AECD - 2144

UNITED STATES ATOMIC ENERGY COMMISSION

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by

Henry R. Hoekstra

Argonne National Laboratory

This document consists of 22 pages.
Date of Manuscript: June 1947
Date Declassified: September 19, 1947

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Technical Information Division, Oak Ridge Directed Operations
AEC, Oak Ridge, Tenn., 9-27-48-1500

Printed in U.S.A.
PRICE 15 CENTS

#309

THE PREPARATION AND PROPERTIES OF ALKALI METAL BOROHYDRIDES

By Henry R. Hoekstra

PART I. PRINCIPLES UNDERLYING NEW METHODS FOR THE PREPARATION OF BOROHYDRIDES

The borohydrides,[1] because of their unique chemical properties, have become compounds of considerable interest, both theoretical and practical. Among the practical applications is the use of sodium borohydride for the generation of hydrogen under conditions in which it is important to obtain the largest possible volume from the smallest weight and volume of generating material and apparatus. This application is discussed in detail later in this paper; the use of the alkali metal borohydrides as reducing agents in organic and in analytical chemistry will be described elsewhere.

To further the theoretical investigation of the borohydrides, as well as to take advantage of their practical potentialities, it became necessary to develop preparative methods by which they could be obtained more conveniently and in larger quantities than had hitherto been possible. In this development, the steps of which are described herein, the Lewis concept of generalized acids and bases has proved a useful guide.[2] This concept defines a basic molecule as one that has an electron-pair which may enter the valence shell of another atom to consummate the electron-pair bond; and acid molecule as one which is capable of receiving such an electron-pair into the shell of one of its atoms. Bases are, in general, restricted to molecules which contain the more electronegative atoms of the periodic table: the fluorine, oxygen, or nitrogen families and occasionally carbon. On the other hand, nearly all elements can act as acids; exceptions are the rare gases and the heavier alkali and alkaline earth metals.

Lewis also stated several fundamental properties of acids and bases from an experimental, rather than a theoretical viewpoint. Two of these are relevant to the present discussion:

1) When an acid and base combine, the process of combination, or neutralization, is a rapid one.

2) An acid or a base will replace a weaker acid or base from its compounds.

The latter reaction is not necessarily a rapid one, since there will be an energy of activation.

From the point of view of the Lewis theory, monomeric binary compounds of trivalent boron are acids since in all such compounds the valence shell of the boron atom contains only six electrons instead of the eight characteristic of covalent compounds of elements of the first short series of the periodic system. Among such acid compounds, diborane may be included since, as has been shown elsewhere,[3] this compound behaves in many of its reactions as if it consists of two borine molecules (BH_3). The base with which this molecule might react to form a borohydride is evidently the hydride ion $(H:)^-$, which is a component of the alkali metal and of the alkaline earth metal hydrides. Since the only corresponding borohydride then known was the lithium compound, our first effort was directed toward the study of the interaction of diborane with lithium hydride.

Contrary to our expectation, however, lithium hydride does not react with diborane at temperatures as high as 75°C; from mixtures of the two reagents, the diborane is recovered quantitatively even when a large excess of lithium hydride is used. Since it was known that diborane reacts with ethers to form etherates of the type $R_2O:BH_3$,[4] it seemed possible that the use of ethers as a medium might favor the reaction by decreasing the required activation energy. Actually diborane reacts quantitatively with finely divided lithium hydride in the presence of ethyl ether to form lithium borohydride. The reaction is a fairly rapid one and generates sufficient heat to raise the temperature of the reaction mixture to above 50°C. The procedure, as described more fully in the experimental part, is particularly convenient because lithium borohydride is soluble in ethyl ether, and may thus be separated from the excess of lithium hydride used in carrying the reaction out. Evaporation of the ether from the solution leads to the precipitation of a crystalline etherate, $LiBH_4:O(C_2H_5)_2$, from which the ether-free borohydride may be obtained by raising the temperature and evacuating the reaction vessel.

Although the hypothesis that the formation of an etherate of borine might favor the desired reaction led to a satisfactory result, there are several reasons for doubting its validity. In the first place, the known etherates of borine are compounds which exist in appreciable concentrations only at very low temperatures; more important, however, since this instability is not an insuperable objection, is the fact that sodium hydride, even if very finely divided and used in the presence of ether, fails to react with diborane. It, therefore, seems more likely that the ether favors the reaction of lithium hydride with diborane because of the heat of solvation of the lithium ion and the consequent solubility of lithium borohydride in ether, in which solvent sodium borohydride is not soluble.

The hydride ion is not the only "base" with which diborane (or borine) might react. Instead of the hydride ion, such generalized bases as alkoxide ions $(RO:)^-$ might be employed. Likewise, diborane is not the only acid to be considered, since compounds such as the boron halides, alkyl borates, and the like, are also acids according to the Lewis interpretation. As a result of these considerations we first studied the interaction of boron halides with alkali metal hydrides, but since these reactions did not quickly lead to the desired result, turned to the interaction between sodium hydride and methyl borate. These reagents were found[5] to react rapidly to form sodium trimethoxyborohydride* according to the equation:

$$NaH + B(OCH_3)_3 = NaBH(OCH_3)_3$$

Methyl borate is, however, a relatively weak acid, presumably because of the possibility of resonance structures such as $H_3C:O\underset{-}{::}\underset{+}{B}(:OCH_3)_2$. Consequently it might be possible to displace it from the ion $[BH(OCH_3)_3]^-$ by the stronger acid borine. Again the hypothesis led to satisfactory results, since diborane reacts rapidly with sodium trimethoxyborohydride, even at −80°C, to liberate methyl borate and to form a solid product shown in the experimental part of this paper to be the hitherto unknown sodium borohydride, $NaBH_4$. The reaction equation is:

$$2NaBH(OCH_3)_3 + B_2H_6 = 2NaBH_4 + 2B(OCH_3)_3$$

Methyl borate is known to interact with diborane to produce dimethoxyborine according to the reaction:

$$4B(OCH_3)_3 + B_2H_6 = 6BH(OCH_3)_2$$

It is therefore not surprising that small amounts of the latter substance were also found among the reaction products; that the quantity of this undesired by-product was small and the yield of sodium borohydride high is due to the fact that dimethoxyborine reacts quantitatively with sodium trimethoxyborohydride according to the equation:

$$NaBH(OCH_3)_3 + 3BH(OCH_3)_2 = NaBH_4 + 3B(OCH_3)_3$$

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* The name sodium trimethoxyborohydride is not altogether satisfactory for this compound, but is used here since no other has as yet been accepted.

The alternative acid-base reaction suggested is that of an alkoxide with diborane. Thus one might anticipate that the basic alkoxide ion, e.g. $[:\underset{..}{\dot{\dot{O}}}:CH_3]^-$, might be added to the acid, borine, as illustrated by the equation:

$$(:OCH_3)^- + BH_3 = (BH_3OCH_3)^-$$

This intermediate might then react further with diborane:

$$(BH_3OCH_3)^- + BH_3 = BH_4^- + BH_2OCH_3$$

When the suggested reaction was carried out, alkali metal borohydrides were actually obtained but practically no methoxy derivative of borine was found among the products.* This result, however, is to be expected since further reaction should occur, probably according to the following steps:

$$\begin{gathered} BH_2OCH_3 + OCH_3^- = \left[BH_2(OCH_3)_2\right]^- \\ \left[BH_2(OCH_3)_2\right]^- + BH_3 = BH_4^- + BH(OCH_3)_2 \\ BH(OCH_3)_2 + OCH_3^- = \left[BH(OCH_3)_3\right]^- \\ \left[BH(OCH_3)_3\right]^- + BH_3 = BH_4^- + B(OCH_3)_3 \end{gathered}$$

The overall reaction between sodium methoxide and diborane then becomes:

$$3NaOCH_3 + 2B_2H_6 = 3NaBH_4 + B(OCH_3)_3$$

The procedure postulated in the preceding discussion led to excellent results when sodium methylate or ethylate was used. In the case of the lithium compounds, curious, as yet unexplained, difficulties were encountered. Although the reaction between lithium ethylate and diborane proceeds rapidly and quantitatively with the evolution of considerable heat, the corresponding reaction of lithium methylate proceeded very slowly and could not be driven to completion. Thus in 30 minutes lithium methylate absorbed only 50% of the theoretical amount of diborane, and after 18 hours at room temperature only 83% of the expected amount of diborane had been absorbed. Whether this difference is due to a difference in particle size of the solid alkoxides employed or to some other cause has not yet been ascertained.

It follows from the preceding discussion that there is still another type of starting material from which borohydrides might be obtained. The tetramethoxyborohydrides (e.g., $NaB(OCH_3)_4$) are readily prepared by interaction of the corresponding alkoxides and alkyl borates. Diborane should react with compounds of this type to displace methyl borate by borine. The resulting ions, e.g. $(BH_3OCH_3)^-$, could then react further with diborane as described in the interaction between the latter and an alkoxide. The reaction was first tested in the case of lithium tetramethoxyborohydride. Over a period of 18 hours, a sample of the latter absorbed 97% of the amount of diborane expected according to the equation:

$$3LiB(OCH_3)_4 + 2B_2H_6 = 3LiBH_4 + 4B(OCH_3)_3$$

Extraction of the crude product with ethyl ether yielded a material containing 91.6% of the hydrogen expected of pure lithium borohydride. With sodium tetramethoxyborohydride the reaction occurs at −80°C.

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* Monomethoxyborine has never been isolated although, in the formation of dimethoxyborine, small amounts of an unstable solid by-product of empirical formula $(BH_2OCH_3)_x$ have been observed.[6] This compound disproportionates fairly rapidly to yield dimethoxyborine, diborane, and methyl borate at room temperature. In the experiments herein reported, the reaction product was heated for final purification, and under these conditions the solid $(BH_2OCH_3)_x$ would have completely decomposed.

These results indicate that this procedure constitutes a satisfactory method for the preparation of sodium or of lithium borohydride. Since there are other satisfactory methods for these compounds, the reaction is of little practical importance in these instances. It has, however, been useful in the preparation of potassium borohydride; it was important in this case because potassium hydride was not available and because potassium methoxide* appears not to react readily with diborane. Potassium tetramethoxyborohydride, on the other hand, reacts readily with diborane to produce a product which yields 95% of the hydrogen expected from pure potassium borohydride. The compound was not further studied.

All of the procedures thus far described for the preparation of borohydrides require the use of diborane, which is a substance not well adapted to simple laboratory procedures nor to quantity production of the desired compounds. Although this paper will not deal specifically with the solution of this problem, the ideas herein presented and their experimental varification, have led to a method of preparation for which diborane is not needed.[7] From the relative acid strengths of the boron compounds herein discussed, one would expect trimethoxyborohydrides to disproportionate, as illustrated by the equation:

$$4NaBH(OCH_3)_3 = NaBH_4 + 3NaB(OCH_3)_4$$

The tetramethoxide at higher temperatures decomposes into the corresponding methoxide and methyl borate, provided that the latter is continuously removed. The final procedure is represented by the equation:

$$4NaH + B(OCH_3)_3 = NaBH_4 + 3NaOCH_3$$

as is discussed in the article to which reference has just been made. Lithium borohydride may be prepared in similar fashion although the yields are not as good as for the sodium compound. It is, furthermore, possible to prepare lithium borohydride from the sodium salt by metathetic reactions carried out in liquid ammonia or in primary amines as a solvent.

This part of the present investigation has thus led to the isolation of the hitherto unknown borohydrides of sodium and of potassium, the properties of which are described briefly in the experimental part of this paper. New methods of preparation, which make these and the corresponding lithium compound readily available for further study or for practical uses, have been developed. In addition to these results, the investigation has established the following displacement series of relative acid strengths, in which the compounds are listed in the order of increasing acidity:

$B(OCH_3)_3$, $BH(OCH_3)_2$, $BH_2(OCH_3)$, and BH_3 (i.e. B_2H_6).

PART II. ALKALI METAL BOROHYDRIDES AS SOURCES OF HYDROGEN

The alkali metal borohydrides react with water according to the equation:

$$MeBH_4 + 2H_2O = MeBO_2 + 4H_2$$

Since lithium and sodium borohydride have molecular weights which are small compared to the volume of hydrogen theoretically obtainable, they should be excellent sources for the generation of hydrogen under conditions under which easy generation and a large ratio of hydrogen volume to weight of reagent are important. Table 1 compares these compounds with other hydrogen sources in this respect.

It is evident from the table that lithium borohydride is theoretically superior to all of the other

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* Prepared from metallic potassium and methyl alcohol. The difference in reactivity of potassium tetramethoxyborohydride and potassium methoxide may be due merely to difference in particle size of the sample employed.

Table 1. Comparison of volume of hydrogen obtainable by the action of water on various reagents.

Compound	Liters of H_2 per gram
Lithium borohydride	4.1*
Lithium hydride	2.8
Sodium borohydride	2.4
Silicon	1.6†
Calcium hydride	1.1
Sodium hydride	0.93

* The scarcity of lithium hydride at the present time as well as the vigorous initial reactivity of lithium borohydride make their use less desirable than that of sodium borohydride.

† Silicon is usually used as ferrosilicon which yields much less hydrogen per gram.

compounds mentioned, and that sodium borohydride is superior to all except lithium hydride. The borohydrides have additional advantages, a statement which is particularly pertinent to sodium borohydride. The latter may, in pellet form, be handled without the use of gloves, the solution obtained after evolution of hydrogen is not excessively irritating to the skin or corrosive to textiles, and the rate of hydrogen evolution is easily regulated as will be described. Furthermore, the heat of hydrolysis of sodium borohydride is approximately 57 kcal per mole or about 16 kcal per mole of hydrogen evolved, as compared with the 28 to 31 kcal per mole of hydrogen when generated from the hydrides of lithium or sodium. As a result of this smaller heat of hydrolysis, the cooling of the hydrogen before it is introduced, for example, into a meteorological balloon is greatly simplified.

Although the interaction of sodium borohydride with water is moderately rapid for a very short interval after the two are mixed at ordinary temperatures, it soon becomes slow, and long before all of the hydrogen has been generated, becomes practically inappreciable. Similarly, even though the initial reaction of lithium borohydride with water is so vigorous that the hydrogen may ignite spontaneously, completion of the reaction requires a long time. The retardation of the reactions is due to the accumulation of the metaborates in the solution whose alkalinity is thereby increased. At an hydrogen ion concentration of less than 10^{-9} moles per liter, the reaction becomes negligible, but as shown by studying the reactions in buffered solutions, the rate may be maintained at a reasonable value by keeping the hydrogen concentration at values up to that of the neutral point (see Table 2).

The rate of these reactions are affected by many factors not easily controlled. For example, it is difficult to prevent temperature rise during the reaction, and the rate at which this rise occurs in the initial stages of the reaction depends on the rate of mixing the reagents. Consequently it seemed futile to adjust the pH of the buffers more than approximately. In view of this fact, it is justified to conclude from the data of Table 2 that the rate of reaction is determined primarily, if not exclusively, by the temperature and the pH of the reaction mixture, and is independent of the nature of the buffer used.

Further evidence tending to confirm this conclusion is found in experiments conducted to achieve a fairly constant and reasonably rapid rate of hydrogen evolution. For this purpose, the solid borohydride was mixed with a variety of solid acidic substances before the addition of water. Among these were solid acids, solid acid anhydrides, and salts of weak bases. In Table 3 the effect of acids on the rate is recorded. It will be seen that as the equivalent concentration of acid increases, the rate

Table 2. Rate of evolution of hydrogen from sodium borohydride in buffered solutions. (In these experiments 5 ml of a 0.9M solution of sodium borohydride was added to 100 ml of the buffer solution of pH 7. After completion of hydrogen evolution, the pH was approximately 8 in each case. The initial temperature was 25°C.)

Time in minutes	Per cent hydrogen evolved		
	Clark and Lubs	Sorenson	MacIlvaine
1	70.8	79.5	76.0
2	80.5	88.0	84.5
3	85.5	90.5	88.5
4	87.5	92.0	90.5
5	89.5	93.0	92.0

increases even though the acids were of various types, a fact which confirms the assumption that the rate is determined by the concentration of hydrogen ion rather than by the negative ion associated with it. In a few cases there were slight deviations from this order due to slight differences in the strengths of the acids or their heats of solution. Table 3B shows the effectiveness of solid acid anhydrides and of a few salts.

In practice, the use of organic acids is undesirable because they often inflame when ground with sodium borohydride; the making and pelleting of such mixtures on a large scale entails a serious hazard. Considerations of safety, stability of the pellets toward air, and ease of handling led to the selection of boric oxide as the most desirable of accelerators of this type.

All of these accelerators have, however, two disadvantages. In the first place, even though a sufficiently rapid overall reaction rate may be achieved by their use, the rate is not uniform. Unless a large amount of acidic accelerator is used, the pH increases somewhat during the reaction which, therefore, becomes fairly slow toward the end of the reaction period. More serious is the relatively large amount of accelerator which must be used to achieve the desired reaction rate. When seventy-five to one hundred parts by weight are used per hundred parts of the borohydride, the volume of hydrogen obtained per gram of starting material is so much reduced that one of the major advantages of the borohydrides is lost.

These difficulties may be almost completely avoided by the use of what may be called catalytic accelerators. Small amounts of finely divided metals, such as Raney nickel, greatly increase the rate of hydrogen evolution; even more effective are metal salts reducible by sodium borohydride. As will be shown later, it is the reduction product of the salts that is the actual catalyst; for this reason it is immaterial which soluble salt of any given metal is used. A large number of salts was tested; those found most effective are listed in Table 4. Since, as shown in the table, cobaltous salts proved far superior to the others, they were the only ones studied in detail.

The addition of a soluble cobaltous salt to a solution of sodium borohydride in water gives rise to the immediate formation of a black substance which initially appears to the naked eye to be homogeneously dispersed through the liquid, but which later coagulates to larger particles. Simultaneously evolution of hydrogen begins, and is maintained at a rate which, instead of falling as the reaction proceeds, grows more rapid if the temperature is not controlled, and remains rapid until the reaction is practically complete.

After coagulation, the black substance may be separated from the solution by filtration. If all steps, including the washing and drying of the product, are carried out with strict exclusion of air, the black material is highly pyroporic. If even small amounts of air were present during the process, the product is much more inert. The most active material has a composition corresponding to the formula,

Table 3A. Hydrolysis of sodium borohydride in the presence of solid acids as accelerators. (All runs were begun at 25°C, with 20 grams of water per gram of $NaBH_4$.)

Accelerator used	Equiv. accel. Mole $NaBH_4$	Final solution temp	Per cent hydrogen evolved 3 min	6 min	10 min
Sulfamic acid	0.2924	47	69.5	77.2	80.7
Tartaric acid	0.3026	47	72.1	77.4	82.3
Citric acid	0.3546	46	74.7	80.7	84.0
Mucic acid	0.3602	51	89.2	93.0	95.1
Succinic acid	0.3846	52	86.8	92.7	95.6
Malic acid	0.4234	52	88.4	93.0	95.8
Malonic acid	0.4366	52	88.9	93.2	94.6
Citric acid	0.4434	49	83.7	87.2	89.8
Oxalic acid	0.5044	51	90.5	94.0	95.0

Table 3B. Hydrolysis of sodium borohydride in the presence of solid acid anhydrides and of salts. (Conditions as in Table 3A.)

Accelerator used	G accel. 100 g $NaBH_4$	Final solution temp	Per cent hydrogen evolved 3 min	6 min	10 min
Boric oxide	33	41	14.5	36.7	50.8
Boric oxide	75	48	73.2	83.2	89.3
Borix oxide	100	56	84.0	95.0	97.5
Phosphorous pentoxide	33	46	57.2	65.5	71.8
Ammon. chloride	100	40	22.2	53.8	74.7
Ammon. carbonate	100	46	69.3	87.1	92.3
Aluminum chloride	60	54	71.0	85.6	91.2

Table 4. Comparison of catalytic accelerators. (0.15 gram of metal chloride, 20 grams of water per gram of $NaBH_4$.)

Time in minutes	Per cent of hydrogen evolved			
	Accelerator added:			
	Cupric	Ferrous	Nickelous C	Cobaltous
5	32	38	42	46
10	43	53	74	97
15	49	65	99 (13 min)	--

Co_2B, and appears to be identical with the product obtained by Stock[8] by the reaction of cobaltous salts with the compounds he considers to be hypoborates. The pure compound when added to borohydride solutions exerts a catalytic effect like that observed with cobaltous salts, and retains its catalytic properties unchanged for long periods of time if kept under oxygen-free water. In the absence of water, oxygen acts on it, apparently to form a mixture of cobaltous oxide and another boride which seems to contain only one cobalt atom per atom of boron. In solution the reaction is further complicated by the slow formation of another compound, probably the borate. As a result, the catalytic effect of the material is greatly reduced. This effect of oxygen probably accounts for the fact that larger amounts of cobaltous salts must be used to obtain a given reaction rate when the cobaltous compound is added separately to the reaction mixture than when the cobaltous salt and the borohydride are together compressed into a pellet.

Pellets containing from three to seven parts of anhydrous cobaltous chloride per hundred parts of sodium borohydride by weight react as rapidly and completely as do pellets containing one hundred parts of an acidic accelerator. The amount of hydrogen evolved per gram of the mixture is, thus, only insignificantly less than that theoretically obtainable from the borohydride itself. It is a little difficult, however, to make exact comparisons of practical results because the rate of evolution of hydrogen is affected by the temperature of the mixture, and the temperature is, in turn, affected by the amount of water used and by the reaction rate.

The rate of hydrogen evolution which, when acid accelerators are used, decreases markedly as the reaction progresses, may be made to increase, decrease, or remain fairly constant by the use of catalytic accelerators depending on the quantity of accelerator, the quantity of water, and the initial temperature. A summary of some of the results obtained with cobaltous chloride as an accelerator under various conditions is given in Table 5. A few of these runs have been graphed (Figure 1) to show clearly the relative effect of temperature and pH on acidic and catalytic accelerators. It is evident that the pH is by far the more important factor when acidic accelerators are used, since even though the solution temperature goes up as high as that obtained with the catalytic accelerators, the rate of hydrogen evolution falls off rapidly as the solution becomes basic. Temperature is the primary factor with catalytic accelerators, since the rate of hydrogen evolution remains nearly constant throughout the run when the temperature is kept constant, but increases sharply when the temperature increase is significant.

PART III. EXPERIMENTAL PROCEDURES AND DATA

Apparatus and Techniques

The apparatus and techniques employed for those reactions which were carried out in vacuum systems are those described by Stock[9] and by Burg and Schlesinger.[3,10]

Table 5. Cobaltous chloride as an accelerator (all runs begun at 25°C unless otherwise stated).

Parts accel. 100 parts $NaBH_4$	Parts water Part $NaBH_4$	Final solution temperature	Minutes to complete reaction
A: Effect of increasing amount of accelerator			
2.5	20	47	17.5
3.5	20	51	12
4	20	55	10
5	20	57	7.5
10	20	58	2.5
B. Effect of increasing amount of water used.			
5	20	57	7.5
5	200	31	15.
5	2300	25	35
10	20	58	2.5
10	100	38	4
10	200	30	6
C. Effect of keeping temperature constant during run (by means of an ice bath).			
5	20	26	27
5	200	26	22
5	400	26	20
5	2300	25	35
10	200	26	9+
10	400	26	9
10	800	25	8+
D. Effect of varying initial temperature, with temperature kept constant during run by means of an ice bath; initial temperature = final temperature.			
5	200	15	35
5	200	25	22
5	200	40	5.5

Materials

Lithium hydride (94%) was obtained from the Lithaloy Corporation. Some of the hydride was a powder of 200 mesh; the remainder was a coarser variety, "crystalline lump." The latter was ground under a nitrogen atmosphere in a ball mill (porcelain balls) before use. Sodium hydride was supplied in particle size between 100 to 200 mesh by the Ethyl Corporation. Its purity was from 97 to 99%; the chief contaminant was metallic sodium. Methyl borate was prepared by treatment of borax, boric oxide, or boric acid with sulfuric acid and methyl alcohol. The azeotrope of methyl borate and methyl alcohol, which is distilled from the reaction mixture, was separated into its components by the use of lithium chloride.[11] Sodium trimethoxyborohydride was prepared by the interaction of sodium hydride with methyl borate.[5] Sodium tetramethoxyborohydride was obtained by treatment of the trimethoxy derivative with methyl alcohol; to remove any sodium methylate which might have been present the product was treated with methyl borate, and the excess of the latter was removed in vacuo. The product so obtained had a boron and sodium content 99.5 and 101.3%, respectively, of the theoretical. The corresponding potassium compound was obtained by interaction of methyl borate with potassium methylate prepared from metallic potassium and methyl alcohol. An especially pure and finely divided sample of sodium methylate was obtained by thermal decomposition of sodium tetramethoxyborohydride in vacuo at 210 to 240°C.

Preparation of Lithium Borohydride From Lithium Hydride and Diborane

The reaction between diborane and lithium hydride in ether suspension, although moderately rapid, is not fast enough for complete absorption of the diborane if the latter is merely bubbled through the suspension. Consequently it is necessary to maintain a fairly large volume of gas in contact with the liquid for some length of time. To achieve this result when only small quantities of the borohydride were to be prepared, the reaction was carried out in a sealed tube of about 250 ml capacity. About one gram of lithium hydride was introduced into the apparatus through side-arm C (Figure 2) which was then sealed off. About 50 ml of anhydrous diethyl ether was then added through the ground joint B, through which the tube may be attached to the vacuum line. After the contents of the tube had been cooled to −80°C, the tube was opened to the pump until the ether had boiled a few moments. The tube was then cooled to liquid nitrogen temperature and sealed off after the introduction of approximately one liter of diborane (measured at standard conditions). To achieve greater reaction surface, the tube was placed in a horizontal position. As the temperature rose reaction set in and was complete in three to four hours. During this time a considerable quantity of the crystalline etherate of lithium borohydride deposited in the tube. This was dissolved by raising the temperature of the mixture, and the resulting solution removed from the excess lithium hydride by filtration.* Details of obtaining the ether-free compound are described later, but it may be pointed out here that the yields obtained by this procedure were practically quantitative.

For the preparation of larger quantities of lithium borohydride by this reaction a more elaborate apparatus (Figure 3) was used. By the use of liquid nitrogen thirteen liters (S.C.) of diborane was condensed from a diborane storage system into bulb B which was then connected with the apparatus through the ground joint. A mixture of ten grams (1.26 moles) of lithium hydride and 400 ml of ethyl ether was stirred for a few minutes in the reaction vessel RV to remove traces of moisture, after which time an ice-bath was placed around the vessel. When the manometer had ceased rising, stopcock S_1 was opened and the air pumped out. In order to transfer the diborane from bulb B to RV, the air in the line between SV_1 and stopcocks S_4 and S_3 was exhausted through stopcock S_2 which was then closed. Stopcock S_4 was then opened and the bulb was allowed to warm till its pressure, as registered by manometer M_2, was about 700 mm. Stopcock S_3 was now opened; by placing a Dewar vessel containing liquid nitrogen at an appropriate height at the lower portion of bulb B, the rate of evaporation of the

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* As a precautionary measure, even though an excess of lithium hydride was present, the tube was opened on the vacuum line with a tube opener at D, so that any unchanged diborane could be safely removed.

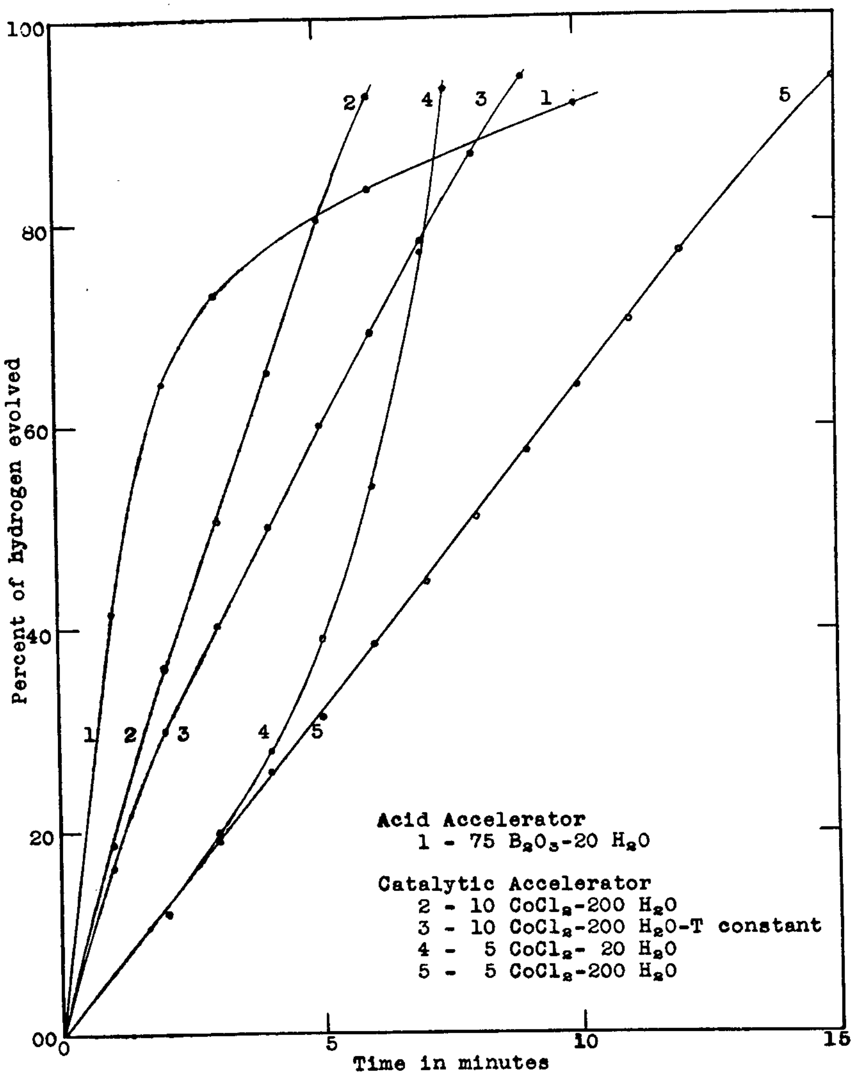

Figure 1. Evolution of hydrogen from sodium borohydride solutions.

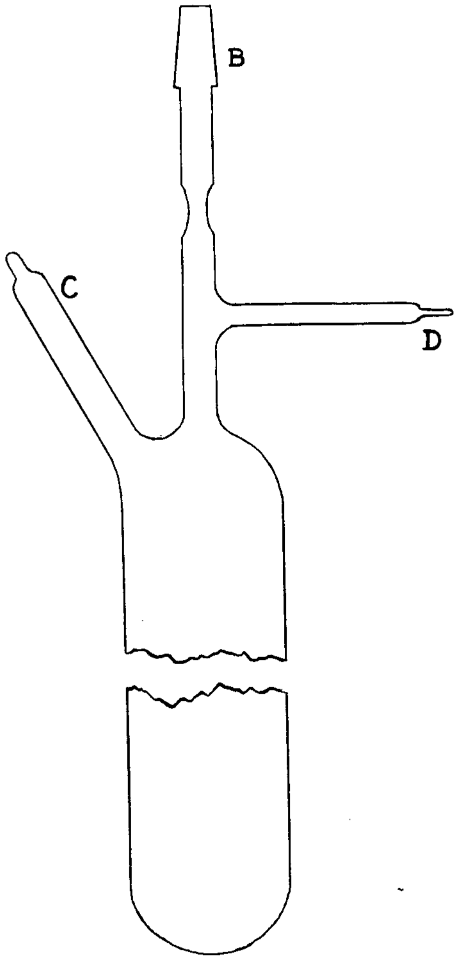

Figure 2. Apparatus for the preparation of small quantities of lithium borohydride.

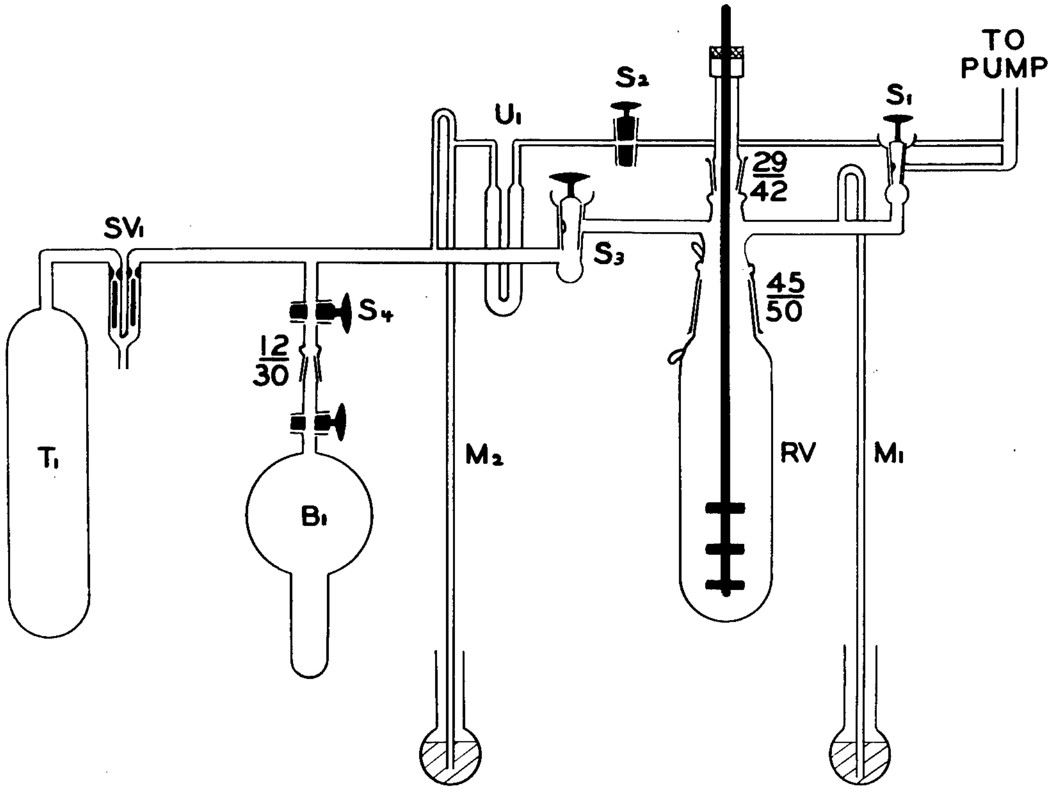

Figure 3. Apparatus for the preparation of large quantities of lithium borohydride.

diborane was regulated to equal its rate of absorption by the lithium hydride. During this process, the mixture in RV was continuously stirred.

Usually after about nine liters of diborane (S.C.) had been absorbed, a heavy slurry of lithium borohydride etherate had formed in the reaction vessel and impeded the stirring. For this reason the mixture was warmed to 15 to 20°C to redissolve the precipitate. The absorption of diborane then continued steadily until all of the liquid in B had vaporized. To remove the residual gaseous diborane, the liquid nitrogen bath was raised, with the result that the diborane together with a little ether from the reaction vessel condensed in B. By warming the latter, the evaporating ether was caused to sweep the remaining diborane into RV where practically all of it was absorbed. As a precaution, stopcock S_1 was always opened for a few seconds to the pump to remove residual traces of diborane.

The reaction vessel, which by the time the reaction was completed, contained an excess of solid lithium hydride, some crystals of the etherate of lithium borohydride, and a saturated solution of the latter, was then disconnected from the line and transferred to the extraction apparatus (Figure 4). The vessel RV was warmed to about 30°C with stopcock S_2 open. When the pressure in the system had become equalized, stopcock S_2 was closed and S_1 opened to the air through a drying tube on the line. The ether solution passed through the sintered dish into the receiver R.

An ice bath was then placed on the reaction vessel RV, and warm water (35 to 40°C) around the receiver R to distill the ether through the sintered disk back into the reaction vessel. Most of the air was removed by opening S_1 to the pump for a few seconds. This step also served to displace the cake formed on the bottom of the disk. After the ether had been returned to the reaction vessel, it was warmed with a water bath and the filtration was repeated. Five extractions completely removed the borohydride from the residue.

To remove the ether after the last extraction, it was distilled into a duplicate reaction vessel and the temperature of the receiver R, containing the pure lithium borohydride was slowly raised to 100°C. The last traces of ether were removed by connecting the receiver directly to the pump.

In a typical experiment carried out as has just been described, the yield was 25.0 grams of lithium borohydride (theoretical 25.2 grams) or above 99%.

Composition and Decomposition Pressure of the Etherate of Lithium Borohydride—$LiBH_4 . O(C_2H_3)_2$

A 0.2630-gram sample of lithium borohydride was placed in a small reaction tube equipped with a ground joint, and the tube attached to the vacuum line where it was directly connected to a manometer and to a calibrated volume through a mercury float valve. Small portions of ether were measured in the

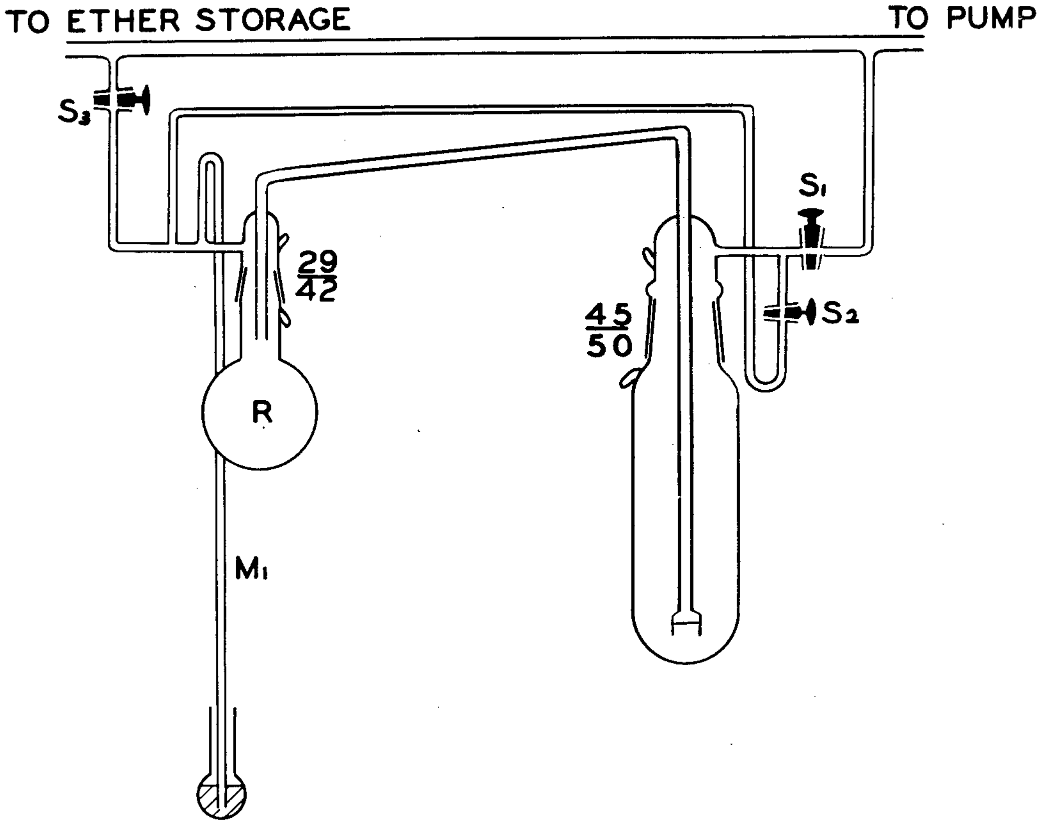

Figure 4. Apparatus for extraction of lithium borohydride.

Table 6. Determination of formula of lithium borohydride etherate.

Ether Being Added		Ether Being Removed	
Mole fraction ether	Pressure (mm)	Mole fraction ether	Pressure (mm)
0.062	9	0.593	182.5
.153	10	.519	181
.225	10	.504	181
.375	10	.492	170
.473	23	.487	23
.489	178	.485	12
.502	181	.479	11
.512	182	.477	10
.550	183	.450	10
.605	184	0.330	10
0.718	183		

calibrated system and transferred to the lithium borohydride tube cooled by liquid nitrogen. After each transfer the bulb was brought to 0°C by means of an ice bath and the equilibrium pressure recorded (Table 6). The pressure readings were plotted as the ordinates against the mole fraction of ether (Figure 5). The slight displacement of the vertical portion of the curve from the value 0.5 was probably due to a small amount of impurity in the lithium borohydride.

The Preparation of Sodium Borohydride from Sodium Trimethoxyborohydride

Sodium trimethoxyborohydride, 4.843 grams (37.86 mmoles), which had been prepared in the usual manner,[5] was weighed into a glass reaction tube fitted with a standard taper joint; the tube was then placed on the vacuum line, and evacuated. After about 100 ml of diborane had been condensed on the trimethoxy compound by means of a liquid nitrogen bath, the tube was closed from the rest of the line, and the nitrogen bath removed. As the tube warmed, the pressure of diborane, observed on a mercury manometer, increased rapidly at first. Then as reaction began, the pressure decreased, dropping nearly to zero within several minutes. It then increased slowly as the tube reached room temperature; the final pressure was due to the reaction products, methyl borate, and dimethoxyborine.* The tube was allowed to stand at room temperature for thirty minutes to ensure completion of the reaction. It was then opened to the rest of the line and the volatile products including a few ml of noncondensable gases were pumped off.† Another portion of diborane was introduced into the reaction vessel and allowed to react, the volatile product was again removed as described. This procedure was repeated three times further; as a result of which a total quantity of 514 ml (22.95 mmoles) of diborane had been added. In order to remove the last traces of methyl borate, which are held tenaciously by the residual

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* In some instances the reaction took place at -80°C. The reaction was rapid, even at this low temperature, but in most cases did not go to completion, since the solid methyl borate formed by the reaction tended to prevent access of the diborane to all of the trimethoxy compound.

† To prevent the volatile products from carrying the finely divided solid reaction product with them, a glass wool plug had been inserted near the mouth of the reaction tube.

solids, the latter were heated to about 200°C after the last treatment with diborane. The mixture of all of the volatile products (except for a trace of hydrogen) were fractionated through −80°C, −145°C, and −195°C baths, and thus separated into 67.0 ml of diborane, 114.8 ml of dimethoxyborine, and 738 ml of methyl borate.* It is thus seen that 514−67 or 447 ml of diborane were absorbed, as contrasted with the 424 ml demanded by the postulated equation. The 114.8 ml of dimethoxyborine obtained would account for 19.1 ml of the 23 ml excess of diborane by interaction of the latter with methyl borate† according to the equation:

$$B_2H_6 + 4B(OCH_3)_3 = 6BH(OCH_3)_2$$

That the reaction had gone practically to completion according to the postulated equation is further shown by the fact that the 114.8 ml of dimethoxyborine and the 738 ml of methyl borate account for more than 96% of the methoxy groups present in the 37.86 mmoles of sodium trimethoxyborohydride originally employed. That the solid product was sodium borohydride is shown by the analysis described in the next paragraph.

Analysis of Sodium Borohydride

A weighed sample of the solid product was placed in a small tube into which, after it was cooled to − 80°C, a small quantity of water was distilled. The tube was sealed, and heated at 70 to 80°C for three hours to hydrolyze the sample completely. After completion of the reaction, the tube was opened to a vacuum line; the hydrogen was removed by a Toepler pump and measured. The aqueous solution was acidified with a measured amount of acid of known concentration, and then titrated with carbonate-free standard barium hydroxide, first to the methyl red end-point, and next, after the addition of mannitol to the phenolphthalein end-point.

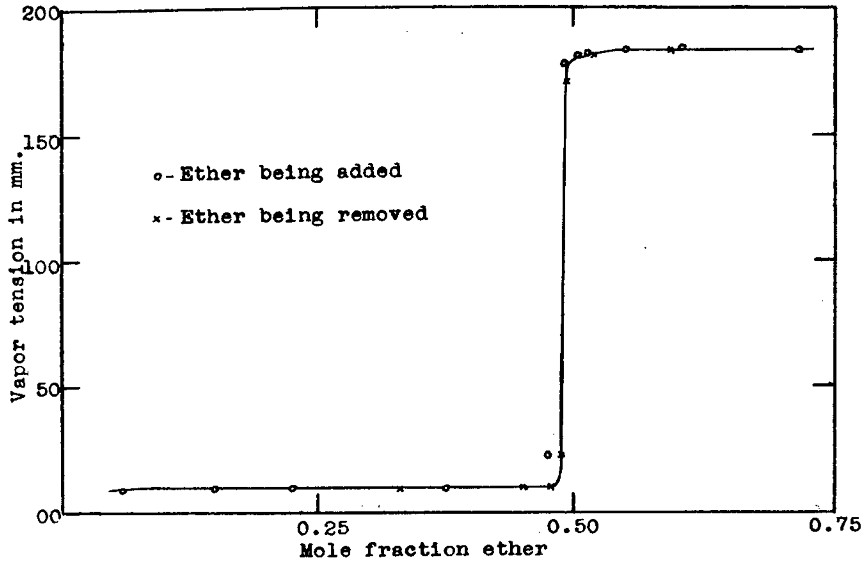

Figure 5. Vapor tension of lithium borohydride etherate.

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*Each of these products was identified by measurement of its vapor tension at several temperatures.

† In the gas phase, equilibrium between diborane and methyl borate is attained very slowly,[6] but it has been found that reactions of boron compounds of this type occur far more rapidly when a liquid phase is present or on glass surfaces.[12]

A sample of the solid weighing 0.0529 g gave 124.5 ml (5.31 mmoles) of hydrogen and required an amount of acid corresponding to 1.32 mmoles of sodium and 1.35 mmoles of boron. Assuming that one-half of the hydrogen evolved by hydrolysis came from water according to the equation:

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2$$

these quantities lead to the formula $Na_{.99}B_{1.02}H_{4.00}$, in excellent agreement with the assumption that the solid product is sodium borohydride. The quantities of hydrogen, sodium, and boron correspond to a product of 95.6% purity; the contaminant is undoubtedly methyl borate which, as already stated, is held tenaciously by the solid material.

Reaction of Dimethoxyborine With Sodium Trimethoxyborohydride

As was pointed out in Part I, one might expect that during the course of the reaction between diborane and sodium trimethoxyborohydride, dimethoxyborine would be formed. That only small quantities of this product are obtained is probably due to the fact that it reacts with the trimethoxyborohydride as shown by the following experiment.

A U-tube (6 mm tubing) equipped with a ground joint at either end was filled with 0.5908 g (4.62 mmoles) of sodium trimethoxyborohydride and attached to the vacuum line. Purified hydrogen was allowed to pass through the U-tube at a rate of eight liters per hour at a pressure of eight pounds. The hydrogen stream carried 495 ml (22.14 mmoles) of dimethoxyborine through the U-tube in 45 minutes. The excess dimethoxyborine and the methyl borate formed by the reaction were trapped in another portion of the vacuum system. After completion of the reaction, the U-tube was removed and weighed; the loss in weight was 0.3940 g as compared with 0.4150 g for complete conversion to sodium borohydride according to the equation:

$$NaBH(OCH_3)_3 + 3BH(OCH_3)_2 = NaBH_4 + 3B(OCH_3)_3$$

Hydrolysis of the solid material, however, resulted in the evolution of the exact volume of hydrogen demanded by complete conversion to sodium borohydride. Evidently, the excess weight (0.0210 g) was due to methyl borate held mechanically by the borohydride, rather than to unchanged trimethoxy compound. The calculated purity of the sodium borohydride was 90%.

Reaction of Diborane With Alkali Metal Methylates

Diborane was condensed by liquid nitrogen on a sample of the specially prepared sodium methylate (see Part III, Materials) contained in a reaction tube connected to the vacuum system. When the tube was warmed nearly to room temperature, a vigorous reaction set in. The volatile products were removed, fractionated, and identified in the manner described in the previous section. From 0.1902 g (3.521 mmoles) of sodium methylate and 65.5 ml (2.92 mmoles) of diborane, 13.6 ml of the latter were recovered unchanged, and 5.2 ml of dimethoxyborine plus 23.8 ml of methyl borate were obtained in the volatile products. According to the equation:

$$3NaOCH_3 + 2B_2H_6 = 3NaBH_4 + B(OCH_3)_3$$

3.52 mmoles of the methylate should react with 2.34 mmoles of diborane to produce 1.17 mmoles of methyl borate. The actual quantities, 2.31 mmoles of diborane absorbed and 1.05 mmoles of methyl borate recovered, are in as good agreement with the theory as is to be expected in view of the small total quantities involved. Analysis of the solid sodium borohydride showed it to be of 96% purity.

Potassium methylate failed to react with diborane during a period of thirty-six hours. This negative result may be due to the state of division of the starting material; the experiment should be repeated with potassium methylate prepared by the special method used for the sodium compound. The reaction of the lithium alkoxides has been adequately described in Part I.

The Reaction of Alkali Metal Tetramethoxyborohydrides With Diborane

The procedures used for mixing the reactants and fractionating the volatile reaction products were like those described for the reaction of diborane with sodium trimethoxyborohydride. In the reaction with sodium tetramethoxyborohydride, the mixture of reactants was maintained at −80°C for about fifteen minutes during which time no visible change occurred. At the end of this time, however, a rapid reaction set in. The mixture was ultimately warmed to room temperature and there maintained for thirty minutes to assure completion of the reaction. In the case of the corresponding potassium compound the mixture had to be warmed to room temperature before interaction occurred; as already mentioned in Part I, the reaction with the lithium compound required eighteen hours at room temperature for completion. Whether factors other than the state of subdivision of the solids accounts for these differences in rates has not been established.

A typical experiment was as follows: the starting materials were 0.5017 g (3.178 mmoles) of sodium tetramethoxyborohydride and 54.2 ml (2.42 mmoles) of diborane; the volatile reaction products contained 3.3 ml of diborane, 84 ml of methyl borate, and 14.4 ml of dimethoxyborine. According to the equation:

$$B_2H_6 + 4B(OCH_3)_3 = 6BH(OCH_3)_2$$

the formation of 14.4 ml of the latter substance should have consumed 2.4 ml of diborane and 9.6 ml of methyl borate. The amount of diborane which had reacted with the 3.178 mmoles of sodium tetramethoxyborohydride thus was 54.2 − (3.3 + 2.4) = 48.5 ml or 2.16 mmoles instead of the 2.12 mmoles required by the equation:

$$3NaB(OCH_3)_4 + 2B_2H_6 = 3NaBH_4 + 4B(OCH_3)_3$$

Similarly the amount of methyl borate formed, after correction for the amount of dimethoxyborine formed, was 84 + 9.6 = 93.6 ml or 4.18 mmoles instead of the 4.24 mmoles expected according to the equation. This excellent agreement made it unnecessary tc analyze the sodium borohydride. The outcome of the reactions of diborane with the lithium and the postassium tetramethoxyborohydrides has been adequately described in Part I.

Properties of Sodium Borohydride

Sodium borohydride is in most respects, physical and chemical, very much like lithium borohydride, and its properties need, therefore, not be described in great detail. The chief differences are in thermal stability, in initial rate of reaction with water, and in solubilities. Sodium borohydride melts above 400°C with but little evidence of decomposition below this temperature, whereas lithium borohydride begins to lose hydrogen at about 275°C. Even when the sodium compound is heated in air to 300°C it undergoes no change or only very slow change; when it is exposed in air to an open flame it burns quietly.

Although the reaction of sodium borohydride with water constitutes a seperate section of this paper it may be mentioned here that it can be dissolved in cold water with only slow decomposition; moderately concentrated aqueous solutions at room temperature lose only about 10% of their available hydrogen per day and the reaction becomes slower with increasing time. Evaporation of the water at 0°C in vacuo from a freshly prepared solution leads to the precipitation of a dihydrate of sodium borohydride; further evacuation produces an anhydrous product of 99% purity.* At 100°C, however, the sodium borohydride is completely hydrolyzed in one or two minutes, a fact that is advantageous when the compound is used as a reducing agent in analytical procedures. The initial reaction of lithium borohydride with water is much more rapid; unless it is added to a large quantity of water, the hydrogen evolved may burst into flame. But even in the case of the lithium salt, the reaction undergoes marked retardation as the alkalinity of the solution increases, and requires many hours for completion

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* Preliminary data indicate that a diammoniate is obtained by evaporation of a liquid ammonia solution.

Table 7. Solubility of sodium borohydride.

Solvent	Boiling pt of solvent	Temp of measurement (°C)	Solubility (g/100 g solvent)
Liquid ammonia	−33.3	25	104
Methyl amine	−6.5	−20	27.6
Ethyl amine	16.6	17	20.9
n-Propyl amine	48.7	28	9.7
i-Propyl amine	34	28	6.0
n-Butyl amine	77.8	28	4.9
Ethylene diamine	118	75	22
Cyclohexyl amine	134	28	1.8
Aniline	184	75	0.6
Pyridine	115.3	25	3.1
		75	3.4
Morpholine	128.3	25	1.4
		75	2.5
Acetonitrile	82	28	0.9

unless the temperature is raised, or the accumulated base is neutralized.

Unlike lithium borohydride, the sodium salt is not soluble in ether. It likewise fails to dissolve in dioxane, ethyl and diethyl Cellosolve, ethyl acetate, and methyl borate. It was necessary, however, to find a solvent to separate the sodium borohydride produced by the reaction

$$4NaH + B(OCH_3)_3 = NaBH_4 + 3NaOCH_3$$

from excess sodium hydride and from sodium methylate. For this purpose approximate information on solubilities is adequate and no effort was made to obtain an accuracy of more than 5 per cent in the solubility measurements. The solvents listed in Table 7 were obtained from commercial sources. Pyridine and morpholine were dried by distilling them from barium oxide; the primary amines were distilled from sodium hydride; anhydrous ethylene diamine, melting at 9°C, was used without further drying; acetonitrile was dried over phosphorus pentoxide and the fraction distilling between 80 to 82°C was used.

To determine the solubility an excess of the solid was refluxed (with exclusion of moisture) for some time at a temperature above that at which the measurement was to be made. The mixture was then cooled to the desired temperature at which it was maintained for a reasonable length of time. About 5 ml of the solution was then removed with a pipette equipped with a glass wool plug to prevent entry of solid. The solution was weighed, the solvent evaporated, and the weight of the residue was then determined. The weighed residual solid was in each case checked for purity by determining the volume of hydrogen released by treatment with hydrochloric acid. The data are given in Table 7.

Procedure for Measuring the Rate of Hydrogen Evolution by the Reaction Between Sodium Borohydride and Water

The rate of hydrolysis of mixtures of sodium borohydride and accelerators was determined by dropping a pellet of the mixture into water and collecting the hydrogen generated. The pellet was

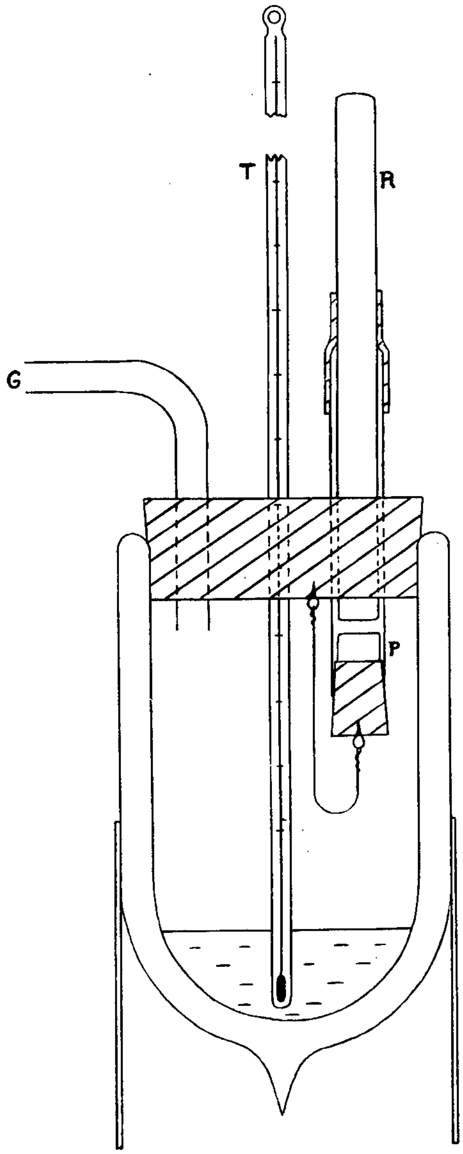

Figure 6. Apparatus for hydrolysis of sodium borohydride.

formed in a dry box with a small pellet press, and was then weighed in a weighing bottle on an analytical balance. The hydrolysis was carried out in a widemouth pint capacity Dewar equipped with a three-hole rubber stopper which held a thermometer, T, a gas outlet tube, G, and a piece of 12 mm tubing large enough to hold a pellet (Figure 6). A solid glass rod, R, which fitted inside the 12 mm tubing was attached to the latter by rubber tubing lubricated with glycerine so that the rod could be pushed through the tubing with a piston action. In performing a hydrolysis the weighed pellet, P, was placed in the 12 mm tubing, a cork was placed at one end and the glass rod was attached at the other end. The rubber stopper with its attachments was placed tightly in the Dewar, which was filled with the desired amount of water. The hydrolysis was started by pushing the glass rod against the pellet and the cork, thus causing the former to drop into the water, while the latter was held above the water level by wire connections to the stopper. The temperature of the hydrolysis solution and the volume of gas collected in a eudiometer (corrected to standard conditions) was noted at thirty-second intervals. In the experiment with buffered solutions a pure sodium borohydride pellet was dropped into the buffer solutions held in the Dewar. For the experiments done at constant temperature, the Dewar was replaced with a round-bottomed flask of appropriate size. The temperature was controlled by means of an ice bath.

Preparation and Analysis of Cobalt Boride

The preparation was carried out in a vessel shaped somewhat like a dumbbell with a right-angle bend at its center. The two ends of the vessel were fifty milliliter flasks and were connected to the L-shaped portion by standard taper joints. A side-neck from the tube carried a stopcock and could be connected to a vacuum pump. The neck of the flask in which the reaction was carried out was equipped with a sintered glass disk, and a side-neck with a standard taper joint through which the reagents could be added.

The boride was prepared by adding solid sodium borohydride in an atmosphere of hydrogen to twenty milliliters of 0.77M cobaltous chloride solution which had previously been degassed. The solution had been cooled to 0°C to minimize the catalytic effect of the boride in decomposing the borohydride, and to allow completion of the reaction to form the boride. After all the cobalt ion had been transformed into the black boride, and the excess borohydrides decomposed, the reaction vessel was evacuated. The boride, which had settled out of the solution, was then filtered off through the sintered glass disk. The water was distilled back to the boride (at about 40°C) leaving solid sodium metaborate in the other arm of the tube. The boride was washed with the water and filtered off a second time. The washing was repeated 5 times to remove all dissolved borate. The reaction vessel was finally connected to a vacuum system and the water completely removed. Hydrogen was admitted to the vessel and the flask containing the boride quickly removed and capped.

A 0.2712 g sample of the boride was dissolved in dilute hydrochloric acid and analyzed for cobalt[13] and boron; 0.2404 g of cobalt and 0.0222 g of boron were found, thus accounting for 96.8% of the sample weight. The cobalt to boron ratio was 1.99 to 1.

Another sample of the boride, 0.1862 g, was exposed to air and heated to about 300°C to insure completion of the oxidation. The weight of the products was 0.2110 g; theoretical for conversion to CoB and CoO is 0.2096 g.

Calorimetric Measurements

Preliminary measurements were made on the heat of hydrolysis of sodium borohydride, which, when combined with previously determined heats of reaction,[14] permitted an approximate calculation of the heat of formation of the borohydride from its elements in their standard states. The purpose of these measurements was to obtain a preliminary survey of the possible usefulness of sodium borohydride for generation of hydrogen. For this objective an accuracy of 2 to 3% was entirely satisfactory and no effort was made to reduce the error beyond this magnitude. The calorimetric measurements were made in a quart Dewar vessel equipped with a three-hole rubber stopper. The stopper held a manually operated ring-type stirrer, a Beckmann thermometer, and a length of 9-mm glass tubing which had a thin-walled bulb blown at its lower end. A solid glass rod which fitted inside of the 8-mm tubing was attached to it with rubber tubing lubricated with glycerine so that the rod could be pushed through the tubing (as described in the hydrolysis experiments). The bulb was filled with powdered sodium borohydride (about 0.5 g), a small wire cage was fastened around the bulb, and the glass rod was so placed that its lower end extended to a point just above the borohydride. Then 400 mml of standard hydrochloric acid solution was pipetted into the Dewar vessel, and the rubber stopper with its attachments put carefully in place. The stirrer was used to maintain a slow, steady agitation of the liquid. Temperature readings were recorded at 30-second intervals.

When the temperature was changing at a uniform rate, the glass bulb was broken by pressing down on the plunger and the borohydride was released to dissolve in the solution. Temperature readings were continued until a uniform change was re-established. The data were plotted in the usual manner and the correct temperature change calculated. The formula used was:

$$-H = \frac{(\text{Sp. Heat .1N HCl})\ (\text{Vol. HCl})\ (\text{Dens. soln}) + (\text{Cal. const})\ \text{Temp. rise})}{(\text{Moles NaBH}_4\ \text{used})}$$

Results obtained in two experiments were:

Run number	G $NaBH_4$ used	Rise in temperature	− H calculated in kcal
1	0.3365	1.262	61.6
2	.3041	1.127	60.9

From these data it is possible to calculate the heat of the reaction:

$NaBH_{4(s)} + HCl_{(.1N)} + 3H_2O = NaCl_{(aq)} + 4H_{2(g)} + H_3BO_{3(aq)}$ $H = -61.2$ kcal

This value was then used to determine the desired heat of reaction and heat of formation by the following series of reactions.

Heat of hydrolysis of sodium borohydride:

$NaBH_{4(s)} + HCl_{(.1N)}\ 3H_2O_{(l)} = NaCl_{(aq)} + H_3BO_{3(aq)} + 4H_{2(g)}$ $H = -61.2$ kcal
$NaCl_{(aq)} + H_2O_{(l)} = NaOH_{(.1N)} + HCl_{(.1)}$ $H = 13.8$ kcal
$NaOH_{(.1N)} + H_3BO_{3(aq)} = NaBO_{2\,(aq)} + 2H_2O_{(l)}$ $H = -\ 9.7$ kcal

$NaBH_{4(s)} + 2H_2O_{(l)} = NaBO_{2(aq)} + 4H_{2(g)}$ $H = -57.1$ kcal

Heat of formation of sodium borohydride:

$Na_{(s)} + B_{(s)} + O_{2(g)} = NaBO_{2(aq)}$ $H = -231.7$ kcal
$2H_2O_{(l)} = O_{2(g)} + 2H_{2(g)}$ $H = 136.8$ kcal
$NaBO_{2(aq)} + 4H_{2(g)} = NaBH_{4(s)} + 2H_2O_{(l)}$ $H = 57.1$ kcal

$Na_{(s)} + B_{(s)} + 2H_{2(g)} = NaBH_{4(s)}$ $H = -38$ kcal

SUMMARY

1) Interpretation of trivalent binary boron compounds as acids and of the alkali metal hydrides as bases in the generalized sense proposed by G. N. Lewis, has led to the discovery of a series of new reactions involving diborane, methyl borate, the alkali metal hydrides, alkoxides, and other related compounds.

2) As a result of these studies sodium and potassium borohydrides have been isolated for the first time, and several new methods for preparing lithium borohydride have been developed. The new procedures are far simpler and more convenient than any hitherto known, and make these compounds readily available for investigation. As a result of these studies, a method for quantity production of sodium borohydride was developed and is referred to herein.

3) The properties of sodium borohydride, including its stability, heat of formation, and of hydrolysis, and its solubility in various solvents, are briefly described. The existence of an etherate of lithium borohydride and of an hydrate and an ammoniate of sodium borohydride has been established.

4) The rate of interaction of sodium borohydride with water under varying conditions has been studied to determine the usefulness of this compound in the generation of hydrogen. It has been found that the rate decreases rapidly because of increasing alkalinity of the solution. This difficulty has been overcome by addition either of acidic substance or of catalysts to the solid borohydride. Cobaltous salts are the most effective catalysts thus far found; their action has been shown to be due to the formation of the compound Co_2B which is the actual catalyst.

ACKNOWLEDGMENTS

The writer wishes to express his most sincere appreciation to Dr. H. I. Schlesinger under whose guidance this investigation was carried out, and to Dr. H. C. Brown for his generous assistance.

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