received from A. D. Mackay and Company without purification. The same observations were made.

The gases from both cell compartments were collected together and tested for condensability. Including the vapor pressure of dimethylformamide, 56 percent of this gas was condensable with 28 percent condensing between -78°C and -196°C. Assuming that the -78°C bath froze out only the solvent vapor, 33 percent of the remaining gas froze out with a -196°C bath and about 66 percent was noncondensable.

The condensable portion of this gas readily decolorized permanganate solution and gave a positive silver nitrate-amylamine test for the boranes. It was noted that approximately twice as much gas was liberated at the anode as at the cathode.

The solid formed at the cathode showed a positive quinalizarin test for boron and a positive flame test for sodium. It readily dissolved in water with the evolution of a gas, and the resulting solution was strongly alkaline. No further tests were made on this solid.

It was noticed that shortly after completing an electrolysis a white, transparent solid began to form in the vicinity of the anode. Some of this material was isolated, washed with anhydrous ether, and tested for boron and sodium. It gave a negative sodium flame test and a positive quinalizarin boron test. Furthermore, this solid dissolved in water with the evolution of a gas and the resulting aqueous solution was slightly alkaline. It should be pointed out that this observation prompted the study of the diborane-dimethylformamide reaction reported in the section on the diborane-dimethylformamide reaction.

Conclusions. From this work it was concluded that:

1. The electrolysis of sodium borohydride in dimethylformamide produced gases at both electrodes, a yellowish, white solid at the cathode, and a white transparent solid formed slowly at the anode after electrolysis was complete.

2. The gases produced, assuming that a -78°C bath froze out only the dimethylformamide vapors, were 33 percent condensable with a -196°C bath and 67 percent noncondensable.

3. The condensible portion of the gases decolorized permanganate solution and gave a positive silver nitrate-amylamine test for the boranes.

4. Approximately twice as much gas was produced at the anode as at the cathode.

5. The yellowish, white solid formed at the cathode contained both boron and sodium, and dissolved in water with the evolution of a gas leaving an alkaline solution.

6. The white, transparent solid formed in the vicinity of the anode contained boron and no sodium, dissolved in water with the evolution of a gas leaving an alkaline solution.

DISCUSSION AND CONCLUSIONS OF ELECTROLYTIC STUDIES

It is evident from the conclusions reached concerning the various electrolytic studies that of the three solvents used, ethylene glycol dimethyl ether, acetonitrile, and dimethylformamide, only ethylene glycol dimethyl ether was suitable for electrolytic studies of sodium trimethoxyborohydride. The same conclusion applies to the electrolysis of sodium borohydride. Apparently, electrolyses of sodium trimethoxyborohydride in dimethylformamide and acetonitrile, and the electrolysis of sodium borohydride in dimethylformamide, were complicated by various side reactions of the solvent. These side reactions were not elucidated. Since the main interest was to find a solvent in which sodium trimethoxyborohydride could be electrolyzed without any reactions of the solvent, the electrolyses occurring with the solvents acetonitrile and dimethylformamide were not studied in detail and a brief discussion of these electrolyses will take the form of postulations as to what might be occurring in these electrolyses in conformance to the observations made and in light of what occurred with ethylene glycol dimethyl ether. The electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether was elucidated and will be discussed at some length since some interesting conclusions are drawn.

Acetonitrile-Sodium Trimethoxyborohydride Electrolysis

As noted, this electrolysis did not occur under anhydrous conditions under the experimental conditions employed. It is probable that an electrolysis of this system would occur under anhydrous conditions provided a sufficiently high potential were employed. If such an electrolysis did occur, the cathode products, methane, sodium cyanide, et cetera, reported by Schmidt (43) would be expected, since sodium ions are present in the solution. If the anode process occurred as with ethylene glycol dimethyl ether, hydrogen and trimethylborate would be formed. Even if this electrolysis were possible, the many side reactions of acetonitrile make it a poor solvent in which to elucidate the reaction occurring during the electrolysis of sodium trimethoxyborohydride.

Some evidence to support the above postulated reaction for the electrolysis of the anhydrous system was obtained from the electrolyses of this system under hydrous conditions. It was concluded that electrolysis occurred under hydrous conditions because of the catalytic effect of the moisture present. This effect is probably produced by the reaction of the trimethoxyborohydride ion and the moisture present, as shown in the equation,

$$BH(OCH_3)_3^- + HOH \longrightarrow H_2 + OH^- + B(OCH_3)_3. \qquad (XIX)$$

Thus, the potential at which electrolysis will occur is lowered by the presence of the hydroxyl ion. From this, the noncondensable gas produced at the anode during this electrolysis is probably hydrogen and is formed by the oxidation of the hydroxyl ions present. Under anhydrous conditions no hydroxyl ions would be present, and if the electrolysis occurred, the trimethoxyborohydride ion would be oxidized at the anode, as shown by the equation,

$$BH(OCH_3)_3^- \longrightarrow B(OCH_3)_3 + 1/2\ H_2 + e^-, \qquad (XX)$$

as is observed in the case of ethylene glycol dimethyl ether.

The most important information gleaned from this work was the fact that the addition of ether to the nonconducting solution of sodium trimethoxyborohydride in acetonitrile did not noticeably increase the conductivity of the solution. It can be concluded from this that either sodium trimethoxyborohydride does not form an etherate under these conditions, or that, if it does, this etherate formation has no material effect on the electrolysis. As discussed later, this fact aided in considering what effect ethylene glycol dimethyl ether might have had on the electrolysis of sodium trimethoxyborohydride in that solvent.

Dimethylformamide-Sodium Trimethoxyborohydride Electrolysis

This electrolysis was complicated by many side reactions. When the cell temperature and current density were not controlled a reddish solid which contained both sodium and boron was formed at the cathode. When the current density was controlled and the temperature of the cell maintained at 0°C a red oil formed at the cathode. This oil contained sodium but no boron.

The above observations cannot be completely explained, but it is possible that the electrolysis of sodium trimethoxyborohydride in this solvent occurred in the same manner as its electrolysis in ethylene glycol dimethyl ether with the production of sodium at the cathode and of hydrogen and trimethylborate at the anode. Then the sodium formed at the cathode might react with the dimethylformamide, sodium trimethoxyborohydride, a reduction product of dimethylformamide, or a combination of any or all of these materials to give the red oil under one set of conditions and the red solid under the other set of conditions.

That some of the reduction products of dimethylformamide might be present is indicated by the work of Gavrilov, Koperina, and Klyuchareva (20). These workers found that dimethylformamide was reduced to the amine in about a 53 percent yield when electrolyzed

in an acid solution using pure lead electrodes and a current density of 0.187 amperes per square centimeter. Though the above conditions used by these workers differed radically from the conditions of the solution used for electrolysis in this work, it is still conceivable that some reduction of dimethylformamide might take place.

The gases produced at both the anode and cathode were for the most part noncondensable. The anode gas was found to contain hydrogen and the vapors of some material which was different from dimethylformamide. It is quite possible that the vapor of trimethylborate was present in this gas, but this conclusion could not be made from the infrared spectrum of this gas.

Dimethylformamide-Sodium Borohydride Electrolysis

The same cathode observations were made in this electrolysis as those noted in the sodium trimethoxyborohydride-dimethylformamide electrolysis, except that in this electrolysis a yellowish, white solid was consistently observed at the cathode. This solid contained both sodium and boron, and it dissolved in water with the evolution of a gas to give an alkaline solution. Only gassing was observed at the anode during electrolysis. However, after the electrolysis had been completed, the formation of a white, transparent solid was noted in the vicinity of the anode. This solid gave a positive boron test but a negative sodium test. It dissolved in water with the evolution of a gas and leaving an alkaline solution. The observation of this solid initiated the study of the diborane-dimethylformamide reaction reported in the section of diborane-dimethylformamide reaction to be presented later. The results of this study showed striking similarities between the diborane-dimethylformamide reaction product and this solid which formed in the vicinity of the anode after electrolysis was completed. For example, both solids had the same physical appearance, both reacted to heat in the same manner, and both dissolved in water with the evolution of a gas and the production of a slightly alkaline solution. It is possible that these two materials are identical.

Excluding the possible reduction of dimethylformamide during the electrolysis, the above observations might be explained by assuming that the electrolysis proceeds according to equation (XXI).

$$NaBH_4 \longrightarrow Na + 1/2\ H_2 + BH_3 \qquad \text{(XXI)}$$

Sodium would be produced at the cathode and hydrogen and diborane at the anode. Then the sodium produced at the cathode could further react with the borine group in the solution, as a result of electrolysis or of the equilibrium shown in equation (XXII), as indicated in equation (XXIII).

$$NaBH_4 \rightleftharpoons NaH + BH_3 \qquad \text{(XXII)}$$

$$Na + BH_3 \longrightarrow NaBH_2 + 1/2\ H_2 \qquad \text{(XXIII)}$$

The product of this latter reaction, sodium dihydridoborane, would account for the presence of sodium and boron in the solid observed at the cathode during electrolysis. It would also account for the dissolution of this solid in water with the evolution of a gas and the resulting alkaline solution.

If the electrolysis occurs according to equation (XXI) with the production of hydrogen and the borine group at the anode and sodium at the cathode, and this sodium at the cathode reacts according to equation (XXIII), then it is noted that approximately one mole of gas will be produced at the anode for every one-half mole of gas at the cathode. Furthermore, the ratio of hydrogen to diborane should be about 2:1. Actually, it was observed that approximately twice as much gas was liberated at the anode as at the cathode. The 2:1 ratio of hydrogen to diborane also agrees with the analysis mentioned if one assumes that the -78° C bath freezes out only the dimethylformamide vapor in the gas. This assumption appears to be valid. Of the remaining gas, 33 percent is condensable with a -196° C bath and 67 percent is noncondensable, indicating a 2:1 ratio of hydrogen to diborane.

The manner of formation of the white solid in the vicinity of the anode after electrolysis had been completed and the cell had

cooled to room temperature also fits into the picture. This solid formed slowly and in the vicinity of the anode where the concentration of diborane should be the greatest if it were produced during the electrolysis. In the study of the diborane-dimethylformamide reaction it was noted that this reaction was also very slow at room temperature.

The fact that the portion of the gas produced during this electrolysis which condensed between -78°C and -196°C reduced permanganate solution and gave a positive test for the boranes by the silver nitrate-amylamine test indicates that regardless of how the reaction proceeded, some of the boron hydrides were formed. As will be seen, this fact lends some support to some of the conclusions made for the electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether.

Ethylene Glycol Dimethyl Ether-Sodium Trimethoxyborohydride Electrolysis

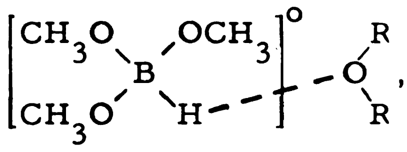
From the identification of the products of electrolysis, the current-hydrogen relation, and the fact that the solvent appeared to be unaltered by electrolysis, it can be stated that electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether occurs according to equation (XVII).

$$NaBH(OCH_3)_3 \longrightarrow Na + 1/2\ H_2 + B(OCH_3)_3 \qquad (XVII)$$

It is postulated that anode mechanism II, given on page 38, is the mechanism by which this reaction proceeds at the anode.

The observation that the ether is unaltered during electrolysis does not exclude the possibility that the ether performs some function, other than providing a suitable medium for electrolysis, such as the formation of an etherate of sodium trimethoxyborohydride. Etherate formation has been observed with lithium borohydride and diethyl ether (37), and is given as a possible explanation for the production of diborane by the reaction of cuprous chloride and lithium borohydride as discussed on page 63. It is realized that lithium borohydride is possibly more covalent than sodium trimethoxyborohydride and that an exact analogy should not be drawn between the two materials. However, if etherate formation were the case with sodium trimethoxyborohydride, it would appear that the addition of ether to the non-conducting system acetonitrile-sodium trimethoxyborohydride might allow the electrolysis to occur. As it has been seen, the addition of ether to the above system did not allow electrolysis to occur. Furthermore, if etherate formation plays a role in the electrolysis of sodium trimethoxyborohydride, it is not clear why ethylene glycol dimethyl ether should be required. Why would diethyl ether not serve the purpose just as well? It was not determined whether sodium trimethoxyborohydride formed etherates with diethyl ether or ethylene glycol dimethyl ether. However, from the above considerations it might be concluded that etherate formation does not materially affect the electrolysis of sodium trimethoxyborohydride.

It would seem that if ethylene glycol dimethyl ether did play a dominate role in the electrolysis of sodium trimethoxyborohydride it might do so in the following manner. The oxygen atoms of the ether might form "bonds" to the hydrogen atom of the trimethoxyborohydride ion, $BH(OCH_3)_3^-$, or preferably the neutral entity, $BH(OCH_3)_3$, as postulated in the anode mechanisms on page 38. This would result in the structure,



, where OR_2 represents the ether.

Thus, the B-H bond would be weakened and would break preferentially to the B-O bond. This mechanism accounts for the products actually observed.

This hypothesis could be tested if a solvent without basic centers such as oxygen could be found which would permit electrolysis of sodium trimethoxyborohydride. If such a solvent could be found, and if the above hypothesis is correct, then it might be possible to break the B-O bond in the neutral entity, $BH(OCH_3)_3$, in preference to the B-H bond. If this occurred, dimethoxyborine

would be formed as shown in anode mechanism I, page 38. Thus, diborane would be produced by the electrolysis.

In this investigation no solvent could be found which was suitable for the proof of this hypothesis. Dimethylformamide hardly qualifies as such a solvent since it contains a carbonyl oxygen. While this type of oxygen has less complexing power than the ether type oxygen, it would affect the reaction in the same manner as the ether.

The electrolysis observed with sodium trimethoxyborohydride in ethylene glycol dimethyl ether may be considered as essentially an electrolysis of sodium hydride, and equation (XVII) on page 83 may be rewritten in the form of equation (XIX).

$$NaH{\cdot}B(OCH_3)_3 \longrightarrow Na + 1/2\ H_2 + B(OCH_3)_3 \qquad \text{(XIX)}$$

In this form the equation suggests an interesting analogy. If the borine group, BH_3, were substituted for the trimethylborate group, $B(OCH_3)_3$, in equation (XIX), the resulting equation would be that shown in equation (XX).

$$NaH{\cdot}BH_3 \longrightarrow Na + 1/2\ H_2 + BH_3 \qquad \text{(XX)}$$

Equation (XX) indicates that the electrolysis of sodium borohydride, $NaBH_4$, in ethylene glycol dimethyl ether would produce diborane. Undoubtedly, the diborane produced would complex with the solvent, but the conditions of electrolysis might be regulated so that a large yield of diborane could be recognized. For example, it might be possible to electrolyze at temperatures at which the complexing of diborane with the ether did not occur.

It is felt that the above analogy is perfectly valid and that the electrolysis as shown in equation (XX) would occur. With sodium borohydride, the solvent used should have little effect upon the outcome of the electrolysis provided the solvent did not react or tie up the diborane so that it could not be obtained.

Since it was found that other workers were well advanced in a study of the reaction indicated by equation (XX), this electrolysis was not attempted. However, the conclusions were tested by using dimethylformamide as a solvent for sodium borohydride and electrolyzing as previously discussed. The gas obtained during this electrolysis gave positive tests for the boranes as indicated, and this fact lends some support to the conclusions drawn.

SOME PHYSICAL PROPERTIES OF TRIMETHYLBORATE

Although many investigators have been directly concerned with trimethylborate, little in the way of consistent values of the physical properties has been published. For example, literature values of -34°C (29), -30°C (24), and -29°C (23) are reported for the melting point of trimethylborate. A compilation of temperature-vapor pressure data could not be found for this compound.

Since a knowledge of these properties was desirable for the present research, and either a lack or inconsistency of them appear in the literature; the temperature-vapor pressure relationship, boiling point, melting point, ΔH_v, and Troutons constant were determined.

Vapor Pressure of Trimethylborate

The trimethylborate used for these determinations was purified as previously noted.

An isotenoscope was constructed according to the directions of Dodd and Robinson (16), evacuated, and dried. Purified trimethylborate was distilled into the isotenoscope and the system was sealed. Mercury was used in the U-tube of the isotenoscope, and this U-tube was connected to a manometer in such a manner that atmospheric pressure could be used to equalize the mercury levels in the isotenoscope U-tube. Thus, the pressure required to equalize the isotenoxcope U-tube mercury levels was equal to the vapor pressure of the system and was measured on the manometer.

Vapor pressures up to 150 mm were measured by the difference in mercury levels in the isotenoscope U-tube alone without the use of the manometer. Above this pressure, measurements were made by equalizing the mercury levels in the U-tube of the isotenoscope as closely as possible, reading the pressure from the manometer, reading the difference in the level of the mercury in the U-tube, and either adding or subtracting the latter reading from the former as circumstances required. A cathetometer was employed for all pressure measurements.

The isotenoscope was too large to be totally immersed in the available dewars, and other available containers allowed too much variation in the temperature of the bath. Above 30°C this variation was particularly great.

Up to room temperature the bulb of the isotenoscope was immersed in a cool bath in a dewar. The rest of the isotenoscope was not thermostated. Above room temperature the remainder of the isotenoscope was wrapped in a heating tape, and the temperature maintained about 10°C above the temperature at which vapor pressure measurements were being made. Up to approximately 40°C the bath temperatures remained constant for an hour or longer. Above this temperature, the temperature of the bath dropped about 0.2°C per five minutes. Temperature measurements were made with National Bureau of Standards calibrated thermometers and are considered to be accurate to within ±0.2°C. The pressure measurements are believed to be accurate to at least ±0.5 mm below 150 mm and ±2 mm above 150 mm of mercury.

The values obtained are recorded in Table IV. These values are plotted in Figure 13. The starred values lie considerably off the curve. It is believed that errors in measurement occurred at these points, since points in the near vicinity of these points indicate that they are high. The other points lie on a smooth logarithmic curve. The vapor pressure value at 67.6°C was obtained by noting that the purified trimethylborate boiled at this temperature at a pressure of 751 mm of mercury.

Heat of Vaporization of Trimethylborate

Plotting the reciprocal of temperature against the logarithm of the pressure, a straight line was obtained with a slope of -1788. From this curve, the following equation, which approximates the vapor pressure of trimethylborate, was derived.

TABLE IV

VAPOR PRESSURE OF TRIMETHYLBORATE

Temperature (°C)	Pressure (mm of mercury)
-22.6	9.6
-17.0	14.5
-15.5	15.0
-11.6	18.7
- 7.5	25.3
- 6.0	26.0
- 0.1	38.4
- 0.1	38.8
8.4	60.0
8.5	60.9
15.5	84.7
15.8	86.2
19.7	106.6
19.7	106.7
24.5	134.3
25.0	136.1
27.5	151.1
37.7	240
39.3	257
39.4	258
39.6	262
43.9	314
45.3	330
50.5	407
50.7	440*
57.4	566*
58.2	552
67.6	751

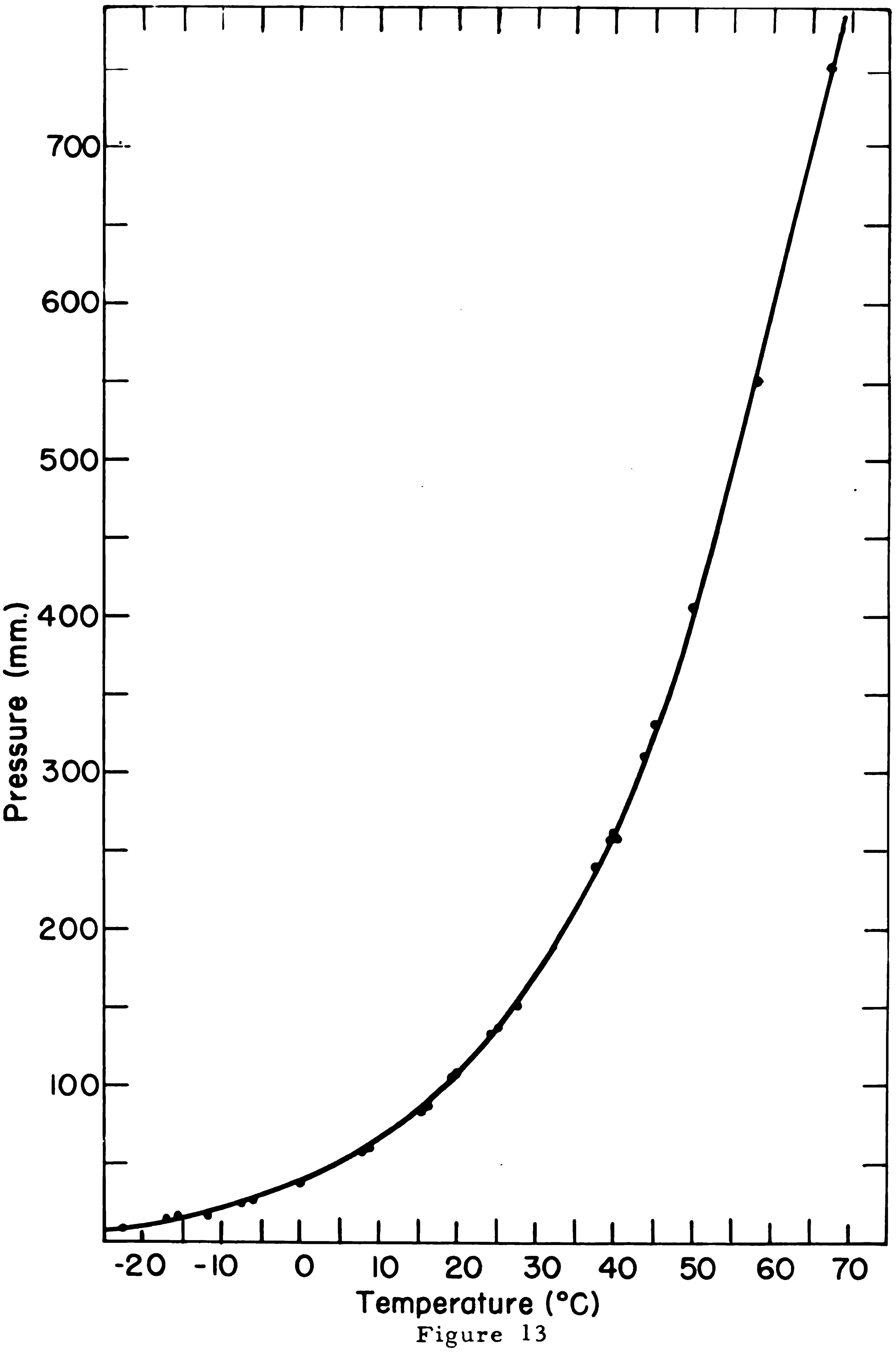


Figure 13
Vapor Pressure Curve for Trimethylborate

$$\log p = -1788/T + 8.129$$

Using the slope of the line which is given above, a heat of vaporization of 8±0.3 kilocalories per mole was obtained for trimethylborate.

Extrapolating the vapor pressure curve, a boiling point of 68.2±0.5°C is obtained for trimethylborate. Goubeau and Keller (23) found a value of 68.7°C for the boiling point of trimethylborate.

Trouton's Constant for Trimethylborate

From the heat of vaporization and the boiling point obtained, it was found that trimethylborate has a Trouton's constant of approximately 24. This value is somewhat higher than the value expected and could indicate some association of trimethylborate in the liquid state. Though this association is surprising, it would be possible if the energy required for the conversion of the planar configuration of boron to the tetrahedral configuration was small. Then, the oxygen of one trimethylborate molecule could occupy the fourth coordination position of the tetrahedral configuration of another trimethylborate molecule, et cetera.

The linearity of the plot of the log p versus the reciprocal of the absolute temperature indicates that the ΔH_v of trimethylborate does not change appreciably with the temperature.

Melting Point of Trimethylborate

Ten milliliters of purified trimethylborate was introduced into the apparatus (Figure 15) used for the dimethylformamide-trimethylborate phase study. A freezing point of -29±0.1°C was obtained. This value agrees well with the value of -29°C obtained by Goubeau and Keller (23).

DIMETHYLFORMAMIDE-TRIMETHYLBORATE PHASE STUDY

Since it was thought that trimethylborate was a product in the electrolysis of sodium trimethoxyborohydride in dimethylformamide, it became necessary to know whether or not a complex of these two materials existed, and a phase study was initiated.

Initially, an apparatus (Figure 14) very similar to those used for freezing-point depression studies in a physical chemistry laboratory was used. There were several major differences. The inner tube (I) was closed at the top with a 45/50 ground-glass joint and cap. Into this cap a thermometer well (TW) was sealed, and the inner tube (I) was placed into the vacuum jacket (V) by a rubber stopper (RS). At the top of the stirring rod (S), a soft iron core (MC) was enclosed in the glass. Using a magnet on the outside of the apparatus, the stirrer could be raised and lowered Stirring was done manually. A pentane thermometer was used for temperature measurements and acetone for thermal contact in the thermometer well The system was calibrated by placing mixtures of known temperatures in the cell.

A melting curve was determined in the following manner. The mixture to be studied was prepared by mixing known weights of the

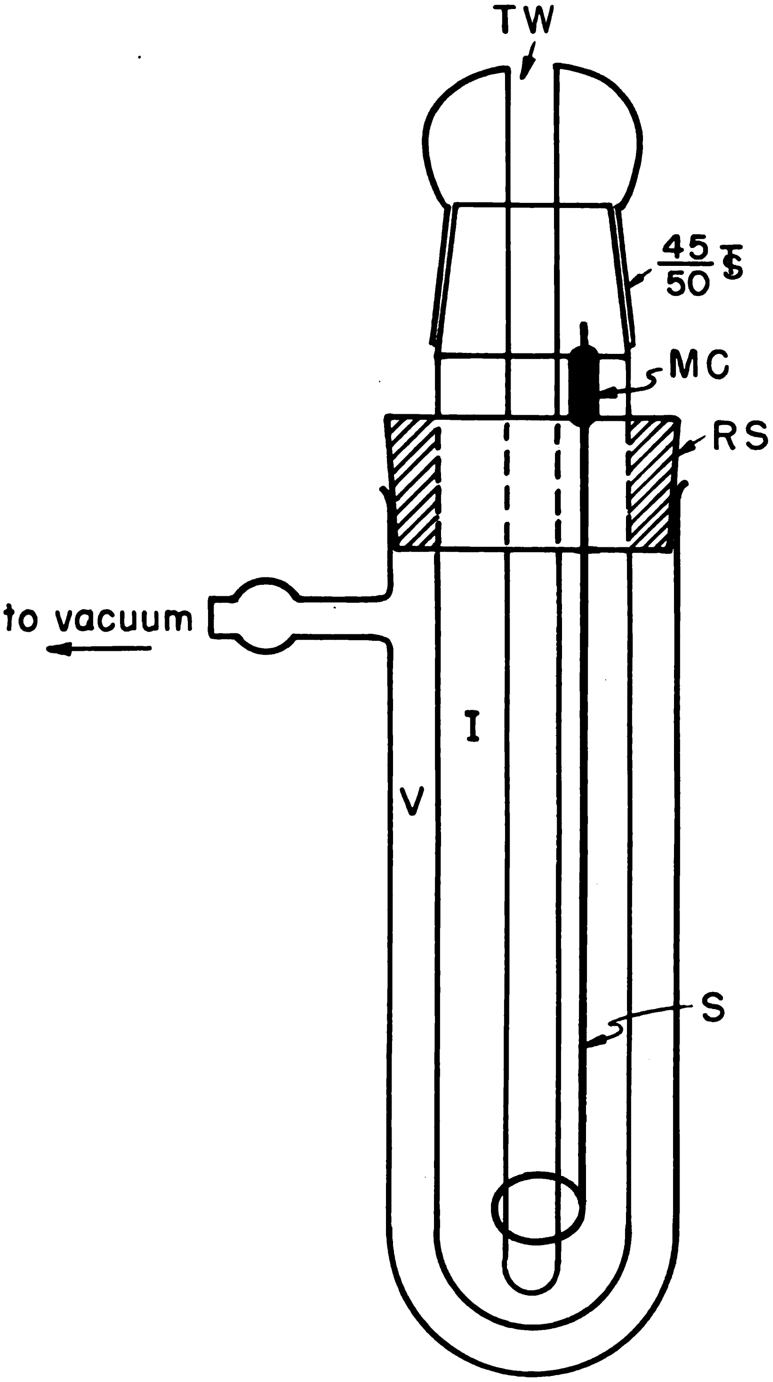


Figure 14

Melting Curve Apparatus

two components in the cell which was placed in the dry box. The same total volume of mixture was used for each curve. The cell was then closed, removed from the dry-box, and the contents of the cell were completely frozen by using a combination of dry ice-acetone and liquid nitrogen baths. The vacuum jacket of the apparatus was then evacuated, the cell and its contents allowed to warm to room temperature at a rate of approximately 1°C per minute, and temperature readings were taken at one-minute intervals. A time-versus-temperature curve was constructed and the temperatures at which breaks occurred noted. Approximately thirty different mixtures were studied in this fashion.

The results were not entirely satisfactory in that they indicated the existence of either a phase diagram with a meritectic point or a phase diagram containing only a eutectic point. The results at the eutectic temperature could be reproduced but the results at the higher temperatures were not reproducible, and no choice could be made between the two possible phase diagrams. This lack of reproducibility at the higher temperatures was attributed to the nonuniformity of the manual stirring.

In order to study the system better, the more convenient apparatus shown in Figure 15 was designed and constructed. The stirring mechanism consisted of a radially slotted, three-inch plate

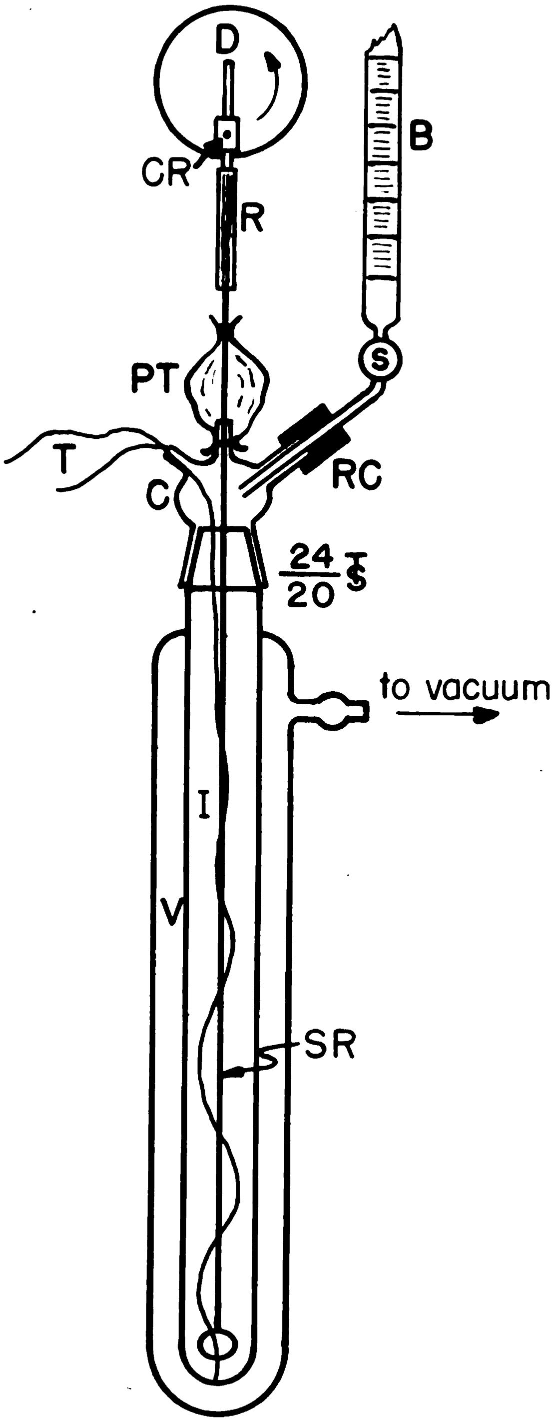


Figure 15

Cooling Curve Apparatus

(D) with an adjustable eccentric. This plate was attached to a Cenco variable-speed stirring motor. To provide flexibility, the connecting rod (CR) and glass stirring rod (SR) were connected by a length of rubber tubing (R). Thus, the amplitude and rate of stirring could be varied within limits. The cell consisted of an inner tube (I) surrounded by a vacuum jacket (V). This inner tube was closed at the top with a 24/40 ground-glass joint and cap (C). The cap had three openings. The stirring rod passed into the cell through the center opening. An air-tight joint was formed at this point by sealing one end of a plastic tube (PT) to the opening flange of the cap and the other to the glass stirring rod. A bellowslike action resulted when the stirrer was in action. A copper-constantan thermocouple (T) was sealed into the cell through one side opening of the cap and a burette (B) into the other.

A Honeywell-Brown Electronik recorder with a Leeds and Northrup amplifier circuit was used. At times the recorder range was lowered by ''bucking out'' a portion of the thermocouple emf using a known potential in series with the thermocouple.

A typical run proceeded as follows. Ten milliliters of purified trimethylborate was buretted into the cell. Then a known volume of dimethylformamide was introduced and stirring started. A dry ice-acetone bath was placed around the cell and the recorder turned on. At -50°C the dry ice-acetone bath was replaced with a liquid nitrogen bath. At times it was necessary to use a variety of baths to regulate the rate of cooling closer. After the cooling curve was completed, the cold bath was removed and the melting curve was obtained as the cell warmed to room temperature. For the majority of mixtures both the cooling and melting curves were obtained.

One purified component was placed in the cell, and a cooling and melting curve obtained. Then increments of the other component were added and cooling and melting curves obtained after the addition of each increment. For one series of curves 10 ml of pure component A was added to the cell and increments of the component B were added until a total of 20 ml of the mixture was in the cell. Then the cell was cleaned and the procedure repeated beginning with pure component B.

The melting points of the pure constituents are believed to be accurate to ±0.1°C. The values for the mixtures are accurate to ±0.5°C.

Using the values of 0.92 and 0.95 for the densities of trimethylborate and dimethylformamide, respectively, and the known volumes of each added; the mole fractions of trimethylborate were calculated.

The results are tabulated in Table V, and the phase diagram is given in Figure 16.

A simple eutectic phase diagram with a eutectic temperature of -63.7±0.5°C was obtained. The eutectic composition was between 9 and 11 mole percent trimethylborate. Within the area marked A of Figure 16, solid trimethylborate and a liquid phase composed of trimethylborate and dimethylformamide are present. In area B solid trimethylborate and a solid with the composition of the eutectic are present. Area C contains solid dimethylformamide and a solid with the composition of the eutectic mixture. Area D contains a solid phase of dimethylformamide and a liquid phase consisting of a mixture of dimethylformamide and trimethylborate. In the area above areas A and D a homogeneous liquid is present.

The eutectic break in the cooling curve was easily detected up to 76 mole percent trimethylborate. As the concentration of trimethylborate exceeded 76 mole percent, the eutectic break became less and less distinct until from 88 to 93 mole percent trimethylborate it was possible to state only that the break occurred in a range of -62°C to -64°C. Beyond 93 mole percent trimethylborate no eutectic break could be observed. This is probably due to the small amount of eutectic mixture present. The existence of the

TABLE V

MOLE PERCENT TRIMETHYLBORATE-TEMPERATURE DATA

Mole Percent Trimethylborate	Temperature (°C)	
	T_1 First Break	T_2 Second Break
0	-60.7	
4	-62.0	
10		-63.4
15	-53.1	-63.4
21	-46.3	-63.7
25	-43.7	-63.7
29	-40.0	-63.7
33	-38.6	-63.7
36	-37.1	-63.7
39	-36.0	-63.7
41	-35.1	-63.7
44	-35.1	-63.7
47	-34.3	
50	-33.7	-63.7
54	-32.9	-62.3
59	-32.3	-62.9
60	-34.0	
64	-32.6	
71	-32.0	
76	-31.8	-64.7
79	-31.0	
85	-31.0	
88	-30.8	-62 to -64
93	-29.7	-62 to -64
94	-30.2	no break
96	-30.3	no break
100	-29.1	

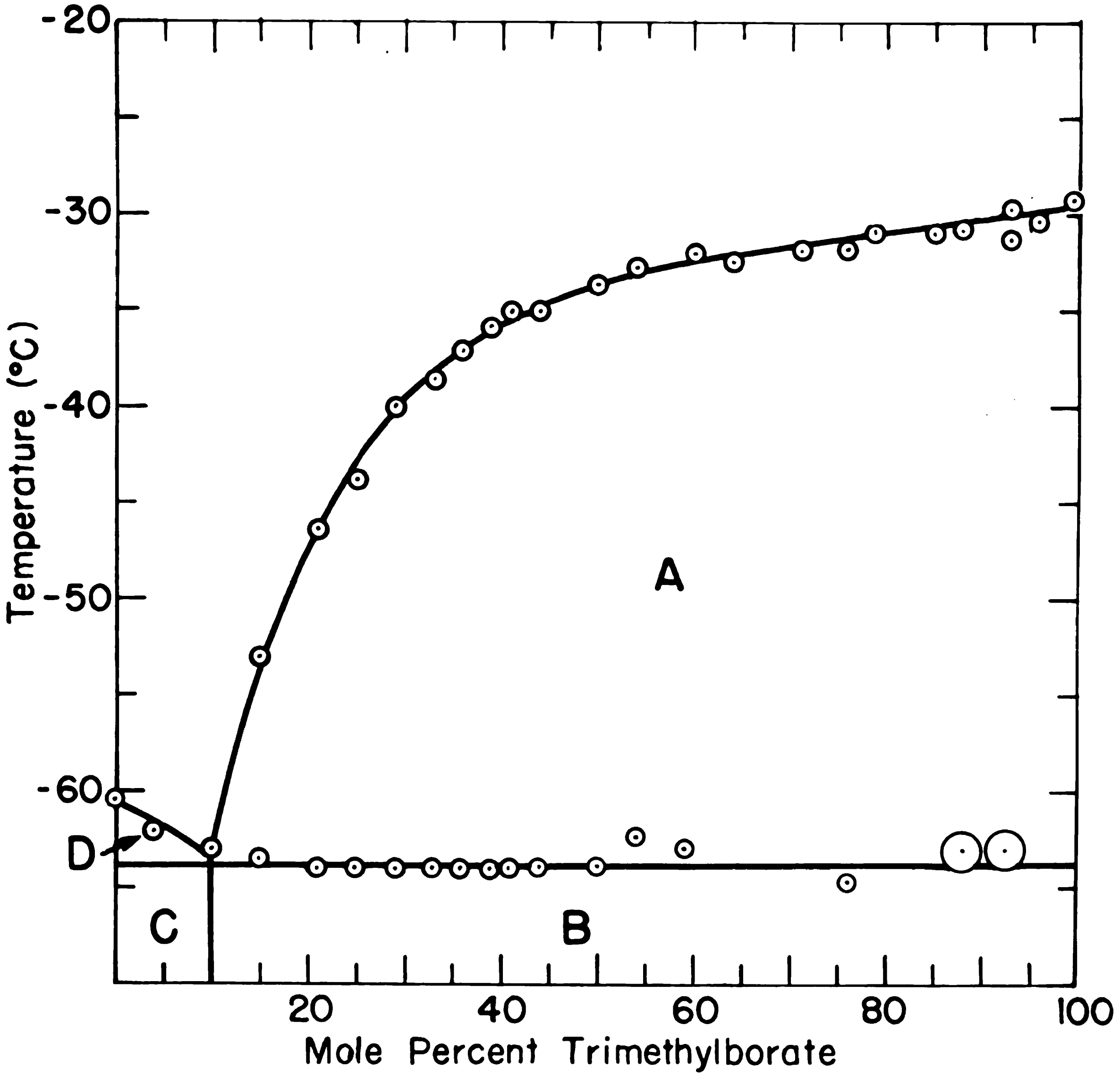


Figure 16

Trimethylborate-Dimethylformamide Phase Diagram eutectic across the diagram and the absence of a parallel meritectic line, rules out the existence of a meritectic point.

Three major sources of error were closely watched. The reference bath was carefully maintained at 0.1°C as measured with a National Bureau of Standards calibrated thermometer. A warming of this reference bath would shift the temperatures recorded downward as observed on several occasions. The "bucking out" potential was carefully controlled and checked. The thermocouple was checked periodically to insure that none of its characteristics were changing. Although supercooling was minimized in most cases, it could not be erased completely, and the melting curve was of great value in elucidating those points at which supercooling occurred.

Both components of the system were purified as previously outlined.

A few visual observations should be noted. When the two reagents were mixed, no visual signs of reaction were noticed. Furthermore, upon mixing, no heat effect was recorded by the recorder. Upon cooling a trimethylborate-rich mixture, a white solid appeared at the first temperature break. The amount of this solid steadily increased until the eutectic temperature was reached at which the total mixture became a white solid.

Goubeau and Link (24) reported that tertiary methyl amine and trimethylborate formed a complex which had a melting point of -50°C. From the above data, it is concluded that, while some association may occur between dimethylformamide and trimethylborate, this attraction is not strong enough to be called a chemical bond, and no complexing occurs between the two materials. Thus, it appears that the substitution of a HCO group for one of the methyl groups on tertiary methylamine prevents chemical combination by rendering the electrons of the nitrogen unavailable for bond formation or increasing steric hindrance to such a degree that combination is impossible.

DIBORANE-DIMETHYLFORMAMIDE REACTION

As noted on page 73, a white solid was observed in the vicinity of the anode after the electrolysis of sodium borohydride in dimethylformamide was completed. Since diborane was a suspected product of this electrolysis, it was logical to find out what occurred when dimethylformamide and diborane were brought into contact. A reference to this reaction had been made by Burg (12).

Initially, dimethylformamide was distilled into a U-tube of the storage and purification apparatus shown in Figure 7, page 36, and diborane was brought into contact with it. The reaction was very slow, and after standing for 24 hours only a white solid remained. This solid was identical in appearance to that observed in the electrolysis of sodium borohydride in dimethylformamide.

It appeared desirable to study this reaction somewhat closer, and preparations were made in that direction.

The literature (25) disclosed that dimethylformamide had vapor pressures of 760 mm at 153°C and 39 mm at 76°C. Plotting the reciprocal of the absolute temperature versus the logarithm of the pressure for these two values and drawing a straight line between them, it was found that the vapor pressure of dimethylformamide was

about 2 mm at 25°C. Rough measurements in the laboratory indicated a vapor pressure for dimethylformamide of about 4 mm at 30°C. Thus, the reaction between diborane and dimethylformamide could be carried out at any temperatures from 0°C to 30°C without any appreciable error being incurred as a result of the pressure of dimethylformamide.

The preliminary reaction between dimethylformamide and diborane indicated that the white solid formed had a low vapor pressure, since when this solid was placed in an evacuated container, little pressure rise was noted over a period of several hours.

Thus, it was reasoned that if successive additions of diborane were made to a known amount of dimethylformamide, and the data plotted as pressure of the system versus mole percent diborane in the nongaseous phase, a curve should be obtained showing little if any pressure until complete reaction had occurred at which point the pressure of the system would rise sharply. This abrupt rise would indicate the composition of the compound formed.

The apparatus constructed for this study is shown in Figure 17. This apparatus was attached to the storage and purification apparatus as shown in Figure 7 on page 36. The reaction cell, V_5, was connected to a small manifold, V_1, by a Stock valve (SV). This small manifold then joined the storage and purification apparatus

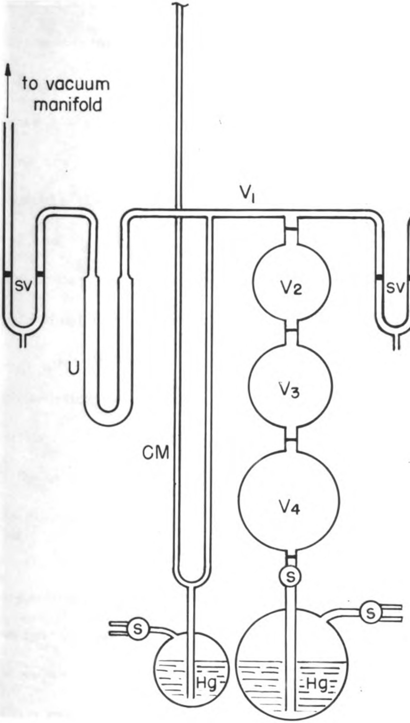


Figure 17

Diborane-Dimethylformamide Reaction Apparatus through a U-tube (U) and a Stock valve (SV). Into this small manifold was sealed a constant volume manometer (CM) and a variable volume apparatus. This variable volume apparatus consisted of three glass bulbs designated by V_2, V_3, and V_4 connected to a mercury reservoir. The total volume of the system could be varied by adjusting the mercury level so as to include or exclude volumes V_2, V_3, and V_4. By bringing the mercury level in the constant volume manometer to a predetermined level, the volume of the system was maintained constant throughout all measurements.

The volumes V_2, V_3, and V_4 were determined prior to the construction of the apparatus by filling the bulbs to the indicated marks and weighing the water required. Knowing the temperature of the water, and therefore its density, the volumes of the bulbs were calculated. V_2 was 52 ml, V_3 was 101 ml, and V_4 was 202 ml.

V_1 included the volume of the system from the Stock valve connecting this apparatus to the storage and purification apparatus to the Stock valve isolating the reaction cell. This volume along with the volume of the reaction cell was determined by introducing a known pressure of dry nitrogen into the system with the volumes V_2, V_3, and V_4 filled with mercury, expanding the volume of the system to include V_2, V_3, and V_4, and noting the pressures at each expansion.

Knowing the volume of the glass bulbs, the volumes V_1 and V_5 were calculated to be 128 and 97 ml, respectively.

Dimethylformamide was distilled into the sample bulb (SB) which was then attached by a 12/30 ground glass joint to the side arm of the reaction cell, V_5. The total system was then evacuated and flamed out. Finally, a small amount of diborane was allowed to stand in the system to insure drying. Then, the system was evacuated, the reaction cell isolated from the system, and dimethylformamide condensed into the reaction cell using a -78°C bath. After the dimethylformamide was introduced, the side arm of the reaction cell was sealed off at the constriction (C) provided for this purpose. Knowing the weight of the sample bulb before and after the addition of dimethylformamide, the weight of the dimethylformamide was calculated by difference. Next, the dimethylformamide in the reaction cell was frozen out with liquid nitrogen and the cell opened to the system and pumped out.

The reaction cell was isolated from the rest of the apparatus and diborane from the storage manifold was introduced into the apparatus The volume, temperature, and pressure of the diborane was known, and the number of moles of diborane added was calculated using the perfect gas law. Since the pressures observed were below 200 mm, the use of the perfect gas law for these calculations is believed to be valid. Next, the diborane was allowed to come in contact with the dimethylformamide and the over-all pressure of the system followed until it became constant. A 25°C bath was kept on the reaction cell. Successive additions of diborane were made and after each addition the pressure changes were followed with a cathetometer. A state of constant pressure was assumed when three pressure readings taken at one-hour intervals were within 0.5 mm of each other.

After each addition of diborane and the attainment of constant pressure, the remaining diborane was frozen into the reaction cell with a -196°C bath and this cell closed from the system so that the next increment of diborane could be measured and added. In most cases, a small residual pressure of 3 to 7 mm was observed after freezing the diborane into the reaction cell. This pressure remained constant throughout all of the measurements, and because of this constancy the presence of hydrogen either as a result of reaction or the decomposition of the diborane was excluded. This small residual pressure was apparently due to the inability of liquid nitrogen to freeze out all of the diborane under the conditions.

As diborane was added, the liquid in the reaction cell became progressively whiter and more viscous until at about 40 mole percent diborane this gummy liquid had changed into a white solid.

Upon evacuating the reaction cell and allowing it to stand, a pressure of 21 mm gradually built up over a period of 24 hours. Upon further evacuation of the apparatus, the white solid reverted to the gummy liquid. This gummy liquid appeared to have little vapor pressure at 25°C and did not appear to break down when subjected to evacuation. By the addition of more diborane to this gummy liquid the white solid could be reformed. Some of this solid was taken from the reaction cell and analyzed immediately for boron. The analysis indicated 16 percent boron. Upon evacuation of this solid, analyses showed that the percent boron dropped from 16 to 14 and finally to 13 percent boron. At this point the solid began to revert to the gummy liquid and no further analyses could be made.

The data collected for this reaction are recorded in Table VI. The method of calculating the amount of diborane added has already been described. The concentration of diborane in the gas phase was computed in the same manner as above. The concentration of diborane in the nongaseous phase was obtained by taking the difference between the accumulative total of diborane added and the diborane in the gas phase.

The curve (Figure 18) obtained by plotting the mole percent diborane in the nongaseous phase versus the pressure of the system differed from that expected in that there was an indication that two

TABLE VI

DIMETHYLFORMAMIDE-DIBORANE REACTION DATA

A	B	C	D	E	F
0	5.4	0	0	0	0.0
$5.01\text{x}10^{-5}$	5.4	$5.01\text{x}10^{-5}$	0	$5.01\text{x}10^{-5}$	0.2
$9.49\text{x}10^{-3}$*	5.5	$9.49\text{x}10^{-3}$	$6.50\text{x}10^{-5}$	$9.42\text{x}10^{-3}$	3.0
$2.63\text{x}10^{-3}$	9.0	$2.68\text{x}10^{-3}$	$5.76\text{x}10^{-4}$	$2.10\text{x}10^{-3}$	7.6
$3.01\text{x}10^{-3}$	21.5	$5.73\text{x}10^{-3}$	$6.51\text{x}10^{-4}$	$5.08\text{x}10^{-3}$	16.5
$2.65\text{x}10^{-3}$	21.1	$8.38\text{x}10^{-3}$	$6.93\text{x}10^{-4}$	$7.74\text{x}10^{-3}$	23.2
$2.73\text{x}10^{-3}$	22.6	$11.11\text{x}10^{-3}$	$6.82\text{x}10^{-4}$	$10.43\text{x}10^{-3}$	28.9
$2.76\text{x}10^{-3}$	33.5	$13.87\text{x}10^{-3}$	$1.01\text{x}10^{-3}$	$12.86\text{x}10^{-3}$	33.3
$2.11\text{x}10^{-3}$	43.5	$15.98\text{x}10^{-3}$	$1.31\text{x}10^{-3}$	$14.67\text{x}10^{-3}$	36.3
$2.59\text{x}10^{-3}$	65.9	$18.57\text{x}10^{-3}$	$2.0\ \text{x}10^{-3}$	$16.57\text{x}10^{-3}$	39.2
$2.63\text{x}10^{-3}$	132.9	$21.2\ \text{x}10^{-3}$	$4.03\text{x}10^{-3}$	$17.17\text{x}10^{-3}$	40.0

A: Diborane added, moles.

B: Equilibrium pressure of system, mm.

C: Accumulative total diborane, moles.

D: Diborane in gas phase at equilibrium, moles.

E: Diborane in nongaseous phase at equilibrium, moles.

F: Diborane in nongaseous phase, mole percent.

* This value was obtained in a separate experiment.

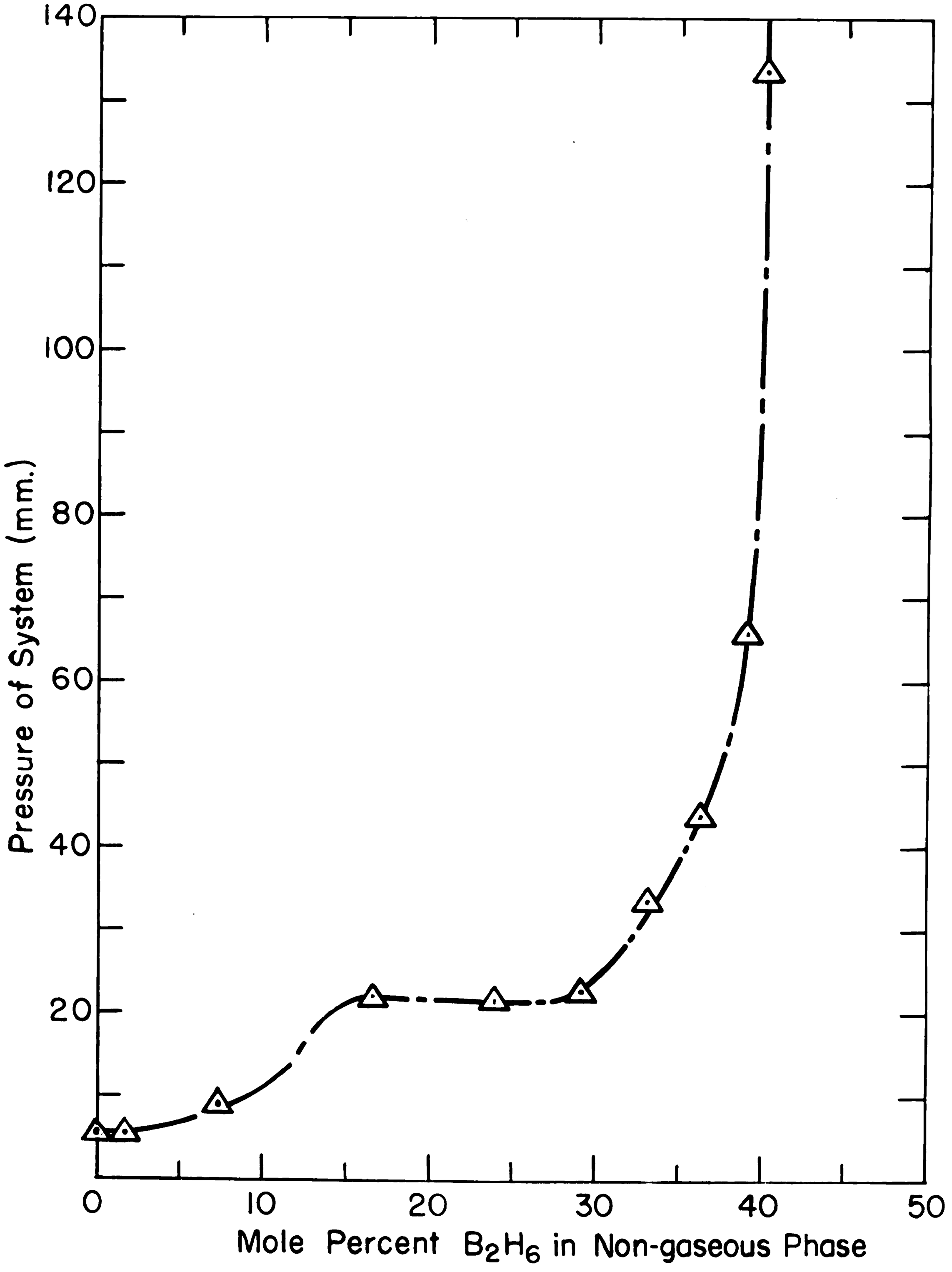
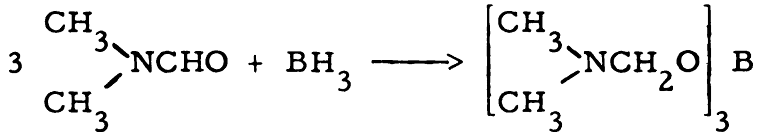


Figure 18

Pressure-Composition Diagram for the System Diborane-Dimethylformamide

compounds were formed; one in the range 10-15 mole percent diborane and one at 40 mole percent diborane in the nongaseous phase. It should be noticed that no points were obtained in the range 10-15 mole percent diborane in the nongaseous phase, and the curve as drawn here is that which is expected.

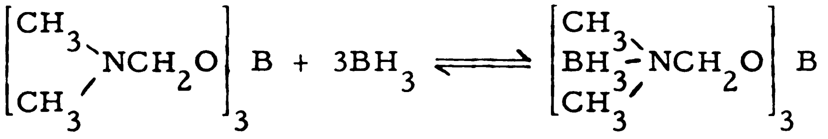
The curve in Figure 18 may be explained by assuming that an initial reaction between diborane and dimethylformamide occurs according to equation (XXIV).



$$3\;\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\!\mathrm{NCHO} + \mathrm{BH_3} \longrightarrow \left[\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\!\mathrm{NCH_2O}\right]_3 \mathrm{B} \qquad \mathrm{(XXIV)}$$

This reaction assumes that the borine group will attack the carbonyl oxygen of the dimethylformamide molecule prior to attacking the nitrogen of that molecule. Even though it is often assumed that the nitrogen atom of the dimethylformamide molecule is more basic than the carbonyl oxygen of this molecule and, thus, the nitrogen should be attacked by the borine group first, there is some basis for the assumption made in equation (XXIV). This is that the B-O bond energy is 110±5 kcal/mole (15), whereas the B-N bond energy is only 89.7 kcal/mole (46), and thus, energy-wise, the formation of the B-O bond would be favored. Reactions with carbonyl oxygens similar to that in equation (XXIV) have been observed (10).

After the completion of the reaction shown in equation (XXIV), the product of this reaction would react with diborane as shown in equation (XXV).



$$\left[\begin{array}{l}CH_3\diagdown\\ \qquad NCH_2O\\ CH_3\diagup\end{array}\right]_3 B + 3BH_3 \rightleftharpoons \left[\begin{array}{l}CH_3\diagdown\\ BH_3\text{-}NCH_2O\\ CH_3\diagup\end{array}\right]_3 B \qquad (XXV)$$

Now the explanation of the curve shown in Figure 18 would be as follows. The rise in the curve between 10 and 15 mole percent diborane would result from the completion of reaction (XXIV). The product of this reaction should contain 4.6 percent boron which would correspond to about 14 mole percent diborane in the nongaseous phase. The rise in the curve does occur in the neighborhood of 14 mole percent diborane in the nongaseous phase. The plateau which is observed at about 21 mm pressure would result from the equilibrium as shown in equation (XXV). Upon the completion of this reaction the curve should rise again as it does at 40 mole percent diborane in the nongaseous phase. The product of reaction (XXV) would contain 15.8 percent boron which would correspond to 40 mole percent diborane. Actually, the curve in Figure 18 becomes practically vertical at 40 mole percent diborane in the nongaseous phase.

THE SYSTEMS B_2O_3-P_2O_5-H_2O, B_2O_3-SO_3-H_2O, AND B_2O_3-SO_3

The report of Newkirk and Hurd (35) concerning the production of the boranes by passing hydrogen over amorphous boron created some speculation as to the possibility of producing elemental boron and consequently the boranes by the electrolysis of boron orthophosphate and the boron "sulfates."

As this subject was developed, it appeared that there was a general belief that elemental boron would be a conductor of electricity and considerably more reactive if a surface coating of oxide could be removed from the boron particles. In fact, the reactivity might be increased to a point where reaction with hydrogen would occur in the absence of elevated temperatures.

If either boron orthophosphate or the boron "sulfates" could be electrolyzed to produce elemental boron, this boron would initially be very pure and have no surface coating. If the boron, while in this state, could be brought in contact with hydrogen, the boranes might be formed. Contact with hydrogen could be accomplished by either passing hydrogen over the electrode at which boron was deposited, or by acidifying the solution so that boron and hydrogen would be produced simultaneously at the same electrode. The latter

method has the advantage that the reaction of boron with "atomic" hydrogen would be much more likely.

It was fully realized that the above considerations opened up a vast, interesting, and possibly a profitable field for research not only in the electrolysis of the compounds mentioned, but also in the electrolysis of the chelates of boron. The above considerations led into the following exploratory research.

The System B_2O_3-P_2O_5-H_2O

Schulze (42) found that boron orthophosphate had a distorted high cristobalite type structure. Each boron and phosphorus atom is surrounded tetrahedrally by oxygen atoms. The boron-oxygen distance may be slightly greater than the phosphorus-oxygen distance, which lends some support to the possible existence of a plus three cationic boron and a phosphate ion.

Boron orthophosphate is a finely divided, white powder which has been prepared in many ways; the most common being evaporation of mixtures of boric acid and phosphoric acid, heating mixtures of boric oxide and diammonium hydrogen orthophosphate, and heating mixtures of the two anhydrides. If a dry crystalline product is desired, the last two methods are the most convenient since the phosphate is difficult to separate from the viscous supernatant liquid in

the first method. On several occasions the heating of anhydrous boric oxide and phosphorus pentoxide has caused unexplained violent explosions (51).

Levi and Gilbert (32) found that boron orthophosphate apparently existed in two forms, a high temperature and a low temperature form, with a transition temperature at about 400° C. The high temperature form is insoluble in water and is only slowly decomposed by boiling alkali; while the low temperature form dissolves with some decomposition in water. Hummel and Kupinski (26) have found that boron orthophosphate begins to vaporize at about 1450° C. Their work indicates that the phosphate vaporizes as such with no decomposition into the corresponding oxides.

Phosphoric acid (75 percent) was heated, and upon the introduction of boric oxide, a finely divided, white solid appeared, giving the solution a milky appearance. Attempts to filter the boron orthophosphate, thus formed, were unsuccessful. This solution was evaporated until a white paste remained. Some of this white paste was placed in an electrolysis cell whose compartments were separated by a glass frit, and concentrated phosphoric acid was added. Again a white, milky solution resulted. Two platinum electrodes were introduced and each covered by a gas collection tube. Potentials of 7.5, 15, and 55 volts were used. Currents ranging from 1.5 amperes with the 7.5 volt source to about 10 amperes with the 55 volt source were obtained. A very vigorous evolution of gas was observed, and a pronounced heating effect was noticed.

Electrolysis gave rise to gases at both electrodes. The cathode gas was identified by ignition as hydrogen; the anode gas was not identified. During electrolysis small brown particles alternately appeared and disappeared on the cathode. When ignited the cathode gas did not produce a green flame. A filter paper saturated with silver nitrate solution showed no evidence of reduction to metallic silver when placed in this cathode gas, and it was concluded that the gas has little, if any, reducing power. The same tests were applied to the anode gas with the same results.

Electrolysis of the white paste was conducted in the same manner as above and gave the same results. Variation of the temperature of electrolysis and the source potential appeared to have no qualitative effect on the products.

It is concluded that boron orthophosphate is relatively insoluble in both dilute and concentrated phosphoric acids, and that the electrolysis of this compound in either of these media will not produce elemental boron or the boranes.

If diborane were formed, its absence in the gas would indicate that it was hydrolyzed by the solution before it could be liberated.

Since tetraborane and some of the higher boranes do not hydrolyze easily, they should have been detected in the gas if they were formed.

The brown particles which formed during the above electrolysis at the cathode can be accounted for in the following manner. It was shown that a small amount of iron was present in the boric oxide employed. The iron could have plated out on the cathode and gradually redissolved in the solution. The amount of this material formed was so small that it could not be collected and tested.

Although only phosphoric acid was used as a solvent in this work, it would be interesting to find a nonaqueous solvent in which the electrolysis of boron orthophosphate could possibly be carried out. In this connection, the boroxines might give the desired results.

The System B_2O_3-SO_3-H_2O

A literature search (32, 34) revealed that, in this hydrous system, the materials $B_2O_3 \cdot SO_3 \cdot 4H_2O$ and $2B_2O_3 \cdot SO_3 \cdot 3H_2O$ were definitely characterized. The former is a finely divided, white, crystalline substance, while the latter appears as large, transparent crystals. Both decompose by hydrolysis upon exposure to atmospheric moisture. One fact somewhat unfavorable for electrolysis is the high viscosity of solutions of boric acid in sulfuric acid.

Boric oxide was dissolved in warm, concentrated sulfuric acid. Upon cooling, large, transparent crystals separated from the solution. Some of this transparent solid, $2B_2O_3 \cdot SO_3 \cdot 3H_2O$, was isolated, washed with sulfuric acid, followed by ether, and then dried in a vacuum desiccator. This material gave a positive flame test for boron. When placed in a stoppered test tube filled with helium and heated, it melted, giving off white fumes which passed up the tube and recondensed to a liquid on the cooler parts of the tube. The residue remaining was a hard glassy material which tested positively for boron.

Into the "boron sulfate" solution at room temperature platinum electrodes were introduced, and these electrodes covered with gas collection tubes. Upon electrolysis at 15 volts a current of 4 amperes was observed, and gases were evolved at both electrodes. Due to the high viscosity of the solution, it was impossible to tell whether or not a solid was produced at the cathode. The solution was heated to about 80°C and the electrolysis renewed with a current of 4.8 amperes passing at 15 volts. With the lower viscosity a white solid was definitely observed at the cathode in addition to gassing. Gassing was observed at the anode, but no formation of a solid. At the cathode the gases H_2S, SO_2, and SO_3 were easily detected by odor. Some hydrogen was evolved as evidenced by ignition tests. Upon burning of the cathode gas, no green flame was observed. The gases at the positive electrode were demonstrated to be oxygen and SO_2.

As electrolysis proceeded, small particles of a dark brown substance alternately appeared and disappeared in the vicinity of the negative electrode. Upon close examination of the negative electrode, particles of this material were observed to be adhering to it. A small amount of these brown particles were collected and gave a positive test for iron. The electrolytic solution was filtered through a glass frit, but the white solid passed through while a small amount of the brown substance remained on the frit. After repeated washings with water and methanol, this brown substance was ignited in the presence of methanol. A green flame resulted, but the brown material did not visibly change. By repeated ignitions with methanol the green flame gradually vanished, leaving the brown particles behind.

The white solid produced at the cathode during electrolysis was isolated, washed, and vacuum dried. It did not give a positive boron flame test. Upon heating, it turned a pale yellow, then a dark red, and finally burned with the characteristic flame of elemental sulfur. Fumes of SO_2 were easily detected by odor. This material readily dissolved in carbon disulfide.

The presence of the gases H_2S, SO_2, and SO_3 along with solid sulfur at the cathode is not surprising, in view of the fact that the "atomic" hydrogen produced at this electrode could easily reduce the sulfate ion to any or all of these states (17).

The appearance and disappearance of the dark brown solid is explained as in the preceding section. The green flame produced in conjunction with this solid is undoubtedly due to the retaining of boron compounds by absorption on the glass frit. The absence of the green flame upon ignition of the gases evolved indicates the absence of the boranes. The white solid produced at the cathode is elemental sulfur as indicated by the results of the tests performed. Thus, neither elemental boron nor the boranes were produced under these conditions.

The System B_2O_3-SO_3

In this system the materials $B_2O_3 \cdot SO_3$ and $B_2O_3 \cdot 2SO_3$ have been isolated. Heating a mixture of the two anhydrides to a temperature of 115°-120°C in a sealed tube gives the mixed anhydride $B_2O_3 \cdot SO_3$. Between 180°-200°C a mixture of the two compounds is indicated, and at 230°C only the anhydride $B_2O_3 \cdot 2SO_3$ is present. According to Pictet and Karl (36), a reaction occurs between these two anhydrides when they are heated to 46°C in an open vessel.

The two compounds have similar properties in that they are both white, amorphous, light substances which are hygroscopic. However, they fume in moist air and decompose at their melting point. When heated in an open vessel above 100°C, they gradually lose all of their SO_3, leaving a residue of boric oxide. Both materials dissolve in cold water, giving a solution of the corresponding acids. Both react with alcohols to form the corresponding borate ester, sulfuric acid, and water (36).

In order to study this system, the following four steps were necessary.

(1) Preparation of anhydrous boric oxide.

(2) Purification of anhydrous SO_3.

(3) Construction of a suitable cell.

(4) Mixing of the reactants, insuring reaction, and electrolysis.

The first step was accomplished by placing boric acid (C.P.) in a glass boat which was in turn placed in a pyrex tube, sealed at one end and connected to a vacuum pump at the other. This tube was placed in a tubular furnace and evacuated. The tube and contents were slowly heated to 220°C and held at this temperature for 72 hours. The temperature was indicated by a thermocouple.

To get pure SO_3, "Sulfan B" was fractionated in the large vacuum manifold according to the method suggested by Archibald

(2). Five fractionations from a 35°C to a 20°C bath were made.

It should be noted that SO_3 attacks "Apieson T" stopcock grease leaving a black deposit. This deposit is easily removed by acetone.

The cell was similar to that shown in Figure 2 with the exception that a side arm was added for the introduction of sulfur trioxide and platinum wire electrodes were used. One electrode was permanently attached to the body of the cell while the other was sealed into the cap. This allowed a variation of the distance between electrodes by simply revolving the cap of the cell.

Anhydrous boric oxide (0.59g) was placed in the dried cell in the dry box. Then approximately 9 ml (17.4g) of purified SO_3 from the large vacuum manifold was distilled directly onto this boric oxide. Upon mixing, no apparent reaction took place. Electrolysis of this mixture could not be accomplished even with a potential of 110 volts. An ammeter with a range of 0-10 milliamperes was used to detect any current passing.

The cell was wrapped with a heating tape and cautiously heated to about 50°C. It was in the vicinity of this temperature where Pictet-Karl observed reaction between these two anhydrides (36). After one hour at this temperature, attempts at electrolysis failed. No noticeable current was observed on the ammeter. Due to the construction of the cell, attainment of temperatures greater than 50° C was not attempted.

An excess of SO_3 was added and heated to about 50° C. This should have insured the formation of $B_2O_3 \cdot SO_3$. The absence of observable current in the system indicates the absence of an appreciable concentration of ions.

Since electrolysis of $B_2O_3 \cdot SO_3$ in SO_3 was not successful, there is no reason to predict that the material $B_2O_3 \cdot 2SO_3$ would be electrolyzable in an anhydrous SO_3 medium. Under the above conditions, it appears that elemental boron cannot be produced.

SUMMARY

1. Ethylene glycol dimethyl ether was found to be a suitable solvent for the electrolysis of sodium trimethoxyborohydride. This ether apparently dissolves sodium trimethoxyborohydride by ionic dissociation, thereby allowing the passage of a current. The ether is apparently not altered during electrolysis.

2. The electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether occurs according to the equation,

$$NaBH(OCH_3)_3 \longrightarrow Na + 1/2\ H_2 + B(OCH_3)_3. \qquad (XVII)$$

While the above electrolysis does not produce diborane, it was concluded that the electrolysis of sodium borohydride in this ether would produce diborane according to the equation,

$$NaBH_4 \longrightarrow Na + 1/2\ H_2 + BH_3. \qquad (XX)$$

3. The electrolysis of sodium borohydride in dimethylformamide was complicated by side reactions, but the gaseous products of this electrolysis gave a positive test for the boranes. This was interpreted as supporting evidence for the electrolysis indicated by equation (XX) above.

4. The electrolysis of sodium trimethoxyborohydride in dimethylformamide is complicated by various side reactions which

were not elucidated. This electrolysis is believed to proceed according to equation (XVII) above with the further reaction of the metallic sodium produced. Some reduction of the dimethylformamide might be occurring. Consequently, this solvent is not recommended for the electrolysis of sodium trimethoxyborohydride.

5. The electrolysis of sodium trimethoxyborohydride in acetonitrile did not occur under anhydrous conditions and the experimental conditions employed at a potential of 110 volts. It is thought that this electrolysis might occur at higher voltages. If it does the cathode products would probably be the same as those obtained by Schmidt (43), while the anode products would probably be hydrogen and trimethylborate. Since the cathode reactions are quite complicated when alkali metal ions are present in this solvent, it would not be a suitable solvent for the electrolysis of sodium trimethoxyborohydride or sodium borohydride.

6. Electrolyses of the systems B_2O_3-P_2O_5-H_2O, B_2O_3-SO_3-H_2O, and B_2O_3-SO_3 did not produce elemental boron under the experimental conditions employed. The system B_2O_3-SO_3 was nonconducting.

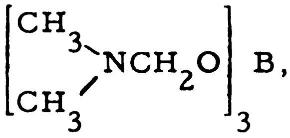
7. A vapor pressure curve for trimethylborate was constructed. The equation describing this curve is

$$\log p = -1788/T + 8.129.$$

Trimethylborate was found to have a melting point of -29±0.1°C, a boiling point of 68.2±0.5°C, a heat of vaporization of 8±0.3 kilocalories per mole, and a Troutons constant of approximately 24.

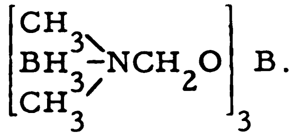
8. The phase diagram for the system trimethylborate-dimethylformamide was found to be a simple eutectic diagram. Thus, it was concluded that no complex was formed between these two substances.

9. The reaction between dimethylformamide and diborane was studied. The experimental data indicate the formation of the compounds



$$\left[\begin{array}{l}CH_3\searrow\\ \qquad\;\; NCH_2O\\ CH_3\nearrow\end{array}\right]_3 B,$$

and



$$\left[\begin{array}{l}CH_3\searrow\\ BH_3\rightarrow NCH_2O\\ CH_3\nearrow\end{array}\right]_3 B.$$

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APPENDIX

During the course of this work some thought was given to the quantitative analysis of the gases produced during the various electrolyses. Since the quantity of these gases was small, a microgasanalysis method had to be used. A Blacet-Leighton microgasanalysis apparatus was available, and since this apparatus allows one to analyze volumes of gas which are smaller than 0.1 ml with an accuracy comparable to that obtained in macrogasanalysis methods, it seemed ideal for the work at hand.

Since the results of the analyses conducted with this equipment neither verified nor disputed the conclusions reached concerning the gases analyzed, they were not reported; but it is felt that this method of gas analysis has merit and should be included as a matter of record. A picture of the equipment used is shown in Figure 19.

A detailed description of the equipment is given in reference (44) while the operational procedure is discussed in reference (3). References (6) and (47) give directions for the construction and use of a combustion coil, and reference (4) describes the circular heating coil and its use.

Most of the reagents for gas absorption are used in the form of solid beads, but liquid reagents contained in sintered glass beads have been used successfully. Table VII (4) lists some of the gases

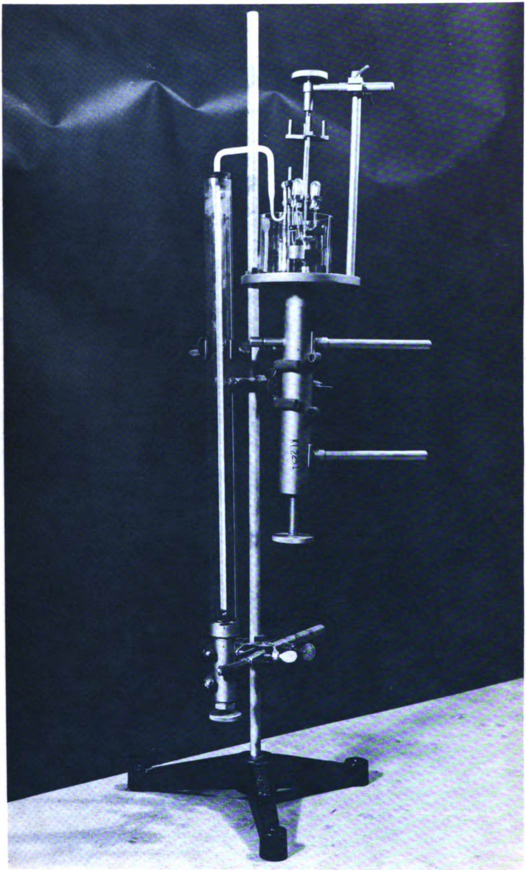

Figure 19
Blacet-Leighton Equipment

TABLE VII

REAGENTS USED FOR ABSORPTION OF GASES BY THE BLACET-LEIGHTON METHOD OF GAS ANALYSIS

Gases	Reagents
Water vapor	KOH or P_2O_5 (3)
Acid-producing gases	KOH (3)
Acetaldehyde and other similar compounds	KOH (30, 31)
Oxygen	Phosphorus (3)
Base-producing gases	P_2O_5 or concentrated H_2SO_4 in sintered glass (5)
Acetylene	Cu_2Cl_2 and KOH (5)
Unsaturated hydrocarbons	Fuming H_2SO_4 in sintered glass (5)
Carbon monoxide	Ag_2O, CuO and KOH, or explosion (3)
Hydrogen	CuO and KOH or explosion (3)
Methane, ethane, or any two readily combustible gases	Combustion (3)
Nitrogen and other inert gases	By difference

which have been determined by this method, the reagents used for their determination, and the reference for the preparation and use of these reagents.

In this work analyses of the gases were conducted by first removing all base-forming gases with a phosphorus pentoxide bead, then all acid-forming gases with a potassium hydroxide bead, and finally analyzing for hydrogen with a copper oxide-potassium hydroxide bead with the application of heat. Where spectroscopic analyses indicated that a gas was hydrogen, as in the case of the anode gas from the electrolysis of sodium trimethoxyborohydride in ethylene glycol dimethyl ether, this method of analysis indicated 98 to 99 percent hydrogen. However, where a gas was suspected of containing diborane, analyses by this method also indicated 98 to 99 percent hydrogen. Thus, it was not possible to determine diborane in a gas containing hydrogen as a constituent, and no suitable physical absorbant for diborane was found.

The reason why a gas containing diborane and hydrogen cannot be analyzed by this method was found to be the behavior of diborane toward alkaline solutions as shown in the equation,

$$B_2H_6 + 2KOH \longrightarrow 2KOBH_3 + H_2.$$

From this equation it is seen that, while one volume of diborane is absorbed, an equal volume of hydrogen is released. Thus, no volume change would occur by treating a gas containing diborane with potassium hydroxide. This was actually observed.

Potassium hydroxide was used during the analyses in the form of a bead and also as a constituent in the bead used for the determination for hydrogen. Thus, if diborane were present in the gas, it would react with the potassium hydroxide bead giving one mole of hydrogen for every mole of diborane reacted, the boron would be removed from the gas with the withdrawal of the potassium hydroxide bead, and the remaining gas would analyze for 100 percent hydrogen as was observed.

For the above reason, this method of analysis did not prove suitable for the analyses of the gases containing diborane. It is believed that a suitable absorbent for diborane, which will fit into this scheme of analysis, can be found.

Ulmer, H.E.

The electrolysis of oxygenated
boron-containing materials.
Ph.D. 1955