REACTION BETWEEN THE ETHER COMPLEX OF BORON TRIFLUORIDE AND LITHIUM HYDRIDE

COMMUNICATION 1. PREPARATION OF PURE DIBORANE

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The simplest boron hydride – diborane – is one of the most stable compounds of this class and is one of the least active in its attack on the grease in joints and taps. Until recently, most of the methods for its synthesis gave complex mixtures of volatile substances containing relatively little diborane, and its isolation from these mixtures was a very difficult task.

Stock, the pioneer in the systematic investigation of the boron hydrides, obtained diborane by prolonged fractionation of the hydrolysis products of so-called magnesium boride [1-4]. Later, Schlesinger and Burg [5] and Stock [6] obtained diborane by passing a mixture of boron halides and hydrogen through an electric discharge, but the yield did not exceed 6%. Hurd [7] prepared diborane by the reduction of boron halides with hydrogen in presence of metals and metal hydrides at high temperatures, and the product was again a difficultly separable mixture having a relatively low diborane content. In 1947 Schlesinger and coworkers [8] made use of the reaction of lithium aluminum hydride with boron trichloride for the preparation of diborane.

With the object of preparing diborane, at the end of 1949 we carried out a systematic study of the reduction of simple inorganic boron compounds with lithium hydride. For this purpose we used boron halides and sulfides, alkali-metal fluoborates, and other compounds. We found that, apart from boron trifluoride in ether solutions, all these substances react with lithium hydride with deflagration and the separation of elementary boron. After a considerable induction period lithium hydride reacted with a dilute ethereal solution of boron trifluoride at room temperature with separation of diborane; when the ether complex of boron trifluoride ("boron trifluoride etherate", a liquid, b.p. 126°) was used, reaction set in very quickly. The gas evolved was almost pure diborane, free from impurities apart from ether vapor. However, the reaction was found to be very capricious, giving yields that varied over the range 20-60%, and systematic work was necessary in order to ensure a reproducible yield.

Since we began this work some patents and papers have been published on the preparation of diborane by reaction between boron trifluoride and lithium hydride in an ether medium. Two patents were published in 1951 on the preparation of diborane by heating a mixture of lithium hydride and boron trifluoride in ether with simultaneous removal of diborane by distillation [9,10]. In a paper by Schapiro and coworkers in 1952 [11] a method is described for the preparation of diborane by reaction between boron trifluoride etherate and lithium aluminum hydride, and in a paper by Elliott, Boldebuck, and Roedel [12] its preparation by reaction of lithium hydride and boron trifluoride etherate is described. In this last investigation numerous experiments were carried out under various conditions, and the results were examined from the point of view of the possibility of the occurrence of two reactions:

$$6LiH + 2BF_3 \xrightarrow{\text{activator}} B_2H_6 + 6LiF$$

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

In presence of sufficient activator, the reaction proceeds in stages:

$$6LiH + 1.5BF_3 \xrightarrow{\text{activator}} 1.5LiBH_4 + 4.5LiF$$

$$1.5\ LiBH_4 + 0.5\ BF_3 \rightarrow B_2H_6 + 1.5\ LiF.$$

The authors point out the great complexity of the reaction and state that the presence of an ether-soluble activator ($LiBH_4$ or $LiBH(OCH_3)_3$) results in preferential conversion to $LiBH_4$, whereas in absence of an activator the reaction proceeds in the direction of the formation of B_2H_6 and $LiBF_4$. High pressures and the use of a tetrahydrofuran medium, in which diborane is highly soluble [13], favor the formation of lithium borohydride. The inconsistency of the yields is particularly emphasized in this paper. In a paper by Schlesinger and coworkers [14] it is stated that boron trifluoride etherate reacts with lithium hydride according to Equation 1 at a rate that depends on the degree of grinding of the lithium hydride, and the maximum yields that they give are not greater than 40-60% with respect to boron. The following intermediate stages are indicated in this paper:

$$3\ LiH + 3\ BF_3 \cdot O(C_2H_5)_2 \rightarrow 3\ LiBHF_3 + 3\ (C_2H_5)_2O;$$

$$3\ LiBHF_3 + BF_3 \cdot (C_2H_5)_2O \rightarrow \frac{1}{2}\ B_2H_5 + 3\ LiBF_4 + (C_2H_5)_2O.$$

It is pointed out that successive additions of the etherate react progressively less vigorously, in spite of the presence of excess of lithium hydride in the reaction mixture. The authors regard this reaction as difficult and non-quantitative, and they prefer the reaction of boron trifluoride with $NaBH(OCH_3)_3$, which gives more consistent yields of diborane. In all the published investigations, therefore, references are made to the complexity of the reaction and the inconsistency of the yields of diborane. For this reason we considered it desirable to publish our results on the reaction of boron trifluoride with lithium hydride, which were verified in numerous experiments under laboratory conditions.

EXPERIMENTAL

Original Substances. Lithium hydride LiH was the commercial quality, a fused crystalline mass containing 90-98% of LiH. It was ground as finely as possible in a mortar, sieved, and used immediately in the reaction. The use of hydride powder that has been kept for a long time results in a long period of induction with subsequent violent reaction.

Boron trifluoride BF_3 was prepared by reaction of boric anhydride with potassium fluoborate and concentrated sulfuric acid [15]. In order to remove hydrogen fluoride and water vapor impurities, the gas was passed through a trap containing concentrated sulfuric acid saturated with boric anhydride in the cold.

Boron trifluoride etherate $BF_3 \cdot (C_2H_5)_2O$ was prepared by saturating absolute ether with boron trifluoride and then distilling at atmospheric pressure; b.p. 126°. When kept, the etherate darkens in color; freshly distilled material must be used in the reaction.

Diethyl ether was first dried with calcined calcium chloride and then distilled and kept over sodium for a long time.

Investigation of Solid Reaction Products. After the reaction, during which gaseous diborane was removed, and removal of ether, a white solid remained in the reaction vessel. In order to determine the exact yield of the reaction with respect to the reactants consumed, it was necessary to determine the composition of this solid.

A test for $LiBH_4$ was carried out by adding 3-4 drops of water or dilute acid to a small amount of an ether extract of the solid. The presence of $LiBH_4$ was indicated by vigorous evolution of hydrogen. Lithium borohydride was isolated quantitatively from the solid by repeated washing with ether on a glass funnel with a porous bottom, filtration under a pressure of dry nitrogen, removal of ether from the filtrate under atmospheric pressure, and drying of the product in a vacuum at 90-100°. The active-hydrogen content of the lithium borohydride was determined by decomposing a sample with a weakly acid solution of a nickel salt [16].

In order to test for the presence of $LiBF_4$, an aqueous solution of a little of the solid was neutralized to methyl orange with hydrochloric acid and mixed with concentrated calcium chloride solution. In presence of $LiBF_4$ the reaction

$$LiBF_4 + 2CaCl_2 + 3H_2O \rightarrow H_3BO_3 + LiCl + 3HCl + 2CaF_2.$$

occurred: there was an indicator change to pink, which became bright red with simultaneous precipitation of CaF_2, when the solution was heated.

For the quantitative determination of $LiBF_4$, a sample of the solid weighing 0.2-0.3 g was dissolved in the least possible amount of water, the solution was neutralized to methyl orange, a strong neutral solution of calcium chloride was added, and the solution was brought almost to the boil, at which it was maintained for 10-15 minutes. The hot solution was titrated with 0.1 N NaOH until almost neutral, and it was then again heated almost to the boil and again titrated. Heating and titration were continued until 1-2 ml of alkali was required for neutralization. The solution was then boiled again for 30 minutes, cooled to room temperature, and titrated for the last time. At this point the hydrolysis of the BF_4^- ion would be practically complete [17]. The calculation of the lithium fluoborate concentration was carried out on the basis of the above equation.

Determination of unchanged lithium hydride in the solid was carried out after removal of lithium borohydride by ether extraction and removal of ether under vacuum. A sample weighing 0.02-0.03 g was decomposed with water, and the hydrogen evolved was collected in a gas buret. The volume was adjusted to normal conditions, and the LiH content of the solid was calculated.

Determination of boron was carried out on the solution after determining the BF_4^- ion and filtering off the precipitate of potassium fluoride. The solution was made up to 250 ml in a measuring flask. An aliquot of this was neutralized to methyl red, mannitol was added, and the solution was titrated to phenolphthalein with 0.1 N NaOH.

For the determination of total fluorine, the precipitate of CaF_2 remaining after the determination of fluorine bound in the form of $LiBF_4$ was filtered off, carefully washed with water, and placed together with the filter paper in a platinum crucible. After being dried and then ignited at 500-600°, the precipitate was weighed. A simple calculation gave the fluorine content.

Lithium was determined gravimetrically in the form of Li_2SO_4, boron being first removed in the form of trimethyl borate and fluorine by repeated evaporation to dryness with sulfuric acid and methanol, the latter being added periodically.

Experiments with Stoichiometric Proportions and with Excess of One or Other Reactant. In the first series of experiments on the preparation of diborane (Table 1), the reaction vessel was a three-necked flask fitted with mercury-sealed mechanical stirrer, dropping funnel, an arrangement for scattering the lithium hydride, and a very efficient reflux condenser, the free end of which was connected to traps cooled with solid carbon dioxide for trapping ether vapor. The yield of diborane in these experiments was determined by absorbing the gas evolved in 20-30% caustic potash solution, acidifying the solution, and determining the boric acid content [18,19], from which the yield of diborane was calculated. In the experiments in which diborane was actually isolated, for the complete removal of ether vapor it was first passed through traps containing concentrated sulfuric acid and then through traps cooled with a mixture of solid carbon dioxide and acetone; it was collected in receivers cooled with liquid nitrogen. In these experiments air was first displaced from the apparatus with dry hydrogen.

In some experiments lithium hydride powder was added to boron trifluoride etherate (Experiments 1 and 3). In most of the experiments, after displacement of air with dry hydrogen or nitrogen, the whole of the amount of finely ground lithium hydride required for the reaction was placed in the reactor and made into a suspension with the minimum amount of ether, and 25-30% of the amount of etherate necessary for reaction in accordance with Equation 1 was added rapidly. The temperature of the mixture then rose to 40°, the mixture boiled, and evolution of diborane set in immediately. The remainder of the etherate was then added gradually. The diborane formed was carried away by a current of dry hydrogen or nitrogen.

An examination of Table 1, which gives the conditions and results of experiments with stoichiometric proportions of reactants (Equation 1), with excess of lithium hydride, and with excess of boron trifluoride, reveals certain regularities. Considerable dilution of the boron trifluoride etherate with ether (Experiment 1) delays the start of the reaction, whereas the addition of small amounts of ether to the lithium hydride at the beginning and in the course of the reaction facilitates mixing and the evolution of diborane. The best yields of diborane with respect to boron are attained with an excess of lithium hydride of 25% and more. The use of a considerable excess of the etherate lowers the yield of diborane with respect to boron to 20% (Experiment 13); moreover, in spite of the excess of etherate, much of the lithium hydride (as much as 50% or higher) does not react. The probable cause of this is the envelopment of hydride particles by solid reaction products – first lithium fluoride, and then lithium fluoborate – which make the particles incapable of further reaction with

TABLE 1

Experiments on the Preparation of Diborane using Various Relative Amounts of $BF_3 \cdot (C_2H_5)_2O$ and LiH

Experiment No.	Amount taken (g) of		$\frac{BF_3}{LiH}$	Yield of B_2H_6 (%)		Yield of $LiBH_4$ (% on BF_3 taken)	Yield of $LiBF_4$ (% on BF_3 taken)	Procedure
	LiH	BF_3		Based on BF_3 (Equation 1)	Based on LiH			
1	4.2	21.8	1 : 3.5	49	43.5	Not determined	Not determined	Etherate highly diluted with ether. Long induction period. Hydride added to BF_3 etherate.
2	4.55	12.7	1 : 6.3	53	40	30.7	″	Etherate diluted with 25 ml of ether. All hydride added at once.
3	2.4	14.0	1 : 3	19.7	23.79	Nil	″	Hydride added to undiluted BF_3 etherate
4	5.1	28.36	1 : 3.2	25	22.6	3.83	″	Ditto
5	2.7	11.22	1 : 4.2	43.4	30.5	Nil	″	Gradual addition of hydride to etherate. Mixture stood 24 hours During reaction 20 ml of ether added.
6	3.2	18.7	1 : 3	28.9	27.7	″	″	Ditto
7	7.5	42.6	1 : 3.1	39.1	33	″	″	Hydride gradually sprinkled into etherate; mixture warmed periodically.
8	22	118	1 : 3.3	46.5	42.2	″	″	Etherate added in two portions; hydride added gradually.
9	13	71	1 : 3.2	44.4	41.1	″	40	Ditto
10	12	71	1 : 3	42.9	42.9	″	44.6	Alternating gradual additions of etherate and hydride.
11	10	42.6	1 : 4.1	58.72	42.30	Not determined	Not determined	Ditto
12	7.5	42.6	1 : 3	47.53	47.53	″	″	Etherate gradually added dropwise to suspension of LiH in 30 ml of ether.
13	2.7	28.24	1 : 1.7	22.46	30.5	Nil	61.24	Ditto
14	1.2	28.24	4 : 3	23.02	62.1	″	46.13	Ditto
15	5.0	14.12	1 : 6	Not determined		15.2	Not determined	Reaction at 0°; etherate gradually added to suspension of hydride in 10 ml of ether.
16	6.7	28.4	1 : 4.1	63	45.0	22.7	Traces	Etherate slowly added to suspension of hydride in 60 ml of ether at 15°

the etherate. For the best utilization of the boron, therefore, it is necessary to take excess of lithium hydride over the amount required according to Equation 1.

Experiments on the preparation of diborane from reaction mixtures containing small additions of lithium borohydride, lithium aluminum hydride, sodium hydride, or trimethyl borate showed that lithium borohydride and trimethyl borate are highly active, particularly the former. The addition of lithium borohydride, even in small amounts, causes the initiation of the reaction and practically eliminates the induction period.

The effect of temperature can be derived from comparisons between various experiments. For example, in 2 reaction was between 12.7 g (0.09 mole) of $BF_3 \cdot (C_2H_5)_2O$ and 4.55 g (0.57 mole) of LiH (BF_3 : LiH = 1 : 6) at 18°, and 2.6 g of lithium borohydride etherate was isolated. When reaction between the same amounts of reactants was carried out at the boiling point of ether, $LiBH_4$ was completely absent from the ether layer. At 0° (Exp. 15) formation of diborane was at a minimum and reaction proceeded preferentially in the direction of $LiBH_4$ formation.

Comparison between Experiments 4 and 5 shows the effect of the order of addition of reactants: alternation of the addition of etherate and hydride improves the yield of diborane, but gradual addition of etherate to the whole amount of the hydride as a suspension in ether (Experiment 16) gives the best yields of diborane.

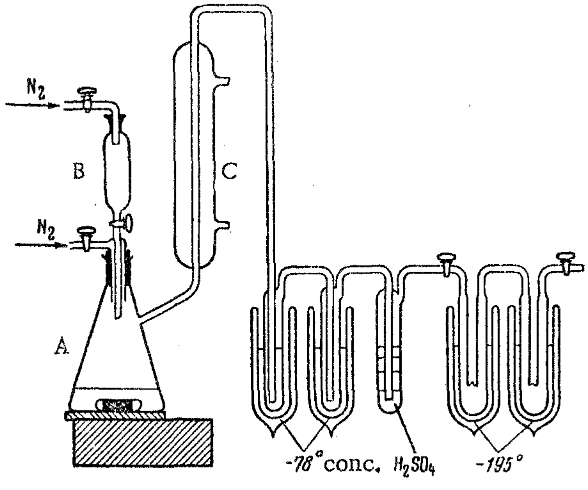

Fig. 1. Laboratory apparatus for the preparation of diborane.

Experiments with Excess of Boron Trifluoride Etherate.* The next series of experiments, for which reaction balance sheets were calculated, was based on an analysis of the results of the first series (Table 1) with the object of improving the yield of diborane, both with respect to boron and with respect to lithium hydride. The yield calculated on the amount of lithium hydride taken is very important, for excess of hydride in the solid reaction product is difficult to utilize or recover, whereas unchanged boron trifluoride can be recovered by distillation during the course of the calcination of the precipitate. In this series of experiments the apparatus used consisted of a reactor A containing a magnetic stirrer (Fig. 1) and fitted with a dropping funnel B, a tube with a tap for introduction of nitrogen, and a reflux condenser C attached to traps. A suspension of the whole of the lithium hydride in a little ether was prepared in the reactor, and 15-25% of the total amount of etherate was added rapidly. A uniform stream of liberated diborane was then maintained by the addition of fresh portions of etherate. In these experiments the diborane was absorbed in dry pyridine, with which it formed the complex $C_5H_5N \cdot BH_3$ [20]. The active hydrogen in the pyridine solution was subsequently determined.

Table 2 gives the amounts of the reactants and products for some experiments of this series. For Experiments 3 and 4 curves showing the time-dependence of the liberation of diborane are given (Fig. 2). In order to indicate the procedure, we describe one of these experiments below. In most of the experiments, not only the gaseous, but also the solid reaction products were investigated, so that the actual equation of the reaction could be given (last column of Table 2).

These equations were obtained by multiplying the numbers of moles of lithium hydride and boron trifluoride etherate brought into reaction by a factor that brings the number of moles of lithium hydride to six, so that a comparison can be made with Equation 1. As lithium borohydride was not found in any of the experiments and the lithium hydride was utilized almost quantitatively, we regarded the yield of diborane as almost quantitative. This is in satisfactory agreement with results on the determination of the yield of diborane when correction is made for unavoidable leakage; Experiment 1 is exceptional, since a considerable loss of the diborane occurred.

Description of Experiment 4 (Table 2). Boron trifluoride etherate (21.3 g) was added rapidly to an electromagnetically stirred suspension of 6.4 g (0.8 mole) of lithium hydride in 15 ml of absolute ether. The remainder of the etherate was added gradually in such a way that uniform liberation of diborane was maintained.

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* Excess of etherate is to be understood as referring to the stoichiometry of Equation 1.

In all, 42.3 g (0.30 mole) of etherate was added. Further addition of etherate did not result in liberation of more diborane. As necessary, more ether was added to the reaction mixture (three 15-ml portions). The diborane evolved was absorbed with dry pyridine. The pyridine traps were changed periodically so that the course of the liberation of diborane could be followed (Fig. 2). The yield of diborane with respect to boron trifluoride etherate (according to Equation 1) was 83.4%, and with respect to lithium hydride it was 94.6%. Other experiments of this series were carried out in a similar way. By this procedure, therefore, all the lithium hydride can be caused to react without an appreciable reduction in the yield of diborane calculated on a boron basis.

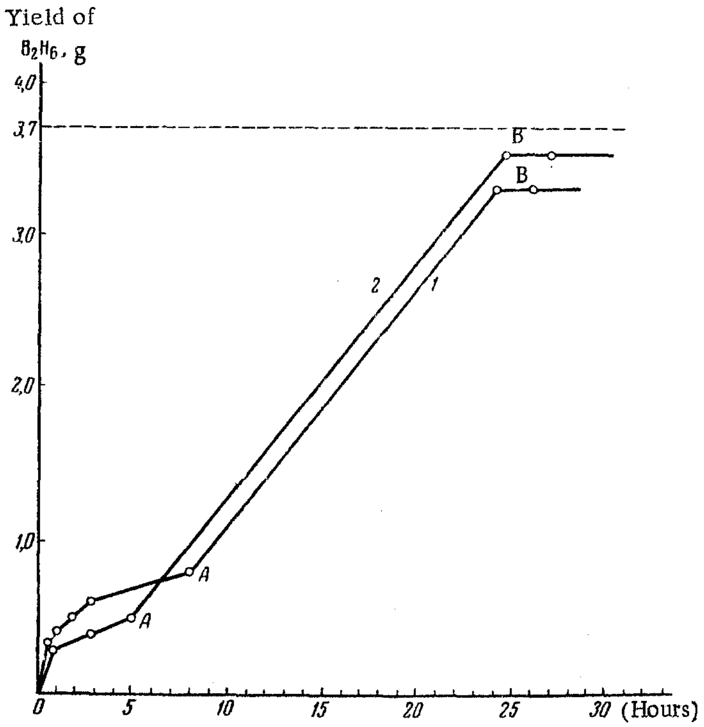

Fig. 2. Time-dependence of liberation of diborane: 1) Experiment 3; 2) Experiment 4.

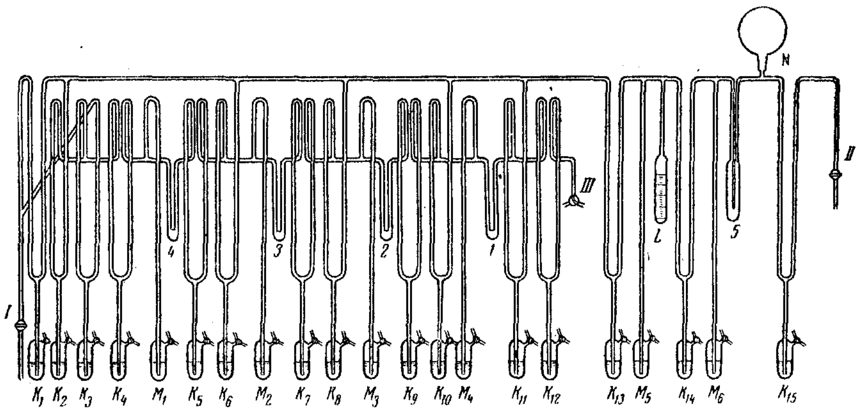

Fig. 3. Diagram of vacuum apparatus for the refining of diborane and the determination of its constants.

Determination of the Purity of the Diborane. The diborane obtained by the reaction investigated contains only ether vapor as impurity. The solutions obtained by absorption of the diborane in traps containing water gave no reaction for fluorine with saturated calcium chloride solution. Passage of the diborane through traps containing concentrated sulfuric acid and traps cooled with a mixture of solid carbon dioxide and acetone (-78°) freed it from ether vapor. In order to establish the purity of the diborane, it was fractionated by the fractional-condensation method and the physical constants of the fractions were determined, this being carried out in a special vacuum apparatus (Fig. 3) constructed in accordance with Stock's recommendations [4], in which the diborane came into contact only with glass and mercury. The fractionation showed that the gas consisted of one fraction only, this being collected at -170° in the form of a white crystalline mass.

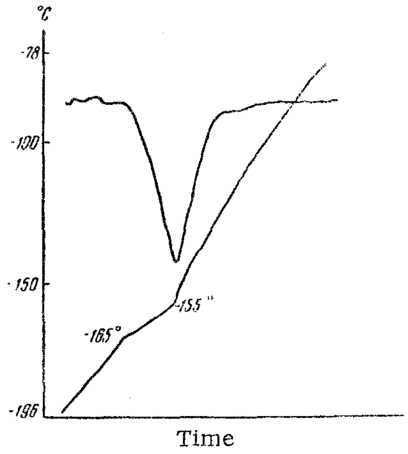

Fig. 4 Heating curve of diborane.

The substance was characterized by vapor-pressure and melting-point determinations. The vapor pressure, which was determined by Stock's method [4] using a gas thermometer (filled with ethylene), was found to be 166.5 mm at -119° (m.p. of diethyl ether), whereas Stock obtained a value of 167.5-168 mm for the same temperature. Heating curves for samples of diborane in the range from -195° to -100° (Fig. 4) have only one halt, corresponding to the endothermic process of fusion; the start of this was at -165°, both for "crude", and also for carefully fractionated diborane (Stock obtained -165.5°). The diborane obtained by the method described was therefore almost completely pure.

DISCUSSION OF RESULTS

An unsatisfactory feature of the preparation of diborane by reaction between boron trifluoride etherate and lithium hydride is the great variation in yield, which varies from 20% to 90% with respect to boron under what appear to be extremely similar conditions. Sometimes the reaction has a long period of induction and then proceeds at an uncontrollable rate. Among the causes of this great variation in yield there is, in the first place, the effect of the presence of moisture in the ether, which results in the formation of films of oxide on the lithium hydride particles. Hence, the quality of the ether and lithium hydride is subject to very exacting requirements. After carrying out several series of experiments with complete analysis of the gaseous, liquid, and solid phases, we were able to discover also other factors that affect the yield of diborane. Our investigation showed that the reaction of lithium hydride with boron trifluoride etherate cannot be described by any one equation, but consists in a series of parallel reactions having successive stages.

Apart from the reactions described by Equations 1 and 2, if the intermediate stages are not counted, the following reactions are also possible:

$$4\,\mathrm{LiH} + \mathrm{BF_3}\cdot(\mathrm{C_2H_5})_2\mathrm{O} \rightarrow \mathrm{LiBH_4} + 3\,\mathrm{LiF}. \qquad (3)$$

$$\mathrm{BF_3} + \mathrm{LiF} = \mathrm{LiBF_4}. \qquad (4)$$

$$\mathrm{BF_3} + 3\,\mathrm{LiBH_4} = \mathrm{B_2H_6} + 3\,\mathrm{LiF}. \qquad (5)$$

The transformation of boron trifluoride goes in three directions: formation of diborane, of lithium borohydride, and of lithium fluoborate. Taking into account the solubilities of the compounds obtained in ether [12] (B_2H_6 - 1.1 g/100 g; $LiBF_4$ - 1.9 g/100 g; $LiBH_4$ - 3.0 g/100 g; LiF - 0.05 g/100 g) and our experiments showing that only diborane is present in the gas phase, we may suppose that the solid phase remaining after distillation of ether may contain, apart from unchanged lithium hydride, lithium fluoride and the boron-containing compounds lithium fluoborate and lithium borohydride. Depending on temperature, dilution with ether, proportions of reactants, and the order of their addition, the reaction may proceed in the direction of a higher or lower relative yield of diborane.

When reaction is brought about at room temperature with an excess of lithium hydride, the temperature of

TABLE 2

Experiments with Excess of Boron Trifluoride Etherate

Experiment No.	Amount taken (g) of		BF_3/LiH	Yield of diborane (%)		Yield (% on BF_3)		Equation of reaction
	$BF_3 (C_2H_5)_2O$	LiH		with respect to boron	with respect to hydride	of $LiBH_4$	of $LiBF_4$	
1	46.15 (0.325)	6.4 (0.8)	1 : 2.45	53.1	65.3	Nil	18.0	$6LiH + 2.44BF_3 \cdot (C_2H_5)_2O \rightarrow B_2H_6 + 0.44LiBF_4 + 5.56LiF + 2.44(C_2H_5)_2O$
2	49.7 (0.35)	5.4 (0.675)	1 : 2	60.82	96.34	Nil	37.5	$6LiH + 3.2BF_3 (C_2H_5)_2O \rightarrow B_2H_6 + 4.8LiF + 1.2LiBF_4 + 3.2(C_2H_5)_2O$
3	60.3 (0.425)	6.4 (0.8)	1 : 2	57.0	88.1	Nil	37.5	Ditto
4	42.3 (0.30)	6.4 (0.8)	1 : 2.7	83.45	94.6	Nil	11.1	$6LiH + 2.25BF_3 (C_2H_5)_2O \rightarrow B_2H_6 + 5.75LiF + 0.25LiBF_4 + 2.25 \cdot (C_2H_5)_2O$

of the mixture rises to 25-35° and there is preferential formation of diborane; under these conditions lithium borohydride does not accumulate in the ether solution. However, much of the boron remains in the precipitate in the form of $LiBF_4$ and the lithium hydride is not utilized fully. When there is a considerable excess of lithium trifluoride, not only is the yield with respect to boron lowered, but the yield with respect to lithium hydride is lowered also. An incomparably better procedure is that carried out in the second series of experiments (Table 2) with a ratio of boron trifluoride to lithium hydride greater than that corresponding to Equation 1 and with gradual addition of the boron trifluoride etherate to the whole of the lithium hydride under vigorous stirring. No lithium borohydride is then formed in the overall reaction, and the yield of diborane is raised both with respect to the utilization of boron, and also with respect to lithium hydride. Under these conditions, the reaction proceeds neither by Equation 1 nor by Equation 2, but by an equation in which the number of moles of boron trifluoride etherate varies over the range 2.25-2.8.

The curve for the time-dependence of the liberation of diborane has a well defined point of inflection A (Fig. 2). This shows that, with gradual addition of etherate, the reaction proceeds in two stages. In the first stage, in which there is a large excess of lithium hydride, the comparatively slow liberation of diborane is associated with the accumulation of active intermediate reaction products – possibly also lithium borohydride – without appreciable formation of lithium fluoborate. The second stage consists in the reaction of fresh portions of etherate with the remaining lithium hydride and with the accumulated active intermediaries, including lithium borohydride. Most of the diborane is obtained at this stage, and there is a corresponding sharp rise in the curve for the liberation of diborane (Fig. 2).

At both stages the reaction probably has a multistage mechanism with formation of the intermediaries $LiHBF_3$, $LiBH_2F_2$, and $LiBH_3F$. The last two compounds may give diborane, since their molecules contain a "ready-made" borine group BH_3:

$$2\ LiBH_3F \rightarrow B_2H_6 + 2\ LiF$$

or

$$2LiBH_3F + 2BF_3 \cdot (C_2H_5)_2O \rightarrow B_2H_6 + 2LiBF_4,$$

$$3\ LiBH_4 + BF_3 \cdot (C_2H_5)_2O \rightarrow 2\ B_2H_6 + 3\ LiF.$$

Simultaneously, particularly in the first stage, a reaction occurs between diborane and excess of lithium hydride:

$$2\ LiH + B_2H_6 \rightarrow 2\ LiBH_4$$

and there is also the reaction (4) in the case of excess of boron trifluoride. Moreoever, in the initial stage of the reaction, while the temperature of the reaction mixture is rising to 40°, disproportionation reactions are possible for the intermediate reduction products:

$$2\ LiHBF_3 \rightarrow LiBH_2F_2 + LiBF_4;$$

$$3\ LiBH_2F_2 \rightarrow B_2H_6 + LiBF_4 + 2\ LiF;$$

$$4\ LiBHF_3 \rightarrow LiBH_4 + 3\ LiBF_4 \text{ etc.}$$

The reactions that we have cited here give some idea of the complexity of the process studied.

From these considerations we may conclude that, for maximum yields of diborane, the initial stage of the reaction must be carried out in presence of excess of lithium hydride, and that, for the best utilization of the hydride, the amount of boron trifluoride etherate taken must be greater than that corresponding to the stoichiometry of Equation 1. These conditions are attained by the procedure used in Experiment 4 (Table 2). Carrying out the reaction in accordance with our description of this experiment ensures the preparation of highly pure diborane in consistent and almost quantitative yield with respect to lithium hydride and to the boron trifluoride etherate that reacts.

SUMMARY

1. The reaction of lithium hydride with boron trifluoride etherate has a complex mechanism, which probably includes various parallel and successive reactions leading to the formation, as the ultimate boron-containing products, of diborane, lithium borohydride, and lithium fluoborate. The yield of diborane is dependent on reaction temperature, relative amounts of reactants, degree of agitation of the reaction mixture, and order of addition of reactants.

2. An almost quantitative yield with respect to both reactants is attained by carrying out the reaction at somewhat raised temperature (25-30°) in the initial stage, at a $BF_3 : LiH$ ratio of 1 : 2.4-2.8, and with gradual addition under constant stirring of lithium trifluoride etherate to lithium hydride.

3. The reaction studied is the simplest and most economical method for the preparation of highly pure diborane under laboratory conditions, and it opens up wide possibilities for the further study of the chemistry of boron hydrides and their derivatives.

LITERATURE CITED

[1] A. Stock and K. Freiderici, Ber. 46, 1959 (1913).

[2] A. Stock and K. Friederici and O. Preiss, Ber. 46, 3353 (1913).

[3] A. Stock and E. Kuss, Ber. 56, 789 (1923).

[4] A. Stock, Hydrides of Boron and Silicon (N. Y., 1933).

[5] W. J. Schlesinger and A. Burg, J. Am. Chem. Soc. 53, 4321 (1931).

[6] A. Stock and W. Sutterlin, Ber. 67, , 407 (1934).

[7] D. Hurd, J. Am. Chem. Soc. 71, 20 (1949).

[8] A. F. Finholt, A. C. Burg,and H. J. Schlesinger, J. Am. Chem. Soc. 69, 1199 (1947).

[9] U. S. Patent 2644472, Offic. Gaz. U. S. Pat. Office 6/III, 644, No. 1, 259, (1951); C. A. 4511 (1951).

[10] U. S. Patent 2543511, Offic. Gaz. U. S. Pat. Office 27/IV, 643, No. 4, 1272 (1951); C. A. 4510 (1951).

[11] J. Schapiro, H J. Weiss and M. Schmith, J. Am. Chem. Soc. 74, 901 (1952).

[12] J. R. Elliott, E. M. Boldebuck and G. F. Roedel, J. Am. Chem. Soc. 74, 5047 (1952).

[13] J. R. Elliott, J. Am. Chem. Soc. 74, 5211 (1952).

[14] H. J. Schlesinger, H. C. Brown, J. R. Gilbreath and J. J. Katz, J. Am. Chem. Soc. 75, 195 (1953).

[15] Inorganic Syntheses 1, 21 (1939).

[16] V. I. Mikheeva and E. M. Fedneva, Proc. Acad. Sci. USSR 101, 99 (1955).

[17] I. G. Ryss, J. Gen. Chem. 16, 531 (1946).

[18] A. Stock and E. Kuss, Ber. 47, 810 (1914).

[19] V. I. Mikheeva and V. Yu. Surs, Proc. Acad. Sci. USSR 93, 67 (1953).

[20] H. C. Brown, H. J. Schlesinger and S. Z. Cardon, J. Am. Chem. Soc. 64, 325 (1942).

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