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NAVAL RESEARCH LABORATORY
REPORT

July 1946

BORON HYDRIDES
Final Report on Contract 173s-10421
from
University of Chicago
by
Professor H. I. Schlesinger

Report P-2964

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CHEMISTRY DIVISION

July 1946

BORON HYDRIDES

Final Report on Contract 173s-10421
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CONFIDENTIAL

* * *

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Numbered Pages.......9
Appendices P.R. #'s 12-
23 inclusive.......70

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--A--

FINAL REPORT ON CONTRACT NO. N173s-10421[1]

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[1] This contract is an extension of Contracts N173s-9058 and s-9820

H. I. Schlesinger in Collaboration with
B. Abraham, A. C. Bond, Jr., C. Dillard, J. Farr,
A. Finholt, M. Gerstein, R. A. Lad and K. Wilzbach

Introduction

Because of the detailed nature of the monthly progress reports on this investigation, and in accordance with the procedure approved by representatives of the Naval Research Laboratory on contracts of which the present one is a continuation, this final report is essentially a guide to the contents of the monthly reports, copies of which are incorporated herein. The subject matter is arranged in accordance with the compounds studied.

A few abbreviations are occasionally used: sodide, lithide and alide for the borohydrides of sodium, lithium and aluminum respectively. P. R. refers to progress reports; the Roman numerals following these letters refer to the number of the monthly report and the Arabic numerals to the page of the monthly report. In a number of instances the most important of several P. R. references are underlined. (Note: Monthly Reports I to XI are parts of Contracts No. N173s-9058 and s-9820; Monthly Reports XII to XXIII deal with the work of the present contract).

Some phases of the investigation are still incomplete and are being continued under an O.R.I. contract.

Report:

A. ALUMINUM BOROHYDRIDE

I. Preparation: P. R. XII, 2; XIII, 1; XX, 1-4; XXI, 1-2.

Renewed interest in this compound made desirable a further study of preparative methods to ascertain whether new methods free from the complications which might attend quantity production by the procedures previously described could be developed (See P. R. XXI, 1). Through the use of the newly discovered lithium aluminum hydride, $LiAlH_4$ (Section D of this report), two new procedures are made available.

(a) The reaction:

$$LiAlH_4 + 2B_2H_6 \rightarrow Al(BH_4)_3 + LiBH_4$$

This reaction (discussed in P. R. XII, 2; XIII, 1; XX, 1-4; and XXI, 1 is superior to the older methods in that it avoids the hazard of mixing alkali metal borohydrides with aluminum chloride (a procedure which must be carried out in the absence of air), as well as the inconvenience caused by sublimation of aluminum chloride, and in that it leaves a residue easily and safely handled. The by-product ($LiBH_4$) may be reused in the preparation of diborane.

The reaction is not as rapid as desirable; furthermore it would be advantageous to avoid the use of diborane. For this reason reaction (b) is under investigation.

(b) The reaction:

$$3LiAlH_4 + 3BCl_3 \xrightarrow{ether} Al(BH_4)_3 + 3LiCl + 2AlCl_3$$

The intermediate steps which are probably involved in this reaction are discussed in P. R. XXI, 1-2, in which the use of excess aluminum chloride for removing aluminum borohydride from its etherate is also described. The yields by this reaction have, however, not as yet been satisfactory. The difficulty seems to be in the fact that the presence of lithium chloride interferes with the removal of ether from aluminum borohydride as well as with the attaining of satisfactory yields, probably because of the reversibility of the intermediate step: $3LiBH_4 + AlCl_3 \xrightarrow{ether} 3LiCl + Al(BH_4)_3$.

For this reason we are investigating a modification of this reaction which consists of the use of an ether solution of aluminum hydride instead of lithium aluminum hydride. The aluminum hydride may be prepared from lithium aluminum hydride (P. R. XIII, 2) or directly from lithium hydride (P. R. XXII, 2). Indications are that good yields, e.g., 70%, may be expected from the reaction:

$$4AlH_3 + 3BCl_3 \xrightarrow{ether} Al(BH_4)_3 + 3AlCl_3 \text{ (P. R. XXII, 2)}$$

and that the borohydride may be successfully removed from the ether by an excess of aluminum chloride. One difficulty still remains to be overcome--from the ether solution of aluminum hydride the latter gradually precipitates as an etherate.

Attempts to replace ether by other solvents have been unsuccessful (P. R. XXII, 2). (Note: Aluminum hydride is probably polymeric; preliminary measurements of the ether tension of its ether solutions indicate a possible formula Al_2H_6 in this solvent).

Whether the method employing lithium aluminum hydride and diborane, or that employing aluminum hydride and boron chloride, are to be preferred to the older method involving alkali metal borohydrides and aluminum chloride must await further study of the aluminum hydride procedure, and an engineering survey of the various processes.

II. Stabilization of Aluminum Borohydride

Although this compound decomposes very slowly at room temperature and not very rapidly at temperatures up to 60°C, the amount of hydrogen produced by even slight decomposition is so great that the problem of storage of the material is a serious one. Venting of the hydrogen to avoid hazardous pressures does not seem feasible because of the spontaneous inflammability of the borohydride.

To make possible safe shipment of the borohydride in glass vessels to the various laboratories desiring to test the compound, means of stabilizing the samples were sought. The most successful procedure discovered, was the preheating of samples for several days at about 40°C, followed by subsequent removal of the accumulated hydrogen and the resealing of the container. Although this procedure greatly decreases the rate of decomposition of aluminum borohydride in glass vessels at room temperatures (25°C and possibly as high as 35°C), it is not effective at 60°C. (P. R. XV, 1; XVII, 2.) The effect of the preheating seems to be due to the formation of a decomposition product which acts as an inhibitor. P. R. XII, 5-9; XIV, 1; XX, 4. A summary of most of the work is found in P. R. XVII, 2-11.

Various aspects of the work on stabilization are found in the following monthly reports:

a. Gradual decrease in the rate of decomposition of untreated samples, P. R. XII, 6; XVII, 4.

    1. Accumulation of hydrogen probably not the stabilizing factor, P. R. XII, 6; XVII, 4.

    2. Effect of glass on stability. Powdered glass does not greatly increase rate of decomposition, P. R. XIII, 3; XVII, 3.

    3. Nature of non-volatile product of spontaneous decomposition, P. R. XVII, 2.

    4. Difference between nature of decomposition process at 25°C and at 60°C, P. R. XVII, 2,3.

    5. Effect of metals on rate of decomposition, P. R. XVII, 2,3.

b. Attempts to stabilize by coating the containing vessel. P. R. XIII, 3; XVII, 3.

c. Stabilization by preheating.

    1. Effect of preheating not due to coatings formed on container, P. R. XIV, 1; XX, 4.

    2. Effect of preheating due to formation of a non-volatile inhibitor, P. R. XVII, 5; XX, 4.

    3. Preheating is effective even if metals are present, P. R. XVII, 5.

    4. Attempts to find other inhibitors, P. R. XVII, 5.

    5. Experimental methods in investigating rates of decomposition, P. R. XVII, 6.

d. Summary of work on Stability and Stabilization, P. R. XVII, 2-11.

III. Reaction of Aluminum Borohydride with Silicon Compounds, P. R. XIX, 3.

IV. Alkyl Derivatives of $Al(BH_4)_3$, P. R. XXI, 3.

B. ALUMINUM HYDRIDE

I. Preparation, P. R. XIII, 2; XV, 2-3, XXII, 2.

II. For its use in preparing aluminum borohydride, see section A, I, (b).

III. Alkyl derivatives of aluminum hydride, P. R. XII, 3.

C. B_5H_9

I. Preparation:

(A survey of most of our work on this problem is found in P. R. XVIII, 4-7.

The only method for preparing B_5H_9 that has thus far proved successful is the thermal decomposition of diborane in a circulating system, as has already been described by Stock and Mathing, and by Burg and Schlesing Various catalysts have been tested; although some of them lower the temperature at which conversion of diborane to mixtures of B_5H_9 and B_5H_{11} occurs none has proved very efficient. It appears that, in general, those conditions which favor conversion of diborane to higher hydrides also favor the decomposition of B_5H_9, with the result that the quantity of B_5 boranes (i.e., B_5H_9 and B_5H_{11}) remains fairly constant for any single treatment. It is for this reason that a circulatory system is effective, since by its use the B_5 boranes may be removed from the diborane to be resubjected to the higher temperature. These facts also indicate that a high rate of flow through the circulating system should improve the process, and that the optimum temperature will depend on the flow-rate. In our experiments approximately 120°C proved to give the best yields of material rich in B_5H_9; higher temperatures might well be advantageous with higher circulation speeds.

The most important observations on catalysts are that hydrogenation catalysts (such as nickel on a porous support) increase the percentage of B_5H_{11} in the B_5 fraction, and that dehydrogenation catalysts, such as aged chromic oxide (30% on aluminum oxide), increase the percentage of B_5H_9.

A few experiments carried out at diborane pressures of approximately 750 lbs. have given unfavorable results. At room temperature decompositi of diborane is very slow, and the major decomposition product is B_4H_{10}. Experiments at higher temperatures and with the use of catalysts have been started.

It appears from the foregoing that manufacture of B_5H_9 by thermal decomposition of diborane in a circulatory system is a feasible, though not yet an efficient process. It is our understanding that the General Electric Company is carrying out an extensive study of this process with equipment permitting the use of larger quantities per run than we can handle. In view of this situation, it seems most efficient for us to concentrate our efforts on an attempt to learn as much as possible about the course of the reaction. We have already ascertained that, whereas pure B_5H_9 is inappreciably decomposed in 24 hours at 100°C, very noticeable decomposition occurs if diborane is present (P. R. XXII, 3-4; XXIII, 1-2). The fact that diborane is simultaneously used up, makes likely the conclusion that B_2H_6 and B_5H_9 react with each other, but this conclusion cannot be considered established until studies on the effect of B_4H_{10} and of other hydrides have been completed. The value of these studies toward achieving an understanding and a possible improvement of the process is obvious.

Details of the work just summarized are found in the following reports:

a. Preliminary runs and description of procedure in the circulatory system, P. R. XII, 3-5; XVIII, 6.

b. Effect of Catlaysts, P. R. XIII, 1-2; XIV, 1-2; XVI, 2; XVII, 1; XVIII, 4; XIX, 4.

c. Influence of various factors on yield, P. R. XVIII, 4-5.

d. Experimental details of single pass, circulating and static systems, P. R. XVIII, 5-7.

e. Summary (including tables of data), P. R. XVIII, 4-5 and 8-12.

f. Effect of B_2H_6 on decomposition of B_5H_9, P. R. XXII, 2-5; XXIII, 1-2.

g. Pressure experiments, P. R. XXI, 2; XXIII, 1.

h. Attempt to prepare B_5H_9 from $LiBH_4$, P. R. XVIII, 7.

II. Properties of B_5H_9, P. R. XIV, 3-5; XV, 2; XVI, 1-2.

The properties investigated were:

a. Stability, P. R. XIV, 3; XXII, 2-5, XXIII, 1-2.

b. Slow rate of hydrolysis confirmed, P. R. XIV, 3.

c. Solubility in a few organic solvents, P. R. XIV, 3; XV, 2.

d. Reaction with isopropyl amine, P. R. XIV, 3.

e. Reaction with lithium hydride, P. R. XIV, 5.

f. Spontaneous inflammability. Although we have frequently exposed B_5H_9 to air without noting any vigorous reaction (P. R. XIV, 3) it may inflame spontaneously, and even detonate under certain conditions (P. R. XIV, 4; XV, 2; XVI, 1-2). The tendency toward spontaneous inflammation may be completely inhibited by the addition of very small amounts of iron carbonyl (tetraethyl lead is less effective). P. R. XV, 2; XVI, 2.

D. LITHIUM ALUMINUM HYDRIDE, $LiAlH_4$

One of the most valuable results of this investigation has been the discovery of this new compound. In connection with the specific objectives of this project, it has been useful in the development of new procedures for preparing aluminum hydride and borohydride (Section A, I, (b) of this report) as well as of diborane, and hydrides of gallium, germanium, silicon, tin, zinc, and several of the hydrides of elements of Group [illegible] A of the periodic system. In general the use of the compound for these purposes leads to very simple preparative methods, in contrast to the older methods which were very cumbersome, gave poor yields of impure products, or were entirely unsuccessful. It is likewise possible, by the use of lithium aluminum hydride, to prepare alkyl derivatives of many of the hydrides just mentioned, thus widening greatly the field for the present investigation. It should be noted that in some cases lithium hydride may be used in place of lithium aluminum hydride, but in almost all cases the latter reacts more rapidly and usually gives better yields. Finally, at our suggestion, others in this laboratory have investigated the reaction of the compound toward organic substances, and have found it to be a unique, extremely useful reagent.

The compound is readily prepared by the action of an ether suspension of lithium hydride on aluminum chloride (in ether solution). Lithium chloride is precipitated, while the new compound remains dissolved in the ether, which can, however, be readily removed by evaporation in vacuo. The material thus obtained is a white solid, which may be handled with safety in ordinary air. Although lithium aluminum hydride reacts very rapidly and vigorously with water, exposure of the solid to moist air does not cause very rapid deterioration, probably because the solid soon becomes coated and protected by aluminum hydroxide. The compound is perfectly stable at room temperatures; at approximately 100° C it loses hydrogen slowly and turns from pure white to gray.

Efforts to prepare sodium aluminum hydride by analogous methods, from the lithium compound by metathesis, or by the action of sodium hydride and aluminum alkoxides, have thus far been unsuccessful (P. R. XIV, 5; XXIII, 2).

Details concerning lithium aluminum hydride are found in the following monthly reports:

I. Preparation: P. R. XI, 1; XII, 1; XVIII, 1.

II. Physical Properties, Composition, Stability: P. R. XII, 1-2.

III. Solubility: P. R. XII, 1.

IV. Reactions with: amines, P. R. XXI, 2; ammonia, P. R. XXI, 2; boron chloride, P. R. XIII, 2 (but see also Section A, I, (b) of this report); boron fluoride, P. R. XII, 2; diborane (see section A, I, (b) of this report); water, P. R. XI, 1; XII, 2. (See also: Section D-V below)

V. Use in the preparation of: $Al(BH_4)_3$ (See section A, I, (b) of this report); AlH_3, P. R. XII, 2; XIV, 5; XV, 2-3; $AlH(CH_3)_2$, P. R. XII, 3; AsH_3, P. R. XVIII, 3; B_2H_6, P. R. XII, 2; XIII, 2; BeH_2, P. R. XIX, 1; GeH_4, P. R. XV, 4; Hydrides of silicon and of tin and their alkyl derivatives, P. R. XII, 1-2; XV, 4; XVI, 3-5; XVIII, 3-4; XIX, 3; SbH_3, P. R. XVIII, 3; ZnH_2, P. R. XIX, 2.

E. USE OF LITHIUM HYDRIDE IN PREPARING HYDRIDES OF OTHER ELEMENTS, P. R. XVI, 3; XXII, 2.

F. PHYSICAL PROPERTIES OF SOME ALKYL SILICON AND ALKYL TIN HYDRIDES, P. R. XVI, 5.

G. LIST OF COMPOUNDS PREPARED OR STUDIED:

(Note: Most of the compounds listed in this section have already been referred to in other sections of this report. Those to which this statement does not apply or for which additional references are included, are indicated by an asterisk*).

$Al(BH_4)_3$ (See Section A of this report)
$Al(BH_4)_2(CH_3)$: P. R. XXI, 3.
$Al(BH_4)(CH_3)_2$: P. R. XXI, 3.
$Al(BF_4)_3$*: P. R. XII, 2; XIII, 3.
AlH_3: P. R. XII, 3; XIII, 2; XV, 2-3, XIX, 3.
$AlH(CH_3)_2$*: P. R. XII, 3.
AsH_3: P. R. XVIII, 3.
BeH_2: P. R. XIX, 1
$Be(AlH_4)_2$*: P. R. XII, 3.
B_2H_6: P. R. XII, 2; XIII, 2 (See B_5H_9)
B_5H_9: (See section C of this report)
Ga_2H_6:* P. R. XV, 4.
GeH_4: P. R. XV, 2.
$LiAlH_4$: (See section D of this report)
$LiAlH_3(CH_3)$*: P. R. XII, 3.
$LiAl(NH_2)_4$*: P. R. XXI, 2.
LiAl(N[illegible])$_4$* : P. R. XXI, 2.
$LiGaH_4$:* P. R. XV, 3.
$NaAlH_4$: P. R. XIV, 5; XXIII, 2.
PbH_4*: P. R. XX, 6.

SbH_3: P. R. XVIII, 3.
SiH_4: P. R. XII, 2; XV, 3.
SiH_4, alkyl derivs.: P. R. XVI, 1, 3-5; XVIII, 3; XIX, 3; XX, 5.
SnH_4: P. R. XV, 4.
SnH_4, alkyl derivs.: P. R. XVI, 1, 3-5; XVIII, 3; XIX, 3.
TiH_4: P. R. XV, 4.
ZnH_2: P. R. XIX, 2
$Zn(BH_4)_2$: P. R. XIX, 2.

PROGRESS REPORT NO. XII
For the period June [illegible] - July 23, 1946

CONTRACT NO. N173 s-10421 [1]
Bu Aero TED NRL No. 3401

[1] This contract is [illegible] of Contract
Nos. [illegible]

H. I. S[illegible] in collaboration with
A. C. [illegible] A. Finholt,
I. Gorenstein and R. A. Lad

Summary

During the period covered by this report the following work has been undertaken: (1) Preparation of lithium aluminum hydride and a study of its properties and [illegible] to prepare beryllium hydrogen compounds such as [illegible] the preparation of [illegible]. (4) Further stability studies [illegible] hydride.

(1) Lithium [illegible] Hydride

Lithium hydride and aluminum chloride react in the presence of anhydrous ethyl ether according to the equation:

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$$

The preparation of this compound in small quantities using vacuum line methods has been described in Progress Report No, XI, p. 1. Larger quantities have been prepared (25 to 30 grams) in ordinary laboratory equipment, working in a nitrogen atmosphere with the usual precautions for excluding moisture and air.

When the product of the reaction was first described in Report No. XI, it was not determined whether the compound was aluminum hydride or the lithium aluminum hydride. The product of the reaction has now been definitely identified as $LiAlH_4$. Analysis of the compound gave the following ratio: $Li_{1.00}$, $Al_{1.00}$, $H_{3.96}$ and the purity was between 98 and 99%.

$LiAlH_4$ is a white solid with interesting physical and chemical properties. It is soluble in diethyl ether (29 g./100 g. ether) and in isopropylamine and insoluble in benzene and chloroform. The solubility of the compound in ether offers evidence that it is not a mixture of LiH and AlH_3 since the former is insoluble in ether. Removal of ether from $LiAlH_4$ at 65° in vacuo does not effect any change in properties since it redissolves completely in ether after such treatment. It has been noted in this connection that the solid compound redissolves completely only if extreme precautions are taken to exclude moisture. If this is not done, there is always an ether insoluble residue, presumably aluminum hydroxide.

It was found that an ether solution of $LiAlH_4$ may be mixed in all proportions with anhydrous benzene to form a stable solution. If the solution is exposed to air of the usual humidity, there is a gradual reaction with moisture to give off hydrogen and precipitate aluminum hydroxide.

The reaction of $LiAlH_4$ with water has been described in a previous report. It is vigorous and complete, without the addition of accelerating agents or acids, provided the mixture is not allowed to overheat. If the reaction is not controlled, black decomposition products are obtained.

The thermal decomposition of $LiAlH_4$ proceeds according to the equation:

$$2LiAlH_4 \rightarrow 3H_2 + 2LiH + 2Al$$

At 150°C hydrogen is evolved at a moderate rate. At 175°C the rate of evolution is rapid. By heating at 220°C for four hours, hydrogen was obtained quantitatively according to the above equation.

A number of reactions of $LiAlH_4$ indicate that it is a valuable reagent in the preparation of other metal hydrogen compounds. For example, it affords a convenient method for the preparation of silane:

$$LiAlH_4 + SiCl_4 \rightarrow LiAlCl_4 + SiH_4$$

This reaction is rapid and probably quantitative but proceeds satisfactorily only in the presence of ether. The reaction as carried out was so vigorous that some decomposition of the reagents occurred; nevertheless, the yield was 86% of the theoretical. With more careful addition of reagents and control of temperature, it seems likely that the yield would have been even higher. The reaction just described was carried out as a preliminary to further studies on the preparation of hydrogen compounds which might be of particular interest to the present project.

One of our first efforts in this direction has been to ascertain whether the new compound might afford a new approach to the preparation of aluminum borohydride since, as previously reported, the present methods have certain disadvantages. The new compound may actually be transformed to the borohydride by the reaction:

$$LiAlH_4 + 3/2\ B_2H_6 \rightarrow Al(BH_4)_3 + LiH$$

Constant removal of aluminum borohydride from the reaction zone seems to be necessary in order to drive the reaction to completion. Plans have been made to circulate diborane over $LiAlH_4$ at 60 to 100°C, constantly removing aluminum borohydride and condensing the latter selectively from the diborane with a -80°C trap. It may be possible to get a quantitative reaction in this way.

Other examples of the reactions of the new compound are the following:

(a) It reacts with boron fluoride etherate according to the equation:

$$3LiAlH_4 + 16BF_3 \xrightarrow{ether} 3LiBF_4 + 3Al(BF_4)_3 + 2B_2H_6$$

The reaction is far more rapid than any of the hitherto known methods for the preparation of diborane and its use would be advantageous on this account. One disadvantage of this reaction, as compared with interaction of lithium hydride with boron fluoride etherate is that the lithium appears in the reaction product as lithium borofluoride instead of lithium fluoride. To overcome this loss of boron, the reaction of $LiAlH_4$ with other boron halides is to be studied.

(b) It reacts with aluminum methyl according to the equation:

$$LiAlH_4 + Al(CH_3)_3 \rightarrow LiAlH_3(CH_3) + AlH(CH_3)_2$$

No attempt was made to follow the exact course of this reaction but a large excess of $LiAlH_4$ was used to convert all of the aluminum methyl into whatever compounds might form. In two experiments $AlH(CH_3)_2$ appeared to be the only volatile product. The reagents were heated together at 70°C for one hour in a sealed tube. The volatile product was then removed and analyzed. The combination of methane and hydrogen obtained by hydrolysis was 1130 cc./g. (theoretical is 1160 cc./g.) and the aluminum found was 45.4% (theoretical 46.5%). The material was a syrupy liquid at room temperature with a vapor pressure of a few millimeters at 25-30°C. This checks the characteristics found by the DuPont group for these compounds. No further study of the properties of the material has been made. Further experiments to determine whether the compound AlH_2CH_3 can be prepared in this way and whether it is possibly present in the non-volatile portion of the crude reaction product are contemplated.

(c) In a preliminary observation, it has been noticed that the addition of an ether solution of aluminum chloride or beryllium chloride to an ether solution of $LiAlH_4$ produces a white flocculent precipitate. We shall attempt to ascertain whether this observation is due to the reactions:

$$3LiAlH_4 + AlCl_3 \rightarrow 3LiCl + 4AlH_3$$

$$2LiAlH_4 + BeCl_2 \rightarrow 2LiCl + Be(AlH_4)_2$$

(2) Preparation of beryllium hydrogen compounds

The preparation of either BeH_2 or $LiBeH_3$ has not yet been achieved. The successful preparation of $LiAlH_4$ suggested the possibility of producing a similar beryllium compound by the reaction of lithium hydride with a beryllium halide. This reaction has been tried using both beryllium chloride and beryllium bromide in several solvents, ether, dioxane, and isopropylamine. Temperature conditions were varied, from the boiling point of the solvent to temperatures as high as 170°C. While a slight amount of ether soluble material containing hydrogen seemed to be formed, in no case was there good evidence of the formation of the desired compounds. The investigation is being continued.

(3) Preparation of B_5H_9

A circulating pump apparatus of the type described by Stock (Stock and Mathing, Ber. 69B, 1456 (1936)) was built for the preparation of the pentaborane. The flow process as described by Stock was followed in the preliminary experiments (Runs 1 to 3 in Table I) and in the later experiments the procedure was only modified slightly. In this process diborane is circulated through a heating zone which is kept at 250 to 300°C. B_5H_9, B_5H_{11} and $B_{10}H_{14}$ are the principal volatile products obtained, and these boron hydrides are continually removed from the gas stream by use of cold traps (-80°C). In the procedure described in the literature, mercury vapor was used as a catalyst. This reagent, as well as other catalytic agents, such as metal helices, glass helices and gaseous hydrogen chloride, were used in some of our present experiments with the objective of preferentially accelerating the reaction:

$$5B_2H_6 \rightarrow 2B_5H_9 + 6H_2$$

TABLE I

Preparation of B_5H_9

Run No.	Operating Conditions	Total Gas Volume	Starting Pressure	Heating Time	Crude Yield (-80° Fraction)	M.P. of Crude Product	% B_2H_6 trans-formed	Purification Treatment	Yield after Purification	M. P. after Purification*
		cc.	mm.	hrs.	%	°C	%		%	°C
1	Hg. vapor	150	120	4	-	-	96.6	8 hrs at 120°	45	-46.9
2	Glass helices	150	120	4	55	-	97.6	8 hrs at 120°	38	
3	Glass helices + 14% HCl	150	120	4	-	-	-	8 hrs at 120°	36.8	-
4	Glass helices + 1.4% HCl	150	120	1	46	-	93.3	5 hrs at 120°	35	-47
5	Glass helices	300	120	1.6	66	-58	94.5	8 hrs at 120°	37.4	-47.5 to -46.0°
6	Glass helices + 50% H_2	300	120	1.5	46	-	93.9	2 hrs at 120°	46.2	-46.9 to -46.2°
7	Glass helices + 27.4% HCl	300	120	1.5	47	-	-	15 min at 120°	37.0	-48.8 to -47.4°
8	Stainless Steel helices	258	103	1.3	56.4	-67.9	95	15 min at 120°	39.1	-47.0 to -46.5°
9	" " "	310	120	1.0	55.6	-	86	room temp.		
10	" " "	334.5	200	1.5	-	-	-	room temp.		
11	Hg. vapor	370	123	1.2	50.3	-	84.6	2 hrs at 120°	43.2	-47.7 to -46.8°
12	" "	326.4	126	1.2	56.6	-	86.6	2½ hrs at 120°	42.6	-47.1 to -46.0°
13	" "	326.0	125	4.0	56.7	-	85.7	2-1/2 hrs at 120°	41.1	-47.5 to -46.[illegible]

*The melting point of B_5H_9 according to Stock is -46.6°C. This constant is a much more reliable criterion of purity than the vapor tension.

In the runs thus far made, no yields have been obtained larger than the 56% reported by Stock (See Table I). Other catalysts, such as BF_3 and $AlCl_3$ will be tested.

The mixture of volatile boron hydrides obtained in the runs was fractionated through a -45°C bath, a -80°C bath, to a liquid nitrogen bath. The hydrides of low volatility, such as $B_{10}H_{14}$ were removed with the -45° bath while unchanged diborane (and hydrogen chloride in some runs) passed through the -80° bath. The mixture of B_5H_9 and B_5H_{11} was trapped in the -80°C bath. The amount of these pentaboranes obtained in this manner was measured and is listed in Table I as "crude yield". Purification of the mixture by converting the unstable B_5H_{11} to B_5H_9 was accomplished by heating the hydrides at 120°C. The conversion of B_5H_{11} to B_5H_9 is not quantitative. The conditions for obtaining the maximum conversion are being studied.

The rate of conversion of diborane to less volatile hydrides was measured by freezing out the diborane with liquid nitrogen at intervals during the run, and measuring the amount of hydrogen formed. In this way a rough rate curve could be obtained. In runs 5 through 12 the heating period was continued only until the hydrogen pressure as measured in this manner was constant.

The purity of the samples was determined by the melting points. For this purpose a melting point apparatus, such as that described by Stock, was used. The temperature was measured with an ammonia vapor tension thermometer.

The diborane for these experiments was distilled twice through a -160°C bath and had a vapor tension of 223 mm. at -112°C. The impurity was probably ethane.

The experiments on an improved preparation of B_5H_9 will continue during the next month. Work will also be started on preparing enough material by the present methods for a study of its properties.

(4) Stability of aluminum borohydride

A further study of the stability of aluminum borohydride at room temperature is being made with the following objectives:

(a) To determine the effect of hydrogen pressure on the rate of decomposition.

(b) To try to stabilize the borohydride by heating in the container for various periods of time before storing at room temperature.

(c) To determine whether other factors, such as the surface of the glass container, influence the decomposition.

These experiments are still in progress and conclusions cannot be made at the present time, but there is considerable evidence that aluminum borohydride can be made more stable at room temperature than previous results have indicated.

(a) Effect of hydrogen

Our experiments to date indicate that the presence of hydrogen gas at pressures up to four atmospheres may have some influence on the decomposition of aluminum borohydride at room temperature, but there seems to be no direct relation between pressure and the rate of decomposition. Other factors undoubtedly are affecting the results.

Figure 1 shows the three tests which are being run at the present time.

Dry oxygen-free hydrogen gas was introduced above a sample of aluminum borohydride to a pressure of 513 .. The subsequent decomposition at room temperature of 22-29 C. is given by curve (a). The data for (b) were obtained by keeping the vapor space above the liquid aluminum borohydride very small. Thus decomposition of the material soon caused a large hydrogen pressure above the sample. It may be seen that curve (b) falls below (a) despite the fact that the hydrogen pressure in (b) is greater than that in (a) for most of the test period. At 20 days, for example, in (b), there was a pressure of 2227 mm. while in (a) the pressure was only 1035 mm. In both cases, however, the decomposition is decidedly greater than (c), in which the hydrogen was measured and removed at two day intervals. Before any conclusions could be drawn from these results, it would be necessary to ascertain what would be the effect of excess pressure produced by the presence of an inert gas, such as nitrogen. At present this line of investigation does not seem promising.

(b) Stabilization of aluminum borohydride

The observation has been made (P.R. X, p. 3) that the rate of decomposition of aluminum borohydride at room temperature seems to decrease with time to such an extent that decomposition almost ceases. It took 60 to 90 days, however, before the formation of hydrogen became very slow. It was hoped that this apparent stabilization could be accelerated at a higher temperature. Storage tubes containing aluminum borohydride were, therefore, heated for a short time (4 to 8 days) at 40°C, the hydrogen was removed and the further decomposition at room temperature was observed.

In Figure 2 the results from several experiments are compared. The following data are plotted.

Curve 1. This curve represents the normal decomposition of aluminum borohydride in a glass tube. It is included for comparison with the stabilized material.

Curve 2. The hydrogen was pumped off from the aluminum borohydride which had stood at room temperature for 120 days. The decomposition in the following 20 days was very small. This result indicates that the accumulation of hydrogen is either not the factor which causes stabilization or that it is not the sole factor.

Curve 3. Aluminum borohydride was heated at 40-45°C for 4 days in a sealed tube. This tube was opened to a manometer and the hydrogen formed in the decomposition at 40°C remained in the system. The curve plotted is the increase in pressure due to subsequent decomposition at room temperature. The borohydride appears to have been stabilized.

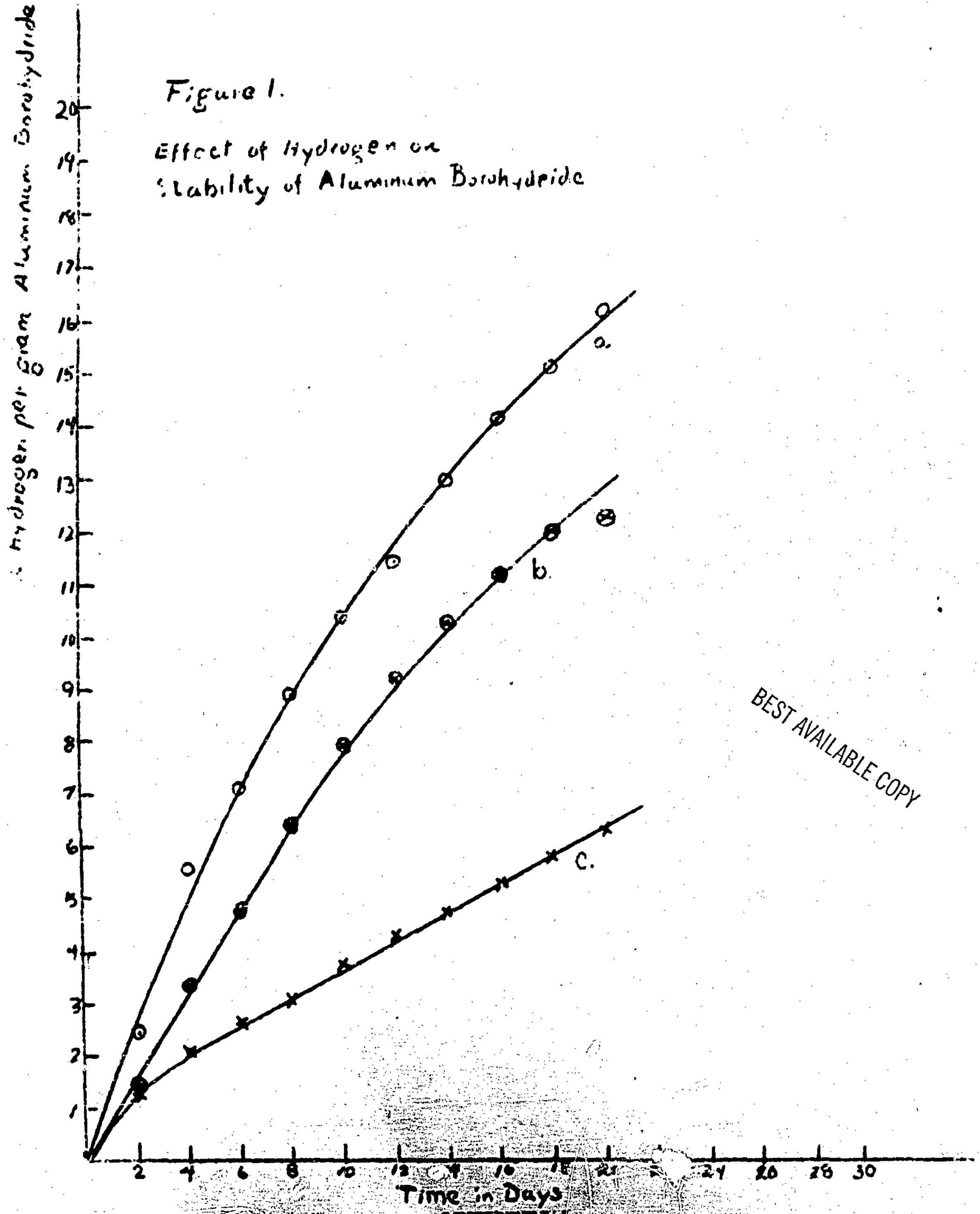
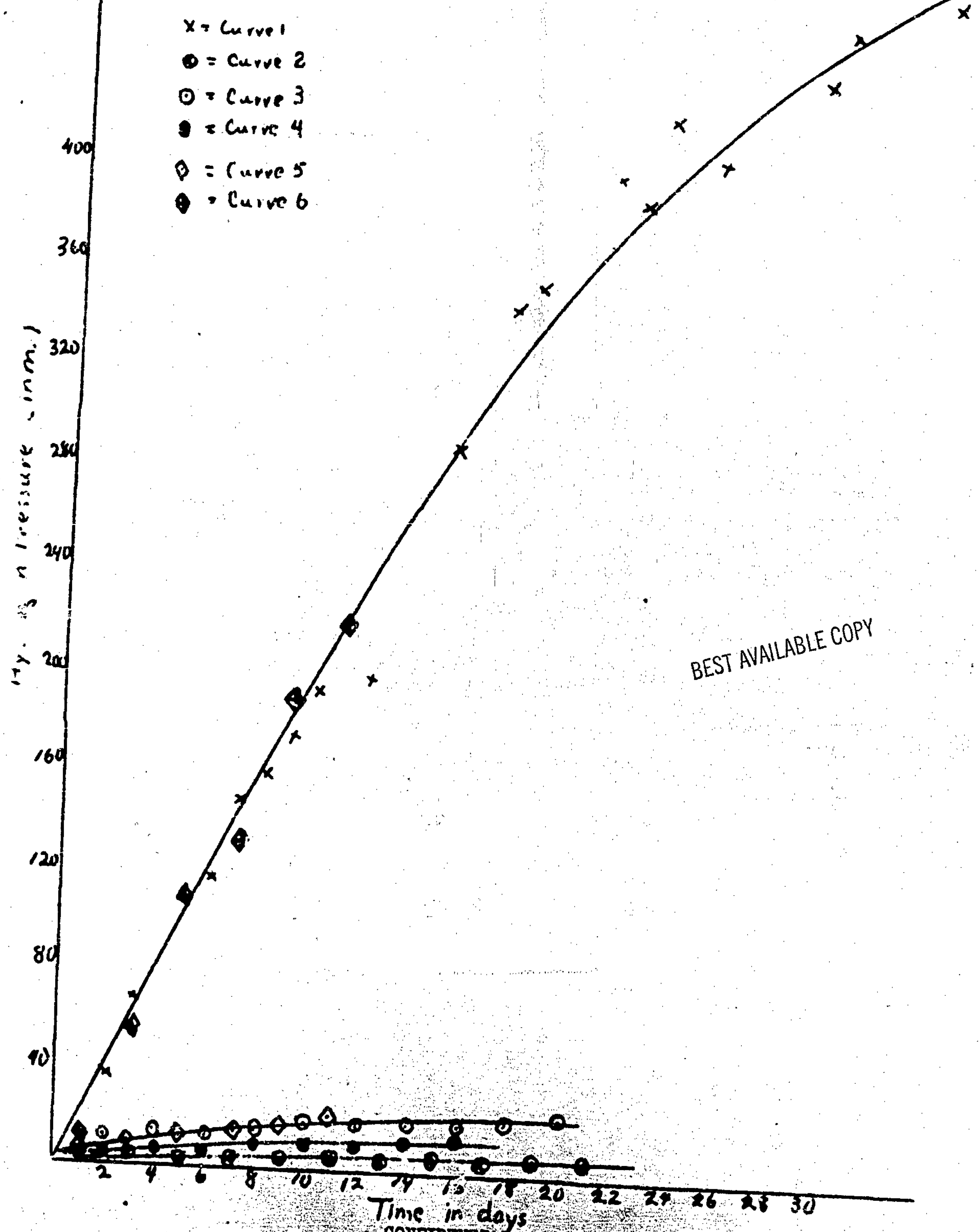


Figure 1.

Effect of Hydrogen on Stability of Aluminum Borohydride

Figure 2. Stabilization of Aluminum Borohydride



Curve 4. Aluminum borohydride was heated for 12 days at 40-45°C. The hydrogen was removed and the system was opened to a manometer. The decomposition at room temperature may be seen to be small.

Curve 5. Two cc. of aluminum borohydride vapor was sealed off in a tube provided with a break-off tip. The tube was placed in an oven in such a manner that only the lower half of the tube was heated. After heating it for one hour at 200°C, brown decomposition products were deposited uniformly over the heated glass surface. The tube was opened and the hydrogen was removed. Liquid aluminum borohydride was then introduced into the tube, and the decomposition at room temperature was observed. The brown material did not appear to be soluble to any extent in the aluminum borohydride. The small amount of decomposition of the latter at room temperature offers some evidence that the process is a surface catalyzed reaction which may be prevented by coating the surface of the container.

Curve 6. This experiment was carried out in the same manner as (5) except that the brown deposit was further heated in an oven at 600°C for 10 minutes. A black deposit was formed which did not adhere to the walls after the aluminum borohydride was added. It may be seen that the decomposition is almost identical with (1). This observation clearly shows that it was the coating obtained in 5 rather than the effect of heat on the glass which inhibited the reaction. This point is to be tested further.

(c) Effect of increased surface

Although previous experiments have not indicated that addition of powdered glass affected the decomposition (PR, VII, p. 11) some further studies have been begun but are not far enough along to report the results at this time.

No. 1 through 25,	Naval Research Laboratory
26-27,	Chief, Bureau of Aeronautics
28-29,	NDRC, Dr. J. Williams
30,	A. C. Bond, Jr.
31,	C. Dillard
32,	A. Finholt
33,	M. Gerstein
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PROGRESS REPORT NO. XIII
For the Period July 24 - August 29, 1945
on
Contract No. N173 s-10421[1]
BuAero TED NRL No. 3401

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[1] Contract No. N173 s-10421 is an extension of contract Nos. N173 s-9058 and s-9820

H. I. Schlesinger in Collaboration with
A. C. Bond, Jr., C. Dillard, J. Farr, A. Finholt, and R. A. Lad

The work undertaken during the period covered by this report has been an extension or a completion of the experiments which were described in Progress Report No. XII.

(1) Lithium Aluminum Hydride

A preliminary report of the reaction of lithium aluminum hydride ($LiAlH_4$) with diborane has been given in Progress Report No. XII. At the time of that report the equation for the reaction was not known, but it has now been established to be the following:

$$LiAlH_4 + 2B_2H_6 - Al(BH_4)_3 + LiBH_4$$

The reaction was carried out in the circulating system in which we have been making B_5H_9. The apparatus was modified slightly so that a tube containing lithium aluminum hydride could be put into the system by means of a removable trap arrangement. Diborane was circulated over the lithium aluminum hydride at pressures of between 200 and 350 mm. and at a speed of about 500 cc. per minute. It was necessary to introduce diborane at intervals to keep the pressure above 200 mm. The lithium aluminum hydride was kept at 65-75° C. Aluminum borohydride was continually condensed from the gas phase in a U-tube maintained at -80° C.

Operating under these conditions, about 1.2 grams of aluminum borohydride were prepared in two to four hours time. This amount of material represented an 80% yield based on the above equation and the amount of lithium aluminum hydride used in the experiment. The amount of diborane used up and the amount of lithium borohydride formed also confirmed this result.

No further work will be done on this reaction unless production of aluminum borohydride is contemplated on a large scale. This experiment has demonstrated, however, a new and feasible method of preparing the borohydride. Under the proper conditions the reaction is probably quantitative.

Desirable modifications of the above procedure would be the following: (1) The lithium aluminum hydride should be finely powdered. (2) The diborane should be passed through, not over, the solid. (3) Higher pressures of diborane should be used.

The reaction of lithium aluminum hydride with boron fluoride etherate to give diborane was described in Progress Report No. XII. A similar reaction with boron chloride gives diborane also, but the equation is not the same.

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$$3LiAlH_4 + 16BF_3 \cdot Et_2O \rightarrow 3LiBF_4 + 3Al(BF_4)_3 + 2B_2H_6 + 16Et_2O$$

$$3LiAlH_4 + 4BCl_3 \rightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$$

The advantage of the latter reaction is that all of the boron goes into the production of diborane.

The reaction was carried out in the vacuum line by condensing boron chloride on an ether solution of lithium aluminum hydride. A vigorous interaction occurred which threw the reagents out of the reaction tube. Despite the difficulty in returning the non-volatile unreacted boron chloride etherate to the reaction tube in order to get complete conversion, the yield was 74%. If the procedure for running the reaction is modified by some method, such as bubbling gaseous boron chloride through an ether solution of lithium aluminum hydride, a quantitative yield probably can be obtained.

The steps in the preparation for quantity production of diborane would be the following:

(1) $4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$

(2) $4BCl_3 + 3LiAlH_4 \rightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$

Steps (1) and (2) would be carried out in the same reaction vessel since, after the process had started, it would only be necessary to add lithium hydride and remove lithium chloride in order to maintain a continuous process. The aluminum chloride would be used and regenerated continuously. The only by-product of the process is lithium chloride. The lithium chloride could be reconverted to the hydride.

The reaction of lithium aluminum hydride with aluminum chloride according to the equation

$$3LiAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3LiCl$$

is being investigated. A product has been obtained in which the aluminum hydrogen ratio is 1:3, which suggests that aluminum hydride is formed. The hydrogen on hydrolysis is low, however, and it seems probable that an etherate of the hydride is formed from which the ether can be removed only with difficulty. Attempts to isolate the hydride will be continued. The preparation of beryllium aluminum hydride ($Be(AlH_4)_2$) from lithium aluminum hydride is also being studied.

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(2) Preparation of B_5H_9

Enough B_5H_9 has been accumulated so that a study of its properties will be made during the coming month. The method of preparation from diborane is still being used. Dehydrogenation and cracking catalysts will be tried in an effort to improve the yields, which still are only 40-50%.

(3) Stability of aluminum borohydride.

In Progress Report No. XII two methods for retarding the decomposition of aluminum borohydride were described. One method was to heat the compound in a storage tube at 40° C. for four to eight days. The hydrogen was pumped off and subsequent decomposition was observed. Samples treated in this manner continue to show an extremely small amount of decomposition, about 0.2 to 0.3 cc. of hydrogen per gram of aluminum borohydride in forty days. The other method of stabilizing the borohydride was to coat the tube with aluminum borohydride decomposition products before introducing a sample. Although the results in the first twenty days indicated little decomposition, the coating slowly peeled off the walls of the container and hydrogen formation increased. At forty days the decomposition was about five times as great as that obtained with the other method of stabilization. Further attempts to put coatings on the walls show that it is difficult to get uniform coatings and that the rate of decomposition of aluminum borohydride varies with the type of coating.

Several stability tests have been run in the presence of different amounts of powdered pyrex glass. The results in all cases were about the same. This indicates that, while glass may catalyze the decomposition of the borohydride, the amount of surface does not affect the rate after a certain limiting quantity has been reached.

(4) Preparation of samples of aluminum borohydride and lithium aluminum hydride.

Samples of aluminum borohydride have been prepared and sent to Dr. Stogeman. Samples of lithium aluminum hydride have been sent to the Naval Research Laboratory.

(5) Work proposed for the coming weeks.

(a) Further study of the reactions of aluminum chloride and of beryllium chloride with lithium aluminum hydride ($LiAlH_4$) with the purpose of obtaining the hydrides of aluminum and of beryllium. A further study of the preparation of lithium aluminum hydride to ascertain the nature of the spontaneously combustible impurity sometimes obtained.

(b) Reaction of lithium aluminum hydride with triethylamine.

(c) Attempts to prepare alkyl derivatives of aluminum hydride by the use of lithium aluminum hydride.

(d) Reaction of lithium aluminum hydride with boron compounds to ascertain whether B_5H_9 may be obtained in this way.

(e) Study of the effects of various types of catalysts in the present reaction for the preparation of B_5H_9.

(f) More detailed study of the properties of B_5H_9.

(g) Investigation of the possibility of preparing hydrides of elements other than beryllium, boron, aluminum, and silicon by use of the new reagent.

(h) Further stability studies on aluminum borohydride to ascertain whether material so stabilized in the lower part of a glass tube will be reactivated on contact with glass walls not in contact with the liquid; also to ascertain whether the catalytic effect of metals can be overcome by heating the borohydride at 40° C. in contact with the metal or by coating the latter at higher temperatures. Although the latter procedure was only partially successful on glass because the coatings ultimately peel, the latter may be more adherent on metals.

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33--A. Finholt
34--R. A. Lad
35--H. I. Schlesinger
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PROGRESS REPORT NO. XIV
For the Period August 30 - September 30, 1945
on
Contract No. 173s-10421[1]
BuAero TED NRL No. 3401

H. I. Schlesinger in Collaboration with
A. C. Bond, Jr., C. Dillard, J. Farr, A. Finholt, R. A. Lad, and K. Wilzbach

(1) Aluminum Borohydride

(a) Approximately 100g of the compound has been "stabilized" by a 5-day heat treatment at 40-45°C. Its shipment to the N.R.L. is awaiting delivery of metal cans ordered for this purpose.

(b) Continuation of Stabilization Tests

Experiments described in the August report (No. XIII) have been continued. To make sure that stabilization is not due solely to deposition of an inhibitor only on those glass surfaces heated in contact with the liquid phase of the compound, tubes partially filled with the liquid were heated at 40-45°C for several days. The tubes were then inverted; decomposition at room temperature thereafter proceeded just as slowly as in tubes which were not inverted.

Preheating the borohydride in contact with iron wire, likewise caused a marked decrease in the rate of subsequent decomposition at room temperature in contact with this metal.

A detailed summary of experiments on this type of stabilization will be submitted in the next report, by which time this phase of the investigation should be completed.

(2) Pentaborane, B_5H_9

(a) Preparation. Search for suitable catalysts in the production of B_5H_9 from diborane by heat treatment has been started. For preliminary, qualitative evaluation of the effectiveness of catalysts, two criteria have been found especially useful: (i) the "crude yield", i.e., the quantity of material retained in a -80°C bath, and (ii) the melting point of the crude product. (The melting point of B_5H_9 is -46.6°C, that of B_5H_{11} is -123°C.) A low melting point of the crude product thus indicates a high degree of contamination with B_5H_{11}. The freezing point is a more sensitive and far more rapid means of estimating the degree of contamination than hydrolytic analysis or than measurement of the vapor tension. No method of avoiding formation of B_5H_{11} has as yet been discovered. The problem at this stage, therefore, resolves itself into two objectives: (i) to decrease its formation to a minimum and/or (ii) to find a satisfactory method for converting B_5H_{11} into B_5H_9. The simple heat treatment recommended by Stock & Mathing, Ber. 69B, 1456 (1936) is very inefficient.

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[1] Contract No. N173 s-10421 is an extension of contract Nos. N173 s-9058 and s-9820

In experiments using mercury vapor as a catalyst in the heated tube through which the diborane is passed, as recommended by Stock, the crude product usually had a freezing point below -60°C; the yield of crude product varied from 60% to 65% of the diborane consumed at 250°C (in most cases from 85-95% of the diborane was used up). It is our present opinion that mercury vapor acts merely as a heat transfer agent, and has no specific catalytic effect. The use of a dehydrogenation catalyst (Cr_2O_3) at 150°C gave a crude product having a melting point of -49°C, thus indicating a much purer product but the crude yield was only 32% even though 90% of the diborane was used up. At higher temperatures, the yield is still poorer.

On the other hand, the use of a standard hydrogenation catalyst at 223°C resulted in a crude yield of 63.4%; the product had a melting point below -80°C. The higher the temperature, the higher the yield; (e.g., at 150°C the yield was 42% and at 185°C, 59.5%). The most favorable temperature has as yet to be determined. It is to be noted that at 150°C in the absence of catalyst no B_5 fraction (i.e., no B_5H_9 or B_5H_{11}) was obtained. The hydrogenation catalyst thus appears to have two effects: it favors the transformation of diborane into B_5 fraction, although the present catalyst was not highly effective in this respect, and it appears greatly to increase the percentage of B_5H_{11}. Both conclusions must, however, await more precise experiments for verification. For example, we have assumed, but not definitely proved, that the contaminant of the B_5H_9 is B_5H_{11} rather than B_4H_{10}. The basis of this assumption is that the crude product has a 0° tension of between 60 and 65 mm. The 0° tension of B_4H_{10} is 388 mm, that of B_5H_9, 66 mm, and that of B_5H_{11}, 53 mm.

These results indicate in a preliminary way that the proportions of B_5H_9 and of B_5H_{11} in the crude product are determined primarily by reaction velocities rather than primarily by equilibrium conditions. This conclusion justifies the further search for catalysts to direct the major reaction into the desired channels. The experiments also suggest the possibility that the best procedure for preparing the compound may be a two-step process, in which the first step is the securing of a maximum yield of B_5 fraction, irrespective of its composition, and the second step conversion of the B_5H_{11} into B_5H_9. To test this possibility, samples rich in B_5H_{11} will be treated with dehydrogenation catalysts of various types.

To have any clear picture of the possibilities along the lines discussed a number of other catalysts of various types must be studied, a project now under way. A few experiments directed toward producing B_5H_9 from sources other than diborane have shown too little promise to deserve inclusion in the report.

We call attention to the fact that we have on hand about 4 g of B_5H_9, some of which could be shipped to the N.R.L. for determination of thermal data. We believe that such measurements should be made now, and we await instructions on when the shipment should be made.

(3) Properties of B_5H_9

(a) Stability. The results are necessarily preliminary in character since considerable time must elapse to obtain sufficient decomposition for precise measurements. Furthermore, as is the case with other similar compounds, the data tend to be erratic, suggesting the influence of wall effects. The following are illustrative of the trend of results:

i. From B_5H_9 in the gas phase at room temperature 3.1 cc of hydrogen per gram were produced after 25 days.

ii. In the presence of liquid B_5H_9 at room temperature 4.3 cc of hydrogen were obtained per gram after 22 days.

iii. In the gas phase at 60°C 3.9 cc of hydrogen per gram were generated in 12 days, but in a similar experiment only 3.5 cc were obtained in 27 days.

iv. In the presence of the liquid at 60°C, 6.2 cc of hydrogen were obtained per gram in 15 days.

In one experiment at room temperature, the decomposition appeared to have ceased since there was no further pressure increase for a period of four days; after removal of the accumulated hydrogen, decomposition appeared to set in again. It is evident that further data are needed before conclusion can be drawn.

(b) We have confirmed Stock's results on the rate of hydrolysis. At ordinary temperatures, it is very slow; hydrolysis, carried out for analytical purposes at 90°C, required several days for completion. In alkaline solutions hydrolysis is more rapid, as is true also of acid solutions.

(c) It is somewhat soluble in water (with decomposition); very soluble in benzene, heptane and ether. Benzene solutions up 50% mole fraction obey Raoult's law approximately.

(d) It reacts with isopropylamine to form an oily product having the composition $B_5H_9 \cdot 4NH_2(C_3H_7)$. The compound is more reactive toward water than B_5H_9 itself, a result to be anticipated since B_5H_9 reacts more rapidly in alkaline solution than with pure water.

(e) Reaction with Air. Contrary to the observations of Stock and his coworkers, as well as to our own earlier experiences, B_5H_9 seems to ignite spontaneously in air, but only under very special conditions. The following sets of facts are cited to illustrate conditions under which spontaneous inflammability did not occur and those under which it was observed:

A tube containing about 2g of B_5H_9 was accidentally broken and its contents spilled on the laboratory bench; although the B_5H_9 evaporated fairly rapidly no flame was observed. Furthermore, no flash or flame was observed in experiments in which air was admitted to a vessel containing frozen B_5H_9 which was then allowed to evaporate and become mixed with the air by very slow warming to room temperature. In these experiments the compositions of the mixtures after complete evaporation of the B_5H_9 varied from 1 to 60% of air, and the total pressure from about 120 to about 460 mm.

If, on the other hand, liquid B_5H_9 was allowed to evaporate rapidly into a vessel containing air, flashing resulted in most of the experiments; only the experiment in which the largest proportion of air (51%) was used, gave no flame or flash. Likewise when air was rapidly admitted to B_5H_9 vapor, a flash resulted. One other striking experiment should be recorded. In one of the cases in which B_5H_9 had been evaporated into air slowly enough to avoid flashing, the B_5H_9 was recondensed and the air removed from the apparatus; the B_5H_9 was then evaporated again but into an evacuated vessel to which air was later rapidly admitted. The B_5H_9 inflamed. This observation indicates that spontaneous inflammability is dependent on the method of mixing the air and the B_5H_9 rather than on an impurity, a point which will receive further discussion.

Some mixtures which were prepared by slow evaporation of B_5H_9 and which had not inflamed were subsequently heated. When the proportion of air was only 12%, the mixture could be heated to 150°C and there maintained for 5 minutes without visible reaction. Another mixture containing 63% of air was heated at the rate of 6°C per minute until it inflamed at 84°C. Only 7% of the B_5H_9 was recovered. In a third experiment another 33% mixture was allowed to expand into an evacuated reaction tube maintained at 50°C, where it reacted with a flash.

In view of the contrast between these observations and earlier ones by Stock and ourselves, further evidence bearing on the question of an impurity as the cause of spontaneous inflammability was sought in addition to that already cited. A sample of B_5H_9 was shaken with water at intervals during 15 minutes, a treatment which should have removed traces of B_4H_{10}, B_5H_{11}, and other highly inflammable hydrides of boron. Nevertheless the washed sample, after removal of the water, behaved as did the samples with which the other tests were made. Although the two experiments cited in this connection make it seem very unlikely that spontaneous inflammability is due to impurities, the latter explanation is not yet entirely excluded. Further studies are in progress.

It should, perhaps, be pointed out that even though spontaneous inflammability was observed as described above, the reactions did not appear to be of violent explosive character; they are better described as a flash sometimes accompanied by a faint sound. The amount of B_5H_9 destroyed when a flash occurred was in general much greater than is accounted for on the assumption that the reaction products are boric oxide and water.

Attempts were made to inhibit the reaction of B_5H_9 with air. Benzene seems relatively ineffective, but lead tetraethyl appeared promising. A mixture containing 7% of this compound in B_5H_9 was rapidly opened to the atmosphere without noticeable reaction. Other tests gave similar indications but further work is necessary.

It is apparent that spontaneous inflammability of B_5H_9 is a complex process. Some results so far obtained indicate that rate of mixing is an important factor in determining whether mixtures will flash but even on this point there is contradictory evidence (e.g., the fact that B_5H_9 accidentally spilled did not inflame). Such factors as the effect of concentration, total pressure and temperature as well as the possible influence of inhibitors need still to be studied. This work is being actively pursued.

(f) B_5H_9 reacts with lithium hydride in the presence of ether to give an ether soluble solid. As has frequently occurred in similar cases, we have not been successful in removing all of the ether from the product. Analysis of the solid obtained gave the atomic ratios Li:B:H = 1.99:5.0:11.7, in fair agreement with the formula $Li_2B_5H_{11}$. The ether containing sample hydrolyzed slowly, and was not spontaneously inflammable in air. No immediate further experiments are planned for the compound unless a test should prove it useful for the purpose of the project. If a sample is desired by the N. R. L., we can readily prepare one.

(3) Lithium Aluminum Hydride

Further work on this compound was confined to efforts to convert it into aluminum hydride. Although an ether solution, in which the ratio of aluminum to hydrogen is 1:3 has been obtained by the reaction already described in Progress Report No. XIII, p. 2, efforts to remove the ether completely without decomposition of what appears to be the etherate of the hydride have been unsuccessful. Various processes were attempted; because the desired result was not achieved, they are merely listed as a matter of record: Use of elevated temperature and low pressure; treatment with tertiary amines and with pyridine; treatment with aluminum chloride or bromide in benzene solution. Another attempted approach was through the compound $NaAlH_4$, but all efforts to prepare this substance (e.g., NaH + $AlCl_3$ under various conditions) were unsuccessful. The matter is being studied further.

It was shown that lithium aluminum hydride, although more reactive than lithium hydride in certain hydrogenations, is no more satisfactory than lithium hydride in attempts to prepare methyl aluminum dihydride from methyl aluminum dichloride.

(4) Proposed Work

In addition to the work already mentioned, methods of preparing hitherto unknown hydrides and alkyl metal hydrides of other elements are being studied. This work also includes experiments designed to develop more efficient methods for preparing compounds which might be useful for the purposes of the project, but for which no efficient methods of preparation are now known. Compounds of titanium and silicon are included in the program, but compounds of some less common elements are also being investigated. Only by having a range of compounds (whether they are themselves feasible or not) and testing them can a logical approach to a solution of the problem be developed.

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PROGRESS REPORT NO. XV.
For the Month of October

on

Contract No. 173s-10421[1)]
BuAero TED NRL No. 3401

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1) Contract No.N173 s-10421 is an extension of contract Nos. N173 s-9058 & s-9820

H. I. Schlesinger in Collaboration with
C. Dillard, J. Farr, A. Finholt, R. A. Lad, and K. Wilzbach

Progress during the month of October has been slower than in past months due in part to a temporary man-power shortage, and in part to a change in the nature of the work. During this period we lost the services of A. C. Bond and D. Peppard, and found only one replacement, Mr. K. Wilzbach, a very able man who had, however, to become familiar with the necessary special techniques. This situation has now been improved since we were able to add Mr. B. Abraham, a man thoroughly experienced in this type of investigation. Even so, very rapid progress cannot be expected since we are now searching for catalysts, and are developing new preparative procedures in a field in which there are no previous experimental data or principles to use as guides.

1. Aluminum Borohydride

The 100 g. of aluminum borohydride, requested by the Naval Research Laboratory, were shipped after the material had been "stabilized" by the methods described in Progress Reports XII (pp. 6 and 9), XIII (p. 3), and XIV (p. 1). An extra tube of the batch from which the shipment was taken was observed by us for 11 days, during which time a pressure of only 45 mm of hydrogen had developed.

The complete report on the stability tests of aluminum borohydride is deferred awaiting completion of the last few experiments.

2. Preparation of B_5H_9

The tests of catalysts were continued, but no materials, more effective than those previously reported (Progress Report XIV, p. 2), have as yet been found. Further study has shown that the effectiveness of the catalysts very rapidly decreases with use, an effect which seems to be due, in part at least, to a coating of solid hydrides of boron or of boron itself. Since experiments carried out in this laboratory before the war had shown that the formation of such solids may be decreased by the use of excess of hydrogen, we have designed and are erecting new apparatus in which the reactions can be carried out under hydrogen pressure, and in which space velocity, extent of catalyst surface and other factors may be more readily altered for the detailed study which now seems necessary. Also we have made arrangements to secure several catalysts effective in hydrocarbon chemistry and shall test these.

3. **Properties of B_5H_9**

(a) **Solubility.** The compound dissolves in hydrocarbons such as benzene, cyclohexane and n-heptane. Solutions up to 50 mole per cent have been prepared and obey Raoult's law approximately, but no attempt was made to determine limits of solubility. The compound is also soluble in solvents like carbon tetrachloride; such mixtures have vapor tensions higher than expected from Raoult's law, but sufficiently lower than the sum of the vapor tensions of the components to show that solutions are formed.

(b) **Spontaneous Inflammability.** By slow evaporation of B_5H_9 into oxygen gas, some data on the limits of spontaneous inflammability were obtained, but the results are still erratic as described in Progress Report XIV (pp. 3-4). When the pressure of B_5H_9 is maintained at 200 mm., while the oxygen pressure if raised, spontaneous inflammation is first observed at an oxygen pressure of 40 mm. although in some experiments a reaction did not occur until the oxygen pressure had risen to 170 mm.

In spontaneously inflammable mixtures containing oxygen at partial pressures from 40 to 170 mm., the reaction was not violent; a mixture containing oxygen at a pressure of 340 mm. (B_5H_9 pressure 205 mm.) exploded with enough violence to shatter the container, however.

The reaction with air, as mentioned in the report referred to, is complex, sometimes giving white and sometimes brown products, the nature of which has not been investigated.

Since it is possible that the spontaneous inflammability may be due to impurities, further fractionations of the material were carried out but all fractions behaved alike. It is recognized, however, that removal of traces by fractionation is difficult. We are consequently searching for chemical tests to identify small amounts of B_5H_{11}, the most likely impurity, in B_5H_9. Toward all but one reagent so far tested, the two substances react similarly; the one exception is lead nitrate which is reduced by impure samples of B_5H_9 but not by the more highly purified ones; the test does not seem to be sufficiently sensitive for our purpose.

Spontaneous inflammability of B_5H_9 samples is completely inhibited by the addition of small amounts of nickel or iron carbonyls. Present results indicate that very small traces of the latter may prove effective. The effect is still under investigation.

4. **Aluminum Hydride.** In previous reports, we have described experiments directed toward the isolation of aluminum hydride (Progress Report XIII, p. 2, and XIV, p. 5). Although the reaction of the new compound $LiAlH_4$ with aluminum chloride in ether solution gives a product in which the ratio of Al:H is 1:3 g at. wts., a pure product could not be obtained, apparently because complete removal of ether is attended by decomposition of the hydride. In order

to make certain that no substances other than the hydride and ether were present in the impure product, its complete pyrolysis was carried out. The volatile products were ethane, hydrogen, ether and a small trace of a sublimate which presumably is aluminum ethylate. The solid residue is a mixture containing metallic aluminum, and aluminum compounds, presumably oxide and the ethylate. The quantities of hydrogen, ethane, and ether, and the total aluminum in the residue agreed, as closely as is to be expected in so complex a situation, with the assumption that an etherate of aluminum hydride decomposes as follows on pyrolysis:

(1) $2AlH_3.x\ Et_2O \rightarrow 2Al + 3H_2 + 2\ x\ Et_2O$

(2) $3AlH_3.x\ Et_2O \rightarrow 2Al + Al(OEt)_3 + EtH + 3H_2 + (x-1)\ Et_2O$

(3) $2AlH_3 3Et_2O \rightarrow Al_2O_3 + 6Et\ \ H$

The details need not be given.

Further confirmation that the material in the ether solution is aluminum hydride was obtained by treating the solution with trimethylamine. Removal of the volatile materials, at 0° - 10°C, left behind a crystalline product, the analysis of which corresponded to the formula $AlH_3 \cdot 2NMe_3$. This formula, the slight volatility and other properties of this substance correspond with those described by Wiberg (Ber. 75, 2003 (1942)) for the trimethylaminate of aluminum hydride. Since Wiberg has shown that the hydride may be isolated from this compound, no further work in that direction is now planned.

5. Preparation of Other Types of Hydrogen Compounds. This aspect of the work, to which considerable time has been devoted, represents a preliminary study in which the immediate usefulness of the products obtained was not a primary objective. Its purpose was to obtain data upon which methods for preparation of compounds of direct interest could be based. Thus the discovery of a new method of preparing silane was not in itself directly applicable to the project, since silane is probably too readily inflammable for practical use; this discovery has led, as shown by experiments carried out after the period covered by this report, to methods more convenient than any hitherto known for preparing the various partially alkylated silanes. We hope that the development of a simple method for the preparation of the very unstable stannane (SnH_4) will similarly lead to methods for obtaining more stable alkyl derivatives of this compound. The preliminary work, herein referred to, is outlined as follows:

(a) Preparation of silane by the reaction, carried out in ether solutions:

$$SiCl_4 + LiAlH_4 \rightarrow LiAlCl_4 + SiH_4$$

This reaction was described in Progress Report XII, p. 2.

(b) Preparation of $LiGaH_4$ by the reaction

$$4LiH + GaCl_3 \rightarrow 3LiCl + LiGaH_4$$

To carry this reaction out, a large excess of lithium hydride was added to an ether solution of gallium chloride at -80°C. The mixture is allowed to warm to room temperature, and is filtered out of contact with air. Evaporation of ether from the filtrate caused the deposition of white, feathery crystals of an etherate of $LiGaH_4$. Removal of ether from this product was accomplished by evacuation at room temperature for 20 hours. The ratio of gallium to hydrogen in the final product was 1:4.08; the total hydrogen obtained by hydrolysis corresponded to a purity of 94.2%. If higher temperatures (40°C) are employed for removal of ether, the product turns slightly grey.

Attempts to prepare digallane by use of an excess of gallium chloride were unsuccessful. A few further experiments are under way, but the matter will not be extensively pursued because of the small likelihood that gallium compounds can be obtained in sufficient quantities to be practical.

(c) Germane (GeH_4) This compound was prepared by the reactions (in ether):

$$GeCl_4 + LiAlH_4 \rightarrow GeH_4 + LiCl + AlCl_3$$

and

$$GeCl_4 + 4LiH \rightarrow GeH_4 + LiCl$$

The germanium chloride was distilled into a flask containing the hydrogen compounds and ether at -180°C. The reaction proceeded smoothly as the mixture warmed to room temperature. The germane, separated from ether by fractional distillation through a -112°C bath, had properties identical with those described in the earlier literature (see Paneth, Ber. 58, 1135 (1925), and Schenck and Imker, ibid. p. 271; the vapor tension reported by the latter is 155 mm. at -112°C, found by us 160 mm.). The yields were low by both methods (20%), possibly because of formation of polymeric GeH_2; the methods are nevertheless marked improvements over older ones.

(d) Stannane (SnH_4) Stannic chloride is reduced to the metal by lithium hydride without formation of stannane. With $LiAlH_4$ in ether solution, under the conditions described for the preparation of germane, stannic chloride reacts vigorously. The volatile product was removed as rapidly as possible to diminish the extent of its decomposition. The stannane was purified by fractionation through a -112°C bath, and had the vapor tensions (182 mm at -80°C and 18.5 mm at -112°C) reported by Paneth, Haken, and Rabinowitch (Ber. 57, 1898, (1924). The yield was 20%.

As already described by Paneth et al, stannane is a very unstable substance; it decomposes completely in 12 hrs. at room temperature.

(e) Titanium (Hydride). Titanium tetrachloride is reduced to the metal by lithium hydride and by $LiAlH_4$. Attempts to prepare a volatile hydride have been unsuccessful.

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PROGRESS REPORT NO. XVI
For the Period October 31 - November 30, 1945
on
Contract No. N173s-10421[1)]
BuAero TED NRL No. 3401

H. I. Schlesinger in Collaboration with
B. Abraham, C. Dillard, J. Farr, A. Finholt, R. A. Lad and K. Wilzbach

Summary

(1) The major progress made during the period covered in this report has been on the procedures for the preparation of hydrides of silicon and of tin, and of their partially akylated derivatives. The methods have now been developed sufficiently to allow the rapid preparation of substances formerly difficult to prepare. In order that our future work may be carried forward in systematic fashion, the compounds now available should be tested immediately. On the basis of such tests, it might be possible to determine what types of compounds have the greatest likelihood of usefulness and, therefore, to what types further effort should be devoted.

The specific compounds which should be tested at present are: mono ethyl silane, $C_2H_5SiH_3$, diethyl silane, $(C_2H_5)_2SiH_2$, mono n-propyl silane, $(n\text{-}C_3H_7)SiH_3$, di n-propyl silane, $(n\text{-}C_3H_7)_2SiH_2$, trimethyl stannane, $(CH_3)_3SnH$ and dimethyl stannane, $(CH_3)_2SnH_2$. Mono methyl stannane has also been prepared but is probably too unstable to be useful. Details of the preparation methods and a brief description of the properties of these compounds is given in a later portion of this report.

It would be desirable to have these tests made at Chicago to save time, but since the University has no department of Chemical Engineering, we do not have the necessary equipment. If the Navy would approve, we could have determinations of the effect of these compounds on cetane and octane numbers of fuels made in Chicago by some organization such as the Phoenix Chemical Laboratories, Inc., which, we understand, already is doing some work for the Army and the Navy. It is far from certain, however, that such determinations would give a reliable, relative measure of the effectiveness of the compounds for the purposes intended.

We, therefore, suggest that the Naval Research Laboratory furnish us with such information in its possession as to whether cetane or octane numbers have been of value for this purpose, and if not, whether any tests, other than actual use in a jet motor, have as yet been devised. If the materials must be tested in Washington, we should receive information immediately as to what quantities of each compound will be needed in order that we may at once set about their preparations.

(2) Further efforts have been made to ascertain whether the spontaneous inflammability of B_5H_9 is due to an impurity. No evidence supporting this interpretation has been found. The compound, if stored in a glass vessel, undergoes slow decomposition accompanied by hydrogen evolution for a relatively short time, after which hydrogen evolution becomes much slower. This initial hydrogen evolution may be

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[1)] Contract No. N173 s-10421 is an extension of contract Nos. N173 s-9058 and s-9820 due to the presence of a slight trace of impurity (B_5H_{11} ?). Since there was a possibility that such an impurity might also be responsible for the observed spontaneous inflammability, we tested a sample of B_5H_9 which had been stored until the initial hydrogen evolution had ceased. Its inflammability was similar to that of fresh samples. To determine whether the initial decomposition is due to an impurity, samples of B_5H_9 and of B_5H_{11} have been sent to the General Electric Company's research laboratory for measurement of the infra-red spectrum. (The University's equipment is not available at present.)

The spontaneous inflammation of B_5H_9 may, however, be completely inhibited at ordinary temperature by iron carbonyl as already mentioned on p. 2 of Progress Report XV (October). We have now found that as small a quantity as 0.01% of the carbonyl completely inhibits the inflammability at room temperature, and it is possible that even smaller amounts would be effective. The reason for this latter statement is that a sample of B_5H_9 from which the carbonyl had been removed as fully as possible by fractionation still failed to flash in air. At higher temperatures the iron carbonyl produces an induction period but does not prevent inflammation. Thus at 60°C addition of 0.02% of iron carbonyl caused an induction period of 14 minutes before the mixture flashed; with 0.1% the induction period was about 4 hours. At 100°C 1% of iron carbonyl produced an induction period of 40 minutes.

The B_5H_9 does not seem to react with iron carbonyl either at room temperature or at 60°C in darkness. If the mixture is illuminated, the iron carbonyl is decomposed at a rate dependent on the intensity of the radiation; but the B_5H_9 is unchanged.

(3) Progress on the catalytic production of B_5H_9 from B_2H_6 has been slow, as was anticipated. A number of catalysts, as well as the effect of hydrogen, are being studied but this work is not sufficiently far along to make any additions to what has been reported in Progress Report XV. Dehydrogenation catalysts thus far are the most effective, but studies on the effect of particle size, length of path, etc., must be completed before final conclusions are reached.

(4) The tests on stability of aluminum borohydride as originally contemplated have been completed and will be the subject of a special report. The observations made on the effect of iron carbonyl on B_5H_9 have led us to study its effect on aluminum borohydride even though the likelihood of success is not great. The final report on this topic is being withheld until the work with iron carbonyl is completed.

The Preparation of Silane, Stannane and Alkyl Derivatives of Each by the Interaction of the Corresponding Halogen Derivatives with Lithium Aluminum Hydride, Lithium Borohydride or Lithium Hydride.

The preparation of Silane and of Stannane by the interaction of lithium aluminum hydride with silicon tetrachloride and with stannic chloride, respectively, has been described in Progress Reports XII (p. 2) and XV (p. 4). This reaction has now been successfully extended to the preparation of partially alkylated derivatives of these hydrides.

Since the use of lithium hydride in place of the aluminum compound would be more convenient, its reactions with silicon tetrachloride and with several of the alkyl derivatives of the latter were investigated. In all cases the lithium hydride produced the desired product. In the reaction with silicon tetrachloride, however, the yield was unsatisfactory unless a large excess of lithium hydride was used. In the preparation of alkyl silicon hydrides, lithium hydride proved as effective as the lithium aluminum hydride so far as yield is concerned, but the reaction of the former was considerably slower and required a higher temperature. So far as can be judged from the data available, the advantage of the lithium aluminum hydride results from its solubility in ethers, which leads to homogeneous reaction mixtures, whereas when lithium hydride is used the reaction is one between a solid and a liquid thus leading to retardation by formation of coatings on the solid reactant. Attempts were made to accelerate the reaction of lithium hydride by the addition of relatively small quantities of aluminum chloride to convert a small part of the lithium hydride to the aluminohydride. The latter should be reconverted to aluminum chloride by the halide used in the reaction, and a "catalyzed" reaction should result. This expectation was, however, not realized, possibly because coating effects prevented access of aluminum chloride to the lithium hydride.

Lithium borohydride is also soluble in ether. It is evident, however, that the boron chloride formed by the interaction of the borohydride with, for example, silicon chloride would immediately react with more of the borohydride to form diborane. The reaction was briefly studied with the expected result; i.e., diborane as well as silane was obtained, thus cutting down on the yield which might be expected for the latter.

Diethyl dichlorosilane and ethyltrichlorosilane were obtained from the Dow Corning Corporation; the corresponding n-propyl derivatives were prepared from the propyl Grignard reagent and silicon tetrachloride. Complete purification of these starting products was not undertaken since all of the corresponding hydrogen compounds were to be prepared. It is much simpler to purify the hydrogen than the chloro compounds. It should be mentioned that silicon alkyl chlorides are manufactured by both Dow and General Electric Company. Preparation of trialkyl silicon hydrides was not attempted since they may be more easily prepared from silicochloroform than by the present method.

The alkyl tin chlorides were prepared by interaction of tetramethyl tin and tin tetrachloride. In this case also the various chloro derivatives were not purified, since separation of the hydrogen compounds from each other seemed likely to be more efficient.

In most cases the reactions were carried out in a vacuum system because of the greater rapidity of this procedure and its advantages in dealing with small quantities of volatile materials. We have, however, carried out a sufficient number of experiments using the more usual types of laboratory glassware and making the separations in a fractionating column to know that these procedures may be used whenever desirable.

For the reaction between lithium aluminum hydride and the alkyl halogen derivatives of silicon or tin, either diethyl ether or dioxane was used as solvent. Diethyl ether has the advantage of dissolving larger amounts of the lithium aluminum halide; dioxane is more readily separated from the reaction product. For the reactions between lithium hydride and the alkyl silicon chlorides, dioxane was used as the medium in order to make possible higher reaction temperatures.

It is not necessary to give details for each preparation since all were carried out in similar fashion. When the reactions were carried out in the vacuum system enough material was used to yield 0.2 to 0.3 g. of product. An excess of about 15-20% of the lithium aluminum hydride was employed; in the case of lithium hydride, the excess was two to threefold the theoretical amount but fairly good results could be obtained with slight excess only. The lithium aluminum halide was dissolved in the solvent in the reaction vessel into which the appropriate silicon compound was then distilled. (When the reaction was carried out in conventional apparatus, the silicon compound was added slowly from a dropping funnel.) In the case of the solid alkyl tin halides, the latter were placed in side arm of the reaction vessel, and were melted to allow them to flow into the solution of the lithium aluminum hydride. When lithium hydride was used in place of the aluminum compound, the former was suspended in the solvent and the procedure just outlined followed thereafter.

With lithium aluminum hydride the reactions proceeded smoothly and rapidly at room temperatures and was complete in about 15 minutes. When lithium hydride was used with ethyl silicon trichloride, rapid reaction ensued at 40-50°C; in the case of the diethyl derivative, the reaction was carried out at the reflux temperature of dioxane (about 98-100°C).

The yields of the monoalkyl silanes, obtained by use of lithium aluminum hydride, were between 95-100%; the yields for the dialkyl silanes were lower because the dialkyl chloro derivatives used as starting material were not pure. With lithium hydride an 86% yield of the monoethyl silane and 72-74% yields of diethyl silane were obtained. (The lower yield of the diethyl derivative is due to the cause mentioned above.) No calculation of the yields of the tin compounds was made since the starting material was in each case a mixture of the various alkyl tin chlorides of unknown composition, and the several hydrogen derivatives were separated from each other after preparation of the mixtures.

All of these compounds are liquids at ordinary temperatures with freezing points which are probably below -112°C. They are either insoluble or only very slightly soluble in water, with which they react very slowly. For example, in the case of the tin compounds, solids are deposited only after the mixture of the compound and water had stood for several days. In benzene, all are soluble. They are not spontaneously inflammable in air, but are readily ignited and seem to burn more rapidly than either diethyl ether or gasoline. Except for monomethyl stannane, the compounds seem stable at ordinary temperatures; monomethyl stannane soon produces a deposit of tin but how extensive its decomposition is has not yet been fully determined.

Observed molecular weights of the compounds in all cases agreed to within experimental error (in all cases less than 1%, and usually less than 0.5%) with the theoretical. Vapor tensions of all of the compounds have been determined at various temperatures; from those data boiling points and heats of vaporization have been calculated. These values are recorded in the following table. At the right are given the equations which reproduce satisfactorily the vapor tensions; for more precise work the constants of the equations should be redetermined, since we have as yet dealt with quantities too small to assume the highest degree of purification.

	Boiling Point °C	Heat of Vaporization (Cal./mole)	Equation for Vapor Tension
$SiEtH_3$	-13.1	5261	$\log p = \frac{-1150}{T} + 7.304$
$SiEt_2H_2$	53.7	7409	$\log p = \frac{-1619}{T} + 7.836$
$SiPrH_3$	24.2	6301	$\log p = \frac{-1377}{T} + 7.513$
$SiPr_2H_2$	110	8500	$\log p = \frac{-1857}{T} + 7.700$
$SnMeH_3$	-0.9	5869	$\log p = \frac{-1283}{T} + 7.594$
$SnMe_2H_2$	36.9	6586	$\log p = \frac{-1440}{T} + 7.524$
$SnMe_3H$	59.2	7236	$\log p = \frac{-1581}{T} + 7.641$

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PROGRESS REPORT NO. XVII
For the Period November 30 - December 31, 1945

on
Contract No. N173s-10421[1]
BuAero TED NRL No. 3401

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[1] Contract No. N173 s-10421 is an extension of contract Nos. N173 s-9058 and s-9820

H. I. Schlesinger in Collaboration with
B. Abraham, C. Dillard, J. Farr, A. Finholt, R. A. Lad and K. Wilzbach

(1) Studies on the conversion of B_2H_6 to B_5H_9 have been continued along the lines reported previously. In general it has been found that changes in temperature, pressure, flow rate, time of contact with catalyst which increased the total amount of B_2H_6 converted into B_5H_9 and B_5H_{11} also increased the percentage of B_2H_6 converted into compounds other than those containing 5 boron atoms per molecule. In other words, the yield of B_5H_9 + B_5H_{11} in terms of B_2H_6 used up remained fairly constant, indicating that the catalysts which proved effective in altering B_2H_6 were also effective in decomposing the B_5 compounds. A very recent, as yet unconfirmed experiment has given a more favorable result from this point of view, but has given a very small conversion. It would be premature to give a more detailed d report on this preliminary experiment at present.

Because of the earlier unfavorable results, we are expanding our studies in several directions: (a) Studies of the conversion of B_2H_6 into B_5H_9 in solvents instead of in the gas phase; (b) A study of the possibility of reducing higher hydrides to B_5H_9 , and (c) Studies on the conversion of B_2H_6 at high pressures.

The last named of these has required preliminary testing of suitable apparatus. Because of the inflammability of diborane and especially of samples of this substance which have been heated, the starting products are best introduced into the pressure system in vacuo. The apparatus must therefore be tight both toward evacuation and toward high pressures. Tests of various types are now under way.

(2) We are preparing some of the silicon-alkyl hydrides and tin alkyl hydrides described in previous reports in quantities large enough for testing in an actual motor. Other compounds of this type are being studied (e.g. bismuth and antimony alkyl hydrides) but the work is still in its initial stages and will be reported later.

(3) A review of the work on the stability of aluminum borohydride is appended.

Stability of Aluminum Borohydride

I. Nature of the Decomposition

This report is a summary of the studies made during the past ten months on the decomposition of aluminum borohydride, hereinafter called alide. The decomposition products of alide are hydrogen gas and non-volatile compounds of aluminum, boron and hydrogen called "polymer". The polymer can be prepared by heating the alide to 100-150°C, but the reaction is very sensitive to temperature changes. More recent studies have shown that polymer formed at high temperatures is not homogeneous but consists of material which is soluble in alide, and an insoluble residue which has the formula (AlB_3H_9). All of the components included in the term "polymer" react with water to give hydrogen. In addition to these, there is often formed another substance of metallic appearance which does not react with water. The average composition of the mixture of these three components, obtained by heating a sample of alide, corresponds closely to (AlB_3H_8). (P.R. III, 12; P.R. VII, 10; P.R. VIII, 18).

At room temperature, only the alide-soluble material is formed, but when the solvent is removed this slowly loses hydrogen to give the insoluble substance, and from it upon prolonged standing, in the absence of alide, traces of the metallic substance are also produced.

Alide is the only solvent known for any form of the polymer (P.R. IV, 2).

II. 60° Studies

Since the decomposition of alide at room temperatures is slow (P.R. VI, 7) accelerated tests at 60° were undertaken. However, the results obtained at this temperature could not be used to predict behavior at lower temperatures because the course of the reaction is quite different. Thus after 20-30 days at room temperature, the decomposition seems to approach a limit corresponding to a loss of between 0.5 and 1.0% of the available hydrogen; whereas at 60°, no retardation of the rate was observed after 70 days. (P.R. X, 3). Also considerable amounts of the insoluble polymer are formed at 60°, as well as some of the substances of metallic appearance. The latter, however, have been obtained in amounts too small for reliable analysis.

Some of the results obtained at 60° are as follows:

1). Decomposition of alide vapor is only about one-tenth as rapid as that of the liquid. (P.R. X, 3).

2). 50% solutions of alide in benzene, isopentane and cyclohexane decompose at approximately the same rate as the pure compound. In amylene solutions of the same concentration, the decomposition is more rapid. (P.R. X, 3)

3). Mild steel and stainless steel seem to be without effect in 360 hours. Copper and its alloys produced a definite increase in the rate of decomposition. (P.R. X, 3)

4). Careful steaming of the glass, used to make sample tubes, did not alter the rate of decomposition, but use of dichromate cleaning solution exerts a harmful effect. (P.R. VIII, 13) In quartz tubes, the rate is approximately the same as in glass. (P.R. X, 3)

5). Fairly large quantities of aluminum chloride accelerated the decomposition, but the effect is too small to account for the fact that some samples of alide decompose more rapidly than others. Carefully purified samples did not behave differently from ordinary samples. (P.R. VII, 10)

6). Addition of soluble polymer did not affect the rate of decomposition in 60 days. (P.R. X, 3)

III. Room Temperature Studies

Observations on the stability of alide at room temperatures are as follows:

1). The decomposition occurs entirely in the liquid phase. No decomposition was perceptible in a sample of alide vapor even after 120 days. (Final Report, Contract Nos. N173 s-9058 and N173 s-9820, page 9.)

2). Samples of the borohydride, carefully freed from chlorides, decomposed somewhat more slowly, at room temperatures, than samples of ordinary purity. On the other hand, addition of aluminum chloride, the most probable impurity, produced no significant acceleration of the decomposition. (P.R. VII, 11)

3). Addition of Pyrex glass wool did not affect the decomposition. (P.R. VII, 11, 13) A large surface of carefully reduced iron accelerated the first stages of the decomposition but the rate rapidly tapers off. (P.R. VII, 11, 15) Other experiments with iron surfaces are described below.

4). Samples of 0.56 g of alide were introduced above 0.5315 and 1.6986 grams of 40-60 mesh powdered Pyrex glass. The development of hydrogen with time in these samples is given in Fig. 1. The sample containing the larger amount of glass powder produced 1.6 times as much hydrogen in 60 days, but this is less than would be expected if the effect were due to surface alone, since the larger sample contains 3 times as much surface. It should be noticed also that the amount of decomposition in the presence of 0.5315 grams of Pyrex powder is less than in samples containing no added surface. Compare curve (2) of Fig. 2.

5). Attempts to coat the walls of the sample tubes with decomposition products of alide in order to counteract any surface effects are described in P.R. XII, 9 and P.R. XIII, 3. Curve (5) of Fig. 3 shows the decomposition of an alide sample in a tube which had been coated with decomposition products at 200°. Although the decomposition was retarded initially, the coating gradually peeled off and the rate increased. However, the rate was still much less than in uncoated tubes. It was difficult to obtain uniform coatings by the methods tried, and the rate of decomposition was found to vary with the nature of the coating.

6). The presence of hydrogen gas at pressures of approximately one atmosphere somewhat accelerates the rate of decomposition, as is shown in Figure 2. Curve 3 represents the data of an experiment in which the hydrogen resulting from the decomposition of a sample of alide was removed from the reaction vessel often enough to prevent a hydrogen pressure of over 40 mm. In the experiments shown in Curve 2 the hydrogen was allowed to remain in the vessel; it is seen that decomposition is more extensive than in the experiment of Curve 3. Still larger hydrogen pressures were brought about in two ways: (a) An amount of hydrogen sufficient to produce a pressure of 571 mm. was introduced into the vessel at the beginning of the experiment which is represented by the open circles in curve 1 of Figure 2; (b) The amount of liquid alide used was made so large and the free space in the vessel was made so small that the hydrogen resulting from decomposition soon attained a relatively high pressure (solid circles of curve 1). In both cases the rate of decomposition is considerably greater than in experiments in which the hydrogen pressure was kept low (curves 2 and 3). (Progress Report XII, 6)*

The accelerating effect of the hydrogen pressure does, however, not continue indefinitely as shown by the fact that both curves 1 and 2 of Figure 2 ultimately level off. This result is probably due to the stabilizing effect to be discussed in following paragraphs.

7). All of the experiments at room temperature showed that the rate of decomposition of alide decreases markedly with time. This effect is illustrated strikingly in curves 1 and 2 of Figure 3: curve 1 represents the rate of decomposition of a fresh sample of alide; curve 2 the rate of decomposition subsequent to 120 days standing at room temperature and after the removal of the hydrogen that had accumulated during the first 120 days.

That this "stabilizing" effect is not due to the presence of hydrogen is clear not only from curve 2, which represents the rate of decomposition after hydrogen removal, but also by the results described in 6). To investigate this point further, samples of alide were heated at 40°C for varying lengths of time, the hydrogen produced was then removed and the subsequent rate of decomposition was observed without removing the alide from the tube in which it was heated. The results are shown in Figure 3. Attention is called to the fact that in the experiments recorded in this figure, hydrogen pressures correspond roughly to extents of decomposition since the quantities of alide and the volumes of the reaction systems were approximately the same in all cases.

Curve 3 of Figure 3 reproduces the results observed with a sample heated at 40°C for two days, and shows a marked retardation of decomposition. The effect is still more pronounced in curve 4. The latter curve, however, shows that heating at 40°C for 12 days (solid circles) has no advantage over 4 days heating at this temperature (⌽) since the points for the two experiments lie on the same curve.

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* Progress Report XII, 6 states that the addition of hydrogen produced a greater acceleration than did the accumulation of hydrogen in a small free space; even though the hydrogen pressure in the latter case soon became greater than in the former. Recalculation of the data after more precise calibration of the apparatus showed that there was no essential difference in the two cases as shown in curve 1, Figure 2.

Curve 4 also bears on the cause of the stabilizing effect of the 40°C heat treatment. The crosses on the curve represent the following experiment: Alide was heated for 8 days in a glass tube at 40°C; the tube was then opened and all of the volatile material (including the residual alide) was removed at low pressure and room temperature as rapidly as possible, and a fresh sample of alide, not preheated, was introduced into the tube and its rate of decomposition observed The fact that this sample underwent as slow decomposition as did the preheated ones shows that some non-volatile inhibitor was formed during the heating of the first sample.

Efforts to ascertain whether this inhibitor acts mostly by covering the walls of the vessel with a protective coating or whether it acts through some other type of mechanism were unsuccessful. It proved impossible to isolate, from the preheated alide, any substance which uniformly inhibited the decomposition. This failure is undoubtedly due to two causes. Unless the residue left in the tube after removal of the preheated alide is kept in a high vacuum for a long time or is itself heated in vacuum, it tenaciously retains some of the alide. For this reason it inflames violently in air, and cannot be effectively removed from the vessel. On the other hand, long pumping and moderate heating result in an alteration of the residue, with loss of hydrogen, and this altered residue is no longer effective as an inhibitor.

It seems probable, however, that some form of the material designated as polymer is the inhibitor.

8). That heating also stabilizes alide against catalytic effects of mild steel surfaces is shown by the fact that a sample of alide heated for 4 days at 40°C in the presence of polished mild steel wire and then observed for 100 days at room temperature in the presence of the curve, produced only 47 mm of hydrogen pressure. It should be stated, however, that alide does not decompose much more rapidly at steel than at glass surfaces.

9). The effect of iron carbonyl on the stability and inflammability of stable pentaborane (B_5H_9), (Progress Report XV, 2 and Progress Report XVI, 2), suggested that analogous studies be made with alide. 0.56 g. of alide and 8.65 cc. of iron carbonyl vapor (4.7 mol %) were introduced into the usual type of stability measuring system. A pale yellow solution was obtained which had a vapor pressure of 362 mm. at 26°C. (V. p. pure alide = 3[illegible]5 mm.) No immediate reaction was observed. The solution was carefully shielded from light.

After standing two days at room temperature, the solution had turned dark brown and the total pressure at 24°C was 1655 mm. (2.18 atm.). The vapor pressure of pure alide at this temperature is 347 mm., so at least 1308 mm. of the pressure was due to decomposition products.

The solution was cooled in liquid nitrogen until a limiting pressure of 487 mm. was obtained. The vapor pressure of pure carbon monoxide is about 575 mm. at -196°C., but should be somewhat lower over the alide solution. It seems, therefore, that alide reacts with iron carbonyl, even in the dark, liberating carbon monoxide. Upon distillation of the mixture, a negligible amount of iron carbonyl was recovered and a dark-brown residue was left in the vessel.

Since iron carbonyl decomposes so rapidly in alide, it cannot be employed as an inhibitor.

10). Experimental. An example of the system used in the room temperature studies is shown in Fig. 4. The system is attached to the usual type of vacuum line through the capillary stopcock, a. The stopcock lubrication is protected from alide vapor by raising mercury into the capillary U-bend. The high pressure manometer, b, is made of 5 mm. o.d. Pyrex tubing and has approximately one atmosphere of dry air in the sealed-off arm instead of a vacuum. The sample tubes are made of 10 mm. o.d., Pyrex tubing. The alide was introduced through the side-arm, c, which is then sealed off and the sampl heated to 40 ± 2°C. After the heating, the tube is attached to the rest of the system at x, and opened by dropping a glass encased iron plunger on the break-off inner seal. The hydrogen, produced during the heating, is pumped off, and the stopcock is closed and sealed with mercury. If the sample is not to be heated, the break-off inner seal is omitted and the alide is introduced directly through stopcock a. The volume of the entire system is approximately 7 cc. when the mercury level in the manometer corresponds to 0 mm. pressure.

In experiments above room temperature, the individual sample tubes were heated in a thermostated oven, maintained at 60 ± 1°. After a given time, the alide was condensed with liquid nitrogen, the tubes were opened and the hydrogen measured with a Toepler pump.

The alide used in these experiments (with stated exceptions) was carefully fractionated through -65°C and had a vapor tension of 119.5 mm. at 0°C.

The temperature of the room varied considerably over the period of these experiments, (from February through October). Thus during the spring months the room temperature range was 22 - 27° in the daytime; while during the summer the daytime temperature range was 27 - 35°C. At night the temperature was usually 5 - 7 degrees below the daytime temperature. These fluctuations are undoubtedly responsible for much of the irregularity in the data.

In earlier room temperature studies the hydrogen pressure was measured by condensing the alide with liquid-nitrogen and reading the residual pressure. This method produced a temperature gradient in the system which limited the precision of the measurements. (Progress Report VIII, 13.) Furthermore, with the accumulation of non-condensible gas in the system, it required increasingly longer times to condense all of the alide.

In later experiments, the total pressure at room temperature was measured and the hydrogen pressure obtained by subtracting the vapor pressure of alide, given by $\log P = 7.808 - \frac{1565}{T}$, from the total. In the range from 20° to 35°C, the vapor tension changes 2 mm. for every 0.1° temperature change so the accuracy of this method was limited to about 1%. In addition, the accumulation of polymer lowered the vapor pressure of the alide, which lowering amounts to about 2% after 40 days.

11). Summary

(a) Alide at 60°C decomposes at a rate which, although not large in percentage of decomposition, involves the generation of enough hydrogen to involve a hazard because of the high pressures that would result in a container in which the free space is relatively small. This decomposition occurs chiefly in the liquid phase and no methods of prevention have been discovered. The products of the decomposition are of several types - compounds, some soluble and others insoluble in alide, all of which react with water to give hydrogen, and a material of metallic appearance which is not soluble in alide and does not react with water at room temperature. The decomposition is accelerated by copper and its alloys, but is not markedly affected by steel surfaces.

(b) Alide at room temperatures decomposes very slowly but only in the liquid phase, giving rise to the alide-soluble type of product mentioned in (a). Although the decomposition over a long period of time is small, the initial rate of decomposition is sufficient to produce dangerous hydrogen pressures if the material is stored in a vessel having little free space. The initial rate of decomposition can, however, be markedly reduced by heating the alide for 4 days at 40°C, after which the hydrogen is removed and further decomposition is slow. The inhibitor, probably the soluble material mentioned in (a), is not volatile; for this reason the alide regains its reactivity if distilled from the vessel in which it was preheated. The inhibitor in the absence of alide or at even slightly elevated temperatures (i.e. above 40°C) loses its inhibiting property, and could for this reason not be isolated. No other effective inhibitors have been found.

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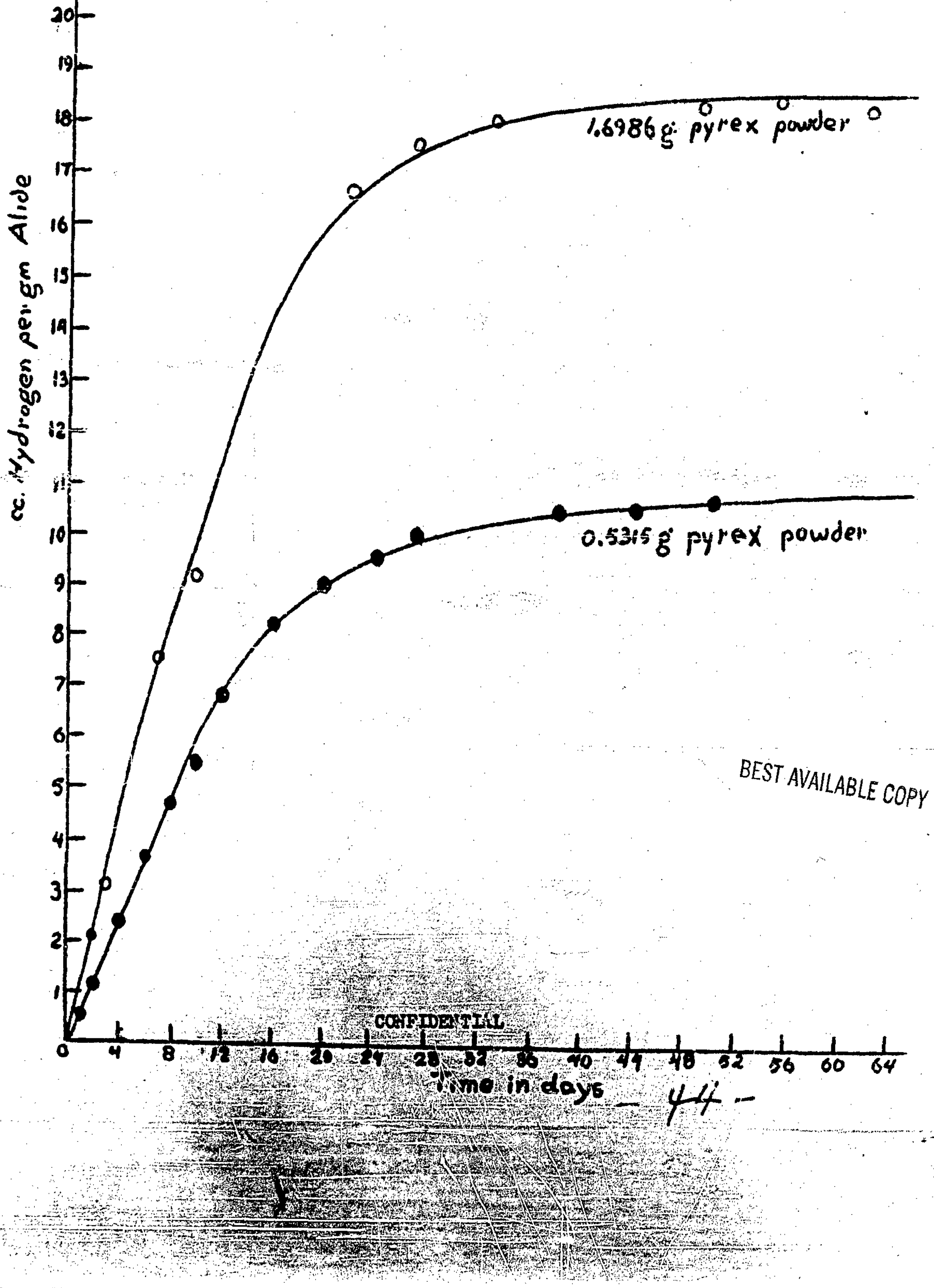
Figure 1. Decomposition of Alide in presence of Pyrex Glass Powder



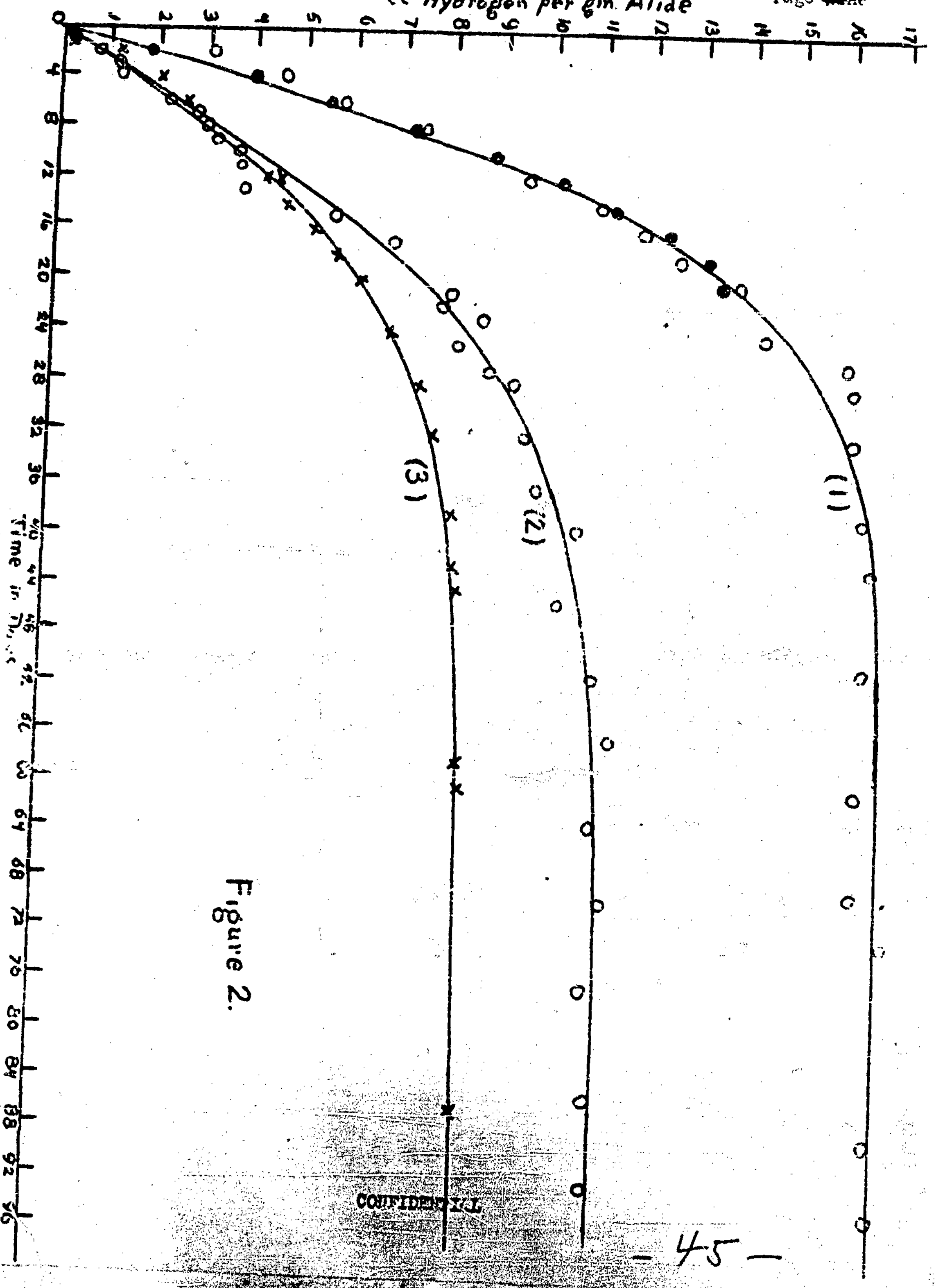

cc Hydrogen per gm. Alide
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Time in
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80
84
88
92
96
(1)
(2)
(3)

Figure 2.

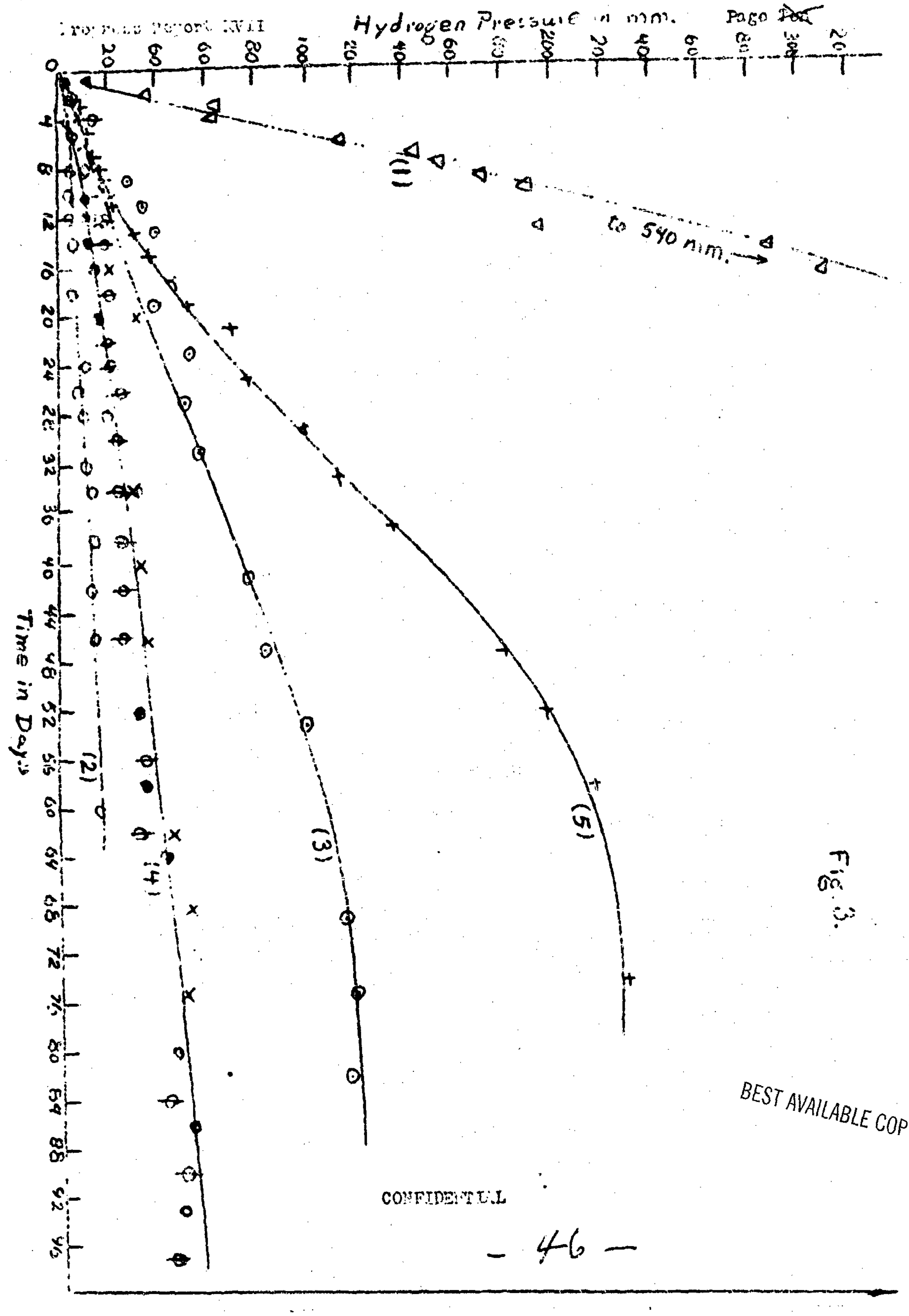

Hydrogen Pressure in mm.
0
20
40
60
80
100
20
40
60
80
200
20
40
60
80
300
20
Time in Days
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80
84
88
92
96
(1)
to 540 mm.
(2)
(3)
(4)
(5)

Fig. 3.

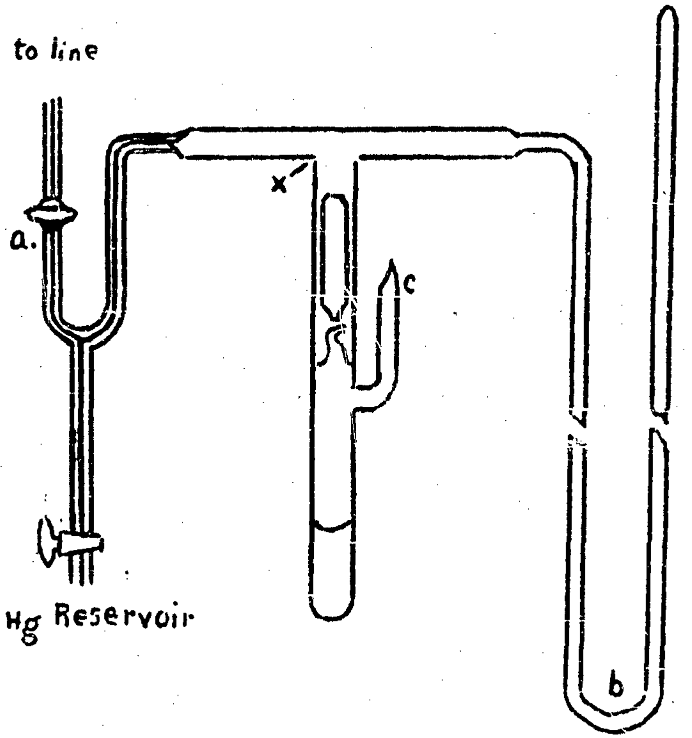


Fig. 4
Alide Stability System

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PROGRESS REPORT NO. XVIII

For the period January 1 - January 31, 1946
on
Contract No. N173s-10421[1]

By H. I. Schlesinger in Collaboration with
B. Abraham, C. Dillard, J. Farr, A. Finholt, R. A. Lad, and A. Wilzbach

I. PREPARATION OF LITHIUM ALUMINUM HYDRIDE

Detailed description of the preparation of the compound $LiAlH_4$ has hitherto not been reported because of a difficulty which has just now been overcome. When the reagents, lithium hydride, aluminum chloride and ethyl ether are mixed, a very slight reaction starts but usually soon dies down. Thereafter no noticeable reactio occurs for a variable period which may cover a few minutes or several hours. The major reaction then sets in very suddenly and so vigorously that it is difficult to control. The difficulty has finally been overcome by the discovery that if lithium hydride is suspended in a solution of ether containing a small amount of lithium aluminum hydride and the ether solution of aluminum chloride is then added, the reaction sets in at once and may be controlled by controlling the rate of addition of the aluminum chloride. If lithium aluminum hydride is not available from previous preparations, it may be prepared in small amounts in the vacuum system, or by carryi out a small preparation in which the mixture must be closely observed during the induction period, and rapidly cooled with an ice bath as soon as there is indication (temperature rise) that the main reaction is about to start. A detailed description follows:

> A three necked, one liter, round bottom flask having a mercury sealed stirro a glass stopper and a bulb condenser attached by ground glass joints was dried and flushed thoroughly with dry nitrogen. Into the flask was placed 100c.c. of a solution containing 7 to 15 grams of lithium aluminum hydride per 100 grams of diethyl ether. 30 grams of lithium hydride (Lithaloy Corp.--ground to 200 mesh) was dropped into the solution and the mixture was stirred for a short time. Through a dropping funnel at the top of the condenser a solution of 100 grams of aluminum chloride (Merck anhydrous, Reagent grade) in 500c.c. of diethyl ether was added slowly with continuous stirring. The addition rate was controll so that boiling observed in the reaction vessel was constant, indicative of a smooth reaction. Stirring was continued a short time after the addition of aluminum chloride was finished until the reaction appeared to cease. The products were filtered through a sintered glass disk under a pressure of dry nitrogen to remove the lithium chloride and excess lithium hydride. The ether was distilled from the filtrate at atmospheric pressure until a thick syrup was formed. The last of the ether was removed in Vacuo heating the solid product at 70°C.

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[1] Contract No. N173s-10421 is an extension of Contract Nos. N173s-9058 and s-9820

Other means for speeding the reaction were tried without success, such as addition of small amounts of iodine, aluminum, mercury and even hydrochloric acid. One variation of the experimental procedure which occasionally caused an immediate reaction was the rapid addition of ether to a mixture of solid aluminum chloride and lithium hydride. Only the method outlined above however, worked every time it was tried.

II. PREPARATION OF THE HYDRIDES OF GROUP V

Halogen compounds of arsenic, antimony, and bismuth were investigated to ascertain whether the substitution of hydrogen for halogen by means of lithium aluminum hydride could be accomplished in Group V as it had in Groups III and IV. Although the hydrides of arsenic, antimony and bismuth and the alkyl hydrides of arsenic are known, the alkyl hydrides of antimony and bismuth have not yet been made.

Arsine and stibine were prepared from lithium aluminum hydride by a reaction with the halogen derivatives of the elements in anhydrous ether. The yields of the hydrides were low (20 to 50%), due to partial reduction of the halides to the metal or other non-volatile solids. The reactions for forming the hydrides were probably as follows:

$$4AsCl_3 + 3LiAlH_4 \rightarrow 4AsH_3 + 3LiCl + 3AlCl_3$$

$$4SbCl_5 + 5LiAlH_4 \rightarrow 4SbH_3 + 5LiCl + 5AlCl_3 + 4H_2$$

Attempts to prepare bismuth hydride from bismuth chloride failed either because the reduction went to the metal or because the instability of the hydride prevented the isolation of measurable quantities.

Preliminary efforts to make Me_2SbH according to the equation: $4Me_2SbCl + LiAlH_4 \rightarrow 4Me_2SbH + LiCl + AlCl_3$ have not been successful. More careful preparation of the starting antimony compounds will be made however before eliminating the possibility of the formation of the desired alkylhydrides.

III. ALKYL SILANES

Mono-n-butyl silane, boiling point 56°C., was made in 76% yield by reaction between butyl silicon trichloride and lithium hydride in refluxing dioxane. The butyl trichloride was prepared in 83% yield from silicon tetrachloride and butyl magnesium bromide.

The preparation of diethyl silane was carried out on a semi-macro scale. One mole of diethyldichloro silane was gradually added to 2.25 moles of lithium hydride in 250 ml. of refluxing dioxane. The reaction mixture was filtered and fractionally distilled, yield 58.5 gms. of diethyl silane. This is 67% of the theoretical amount.

IV. ALKYL STANNANES

Preliminary studies for the large scale preparation of dimethyl stannane have been made. The preparation of large quantities of tin tetramethyl, by the reaction of methyl magnesium with stannic chloride, offered no difficulties, and 310 gms. of this product have been prepared. The reaction between tin tetramethyl and stannic chloride to produce dimethyl dichlorostannane also proceeded smoothly on a large scale. Reaction between 0.1 mole quantities of $SnMe_2Cl_2$ and $LiAlH_4$ in 100 ml. of dry dioxane yielded 0.043 moles of dimethyl stannane on fractional distillation. The low yield (43 percent) is in part accounted for by decomposition of dimethyl stannane at the elevated temperature required for distillation. Attempts to replace the $LiAlH_4$ with more readily available LiH were unsuccessful; there was no reaction between LiH and $SnMe_2Cl_2$ in refluxing dioxane. Similarly, it was impossible to prepare stannane from LiH and stannic chloride in ether.

V. ZINC COMPOUNDS

Experiments directed toward the preparation of the hydride and borohydride of zinc or of partially alkylated derivatives of these compounds have been initiated by a study of the reaction of lithium aluminum hydride with zinc alkyls. Although compounds of this type seem to have been obtained the experiments are as yet not sufficiently advanced for a definite report.

VI. THE PREPARATION B_5H_9 FROM DIBORANE

Note 1: In the following, the term "conversion" is used to represent the fraction of the diborane which has undergone chemical change. The yield is calculate from the equation:

$$5B_2H_6 \rightarrow 2B_5H_x + (15-x)H_2 \quad x = 9 \text{ or } 11$$

The amount of B_2H_6 which has actually undergone chemical change is used as the basis for the yield calculation. Thus, if 100cc. of B_2H_6 (S.T.P.) had undergone 50% conversion with a 50% yield, the actual amount of B_5H_9 + B_5H_{11} would be (0.4) (0.50) (0.50)(100) = 10 cc. (gas at S.T.P.)

Note 2: Figures and tables referred to in this section are found at the end of the report.

A. Survey of Results Obtained and Conclusions Thus Far Drawn:

(1) Catalysts have been found which lower the temperature at which diborane is converted into products containing B_5H_9 and B_5H_{11}. The catalysts so far used have, however, not been effective enough to lead to a satisfactory preparatory method.

(2) It has been shown that certain types of catalysts increase the ratio of B_5H_9 to B_5H_{11} and others decrease this ratio. Among the former are dehydrogenation catalysts such as Cr_2O_3 on Al_2O_3; among the latter are hydrogenation catalys such as nickel on a porous support.

(3) In a single pass system it was found that as the temperature was raised from 120°C to 190°C the yield (as defined) decreases, whereas the conversion

increases. The overall yield (i.e., the product of yield and conversion) remains fairly constant. If there is any significant change, the higher temperatures produce a slightly higher total yield but at the same time produce more undesirable by-products.

(4) At a fixed temperature (e.g., 120°C) the yield decreased rapidly as the contact time was increased from 0.1 min. to 5 min.; whereas, the conversion increased to a maximum and remained almost constant. (see figure 1) The contact time is the average time which a molecule spends in the catalyst bed, and is given by the ratio of bed depth to linear velocity.

(5) Increase of pressure, short of pressure high enough to maintain a liquid phase of B_2H_6 (pressures up to 33 atmospheres), had a detrimental effect on the yield. The high pressures increased the conversion but decreased the yield almost to zero.

From the preceding it follows that an effective preparative method would require the use of relatively low temperatures (e.g., 100-120°C). At these temperatures, however, it has not been possible, as yet, to obtain effective conversion. The use of a circulating system is valuable on this account because the amount of conversion can be increased by recycling the gas. Two lines of further research are indicated:

(1) Continued search for better catalysts.

(2) Study of the behavior of diborane in the liquid state at very high pressure.

EXPERIMENTAL PART

I. STATIC EXPERIMENTS:

Experiments in which B_2H_6 was heated in bulbs under various conditions resulted in rather poor yields of B_5H_9. The results obtained at pressures of 150-280 mm. were more satisfactory than those obtained at pressures of 24-30 atmospheres. The catalysts used were $Ni(CO)_4$, BCl_3, $BrBr_3$ and Cu powder + BCl_3. Those experiments in which the best results are obtained are listed in Table I. Examination of the table will show that the effect of the catalyst was very slight except in the case of BBr_3, in which case a reduction in yield was observed.

In view of the results so far obtained no further work is contemplated in static systems under conditions obtainable in glass apparatus. As soon as high pressure equipment becomes available, we plan to carry out experiments at pressures above the critical pressure of B_2H_6. It has been found that B_5H_9 and $Al(BH_4)_3$ are more susceptible to decomposition in the liquid phase than in the vapor, and it is hoped that B_2H_6 will behave in a similar fashion.

II. EXPERIMENTS IN THE CIRCULATING SYSTEM

Experiments in the circulating system have yielded the best results so far. By the use of a dehydrogenation catalyst, it has been possible to obtain almost pure B_5H_9 in a yield of 50% but with low conversion per pass. The drawback to the method is the length of time required. Experiments in a single-pass system, which will be discussed below, have shown that conditions which results in high yields have, unfortunately, been unsatisfactory from the point of view of the amount of B_2H_6 converted. In other words, high yields in the sense used here accompany low conversion, and vice versa. The results in the circulating system are similar; however high conversion is obtained by recycling the gas.

The best results obtained in the circulating system under each set of conditions are listed in Table II. The use of catalysts makes it possible to operate at low temperatures and to obtain products of higher purity. The best catalyst found for the production of B_5H_9 was a dehydrogenation catalyst (30% Cr_2O_3 on Al_2O_3) which had been artificially aged to the point at which it was no longer useful for hydrocarbon preparations. It was found later, in the course of the experiments with the single-pass system that plant spent catalysts are also effective for the preparation of B_5H_9. A fresh dehydrogenation catalyst gave poor results.

By the use of a hydrogenation catalyst (nickel on a porous support) it is possible to prepare almost pure B_5H_{11}. The product obtained melted at -129°C, the melting point recorded by Stock for this compound.

The circulating system operated at pressures up to 500 mm. Variations of the operating pressure from 120 to 500 mm. did not change the conversion nor the yield. The fact that varying the pressure in the single-pass system from 200 mm. to 2 atmos. also did not change the conversion-yield ratio indicates that pressures of at least 2 atmos. could be used in the circulating system.

III. EXPERIMENTS IN THE SINGLE-PASS SYSTEM

In the circulating system, the composition of the gas changes continuously. Since the variation in the composition might affect the type of reaction taking place, experiments in a single-pass system were undertaken. It was found that the dehydrogenation catalysts most effective in the circulating system were also effective here. The results obtained at 120°C with varying contact times are shown in Figure 1. The contact time was varied by changing either the flow rate or the bed dimensions. It can be seen from the results that both high yield and high conversion are incompatible. Indications from other experiments are that curves of similar shape are obtained at higher temperatures. The problem here is not one of rate; it is rather the specificity of reaction products. A catalyst that increases the rate of pyrolysis will not alter the situation unless it also increases the yield of B_5H_9.

The purity of the material obtained in the single-pass system was lower than that in the circulating system. This is probably due to the fact that B_5H_{11} (m.p. -129°C) is carried through the -80° trap used to condense B_5 fractions in the circulating system, and converted to B_5H_9 or higher hydrides. In one experiment in the circulating system, it was observed that the material collected was liquid at -80° after the first 30 minutes, indicating a relatively high percentage of B_5H_{11} in the product, whereas the material found at the end of the six hours was solid.

A series of experiments using no catalysts, or catalysts such as etched aluminum rivets and brass turnings, was run at various temperatures but at constant contact time. These results are shown in Figure II. Here again one can see that high yields are accompanied by low conversion. With these catalysts, the material obtained at temperatures below 150°C contained a large amount of B_5H_{11}.

Other flow experiments are listed in Table III.

IV. PREPARATION OF B_5H_9 FROM LITHIUM BOROHYDRIDE

In an effort to prepare B_5H_9 more directly than from diborane, we have begun a study of the reaction of boron halides on lithium borohydride. At lower temperature this reaction yields diborane; it was conceivable that at somewhat higher ones, B_5H_9 and B_5H_{11} might be directly obtained. The experiments are as yet incomplete since only two temperatures have been used. Above 150°C the yields are low; at 105°C the results have been far more promising. Only boron bromide as the halide has as yet been studied.

Calculations of the yields in these preliminary experiments had to be based on the somewhat arbitrary assumption that one mole of BBr_3 reacts with three of $LiBH_4$. In one of the most satisfactory experiments 2.27 m. moles of BBr_3 were used. On the assumption stated, this quantity of BBr_3 should have reacted with 6.81 m. moles of $LiBH_4$, a total of about 9 m. moles of boron. After completion of the reaction at 105°C, 2.5 m. moles of boron was obtained as B_2H_6, an equal amount as B_5 fraction, 0.2 m. moles as B_4H_{10}. Some $B_{10}H_{14}$ was obtained but not measured since the total quantity was so small. The materials were heated in a sealed tube for 16 hours without use of any solvent. Other experiments seemed to give more favorable results but the quantities were too small for reliable measurement.

It is intended to continue these experiments with other halides, and with the use of solvents if satisfactory ones can be found. It is too early, however, to estimate the likelihood of success.

DISTRIBUTION

cc: (2) Col. J. H. Sams, Army Liaison Officer, Navy Department
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20 K. Wilzbach
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TABLE I

STATIC EXPERIMENTS

CATALYST	TIME min.	TEMP °C	PRESSURE mm.	CONV. %	YIELD %
NONE	15	170	150	65	25.
NONE	60	170	150	85	15.
BBR_3	240	120	280	71	1.7
BCl_3	4500	120	280	78	31.
$Cu+BCl_3$	4500	120	280	77	21.
$Ni(CO)_4$	60	170	150	85	15.
NONE	120	60	24-30 atmos	0	0.
NONE	2480	60	"	25	0.
NONE	120	110	"	45	12.
BCl_3	1440	120	26 atmos	68	14.

TABLE II

CIRCULATING SYSTEM

(Flow rate = 600 cc/min)

CATALYST	TIME	TEMP	PRESSURE	CONV.	YIELD	M.P. of crude product
	Hrs.	°C	mm.	%	%	
Hg Vapor	2.	250	126	87.	57.	
Glass Helices	3.	250	120	95.	66.	-58
Glass + 1% HCL	1.	250	120	93.	46.	
Glass + H_2	2.5	250	120	94.	46.	
Stainless Steel	2.2	250	103	95.	55.	-68
Dehydrocyclization	1.	120	160	63.	40.	-64
Cracking	4.	140	150	96.	19.	
Dehydrogenation	6.	115	180	86.	54.	-47.8
*Dehydrogenation	6.	135	500	45.	50.	-47.3
Hydrogenation	6.5	195	150	80.	64.	-129

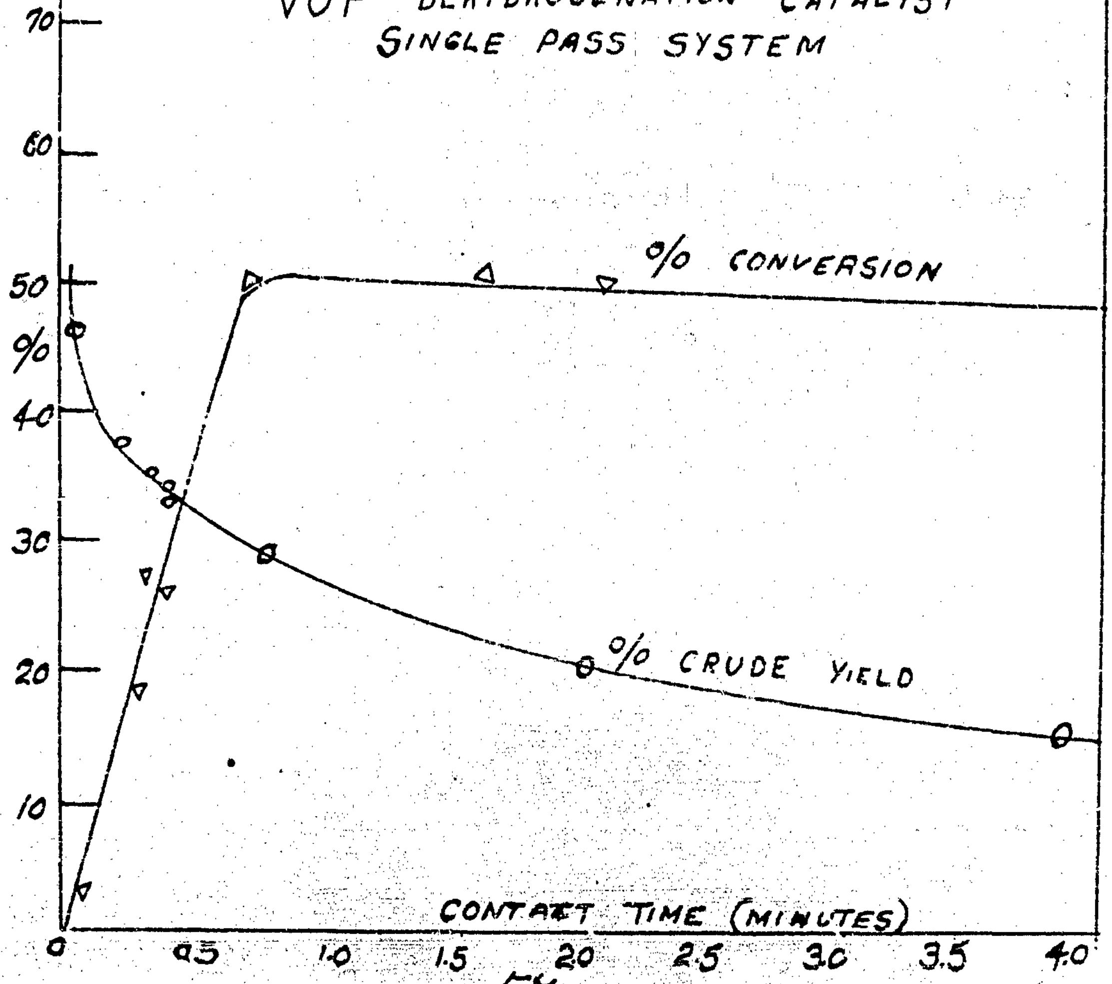
* B_5H_{11} passed through this catalyst with no effect other than thermal cracking.

TABLE III

SINGLE PASS SYSTEM					
CATALYST	FLOW RATE cc/min	TEMP. °C	PRESSURE mm.	CONV. %	YIELD %
NONE	5.8	115	1325	2.7	47.
HYDROG.	4.0	120	1370	52.	7.
GLASS HELICES	2.4	171	320	10.	60.
LONG PATH. - NONE	4.8	126	760	2.	82.
HOT NICHROME WIRE	2.4	161	760	41.	19.
	3.3	151	300	33.	27.
HG-VAPOR ARC (U.V.)	1.8	?	300	64.	10.
Fe TILINGS (induction heat)	27.	125	100	5.	55.
OIL	5.3	140		18.	14.

FIGURE 1
% YIELD AND % CONVERSION
VS
CONTACT TIME

VOP DEHYDROGENATION CATALYST
SINGLE PASS SYSTEM



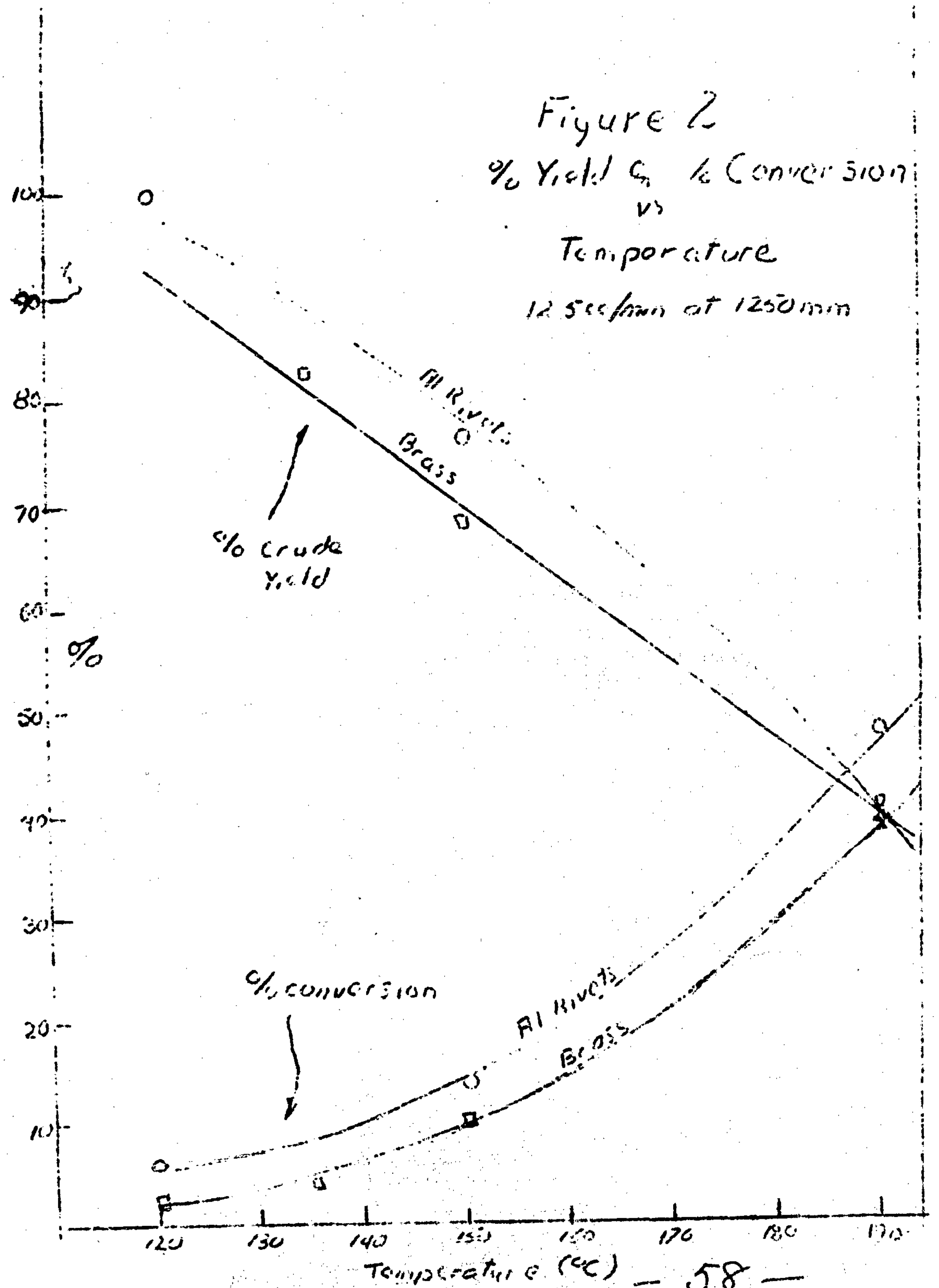


Figure 2
% Yield & % Conversion
vs
Temperature
12.5 cc/min at 1250 mm

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PROGRESS REPORT NO. XIX
For the Period February 1 - February 28, 1946

on

Contract No. N173s-10421[1)]
BuAero TED NRL No. 3401

H. I. Schlesinger in Collaboration with
B. Abraham, C. Dillard, J. Farr, A. Finholt, M. Gerstein, R. A. Lad, and K. Wilzbach

I. Preparation of Beryllium Hydride and of Methyl Beryllium Hydride.

Beryllium methyl hydride was prepared by the reaction of beryllium methyl and dimethyl aluminum hydride according to the equation:

$$Be(CH_3)_2 + AlH(CH_3)_2 \rightarrow Al(CH_3)_3 + BeH(CH_3)$$

An excess of beryllium methyl was used. Since the beryllium methyl hydride is non-volatile, the excess beryllium alkyl together with the aluminum methyl were removed by heating the mixture to 150°C in vacuo. The beryllium methyl was prepared according to Gilman and Schultze, J. Chem. Soc., 1927, p.2663. The dimethyl aluminum hydride was prepared from lithium aluminum hydride and aluminum methyl as described in Progress Report No. XII (p. 3). An analysis of the new compound was made by hydrolyzing it with water and acid for the available methane and hydrogen while the beryllium was weighed as the oxide. Calc'd for $BeCH_3H$: CH_3 and H, 64.0%; Be, 36.0%. Found: CH_3 and H, 61.0; Be, 36.1.

Beryllium methyl hydride is a white non-volatile solid. It begins to decompose when heated to 170°C in vacuo. The material hydrolyzes rapidly in water and bursts into flames when it is thrown on water in air. The material is not spontaneously inflammable in air nor does it fume in air of ordinary humidity. Although it appeared completely soluble in the aluminum methyl which was a product of the preparation, it did not redissolve readily in this solvent after it had once been removed. Solubility in ether also appeared to be small.

The preparation of beryllium hydride has been attempted. The two methods which are being pursued at present are indicated by the following equations:

$$Be(CH_3)_2 + 2AlH(CH_3)_2 \rightarrow 2Al(CH_3)_3 + BeH_2 \text{ and}$$
$$Be(CH_3)_2 + LiAlH_4 \xrightarrow{\text{ether}} LiAl(CH_3)_2H_2 + BeH_2 \downarrow$$

Products have been obtained which on hydrolysis gave 2500 to 3000cc of gas per gram. This is considerably lower than the theory for the hydride (4000 cc/gm) but higher than that for the methyl hydride (1794 cc/gm). The amount of gas expecte from the hypothetical compound, $Be(AlH_4)_2$, is 2515 cc/gm. It is evident that the products thus far obtained are not homogeneous; improvements in the experimental procedure have been planned in the hope that more difinitive results may be obtained.

[1)] Contract No. N173 s-10421 is an extension of contract Nos. N173 s-9058 and s-9820

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II. Preparation of Zinc Hydride

Zinc hydride was prepared by reaction between zinc methyl and either dimethyl aluminum hydride or lithium aluminum hydride. It is a white, non-volile solid, insoluble in ether. It does not seem to react with air, and the hydrolysis is slow except in the presence of acid or base. Hydrolysis yields 665cc of gas per gram of solid.

Zinc Hydride from Dimethyl Aluminum Hydride---Dimethyl aluminum hydride was prepared by heating trimethyl aluminum with an excess of lithium aluminum hydride at 70°C, as described in Progress Report XII (p. 3). When zinc methyl was condensed on this compound there was immediate formation of a white solid. Volatile material was removed from the solid by evacuation at 50°C. (During this operation the zinc hydride sometimes darkened--the darkening could not be correlated with the proportion of the reactants or the conditions of reaction. Because of this apparent decomposition exact yields cannot be given.

Zinc Hydride from Lithium Aluminum Hydride---A more satisfactory method of preparing zinc hydride was by action of zinc methyl on an excess of ether solution of lithium aluminum hydride. The precipitate, which formed at once, was removed by filtration, washed several times with dry ether, and dried in vacuo at 50°C. The product was white.

Analysis of Zinc Hydride---Analysis was accomplished by measuring the hydrogen liberated by hydrolysis and determining the amount of zinc in the resulting solution by precipitation with 8 hydroxy quinoline.

	Hydrogen Evolution per gram	Per cent zinc
Calculated for ZnH_2	665 cc	97.0
Observed (two trials)	664 cc	96.1

These results give $Zn_{0.99}H_{2.00}$ as the empirical formula for zinc hydride.

III. Preparation of Zinc Borohydride

Zinc borohydride was prepared from zinc hydride and excess diborane in ether. Upon evaporation of the resulting solution there remained a white solid, which turned grey when the temperature was raised to 50°C in order to remove the last traces of ether. The grey solid reacted vigorously with water to yield 1910cc of gas per gram, in good agreement with the value of 1890cc per gram calculated for $Zn(BH_4)_2$. Aliquots of the hydrolysis solution were analyzed for zinc by precipitation with 8 hydroxyquinoline and for boron by distillation as methyl borate and titration in the presence of mannitol.

The following results were obtained from two preparations of the borohydride.

	Sample I	Sample II
Weight	0.454 g.	0.545 g.
Hydrogen liberated per gram	1935 cc.	1908 cc.
m. e. hydrogen	39.1	48.5
m. e. boron	9.7	10.8
m. e. zinc	4.6	5.5
Observed formula	$Zn_{0.97}B_{2.04}H_{8.18}$	$Zn_{0.96}B_{1.91}H_{8.02}$

These results check the formula $Zn(BH_4)_2$ fairly well, but an attempt will be made to prepare the compound from zinc chloride and lithium borohydride (in ether) to get an independent analysis.

IV. Reactions of Silicon Compounds with Borohydrides

In Progress Report VII, pp. 4-5, the reactions of ethyl silicate and of silicon tetrachloride with aluminum borohydride were described. The results indicated that silicon borohydride does not exist. Since the experimental basis for this conclusion was meager and additional silicon compounds have become conveniently available, additional experiments have been carried out. Since they led to the same conclusion as the former ones, the results are briefly reported as follows to complete the record:

(a) Diethyl silicon chloride reacts slowly at 50° in the presence of dioxane to give diborane and a mixture probably consisting chiefly of diethyl silicon hydride. With aluminum borohydride at 25°C the Et_2SiCl_2 reacts quantitatively to yield Et_2SiH_2, B_2H_6 and $AlCl_3$.

(b) Silico chloroform and dichlorosilane react with aluminum borohydride at 25°C to yield silane and diborane.

(c) Ethyl Silicon Hydride does not react with diborane and only slightly with aluminum borohydride. Products not identified.

(d) Siloxane, $(SiH_3)_2O$, at 60°C reacted with diborane producing silane and a white solid too small in amount for identification. With aluminum borohydride siloxane produced diborane, silane and a sublimable white compound, spontaneously inflammable in air. Although it is not likely that this substance will be useful, we may study it further if time permits.

Preparation of Larger Quantities of Diethyl Silane and of Dimethyl Stannane.

Since the new methods (see Progress Reports XII, p. 2, XIII, p. 4, XV pp.3- and XVI pp. 3-5) of preparing these compounds were developed on a very small scale, two preparations with somewhat larger quantities were carried out to make certain that no unexpected difficulties would arise.

Of the diethyl silane 500cc was prepared from diethyl silicon chloride and lithium hydride without alteration of the procedures previously described. The yields were approximately 70% of the purified compound. We now have about 700cc of the compound on hand.

In the preparation of dimethyl stannane in larger quantities difficulty was encountered in removing the dioxane used as a solvent for the reactants, dimethyl tin chloride and lithium aluminum hydride. At ordinary pressures removal of the solvent required a temperature of 140°C which resulted in considerable decomposition of the product. At reduced pressure (approx. 20mm.) and a temperature of 90-100°C most of the solvent could be removed and a 74% yield was obtained (66g. of dimethyl stannane from 130g. of dimethyl tin chloride and 24g. of lithium aluminum hydride).

When low temperature traps are used in the distillation process, the use of dioxane is disadvantageous since it solidifies at 12°C. For this reason lithium aluminum hydride was prepared in n-butyl ether solution. Lithium hydride (10g) and 2g. of previously prepared lithium aluminum hydride were added to the solvent and aluminum chloride was then gradually introduced. The mixture was cooled periodically by immersing the reaction vessel in a water bath, a precaution seldom needed when ethyl ether is used because the low boiling point of the latter almost automatically prevents undue temperature rise. After all the aluminum chloride had been added the solution was allowed to stand for some hours. Then 65g of dimethyl tin chloride was added in the usual way. The reaction product was distilled at 15mm. and room temperature; the material collected at -80°C was practically free from the ether after distillation through a column; 28g. (63% yield) of the pure substances was obtained. Undoubtably better yields could be secured by further study of the reaction conditions.

We have at present on hand;

464g. of diethyl silane
66g. of dimethyl stannane
5g. of dipropyl silane.

V. Preparation of B_5H_9

We have been preparing B_5H_9 in small quantities in anticipation of a demand of a sample for Dr. Stegeman. About 4g. of the pure material are on hand.

No noteworthy progress has been made in improvement of the preparative method. Two additional catalysts--boron phosphate and a dehydrogenation--polymerization catalyst, furnished by Universal Oil Products Co. have been tested. They proved less effective than catalysts previously used. Apparatus for the high pressure tests is being made in our shop.

VI. Work Proposed for the Immediate Future.

As a result of the conference at the Naval Research Laboratory on March 12, we are examining in more detail the procedure for preparing aluminum borohydride from lithium aluminum hydride (Progress Report No. XIII, p. 1) and are making additional studies on the stabilization of the former. Likewise we are making observations on the relative rate of deterioration of lithium borohydride and of lithium aluminum hydride by air of ordinary moisture content both in the case of the dry salts and of their ether solutions.

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PROGRESS REPORT NO. XX
For the period March 1 - March 31, 1946

on
Contract No. N173s-10421[1)]
BuAero TED NRL No. 3401

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1) Contract No. N173s-10421 is an extension of contract Nos. N173 s-9058 and s-9820

H. I. Schlesinger in Collaboration with
B. Abraham, C. Dillard, J. Farr, A. Finholt, M. Gerstein, R. A. Lad, and K. Wilzbach

I. Preparation of aluminum borohydride

As a result of the conference at the Naval Research Laboratory on March 12, additional studies have been made on the preparation of aluminum borohydride from lithium aluminum hydride and diborane (P.R. No. XIII, p.1). The results of the experiments which have been performed are listed in Table I. These experiments were intended to determine in a few high spot tests, the most important factors in an efficient use of this preparation. Two runs (Nos. 1 & 2, Table I) were made in a circulating system; six others were made in a single pass system. The yield of aluminum borohydride was found by isolating the compound in the vacuum line by the usual fractionation procedure.

Run No. 4 illustrates most clearly the effect of temperature on the time-yield. Increasing the temperature from 75 to 90°C, with other conditions being identical, increased the yield obtained in 12 minutes from 2.9% to 19.7%. A further increase in temperature was precluded since lithium aluminum hydride begins to decompose around 100°C. Even at 90 and 95°C in this reaction the evolution of some non-condensible was evident. There was also a change in appearance of the residue which became caked and grey at 90°C while at 70°C it stayed white and powdered. The lithium aluminum hydride used in all the runs had been ground in a dry box. Addition of powdered glass was ineffectual in preventing caking at 90°C. Only in Run No. 3 in which the mixture was agitated with a magnetic stirrer was caking eliminated.

The effect of pressure was shown in Runs No. 7 and 8. With otherwise identical conditions, increasing the pressure from one atmosphere to two atmospheres increased the yield by 11 percent. This appears to show that the reaction is faster at the higher pressure although the rate should also be checked at higher and lower pressures than those used in Runs 7 & 8. While not conclusive, the experiments indicate that a semi-works study of the reaction should include an evaluation of the pressure effect.

As might have been expected, the use of a large excess of diborane did speed up the reaction. In Run No. 4, in a 19 minute period at 90°C where the flow rate was 6870 cc/hr., a 42.2% yield was obtained. In Run No. 3, on the other hand, the flow rate was only 2328 cc/hr., and, in 20 minutes at 90°C the yield was only 21.6%. Thus the lower flow rate, with other conditions being the same, cut the yield almost in half.

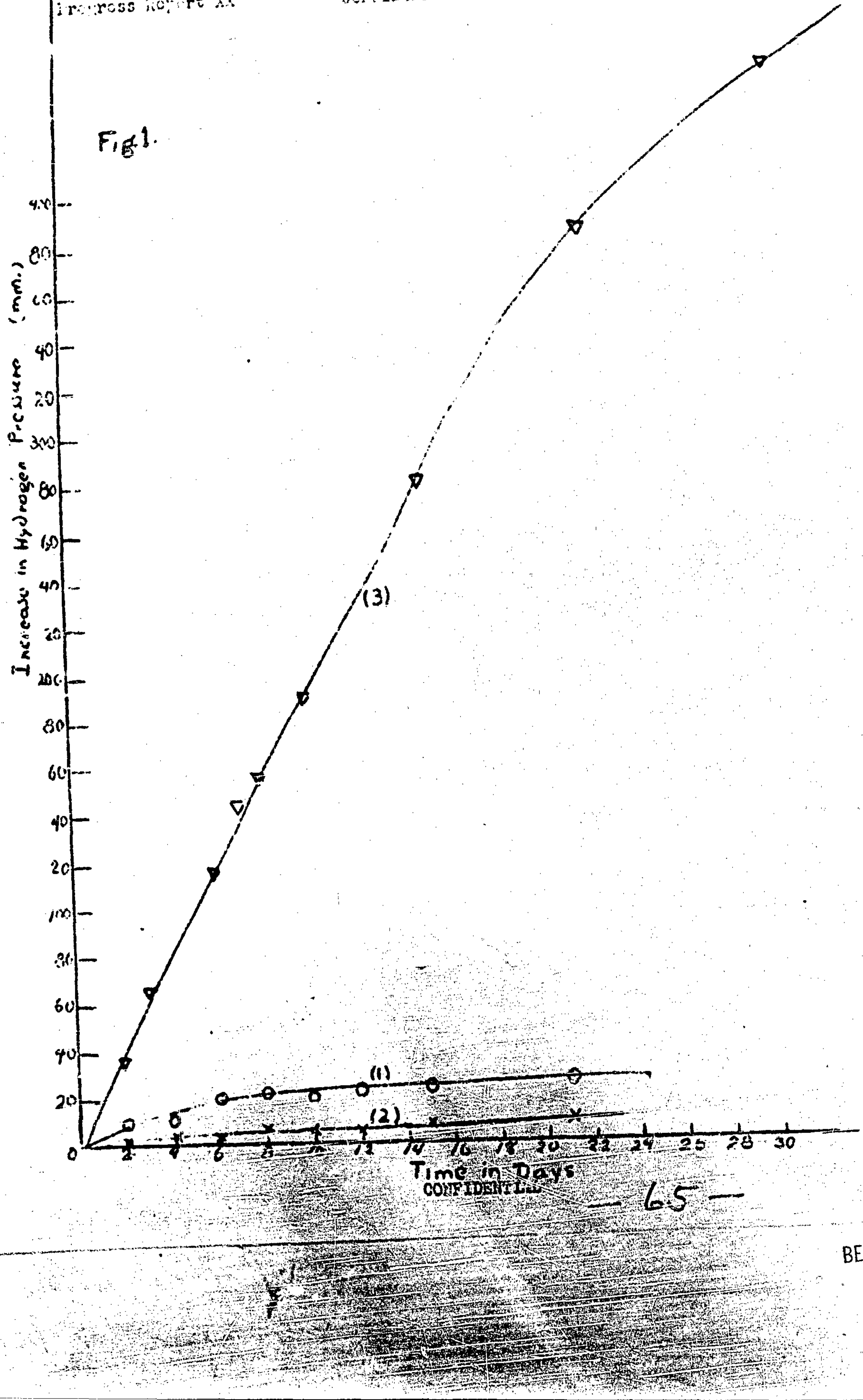
TABLE I

Run no.	Amount of $LiAlH_4$	Rate of flow of B_2H_6 (cc (STP) per hour)	Temp	Time	Pressure	Yield of $Al(BH_4)_3$	
1.	0.747g.	30,000 (Circulating system)	70°C	5 hrs.	250-300 mm.	380 cc	86.3%
2.	0.955g.	30,000 (Circulating system)	70°C 90°C	3 1/4hr. 3 3/4"	400-500 mm.	505 cc	89.3%
3.	0.367g. +5g. powdered glass (stirred)	2,328 (single pass system)	90°C	20 min.	2 atm.	47 cc	21.6%
4.	0.341g.	6,870 (S.p.s.)	75°C 90oC 90°C	12 min. 12 min. 7 min.	2 atm. 2 atm. 2 atm.	9.3 cc 63. cc 72. cc 144.3 cc	2.9% 19.7% 22.5% 45.1%
5.	0.300g.	5,500 (s.p.s.)	90°C 95°C	35 min. 25 min.	2 atm. 2 atm.	90. cc 37. cc 127. cc	51% 21% 72%
6.*	0.479g. +3g. powdered glass	3,300 (s.p.s.)	95°C	37 min.	1 atm.	10.9cc	3.9
7.	0.617g. +3g. powdered glass	2,820 (s.p.s.)	95°C	60 min.	1 atm.	147 cc	40%
8.	0.570g. +3g. powdered glass	2,750 (s.p.s.)	95°C	57 min.	2 atm.	172 cc	51%

* The B_2H_6 used in this experiment was found to be very poor in quality, containing a high percentage of ethane.

The experiments do show that the process probably can be developed into a feasible industrial preparation of aluminum borohydride. They also show that temperature, pressure, and concentration of diborane (or rate of flow) are important factors in obtaining an efficient process. The choice between this method of making aluminum borohydride and the lithium borohydride-aluminum chloride reaction will have to be made on an engineering basis, and may require semi-works experiments.

Fig 1.


Increase in Hydrogen Pressure (mm.)
400
80
60
40
20
300
80
60
40
20
200
80
60
40
20
100
80
60
40
20
0
2
4
6
8
10
12
14
16
18
20
22
24
25
28
30
Time in Days
(1)
(2)
(3)

II. Stability of Alide

It has been found that samples of alide which were aged by long standing or by heating at 40°C for several days were more stable when subsequently stored at room temperatures. (P.R. XVII, 4-5, also Fig. 3). It seemed probable that some form of the material designated as "polymer" was the inhibiting agent. Several further experiments have now been performed to support this hypothesis. In one instance (1) a solid form of this "polymer" was isolated, and when added to unstabilized alide. it inhibited decomposition. In a second experiment,(2) an alide solution containing "polymer" was poured into a fresh glass surface with little subsequent decomposition Both experiments indicate that the stabilizing effect is a property of the "polymer solution and is not due to a change in the glass surface of the vessel in the process of forming the "polymer".

1. A sample of "polymer" was prepared by heating aluminum borohydride for several days at 80°C. The soluble "polymer" was separated from insoluble material by filtering through a sintered disk. As much aluminum borohydride as possible was removed from the "polymer" by distillation in vacuo at room temperature. An atmosphere of nitrogen was admitted to the white solid and it was found to weigh 0.0800 grams. To this solid was added 0.500 gram of unstabilized alide, in which the solid dissolved completely. The mixture was sealed off in a tube of approximately 15cc volume. After standing at room temperature for 11 months,the tubes were opened, and the accumulated hydrogen was measured in the Toepler pump system. The sample to which the "polymer" was added showed no visible evidence of decomposition and yielded 2.1 cc of hydrogen, or 4.2 cc of hydrogen per gram alide. The second sample contained a metallic precipitate. It yielded 6.55 cc of hydrogen, or, 13.1 cc hydrogen per gram alide.

2. Two identical samples of 0,56 grams of alide were heated at 40° for four days in the manner described in P.R. XVII, 6. One sample tube (Sample 1) was then attached to a manometer system and opened The hydrogen was removed as described in P.R. XVII, 6. The other tube (Sample 2) was attached to a new storage tube in such a manner that the alide could be poured in vacuo. The original tube was rinsed by distilling in a little alide and then allowed to drain for one half hour. The original tube was detached by sealing off at a constricted point, and the new tube was attached to the manometer system. The subsequent increase in hydrogen pressure is shown in Fig. 1, where the circles represent sample 1 and the X's represent sample 2. The increase in pressure for a comparable sample of unstabilized alide is given by curve 3. (See P.R. X, 3)

III. Preparation of B_5H_9

High pressure equipment has now been assembled to study the decomposition of diborane at pressures up to 1000 pounds per sq. inch, The studies will be directed towards the preparation of B_5H_9, which may form rapidly under stringent conditions. The first experiments will be run in stainless steel bombs without catalysts and at room temperature. Tests under varying conditions have been planned.

Several other series of experiments are now in progress to ascertain the nature of the thermal decomposition of diborane. These include:

1. Studies of the rates of formation of B_5H_9, B_4H_{10}, and higher hydrides at various temperatures and pressures of diborane.

2. Studies of the thermal decomposition of B_5H_9 at various temperatures.

3. Preparation of B_4H_{10} in appreciable quantities by a Wurtz reaction between sodium amalgam and B_2H_5Br, and subsequent studies of the thermal decomposition of B_4H_{10}.

IV. Deterioration of Lithium Aluminum Hydride and Lithium Borohydride in Moist Air.

The rates of decomposition of solid lithium aluminum hydride and lithium borohydride in air of 80% humidity at 25°C. were compared. Samples of the powdered salts were placed on watch glasses, and, at intervals, portions were weighed out and hydrolyzed with water. The results below indicate that the deterioration of soli lithium borohydride is much more rapid than that of solid lithium aluminum hydride.

$LiAlH_4$				$LiBH_4$	
Min.	cc H_2/g.	Percent Theoretical	Min.	cc H_2/g.	Percent Theoretical
0	2178	92	0	3900	95
15	2070	88	90	1345	33
120	1915	81			
1080	756	32			

On the other hand, lithium aluminum hydride seemed to hydrolyze more rapidly than lithium borohydride in ether containing about 4g. solid per 100g. solution. There was noticeable evolution of hydrogen from the solution of lithium aluminum hydride, and a precipitate formed within 15 minutes. The solution of lithium borohydride was still clear after an hour had elapsed.

The difference in the rates of deterioration of solids and solutions may be ascribed to formation of a protective coating on solid lithium aluminum hydride.

V. Preparation of Substituted Silanes

The preparations of alkyl substituted silanes by reaction between the chlorides and either lithium hydride or lithium aluminum hydride were continued. We now have available:

Compound	g.	Prepared From	Prepared In	Yield
Ethyl silane	16	$LiAlH_4$	dioxane	80%
Diethyl silane	484	LiH	dioxane	75%
Propyl silane	33	$LiAlH_4$	dioxane	70%
Dipropyl silane	44	$LiAlH_4$	ether	80%
Butyl silane	27	LiH	dioxane	73%
Phenyl silane	55	$LiAlH_4$	ether	77%

~~-6-~~

In a preliminary experiment diethyl silane was prepared in 25% yield from the chloride, sodium hydride, an aluminum chloride in refluxing dioxane. No reaction occurred in the absence of aluminum chloride. The reaction will be investigated further.

VI. Preparation of Lead Hydrides

Inconclusive results were obtained in an attempt to prepare lead trimethyl hydride from the chloride and lithium aluminum hydride. Study of the reaction will be continued.

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PROGRESS REPORT NO. XXI
For the period April 1 - April 31, 1946

on

Contract No. N173s-10421[1]
BuAero TED NEL No. 3401

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[1] Contract No. N173s-10421 is an extension of contract Nos. N173 s-5058 and s-9820

H. I. Schlesinger in Collaboration with
B. Abraham, C. Dillard, J. Farr, A. Finholt, M. Gerstein, and K. Wilzbach

I. The Preparation of Aluminum Borohydride.

The most satisfactory methods for the preparation of aluminum borohydride thus far developed are (a) the action of alkali metal borohydrides on aluminum chloride, and (b) the reaction of lithium aluminum hydride on diborane. As already reported the former method involves some hazard in mixing the reactants and in disposing of the residues; the second is slower than desirable under conditions hitherto used. To overcome these difficulties we are reinvestigating the possibility of carrying these reactions out in suitable solvents. Earlier attempts in this direction had involved the use of hydrocarbons which resulted in no improvement, and of dibutyl ether, in which no reaction took place until the temperature was raised to 130°C, under which conditions a complex product containing butane and diborane was obtained.

Diethyl ether offers a number of theoretical advantages. Both lithium borohydride and lithium aluminum hydride are prepared in ether solution and could thus be used without previous removal of the solvent if the reaction with aluminum chloride which is also soluble in ether were carried out in the same solvent. In our previous experiments we nevertheless avoided the use of diethyl ether because we did not then know of any method of regenerating the aluminum borohydride from its extremely stable etherate. Recently we have found that the borohydride may be displaced from the etherate by addition of an excess of aluminum chloride:

$$Al(BH_4)_3 \cdot Et_2O + AlCl_3 \rightarrow Al(BH_4)_3 + AlCl_3 \cdot Et_2O \quad (1)$$

This procedure, if it could be applied to the preparation of the borohydride, is particularly attractive in the case of the lithium aluminum hydride reaction because the etherate of aluminum chloride is one of the starting materials for the lithium compound. The displacement of aluminum borohydride by aluminum chloride has given yields as high as 80-85% and further improvement seems likely.

A study has been started of the direct conversion of lithium aluminum hydride to aluminum borohydride according to the reaction:

$$3\ LiAlH_4 + 3BCl_3 \xrightarrow{ether} Al(BH_4)_3 + 3LiCl + 2AlCl_3 \quad (2)$$

Preliminary results indicate that in the presence of an excess of $LiAlH_4$, boron chloride reacts to form a non-volatile product (presumably $Al(BH_4)_3 \cdot Et_2O$) which gives off diborane on further treatment with boron chloride. Thus far, however, only poor yields of aluminum borohydride have been obtained on addition of aluminum chloride.

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In order to determine the reason for the unsatisfactory results, the probable intermediate steps are being studied. These are the following:

$$3LiAlH_4 + 4BCl_3 \xrightarrow{ether} 2\,B_2H_6 + 3LiCl + 3AlCl_3 \qquad (3)$$

$$LiAlH_4 + 2B_2H_6 \xrightarrow{ether} LiBH_4 + Al(BH_4)_3 \qquad (4)$$

$$3LiBH_4 + AlCl_3 \xrightarrow{ether} Al(BH_4)_3 + 3LiCl \qquad (5)$$

We have shown that reaction (3) proceeds quantitatively. Reaction (4) gave yields of 85 to 89% in the absence of ether (P. R. XX, p. 1-2) and the absorption of diborane in the presence of ether indicates a quantitative reaction. Unforeseen difficulties are encountered when reaction (5), which proceeds satisfactorily in in the dry state, is carried out in ether. Yields of the borohydride up to 75% have been obtained but the reaction is slow and requires a considerable excess of aluminum chloride to liberate the borohydride according to (1).

A study of the experimental conditions for obtaining good yields by these reactions is being continued.

II. Preparation of B_5H_9

Several experiments have been run in high pressure equipment in an effort to prepare B_5H_9 from diborane at pressures in the neighborhood of 750 lbs. per sq. inch. The first experiments were run at room temperature without the addition of catalysts. The only product obtained in periods up to 120 hours has been B_4H_{10} and the yields of this were only a maximum of 2½ percent. These experiments were carried out with diborane contaminated with about 5% of ethane, an impurity which lowers the pressure at which diborane liquifies. Additional experiments with purer diborane and under various conditions of temperature and pressure, as well as some involving the use of catalysis, are planned.

The study of the decomposition of B_4H_{10} is underway but not enough data for a definitive report have as yet been completed.

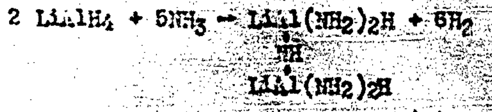
III. Reaction of Lithium Aluminum Hydride with Ammonia and with Amines.

In our search for solvents, other than hydrocarbons and ethers, for lithium aluminum hydride we tested ammonia and amines which dissolve certain borohydrides without decomposition. In contrast thereto these solvents liberate hydrogen from the aluminum compound. With primary and secondary amines 4 moles of hydrogen are liberated per mole of lithium aluminum hydride acting on 4 moles of the amine. The reactions may probably be represented by the equations:

$$LiAlH_4 + 4Me_2NH \rightarrow LiAl(NMe_2)_4 + 4H_2$$

$$LiAlH_4 + 4\ Me_2CHNH_2 \rightarrow LiAl(NHCHMe_2)_4 + 4H_2$$

Ammonia reacts differently in that 3 moles of hydrogen are evolved and only about 2.3 moles of NH_3 (average of three experiments) were retained in the formation of a product. It is possible that the reaction may be explained as indicated below:



$$2\ LiAlH_4 + 5NH_3 \rightarrow \begin{array}{l} LiAl(NH_2)_2H \\ \quad NH \\ LiAl(NH_2)_2H \end{array} + 6H_2$$

No further work is contemplated.

IV. Preparation of Alkyl Aluminum Borohydrides

Compounds containing alkyl groups in addition to borohydride groups, as well as alkyl metal hydrides may prove to have desirable properties. Their study is included in the plans for the future development of the project. In connection with this aspect of the work we have prepared dimethyl aluminum borohydride $(CH_3)_2AlB$ and the monomethyl derivative from the corresponding methyl aluminum chlorides and lithium borohydride.

Dimethyl aluminum borohydride, $(CH_3)_2AlBH_4$, and monomethyl aluminum borohydride, $CH_3Al(BH_4)_2$, have been prepared from the corresponding methyl aluminum chlorides and lithium borohydride.

$$(CH_3)_2AlCl + LiBH_4 \rightarrow (CH_3)_2AlBH_4 + LiCl$$

$$CH_3AlCl_2 + 2LiBH_4 \rightarrow CH_3Al(BH_4)_2 + 2LiCl$$

Byproducts such as diborane and boron trimethyl were also formed in the preparation.

The monomethyl compound was prepared fairly pure but it was not possible to separate completely the dimethyl aluminum borohydride from some volatile impurities containing chloride. The compounds were analysed for aluminum, boron and the combined methyl and hydrogen groups present. Molecular weights were also determined.

	$CH_3Al(BH_4)_2$		$(CH_3)_2AlBH_4$	
	Observed	Calc.	Observed	Calc.
Molecular Weight	72.4	71.6	74.2	71.8
Emperical Formula	$(CH_3 + H)_{8.7}Al_{1.0}B_{1.9}$		$(CH_3 + H)_{5.3}Al_{1.0}B_{0.91}$	

A study of the physical and chemical properties has been deferred for the present because of a lack of the necessary personnel to continue the work. It should be noted that we have lost two experienced men (Lad and Abraham) who have accepted permanent positions elsewhere; Gerstein has left for Washington to obtain his discharge from the Navy, and it is as yet uncertain how long he will remain on the project after he returns to Chicago. The additional persons who will probably join our group for the renewed project will not be available till July 1, 1946. Progress of the work on the present contract will, on that account, be retarded.

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PROGRESS REPORT NO. XXII
For the period May 1 - May 31, 1946

Contract No. N173s-10421[1)]
BuAero TED NEL No. 3401

H. I. Schlesinger in Collaboration with
C. Dillard, J. Farr, A. Finholt and K. Wilzbach

Owing to the fact that we lost the services of Messrs. Abraham and Lad, and that Dr. Gerstein had to be away to attend to his discharge from the Navy, progress has not been as rapid as hitherto. The new personnel to replace these men will not be available until July 1.

I. The Preparation of Aluminum Borohydride.

During the period covered by this report, work has continued on the preparation of aluminum borohydride in the solvent, diethyl ether. In Progress Report No. XXI preliminary results were discussed for the interaction of lithium aluminum hydride and boron chloride:

$$3\ LiAlH_4 + 3\ BCl_3 \xrightarrow{ether} Al(BH_4)_3 + 3LiCl + 2AlCl_3 \qquad (1)$$

Further work on this reaction has confirmed our hypothesis (see P.R. No. XXI) that the difficulty in obtaining aluminum borohydride lies in the intermediate step:

$$3LiBH_4 + AlCl_3 \xrightarrow{ether} Al(BH_4)_3 + 3LiCl \qquad (2)$$

At present we are attempting either to eliminate this step completely or to find a method of driving the reaction more rapidly to the completion.

There is considerable experimental evidence to indicate that reaction (2) does not proceed rapidly or completely in an ether solution. When fairly dilute solutions (2 g. per 100 g. ether) of the reagents were mixed, only a small amount of lithium chloride precipitated instead of the amount indicated by equation (2). In a more concentrated solution a precipitate did form, but aluminum borohydride was not rapidly released from the resultant mixture on the addition of aluminum chloride (see P.R. No. XXI). With a large excess of aluminum chloride and over a period of several days, 75% of the aluminum borohydride could be recovered. In another experiment, after excess aluminum chloride had been in contact with the reaction product for 3 to 4 hours, only 27% of the aluminum borohydride was liberated. Treatment of this same product with boron chloride resulted in the recovery of 96% of the boron as diborane thus showing the presence of BH_4 groups in the mixture.

The experiments which have been cited show that equation (2) may represent a reversible reaction in ether which only with difficulty is driven completely to the right. Further confirmation was found in the reaction of aluminum borohydride and anhydrous lithium chloride in ether solution to give a product from which the aluminum borohydride could not be recovered on addition of aluminum chloride. A more complete study of the reversibility of the reaction is planned.

[1)] Contract No. N173s-10421 is an extension of contract Nos. N173 s-9058 and s-9820

A synthesis of aluminum borohydride has been tried in which reaction (2) is not an intermediate step. Aluminum hydride was used as a starting reagent instead of lithium aluminum hydride and the equation for the reaction is as follows:

$$4AlH_3 + 3BCl_3 \xrightarrow{\text{ether}} Al(BH_4)_3 + 3AlCl_3 \qquad (3)$$

The aluminum borohydride was liberated from the etherate with aluminum chloride. An overall yield of 67% has been obtained in the first experiment. The yield should be raised much higher when larger runs are made in which handling losses are minimize and in which aluminum chloride free from hydrogen chloride is used. In the experimen performed, at least 16% of the missing aluminum borohydride was accounted for as diborane undoubtedly formed by action of hydrogen chloride.

As has been described in earlier reports (P.R. XIII, p. 1) aluminum hydride may be prepared in ether solution by the reaction of lithium aluminum hydride and aluminum chloride:

$$3\ LiAlH_4 + AlCl_3 \rightarrow 3AlH_3 + 3LiCl$$

It may also be more directly prepared from lithium hydride:

$$3\ LiH + AlCl_3 \rightarrow AlH_3 + 3LiCl$$

If a 2 to 15% excess of aluminum chloride is used, the lithium hydride reacts completely to give aluminum hydride. The reaction must be carried out in a very dilute solution however (2 g. of AlH_3 per 100 g. ether) or the etherate of aluminum hydride ($2AlH_3.Et_2O$) precipitates out with the LiCl. In concentrations as dilute as 8 g. of AlH_3 per 100 grams of ether, this occurs very rapidly. The necessity for using a dilute solution is one drawback to the use of aluminum hydride as a reagent.

Triethyl amine was also considered as a solvent in place of diethyl ether. Only 50% of the aluminum borohydride present in an amine solution could be recovered by replacement with aluminum chloride, and the use of this solvent does not appear feasible. A side reaction took place giving a grey metallic precipitate and accompanied by the evolution of hydrogen.

The reaction of sodium borohydride and aluminum chloride in ether gave no detectable amount of aluminum borohydride.

II. Preparation of B_5H_9

Although some progress has been made in the preparation of B_5H_9 from diborane, and its manufacture in a system in which diborane is rapidly circulated through a heated zone seems feasible, the results are not yet satisfactory as desirable. It is our opinion that ultimate progress will be accelerated by an investigati of the possible course of the reaction. The initial steps of this program are outlined below. It may be mentioned that one significant observation has been made: Pure B_5H_9 undergoes very little or no decomposition in 24 hours at 100°C, and the presence of hydrogen has little or no effect. But the B_5H_9 undergoes fairly rapid decomposition in the presence of diborane. It is as yet uncertain, however, whether the effect is due to diborane itself, or whether it is due to some intermediate produced by thermal decomposition of diborane. For this reason we shall attempt to determine the effect of such intermediates, e.g., B_4H_{10} and B_5H_{11} on the decomposition of B_5H_9. In addition the following studies are planned.

1. To study the rate of decomposition of diborane and the rates of formation of B_4H_{10}, B_5H_9 and higher hydrides at 100°C. (At this temperature the decomposition proceeded at a convenient rate and the products are relatively stable).

2. To study the rates of decomposition of B_4H_{10}, B_5H_9, etc. at 100°.

3. To study the effects of temperature, pressure and catalysts on the decomposition of B_2H_6 to B_5H_9.

Preliminary results for (1) and (2) are given in this report.

Ethane and ether-free diborane was prepared from boron bromide and lithium borohydride. (vapor pressure = 225 mm at -112°) The B_5H_9 was purified from B_5H_{11} by heating it for several hours at 100°C. (Vapor pressure = 66mm at 0°; melting pt. = -47°C.) An attempt to prepare B_4H_{10} from B_2H_5Br and sodium amalgam gave poor results and a study of the decomposition of B_4H_{10} therefore has not been started.

Figure 1 shows the results of heating diborane at 100°C for various length of time. In these experiments, 100cc. of B_2H_6 (8.94 millimoles of boron) were sealed off in 250cc flasks, heated at $100 \pm 2°$, then fractionated through -85°, -95°, and -140° and liquid nitrogen. The fractions were identified by their vapor pressure. In the figure, the percentage distribution of total boron among the various fractions and nonvolatile material ($B_{10}H_{14}$, etc.) is plotted against the time of heating.

The early portion of the B_2H_6 curve approximates a first order reaction but later deviates considerably. This leveling off is possibly due to formation of diborane from subsequent decomposition of the higher hydrides.

The maximum in the curve representing total B_5, i.e., B_5H_9 + B_5H_{11} at around three hours may be due to the presence of B_5H_{11} which decomposes on longer heating to give pure B_5H_9. Experiments described below show that B_5H_9 reacts with the unchanged diborane hence low yields are obtained.

The fact that the curves for B_2H_6, B_5H_9 and higher hydrides level off with longer heating times, indicates that some sort of equilibrium must be established between these substances.

Pure B_5H_9 heated by itself (8.94 millimoles as boron) was quantitatively recovered unchanged after 24 hours at 100°. A sample of pure B_5H_9 (8.94 m.moles B) and ½ atmosphere of hydrogen gas was also unchanged after 12 hours at 100°C.

To the non-volatile decomposition products from diborane (estimated to contain 4.8 millimoles of boron) was added 8.94 millimoles of Das B_5H_9. After 12 hours at 100° the B_5H_9 was quantitatively recovered.

However when mixtures of 20 cc. B_5H_9 and 50 cc. B_2H_6 were heated at 100°, appreciable decomposition of B_5H_9 occurred. The results of two such experiments are given in the following table.

Sample	Heating time	Millimoles B as B_2H_6	Millimoles B as B_5H_9	Total millimoles B
1	12 hours	4.9	4.4	9.3
2	24 "	4.9	4.9	9.8

Sample	M.moles B recovered as B_2H_6	M.moles B recovered as B_5H_9	M.Moles B recovered as B_4H_{10}	Total M.moles B recovered
1	2.67	3.24	0.18	6.09
2	1.53	3.20	0.06	4.85

Sample	% initial B_2H_6 recovered	% initial B_5H_9 recovered	% Total B recovered	% Total B as higher hydrides
1	53.5%	73.6%	65.5%	34.5%
2	31.2%	66.5%	49.5%	50.5%

It is of interest to note that the non-volatile residues from the decomposition of pure B_2H_6 were yellow and always collected on the bottom side of the flask as it lay in the oven; while the solids obtained from B_2H_6 -B_5H_9 mixtures were white and coated the entire surface of the containers. Needles of $B_{10}H_{14}$ were observed in both cases.

The fact that B_5H_9 reacts with diborane explains why the circulating system and one-pass experiments gave better yields than the static experiments. It also shows why increased pressures of diborane had a detrimental effect on the yield of B_5H_9, (P.R. XVIII, 5). These results are also in agreement with the fact that in the circulating and one-pass systems, better yields of B_5H_9 are obtained for short contact times, although conversion of diborane is low under these conditions.

As has been already stated, the most effective preparative method would require the use of a circulating system which passed the diborane rapidly through a heated zone (at 100-125°C) with means of continuously separating out the B_5H_9.

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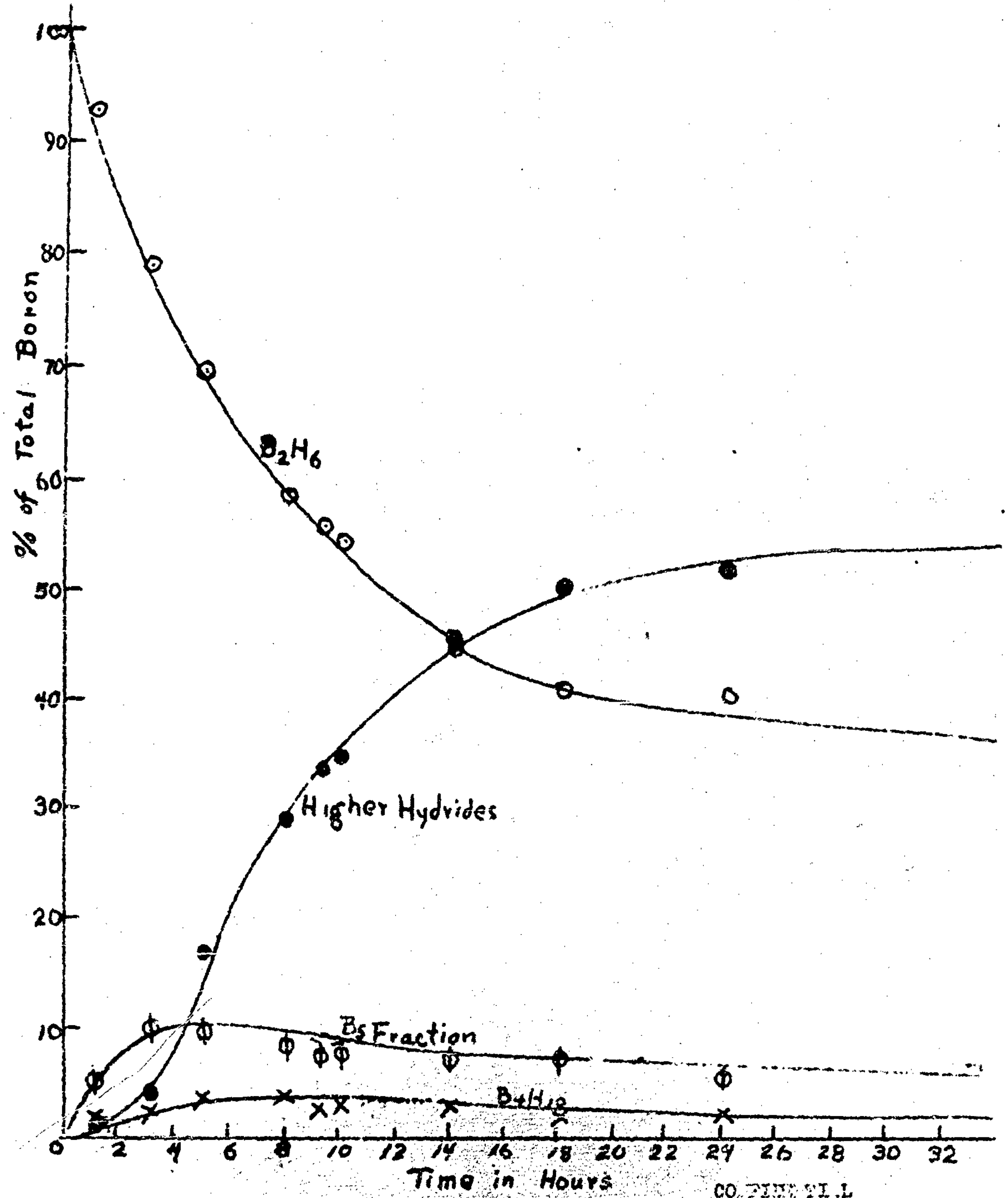
Fig. 1.

Decomposition of B_2H_6 at 100° C.



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PROGRESS REPORT NO. XXIII

For the period June 1 - June 30, 1946
on
Contract No. N173s-10421[1]

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[1] Contract No. N173s-10421 is an extension of Contract Nos. N173s-9058 and s-9820

H. I. Schlesinger in Collaboration with
C. Dillard, J. Farr, A. Finholt, M. Gerstein and K. Wilzbach

I. PREPARATION OF ALUMINUM BOROHYDRIDE

Although the study of the reaction between aluminum hydride and boron chloride has been continued to find the best conditions for this procedure for preparing aluminum borohydride, we are not convinced that the ultimate solution of the problem has as yet been attained. Detailed description of the experiments is deferred until additional data have been secured.

II. PREPARATION OF B_5H_9

The study of the behavior of diborane at high pressures is being continued. The previously reported experiments (Progress Report No. XXI, p. 2) were carried out with diborane containing about 5% of ethane. Diborane free from this impurity has been found to give no better results. For example, 2.44 liters of the purified diborane at an initial pressure of 700 lbs/sq. inch, after standing for nine days at room temperature (ca. 25°C), had produced only 41.5cc. of B_4H_{10} and 14.4cc. of a mixture of B_4H_{10} and B_5H_9. The rest, 2.31 l., or 94% of the diborane, was unchanged. Experiments in which boron trichloride and other catalysts are to be used have been started; observations of the pressure changes indicate that the diborane undergoes more rapid change in the presence of boron chloride than in the absence of a catalyst, but the experiment was still in progress at the time of the writing of this report, and neither the nature nor the extent of the change had as yet been ascertained.

Further work is also in progress on the reaction between diborane and B_5H_9 at 100°C (see Progress Report XXII, p.4). Mixtures of 55cc.B_2H_6 and 21cc.B_5H_9 reacted at 100°C so as to decrease the concentration of both substances. After 45 hours the molar ratio of B_2H_6 to B_5H_9 had reached 1:1 and further reaction seemed very slow.

That this composition does not represent an equilibrium condition, however, is made evident by the fact that mixtures of B_2H_6 and B_5H_9 in the molal ratio 1:1 undergo further change as shown in experiment (1) in the following table. Experiment (a) represents the earlier stages of the experiment described in the preceding paragraph; in experiment (2) only a small proportion of diborane was used, and in experiment (3), in addition to diborane and B_5H_9, higher hydrides such as $B_{10}H_{14}$ were introduced into the reaction vessel. The volume of this vessel in each case was 250cc. It appears as if an excess of diborane accelerates the decomposition of B_5H_9 and vice versa, but there are as yet insufficient data

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for definite conclusions. It does seem, however, that the higher hydrides are without effect.

Sample No.	Initial cc. B_2H_6	Initial cc. B_5H_9	Mol ratio $\frac{B_2H_6}{B_5H_9}$	Heating Time	cc. B_2H_6 Recovered	cc. B_5H_9 Recovered	% B_2H_6 Recovered	% B_5H_9 Recovered
(a)	54	21	2.58:1	20 hrs.	20.5	14.4	37.9%	68.5%
(1)	20.8	20.7	1:1	20 hrs.	6.8	16.4	32.[illegible]%	79.1%
(2)	20.9	39.6	0.53:1	20 hrs.	4.35	31.4	20.8%	79.[illegible]%
(3)	20.9	20.7	1:1	20 hrs.	6.6	16.3	31.6%	76.[illegible]%

Further work, especially to determine the effect of B_4H_{10} is under way.

III. ATTEMPTS TO PREPARE SODIUM ALUMINUM HYDRIDE

Preparation of this compound by metathesis from lithium aluminum hydride in ether solution has failed because no compounds of appropriate solubility in ether exist. The compound theoretically most favorable, i.e., $NaAlCl_4$, was found to be decomposed by ether. The reaction of sodium hydride on molten aluminum ethoxide, (which is analogous to the preparation of sodium borohydride from sodium hydride and an alkyl borate) gives a mixture we have not yet succeeded in separating. The prospects for success by this reaction are not favorable. Hydrogenation of sodium aluminum alloys is the only other procedure we have in mind but we are not yet ready to proceed with it.

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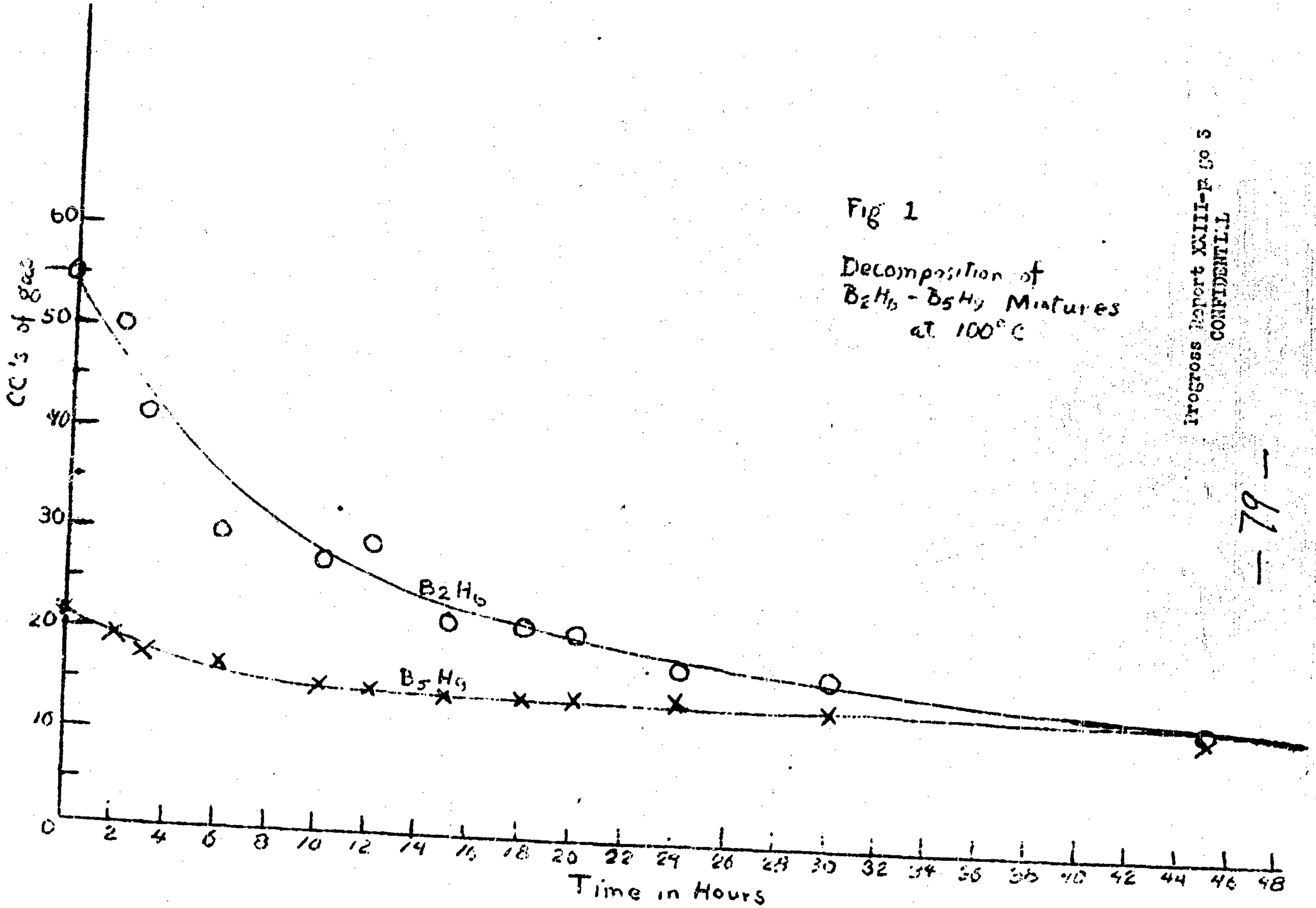

Fig 1

Decomposition of B_2H_6 - B_5H_9 Mixtures at 100°C

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ABSTRACT:

Preparation of lithium aluminum hydride and study of its properties and reactions are presented. Attempts were made to prepare beryllium hydrogen compounds, and experiments conducted on preparation of pentaborane are discussed. Methods were developed on procedures for preparation of hydrides of silicon and tin and of partially alkylated derivatives. Iron carbonyl was used as catalyst in B_5H_9, but reaction was negative. If mixture is illuminated, iron carbonyl is decomposed at rate dependent on intensity of radiation.

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