

The rest of the apparatus was then evacuated to *ca.* 10^{-5} mm. through S7. Stopcock S6 was closed and all material in trap T3 was condensed in T2. For purification of the contents of what was then in T2, these were passed through trap T3 kept at -100° for this purpose and into T4 at -196° . The latter then contained diborane of fairly high purity as shown by the fact that its vapor tension at -112° usually was above 220 mm. For further purification, the residues in T3 may be distilled back into T1 and the diborane may be transferred from T4 back to T2. A second fractionation from T2 back through T3 and T4 may then be undertaken but this time T3 should be maintained at -140° rather than at -100° . The purified diborane may then be transferred to storage bulbs on the vacuum line or used directly for reaction studies.

Residues from the fractionation procedure were all distilled into T1 and the stopcocks adjusted to pass nitrogen through the reaction flask, the cold finger, T1 and out through bubbler B2. Methanol was then added slowly through the dropping funnel to destroy any hydrides remaining in the flask. The stopcocks were readjusted to

allow nitrogen to pass out through B1 and T1 was allowed to warm to room temperature. The nitrogen stream carried with it sufficient methanol into T1 to render harmless any residues there remaining. After standing at room temperature for a short time, the reaction flask and T1 could be removed safely for cleaning.¹⁶

Acknowledgment.—The assistance of H. R. Hoekstra, A. E. Finholt, D. M. Ritter, L. R. Rapp and I. Sheft with individual experiments and preparations reported in this paper is gratefully acknowledged.

(16) This description follows, with a few modifications, one given in Atomic Energy Commission Document MDDC-1338, by H. I. Schlesinger, George W. Schaeffer and Glen D. Barbaras. The document entitled "The Deposition of Pure Boron, Part I" may be obtained by inquiry to the Technical Information Division, Atomic Energy Commission, P. O. Box E, Oak Ridge, Tenn.

CHICAGO, ILL.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

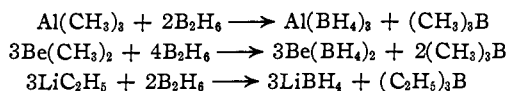
Reactions of Diborane with Alkali Metal Hydrides and Their Addition Compounds. New Syntheses of Borohydrides. Sodium and Potassium Borohydrides¹

BY H. I. SCHLESINGER, HERBERT C. BROWN, HENRY R. HOEKSTRA AND LOUIS R. RAPP

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In the presence of diethyl ether, lithium hydride reacts readily with diborane to form lithium borohydride: $\text{LiH} + \frac{1}{2}\text{B}_2\text{H}_6 \rightarrow \text{LiBH}_4$. The latter is also formed by reaction of diborane with either lithium ethoxide or lithium tetramethoxyborohydride: $2\text{B}_2\text{H}_6 + 3\text{LiOC}_2\text{H}_5 \rightarrow 3\text{LiBH}_4 + \text{B}(\text{OC}_2\text{H}_5)_3$, and $2\text{B}_2\text{H}_6 + 3\text{LiB}(\text{OCH}_3)_4 \rightarrow 3\text{LiBH}_4 + 4\text{B}(\text{OCH}_3)_3$. Lithium borohydride is readily purified by recrystallization from ethyl ether; the etherate, $\text{LiBH}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, is obtained, but the ether is removed easily. Attempts to bring about a direct reaction between sodium hydride and diborane have not succeeded. However, diborane is rapidly and quantitatively absorbed by sodium trimethoxyborohydride in accordance with the equation: $\frac{1}{2}\text{B}_2\text{H}_6 + \text{NaBH}(\text{OCH}_3)_3 \rightarrow \text{NaBH}_4 + \text{B}(\text{OCH}_3)_3$. Dimethoxyborine reacts in similar fashion with the trimethoxyborohydride. The new product, sodium borohydride, may also be prepared by the reaction of diborane with either sodium methoxide or sodium tetramethoxyborohydride. Potassium borohydride, also prepared for the first time, is obtained by the interaction of potassium tetramethoxyborohydride with diborane. These new methods, together with others described in other papers of this series, make the alkali metal borohydrides readily available. Sodium borohydride is a white crystalline solid of remarkable stability. It has been heated in air to 300° and in vacuum to 400° without apparent change. It dissolves in cold water without extensive reaction. From its aqueous solutions it may be recovered as the dihydrate. At 100° it reacts rapidly with water to liberate 4 moles of hydrogen, a reaction which also occurs rapidly at room temperature in the presence of acids or of certain catalysts. Boron fluoride liberates diborane quantitatively. The borohydride is a strong reducing agent both for organic and inorganic compounds. Potassium borohydride has properties similar to those of the sodium salt, but has not yet been investigated as thoroughly.

The borohydrides of aluminum,^{2a} beryllium^{2b} and lithium,^{2c} have hitherto been prepared only by the action of diborane on the respective metal alkyls^{3,4}



This type of reaction is unsatisfactory when borohydrides in even moderate amounts are desired. The metal alkyls, particularly the less volatile ones of the alkali metals, are themselves difficult to pre-

pare and handle on any large scale. Also the reaction is slow and requires repeated treatment with a large excess of diborane to remove completely all alkyl groups from the reaction product.

As a result of an investigation of the reactions of diborane with alkali metal hydrides and with their derivatives, a more satisfactory synthesis of lithium borohydride and methods of preparing the hitherto unknown sodium and potassium borohydrides were discovered. It thus became possible to study the properties of alkali metal borohydrides in more detail than could previously be done.

The knowledge thus gained enabled us later to develop methods for the preparation of borohydrides which have the advantage of not requiring the use of diborane, as is described in subsequent papers of this series.⁵

Results and Discussion

In the absence of solvents no reaction between diborane and lithium hydride was observed, even at elevated temperatures and pressures. The solu-

(5) No. VI, H. I. Schlesinger, H. C. Brown and A. E. Finholt, *THIS JOURNAL*, **75**, 205 (1953), and No. VII, H. I. Schlesinger, H. C. Brown and E. K. Hyde, *ibid.*, **75**, 209 (1953).

(1) New Developments in the Chemistry of Diborane and the Borohydrides. V. For a theoretical discussion of the reactions described herein, and for an explanation of the nomenclature employed, see paper I of this series, *THIS JOURNAL*, **75**, 186 (1953). For the experimental work on the lithium and sodium compounds discussed herein, H. R. Hoekstra is largely responsible. The discussion of the potassium compounds is based on the experiments of L. R. Rapp.

(2) (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *ibid.*, **62**, 3421 (1940); (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940); (c) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(3) The formation of lithium borohydride in the reaction of aluminum borohydride with ethyllithium in benzene solution has been observed (ref. 2c), but is also not feasible for larger scale preparations.

(4) The equations are idealized; the alkyl groups are actually recovered as mixtures of the boron alkyl and alkyl derivatives of diborane.

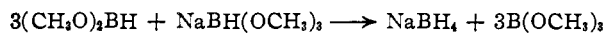
bility of lithium borohydride in ethyl ether suggested that the reaction might proceed in the presence of this solvent. Actually, under these conditions, diborane was quantitatively absorbed by the hydride with the formation of lithium borohydride in a state of high purity. An interpretation of the effect of ether has been given in the first paper of this series.¹

If the lithium hydride is coarse the reaction is relatively slow and is best carried out in sealed tubes under moderate diborane pressure. Under these conditions only about 1 g. of the borohydride can be prepared in each tube without the use of excessive diborane pressures. With finely divided lithium hydride, on the other hand, the reaction is rapid at atmospheric pressure and at room temperature and the desired compound is readily prepared in quantity. Since none of the impurities present in lithium hydride is soluble in ether, simple filtration of the initial solution serves to remove both excess hydride and all impurities. Evaporation of the filtrate leads to the precipitation of a crystalline monohydrate, $\text{LiBH}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$. Since this hydrate has a dissociation pressure of 10 mm. at 0° the ether is readily removed leaving behind finely divided borohydride of analytical purity. Physical properties and several reactions of lithium borohydride are described in the Experimental Part.

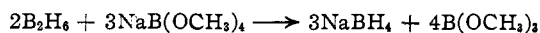
All attempts to bring about a similar reaction between sodium hydride and diborane failed. On the other hand, sodium trimethoxyborohydride, which is a source of readily available hydride ions,⁶ reacts rapidly with diborane to form sodium borohydride



The reaction proceeds so rapidly and so nearly quantitatively that it may be used to absorb diborane almost completely from a stream of gas, even though the concentration of the diborane in the latter is relatively low. As a result, sodium borohydride may be prepared by passing diborane directly from a generator through a column of solid sodium trimethoxyborohydride without the inconvenience and hazard of storing large quantities of diborane. It may be added that dimethoxyborine, which in some reactions is generated simultaneously with diborane, undergoes a similar reaction with the trimethoxy derivative



Another reaction of the same general type is that of diborane with sodium tetramethoxyborohydride

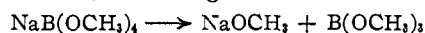


All of the preceding reactions for the preparation of sodium borohydride may be interpreted, in the sense of the Lewis generalized acid-base concept, as representing the displacement of the weaker acid, methyl borate, by the stronger acid, borine (BH_3).⁷

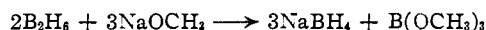
(6) H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, *THIS JOURNAL*, **75**, 192 (1953).

(7) In many of its reactions, diborane behaves as if it consists of two borine fragments. The use of the Lewis concept in giving direction to the investigation of which this paper is a part and in interpreting its results has proved very fruitful. It is outlined in the first paper of the series (ref. 1).

It, therefore, seemed possible that the latter acid might also react with "bases" such as sodium methoxide to form acid-base complexes from which the borohydride might be obtained by further action of diborane. The sample of the methoxide, used to test this hypothesis, was prepared by decomposition of sodium tetramethoxyborohydride and, therefore, had a large surface

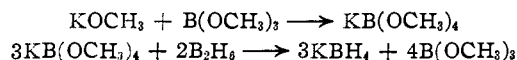


It rapidly absorbed diborane to form the borohydride with considerable evolution of heat



Of these three new reactions for the preparation of sodium borohydride—the reaction of diborane with sodium trimethoxyborohydride, with sodium tetramethoxyborohydride or with sodium methoxide—the first has the advantage of requiring the least diborane.

Potassium borohydride, another hitherto unknown compound, was prepared by the action of diborane on potassium tetramethoxyborohydride. The latter was obtained by the reaction of potassium methoxide with methyl borate



In contrast to sodium methoxide, the corresponding potassium compound did not react with diborane.⁸ A similar difference was observed in the reactions of lithium and sodium tetramethoxyborohydrides with diborane. The latter reacted completely and quantitatively in a few minutes, even at -80° ; the former required about 18 hours to absorb 97% of the theoretical diborane at room temperature and the product was not pure. Another example is the case of lithium methoxide and ethoxide. The former absorbed only 50% of the theoretical diborane in 30 minutes at room temperature and only 83% after 18 hours, whereas the reaction of the ethoxide was rapid and complete. As was discussed more fully in the first paper of this series,¹ differences such as these are probably due to differences in the physical condition of the several solid compounds.

Sodium borohydride is a white crystalline, salt-like compound.⁹ It is very soluble in liquid ammonia (from which it is recovered as a diammoniate), and in the lower aliphatic amines. We found isopropylamine particularly convenient for extraction and recrystallization of the borohydride.

It is remarkably stable. Heated in an evacuated tube, it exhibits no apparent change at temperatures approaching 400° , whereas lithium borohydride^{2c} loses hydrogen at 275° . Only above 400° is a relatively slow evolution of hydrogen noted. In air the substance has been heated to 300° without apparent change. A small quantity burns quietly in a bunsen flame.

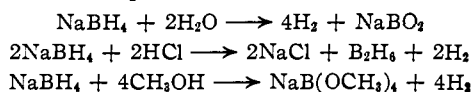
Sodium borohydride dissolves in cold water without extensive evolution of hydrogen and may be

(8) J. Goubeau, U. Jacobshagen and M. Rahtz [*Z. anorg. Chem.*, **263**, 63 (1950)] report failure to obtain potassium borohydride by the action of diborane on potassium hydride within the temperature range of 185 – 200° .

(9) A. M. Soldate, *THIS JOURNAL*, **69**, 987 (1947); P. M. Harris and E. P. Meibohm, *ibid.*, **69**, 1232 (1947).

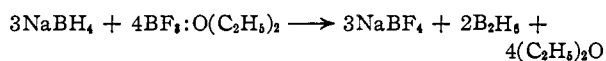
partially recovered as the dihydrate, $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$, from aqueous solutions. Moreover, the water may be removed from the dihydrate *in vacuo* to give sodium borohydride of high purity. The reactivity toward water is markedly dependent upon the pH and the temperature of the solution. Addition of acid to the relatively stable solution of sodium borohydride in cold water rapidly liberates the theoretical quantity of hydrogen. At higher temperatures the hydrolysis rapidly proceeds to completion without added acid.¹⁰ The hydrolysis can also be greatly catalyzed by small quantities of certain metal salts. Cobalt salts are particularly effective.¹¹

Its reactions with water, methanol and hydrogen chloride are quite similar to those of the corresponding lithium compound.^{2c,11}



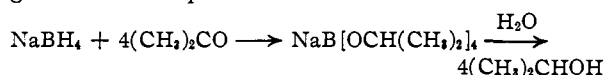
The reaction with methanol proceeds at an appreciable rate at -40° , in contrast to the slow reaction with water at room temperature.

Sodium borohydride reacts quantitatively with boron fluoride etherate to liberate diborane.



With the present commercial availability of sodium borohydride,¹² this reaction constitutes another convenient source of diborane.

The salt reacts with acetone to form a reduction product which, after hydrolysis, yields isopropyl alcohol. A possible course of the reaction is suggested in the equation



Sodium borohydride is a more convenient reagent for the reaction of organic compounds containing carbonyl groups than diborane.¹³ It differs from lithium aluminum hydride¹⁴ in being less powerful and, therefore, more selective in some cases, as well as in its applicability in water and other hydroxylic solvents.¹⁵ Sodium borohydride in aqueous solution also reduces many inorganic ions and has shown considerable promise as an analytical reagent.¹⁶

So far as it has been investigated, the behavior of potassium borohydride is similar to that of the sodium salt.

Experimental Part

Materials.—The sodium and lithium hydrides have been previously described.⁶

For large scale preparations of lithium borohydride, a

(10) The kinetics of the hydrolysis of sodium borohydride have been studied recently by M. Kilpatrick and C. D. McKianey, Jr., *THIS JOURNAL*, **72**, 5474 (1950).

(11) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *ibid.*, **75**, 215 (1953).

(12) Metal Hydrides, Beverly, Mass.

(13) H. C. Brown, H. I. Schlesinger and A. B. Burg, *THIS JOURNAL*, **61**, 673 (1939).

(14) A. E. Finholt, A. C. Bond and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947); R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197, 2548 (1947).

(15) S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949).

(16) Unpublished work of George W. Schaeffer and A. C. Stewart. Also A. C. Stewart, Reducing Properties of Aqueous Solutions of Sodium Borohydride, University of Chicago M.S. Thesis, 1948.

better grade of lithium hydride had become available from the Litalloy Corporation.¹⁷ It analyzed 94% hydride and was in the form of 200-mesh powder. Sodium tetramethoxyborohydride was obtained by treating the trimethoxyborohydride with methanol, followed by methyl borate (to remove small quantities of sodium methoxide). Sodium methoxide was prepared by thermal decomposition of sodium tetramethoxyborohydride *in vacuo* at $210\text{--}240^\circ$. Lithium methoxide and ethoxide were prepared by action of the metal on the appropriate alcohol. Lithium tetramethoxyborohydride was obtained by treating the methoxide with excess methyl borate and then removing the excess *in vacuo*.

For the preparation of the potassium compounds, potassium sand was first prepared in xylene, the xylene was removed and the residue was washed with anhydrous ether. To a mixture of the product with toluene, an excess of methanol was added slowly. After the potassium had all reacted, the alcohol was removed under high vacuum, the last traces at 170° for 2 hours. Analysis indicated 92.3% purity. The preparation of potassium tetramethoxyborohydride, a new compound, is described below.

In the following, volumes of vapor and gases are referred to S.T.P.

A. Preparation and Behavior of Lithium Borohydride

Lithium Hydride and Diborane.—The initial reactions with the coarser lithium hydride were carried out in heavy glass tubes of approximately 250-ml. capacity, fitted with a side arm for introduction of lithium hydride and with a ground joint for attachment to the vacuum line. The tubes were charged with about 1 g. of the hydride and 50 ml. of anhydrous ether. They were then attached to the vacuum line, evacuated at -80° and supplied with about 1 l. of diborane. Next they were sealed and permitted to warm to room temperature. After 3–4 hours the reaction appeared complete. The tubes were opened to the line, nitrogen was admitted and the crystalline borohydride was dissolved by raising the temperature of the mixture to the boiling point of ether. The mixture was filtered with protection from atmospheric moisture. The ether was evaporated from the filtrate, the last portions under vacuum. The yield of lithium borohydride was essentially quantitative.

For the preparation of larger quantities of lithium borohydride, the more elaborate apparatus of Fig. 1 was used. By the use of liquid nitrogen, 13 l. of diborane was condensed from a storage system into bulb B_1 which was then connected to the apparatus through the ground joint. A mixture of 10 g. (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 it was cooled with an ice-bath. When the manometer had ceased rising, stopcock S_1 was opened and the air was pumped out. In order to transfer the diborane from bulb B to RV, the air in the line between SV_1 and stopcock S_4 and S_4 was exhausted through stopcock S_2 which was then closed.

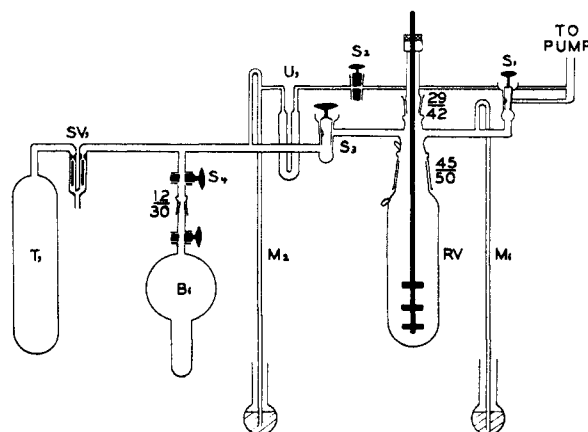


Fig. 1.—Apparatus for the preparation of large quantities of lithium borohydride.

(17) More recently lithium hydride has been obtainable from the Maywood Chemical Works, Maywood, N. J., and from the Metalloy Corporation, Minneapolis, Minn.

Stopcock S_1 was opened and the bulb was allowed to warm until its pressure, as registered by manometer M_2 , was about 700 mm. Stopcock S_2 was now opened. By placing a dewar vessel containing liquid nitrogen at an appropriate height at the lower portion of bulb B_1 , the rate of evaporation of the diborane was regulated to equal its rate of absorption by the lithium hydride. During this process, the mixture in RV was continuously stirred.

After about 9 l. of diborane had been absorbed, a heavy slurry of lithium borohydride etherate usually formed and impeded the stirring. The mixture was warmed to 15–20° to redissolve the precipitate and the absorption was completed at that temperature. To remove the residual 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_1 . By warming the latter, the evaporating ether swept the remaining diborane into RV where it was absorbed. As a final precaution, stopcock S_1 was opened for a few seconds to the pump to remove residual traces of diborane.

The reaction vessel, which 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 (Fig. 2). The vessel RV was warmed to 30° 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 glass disc into the receiver R. To distil the ether through the sintered glass disc back into the reaction vessel, RV, the latter was cooled by an ice-bath and the receiver was warmed to 35–40° by a water-bath. 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 disc. After the ether had been returned to the reaction vessel, it was warmed and the filtration was repeated. Five extractions completely removed the borohydride from the residue. After the last extraction, the ether was distilled into a duplicate reaction vessel, and the temperature of the receiver R, containing the pure lithium borohydride, was slowly raised to 100°. The last traces of ether were removed by connecting the receiver directly to the pump.

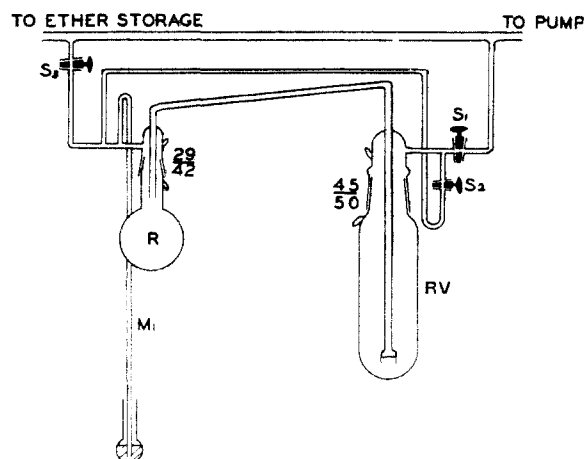
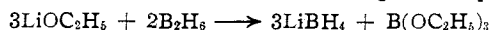


Fig. 2.—Apparatus for extraction of lithium borohydride.

In a typical preparation, carried out as described above, the yield was 25.0 g. of lithium borohydride, an amount which corresponded to a 99% conversion of the diborane used.

The Reaction of Lithium Ethoxide with Diborane.—Over a sample of 95% lithium ethoxide containing 2.23 g. (43 mmoles) of the pure compound 1050 ml. of diborane was passed under such conditions that the pressure remained below 100 mm. During the first passage 509 ml. of diborane was absorbed, during the second 124 ml. and during the third 12 ml., a total of 645 ml. or 28.8 mmoles. The amount calculated is 28.7 mmoles according to the equation

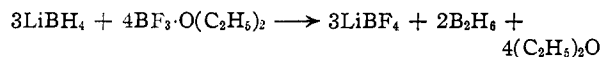


The purity of lithium borohydride was shown by hydrolysis to be 85–90%. A single recrystallization from ether raised it to 95–96%.

Considerable heat is evolved in the course of the reaction. In the first passage of the diborane through the ethoxide the temperature rose to 150° and in the second stage to 50°. In other experiments even higher temperatures have been observed. Under these conditions there is loss of diborane through decomposition to hydrogen and heavier hydrides of boron. This phenomenon limited the amount of lithium borohydride we could prepare in a single operation, a difficulty which could be overcome by utilizing better heat transfer methods. The reaction possesses the inherent advantage of being very fast. It would, therefore, permit the preparation of lithium borohydride without the necessity of maintaining a large quantity of diborane in the reaction system.

Reaction of Lithium Borohydride with Boron Fluoride.—Gaseous boron fluoride did not show any significant reaction with lithium borohydride. However, boron fluoride etherate reacted rapidly and completely to liberate diborane.

In a small reaction tube attached to the vacuum system, 43 mg. of lithium borohydride (2.00 mmoles) and 311 mg. of boron fluoride etherate (2.05 mmoles) were allowed to interact as the temperature rose. The pressure in the tube rose rapidly during the first 15 minutes and changed but little during the next hour. The volatile reaction products consisted of 43.5 ml. of ether (1.94 mmoles) and 23.6 ml. of diborane (1.05 mmoles). From these data it is evident that incomplete separation of the ether from the diborane was responsible for the fact that the amount of the latter slightly exceeds the value, 1.025 mmoles, calculated from the amount of the etherate according to the equation



The equation was confirmed by experiments showing that when an excess of the etherate was used, the molar ratio $\text{B}_2\text{H}_6:\text{LiBH}_4$ was 2:3.

Lithium Borohydride Etherate.—A 0.2630-g. sample of lithium borohydride was placed in a small reaction tube equipped with a ground joint. The tube was attached to the vacuum apparatus where it was directly connected to a

TABLE I
DISSOCIATION PRESSURES OF LITHIUM BOROHYDRIDE ETHERATE AT 0°

Ether added Mole fraction of ether	Press., mm.	Ether removed Mole fraction of ether	Press., mm.
0.062	9	0.593	182
.153	10	.519	181
.225	10	.509	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	.330	10
.718	183		

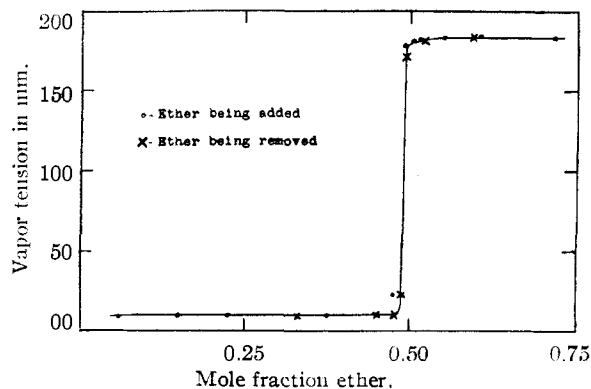


Fig. 3.—Vapor tension of lithium borohydride etherate.

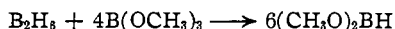
manometer and to a calibrated volume through a mercury float valve. Small portions of ether were measured as a gas in the calibrated system and were transferred to the lithium borohydride tube by condensation with liquid nitrogen. After each transfer the bulb was brought to 0° by means of an ice-bath and the equilibrium pressure recorded. The data are recorded in Table I and plotted in Fig. 3.

It is apparent that lithium borohydride forms a monoetherate with a dissociation pressure of 10 mm. at 0°. The slight displacement of the vertical portions of the curve from the value 0.5 was probably due to a small amount of impurity in the borohydride, possibly picked up in the course of weighing and transferring the sample. (Lithium borohydride is quite hygroscopic.)

Solubilities of Lithium Borohydride.—The solubility of lithium borohydride per 100 g. of solvent is approximately 2.5 g. in diethyl ether at 19°, and 3–4 g. in isopropylamine at 25°.

B. Preparation and Properties of Sodium Borohydride

Sodium Trimethoxyborohydride and Diborane.—Approximately 100 ml. of diborane was condensed on 4.84 g. (37.9 mmoles) of sodium trimethoxyborohydride contained in a glass reaction tube connected to a manometer and to the vacuum apparatus. With rise of temperature the pressure of diborane in the tube first rose rapidly as the liquid vaporized and then dropped quickly to a low value as the gas was taken up by the solid. When the tube had reached room temperature, the pressure had again increased to a value approximately that for methyl borate. After 30 minutes the tube was opened, the volatile products were removed and stored for later study and another portion of diborane was introduced into the tube and permitted to react. The complete procedure was repeated three times. A total of 514 ml. (22.9 mmoles) of diborane was added. The solid was heated to 200° to remove the last traces of volatile material. The combined volatile products were fractionated through U-tubes at –80, –145 and –195°, and separated into 67.0 ml. of diborane, 115 ml. of dimethoxyborine and 738 ml. of methyl borate. A total of 447 ml. of diborane was absorbed, as contrasted with the 424 ml. demanded by the postulated equation $B_2H_6 + 2NaBH(OCH_3)_2 \rightarrow 2NaBH_4 + 2B(OCH_3)_3$. The 115 ml. of dimethoxyborine accounts for an additional 19 ml. of diborane, presumably utilized in the secondary reaction



Thus 99% of the diborane introduced is accounted for. Similarly, the 115 ml. of dimethoxyborine (5.13 mmoles) and 738 ml. of methyl borate (32.9 mmoles) account for more than 96% of the methoxy groups present in the 37.9 mmoles of sodium trimethoxyborohydride originally employed. For analysis, hydrogen was generated by hydrolysis and the boron and sodium were determined in the resulting solution by the usual procedures.

Anal. Calcd. in mmoles for $NaBH_4$ (0.0529-g. sample): H₂, 5.6; Na, 1.40; B, 1.40. Found: H₂, 5.31; Na, 1.32; B, 1.35.

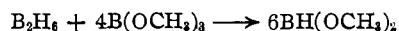
The sample was evidently between 94 and 95% pure.

To ascertain whether the reaction is rapid enough to remove diborane from a stream of inert gas, approximately 2 g. of sodium trimethoxyborohydride was placed in a small U-tube (6 mm. diameter), through which hydrogen containing diborane was permitted to flow at the rate of 12 l. per hr. The diborane rate was 0.324 l. per hr. There was a narrow hot zone of reaction in the tube and the progress of the absorption could be followed both by the movement of the hot zone and by visual observation of the changes in the material. The volatile products were trapped out of the hydrogen stream. From 103.5 ml. of diborane there was obtained 217 ml. of volatile product, largely methyl borate with a small quantity of dimethoxyborine. Identical results were obtained in a similar experiment in which the rate of flow of diborane was 1.9 l. per hr. At least 95% of the diborane was absorbed in a single pass.

Sodium Trimethoxyborohydride and Dimethoxyborine.—A U-tube (6 mm. tubing) equipped with ground joints at both ends 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 the rate of 8 l. per hr. at a pressure of 0.5 atm. The hydrogen stream carried 495 ml. (22.1 mmoles) of dimethoxy-

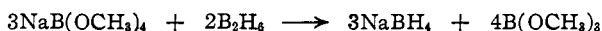
borine through the U-tube in 45 minutes. At the end of the reaction, the volatile products were removed from the U-tube. The decrease in weight was 0.3940 g. as compared to the value 0.4149 g. for complete conversion to sodium borohydride: $NaBH(OCH_3)_2 + 3(CH_3O)_2BH \rightarrow NaBH_4 + 3B(OCH_3)_3$. Hydrolysis of the solid liberated the theoretical quantity of hydrogen.

Sodium Methoxide and Diborane.—To prepare the sodium methoxide for this reaction, 0.555 g. (3.52 mmoles) of sodium tetramethoxyborohydride was heated to 210–240° under vacuum until the theoretical quantity of methyl borate was evolved. The product was cooled to room temperature and 65.5 ml. (2.92 mmoles) of diborane was added. There was very rapid absorption and the tube grew noticeably hot. The volatile products were removed and separated. Diborane, 13.6 ml., was recovered together with 5.2 ml. of dimethoxyborine and 23.8 ml. of methyl borate. The equation, $3NaOCH_3 + 2B_2H_6 \rightarrow 3NaBH_4 + B(OCH_3)_3$, requires a consumption of 52.4 ml. of diborane as compared with the 51.9 ml. actually used and the formation of 26.2 ml. of methyl borate. The slight deficiency in the actual amounts is fully accounted for by the production of the 5.2 ml. of dimethoxyborine according to the equation



The purity of the sodium borohydride was 96%.

Sodium Tetramethoxyborohydride and Diborane.—Sodium tetramethoxyborohydride (boron 99.5% and sodium 101.3% of the theoretical) was treated with diborane. For 15 minutes at –80°, no visible change occurred, then rapid absorption of the gas was observed. The mixture was ultimately warmed to room temperature and maintained there for 30 minutes to assure completion of the reaction. The 0.502 g. (3.18 mmoles) of the tetramethoxyborohydride absorbed 50.9 ml. (2.27 mmoles) of diborane and produced 84 ml. of methyl borate (3.75 mmoles) and 14.4 ml. (0.64 mmole) of dimethoxyborine. The calculated amounts of diborane absorbed and of methyl borate produced are 2.23 and 3.80 mmoles, respectively, if it is assumed that the 0.64 mmole of dimethoxyborine resulted from the secondary reaction of diborane and methyl borate, and that the equation for the main reaction is



Properties of Sodium Borohydride. Solubility.—An excess of the solid borohydride 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 and maintained at the desired temperature. About 5 ml. of the solution was then removed with a pipet 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 II.

TABLE II

SOLUBILITY OF SODIUM BOROHYDRIDE IN SEVERAL SOLVENTS

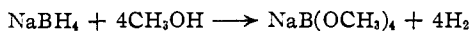
Solvent	B. p. of solvent, °C.	Temp., °C.	Solubility, g./100 g. solvent
Liquid ammonia	–33.3	25	104
Methylamine	–6.5	–20	27.6
Ethylamine	16.6	17	20.9
<i>n</i> -Propylamine	48.7	28	9.7
Isopropylamine	34	28	6.0
<i>n</i> -Butylamine	77.8	28	4.9
Ethylenediamine	118	75	22
Cyclohexylamine	134	28	1.8
Aniline	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

The borohydride is not appreciably soluble in ethyl ether, dioxane, diethyl cellosolve, ethyl acetate and methyl borate.

It reacts with acetone (see below). Its solubility in water, the existence of a hydrate and the utilization of these facts in the purification of the salt have been adequately described. Evaporation of a liquid ammonia solution of the borohydride results in the separation of a crystalline solvate which preliminary data indicate to be a diammoniate.

Sodium Borohydride and Boron Fluoride Ethyl Etherate.—A mixture of 0.110 g. (2.90 mmoles) of sodium borohydride¹⁸ and 0.743 g. (5.24 mmoles) of boron fluoride etherate was prepared at -195° and allowed to warm to room temperature. A vigorous reaction accompanied by evolution of a gas was observed. After one hour, the volatile products were removed and separated into 85.7 ml. of ether and 42.8 ml. of diborane by fractional condensation. Based on the equation, $3\text{NaBH}_4 + 4(\text{C}_2\text{H}_5)_2\text{O}:\text{BF}_3 \rightarrow 2\text{B}_2\text{H}_6 + 3\text{NaBF}_4 + 4(\text{C}_2\text{H}_5)_2\text{O}$, the diborane yield was 98% and the ether recovery was 98.7%. Addition of a solution of potassium chloride to an aqueous solution of the residue produced a precipitate of potassium borofluoride.

Sodium Borohydride and Methanol.—Addition of methanol (38.5 mmoles) to 9.22 mmoles of sodium borohydride gave rise to a very slow evolution of hydrogen at -80° , which became moderately rapid at -40° . Additional methanol (11.2 mmoles) was added and the mixture was allowed to warm to room temperature in order to bring hydrogen evolution to completion in reasonable time. Even so, the quantity of hydrogen obtained was only 90% of that expected according to the equation



The equation is, however, confirmed by the fact that the solid reaction product gave off no volatile material except a small amount of methanol when heated to 145° but exhibited a dissociation pressure of 3 mm. and gave off methyl borate at 250° , as is characteristic of the tetramethoxy derivative. Failure to obtain more than 90% of the expected hydrogen is attributed to the difficulty of securing adequate contact of the methanol with the residual simple borohydride, embedded in the voluminous tetramethoxyborohydride.

Sodium Borohydride and Aluminum Borohydride.—No evidence of the formation of addition products, such as $\text{NaAl}(\text{BH}_4)_4$, was obtained when the two simple borohydrides were mixed. The sodium salt swelled and appeared to dissolve partially in the liquid aluminum compound. The latter could be recovered from the mixture though with some difficulty.

Sodium Borohydride and Acetone.—Sodium borohydride, 0.150 g. (3.94 mmoles), was treated in a closed tube with slightly more than 4 equivalents, *i.e.*, with 0.97 g. (16.8 mmoles) of acetone. At room temperature the acetone was apparently absorbed by the borohydride, forming a porous fluffy solid. The tube was heated briefly to $40\text{--}60^{\circ}$, opened and the excess acetone removed. The solid was treated with water, and the volatile products were removed and dried. The residue contained the original sodium and boron. The volatile product was homogeneous with a v.p. of

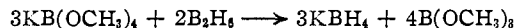
9.0 mm. at 0° , 44.3 mm. at 25° and a b.p. of 82.5° , in excellent agreement with the corresponding values for isopropyl alcohol (v.p. 8.9 mm. at 0° , 44.2 mm. at 25° , b.p. 83°).

C. Preparation of Potassium Borohydride

Preparation of Potassium Tetramethoxyborohydride.—To a solution of approximately 9 g. of potassium in 130 ml. of absolute methanol, 35 ml. of methyl borate was added (a 10% excess). Considerable heat was generated. The excess methanol was distilled off at atmospheric pressure to incipient precipitation. The solution was cooled and the resulting white, needle-like crystals of the potassium tetramethoxyborohydride were removed by filtration in the absence of moisture. The crystals were freed from the last traces of solvent by heating them to 120° at low pressure. An analysis showed 100.7% of the theoretical potassium and 101% of the boron.

Diborane and Potassium Methoxide.—A mixture of 7.6 mmoles of potassium methoxide and 7 mmoles of diborane failed to interact at room temperature, as demonstrated by complete recovery of the diborane after 1.5 hours, as well as after an additional 34 hours of contact.

Diborane and Potassium Tetramethoxyborohydride.—To 7.41 g. (42.6 mmoles) of potassium tetramethoxyborohydride at -80° , 689 ml. (30.8 mmoles) of diborane was added in 60-ml. portions. Even at this low temperature the reaction was rapid. In addition to methyl borate, the volatile reaction products contained 21 ml. of diborane and 128 ml. of dimethoxyborane. Since the latter was undoubtedly formed by the side reaction, $\text{B}_2\text{H}_6 + 4\text{B}(\text{OCH}_3)_2 \rightarrow 6\text{HB}(\text{OCH}_3)_2$, the amount of diborane which had reacted with the 42.6 mmoles of the tetramethoxyborohydride was 647 ml. (*i.e.*, $689 - 21 - 21$ ml.) or 28.8 mmoles. This quantity is in excellent agreement with the value 28.4, calculated according to the equation



The product, a white solid, was heated to 190° and subjected to pumping. A portion of the resulting material was dissolved in water, heated to 100° to liberate hydrogen, and the solution was analyzed for base and for boron in the usual way. The results corresponded to the formula $\text{K}_{1.00}\text{B}_{1.04}\text{H}_4\text{O}_4$.

A large sample, involving 3.1 l. of diborane, was made by passing the gas through a U-tube containing potassium tetramethoxyborohydride. The gas was rapidly absorbed and methyl borate was evolved.

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CHICAGO, ILL.

(18) The sodium borohydride used in these experiments was a finely divided solid prepared from sodium trimethoxyborohydride and diborane.