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SYNTHESIS OF LMH-2
(Unclassified Title)

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Final Technical Report
January 15, 1964 - October 15, 1965
on Contract
AF 04(611)-9700
AFSC Project No. 3148
Program Structure No. 750G
Report No. AFRPL-TR-66-15

By

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Cincinnati, Ohio



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FOREWORD

This report was prepared by the Research Division of U.S. Industrial Chemicals Co., Division of National Distillers and Chemical Corporation, Cincinnati, Ohio under USAF Contract No. AF04(611)-9700. The Project Monitor is 1st. Lt. J. Rombouts, Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, United States Air Force, Edwards, California.

The report covers work performed during the period January 15, 1964 to October 31, 1965 by Dr. Jawad H. Murib, Senior Research Associate, serving as principal investigator, assisted by Mr. C. A. Bonecutter, Chemist and Mr. B. Seeskin, Assistant Chemist. Dr. D. Horvitz, Assistant Research Manager, acted as a consultant on the project.

This effort is being continued under Air Force Contract AF04(611)-11402.

This technical report has been reviewed and is approved.

GEORGE F. BABITS, Lt. Colonel, USAF
Chief, Propellant Division

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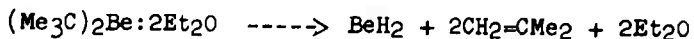
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INTRODUCTION

Considerable effort has been spent on the development of suitable processes for the manufacture of beryllium hydride of high purity and crystallinity for use in chemical propellant systems. The most successful process to date was developed by Ethyl Corporation and based on the pyrolytic method of Coates and co-workers utilizing di-t-butyl beryllium (prepared from Grignard reagents) as a starting material.



This method yields amorphous solid with an absolute density of 0.65 g/cc. and an over-all purity of 93 wt.%. The amorphous product is converted to crystalline BeH_2 by compaction-fusion at an ultra high pressure of 200,000 psi. and 200°C. These methods are uneconomical and time consuming and thus impractical for large scale production of crystalline BeH_2 .

The objective of developing an economical and convenient method for the production of high purity beryllium hydride with high density and crystallinity, therefore, remains to be accomplished.

Investigation in this laboratory revealed the existence of a new soluble hydride, chloroberyllium hydride (CPH) which became the basis for an applied research program of contract AF 04(611)-9700 to develop a process for the manufacture of high purity BeH_2 from readily available materials such as beryllium chloride (BeCl_2) and sodium hydride (NaH).

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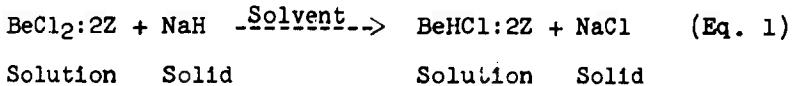
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OBJECTIVE

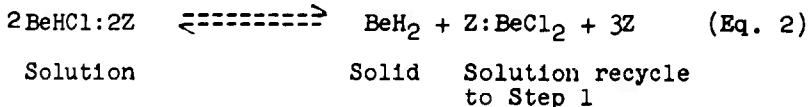
The objective of this program is to develop a process for the manufacture of high purity beryllium hydride with a high degree of crystallinity and with a greater density than that obtained by pyrolytic methods. The proposed process for making BeH_2 , under the contract, involves two steps:

Step 1. Preparation of chloroberyllium hydride from the reaction of beryllium chloride with sodium hydride in ethers or thioethers,



Z = Ether or Thioether

Step 2. Disproportionation of the soluble intermediate CBH, in the absence of residual sodium hydride or by-product sodium chloride, to give insoluble beryllium hydride and soluble beryllium chloride,



PROJECT STATUS

Summary

This report describes the progress made toward the synthesis of BeH_2 outlined below:

Preparation of chloroberyllium hydride from beryllium chloride-etherate and sodium hydride was achieved in conversions up to 95.3% based on beryllium chloride.

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Disproportionation of the CBH intermediate was demonstrated to give beryllium hydride in purities up to 85.1 wt. %. The product was amorphous with residual Be-Cl bonds, retained ether, and Be-O bonds as the major contaminants. The atomic ratio of active hydride to residual chloride (H^-/Cl^-) in the final product reached up to 142/1. This was realized by treatment with $LiAlH_4$.

Although no crystalline beryllium hydride has been conclusively isolated, crystalline material was evident in samples obtained from the disproportionation of CBH in 1,2-dichloroethane solvent. Because BeH_2 is difficult to identify by X-ray and since impurities tend to "mask" the desired product except in samples of high purity, it was not certain whether the observed diffraction lines were related to crystalline BeH_2 or to associated impurities. A definite judgment on the crystallinity of the product awaits preparation of high purity BeH_2 .

The CBH intermediate was isolated in essentially pure state with observed atomic ratios of Cl:Be:H of 1.02:1.00:0.98 in good agreement with the theoretical value 1:1:1 for $ClBeH$.

The reaction time of Step 1 was decreased from 30 hrs., obtained in ether-kerosene at 25°C., using ball-milling to about 4 hrs. in benzene at 80°C. and 2 hrs. in toluene at 105°C. employing simple stirring.

The amount of ether was decreased to only that required to form the dietherate, $BeCl_2 \cdot 2Et_2O$. This is advantageous in that it avoids recycle of large volume of ether solvent.

Particle size of NaH was found to influence the reaction rate. Use of NaH of average particle size of 5 microns gave about 33-fold faster reaction rate than that obtained with an average size of 40 microns.

The character of the CBH disproportionation product was found to be highly dependent on the nature of solvents, temperature and type of disproportionation, whether carried out under vacuum or in solution.

Disproportionation of CBH under vacuum gave gelatinous products difficult to filter and transfer, with extreme reactivity toward moisture. However, when the disproportionation was carried out in different solvents the products exhibited various hydrolytic activities with different filtration and flow characteristics. In aromatic solvents the disproportionation products appeared to have larger particle size and lower hydrolytic activity than those obtained by vacuum disproportionation.

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Complexing agents with different coordination strength toward ClBeH were found to be capable of effecting great variation in the chemical and physical properties of CBH intermediate. In the case of the adduct $\text{ClBeH}:\text{OEt}_2$ the disproportionation under vacuum gave amorphous products with H^- to residual Cl^- ratios of up to 137/1 and minor amounts of ether probably owing to terminal coordination. Likewise disproportionation of the dimethyl sulfide adduct $\text{ClBeH}:\text{SMe}_2$ led to an amorphous product retaining a large amount of residual chloride ($\text{H}^-/\text{Cl}^- = 6.5/1$) but no Me_2S . When dimethyl ether was used as the complexing agent only a small amount of disproportionation product was obtained which was also amorphous to X-ray. Displacement of ether from $\text{ClBeH}:\text{OEt}_2$ by trimethyl amine resulted in the formation of a benzene-soluble adduct probably $\text{ClBeH}:\text{NMe}_3$ which appeared to be stable toward disproportionation. Its characteristics have not yet been determined.

Reduction of the adduct, $\text{BeCl}_2:\text{NMe}_3$ with sodium hydride in a mixed ether-benzene solvent at room temperature led to a soluble hydride presumably $\text{ClBeH}:\text{NMe}_3$ with conversions up to 40.7% based on initial $\text{BeCl}_2:\text{NMe}_3$.

Details

Preparation of Chloroberyllium Hydride

Nature of the Reaction of BeCl_2 with NaH in Ethers

In order to establish whether chloroberyllium hydride undergoes transformation to beryllium hydride in the course of step (1) a rate study of this reaction was undertaken. Diethyl ether was employed in view of its marked influence on the conversion in contrast to those obtained in other basic solvents (see Table I). Kerosene was used as carrier for NaH .

The study revealed that two consecutive reactions are occurring as represented by equation (1) and (2). The course of the reaction was followed by analyzing for CBH. Its concentration rose to a maximum and then fell off, as shown in Fig. 1. The mole ratio of CBH to the total hydride in the reaction mixture is plotted against time. Curve 1 shows the change in content of CBH in Et_2O with ball-mill attrition. A maximum conversion of 74% occurred at 30 hrs. The concentration, then, diminished slowly via formation of insoluble hydride leaving a soluble amount of 15% of the total hydride at 110 hrs. The slow rate of diminution of soluble hydride permitted the isolation of CBH from the reaction mixture before it had changed into insoluble hydride.

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Factors Influencing the Conversion of BeCl₂ to CBH in Basic Solvents

The conversion of BeCl₂ to CBH at room temperature was found to depend on several factors: (a) nature of basic solvent, (b) concentration of BeCl₂, (c) type of mixing, (d) ratio of reactants and (e) catalysts. These factors are discussed below:

Effect of Basic Solvents: Several Lewis bases were tried such as dimethyl sulfide (Me₂S), diethyl ether (Et₂O), trimethyl amine (NMe₃), tetrahydrofuran (THF) and diglyme (see Table I). In Me₂S, formation of soluble CBH was accompanied by deposition of insoluble beryllium-hydride bonds. This would lead to a product contaminated with sodium and chloride ions. In diethyl ether, however, the rate of reaction (1) was faster than that of reaction (2). Thus, it was possible to isolate sodium-free, ether-soluble CBH in conversions up to 77.2% based on BeCl₂. Poor results were obtained in active ethers such as THF, and diglyme. The over-all results are shown in Table I.

TABLE I

Effect of Solvents on the Rate of CBH Production
from NaH and BeCl₂ at Room Temperature

<u>Solvent</u>	<u>Time, hrs.</u>	<u>% Conversion</u>
Et ₂ O	31	77.2
Me ₂ S	5	25.7
ØH-Et ₂ O	17	13.0
Tetrahydrofuran	16	3.0
Diglyme	54	0.0
Et ₂ O-BEt ₃	15.5	72.5
Et ₂ O-AlEt ₃	20.0	33.0
Me ₂ S-BEt ₃	15.5	30.0

Extensive side reactions involving disproportionation of CBH or further reaction with NaH appear to dominate in active ethers. Table II shows the distribution of hydride content in both the liquid and solid phases of the reaction mixture.

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TABLE II **CONFIDENTIAL**

Reaction of Sodium Hydride with Beryllium Chloride in Ether Solvents at Room Temperature
(Ratios and percentages expressed in mmoles.)

Expt. No.	Initial Ratio NaH/BeCl ₂	Solvent	Catalyst	Mixing	Reaction Time, hrs.	% Distribution of Hydride		
						Liquid Phase ClBeH (a) Observed	Solid Phase NaH Unreacted	Hydride Unaccounted for (b)
952-32	1.065	Me ₂ S	-	Ball-mill	15.5	24.20	37.30	38.50
-33	1.020	Me ₂ S	BEt ₃	Ball-mill	15.5	30.22	32.96	36.82
-38	0.957	Et ₂ O	-	Magnetic stirrer	15.75	68.90	20.25	10.85
-39	1.000	Et ₂ O	BEt ₃	Magnetic stirrer	15.75	72.5	19.05	8.45
946-28	0.943	Et ₂ O	-	Ball-mill	30.0	67.40	14.14	18.46
-30	0.998	Et ₂ O	BEt ₃	Magnetic stirrer	44.0	71.40	16.80	11.80
952-63	0.988	Et ₂ O	AlEt ₃	Magnetic stirrer	164.75	36.10	-	-
-52	0.750	Et ₂ O	-	Ultrasonic	29.75	54.80	33.50	11.70
-71	1.795	Et ₂ O	-	Magnetic stirrer	45.25	69.40(c)	-	-
-67	0.989	Et ₂ O	-	Magnetic stirrer	44.5	60.30	28.1	11.6
-61	1.075	THF	-	Magnetic stirrer	16.0	2.97	-	-
-58	1.015	Diglyme	-	Magnetic stirrer	54.0	0.0	59.20	40.80

(a) Based on initial NaH.

(b) The difference between initial NaH and sum of HBeCl observed and NaH unreacted is believed to be BeH₂.

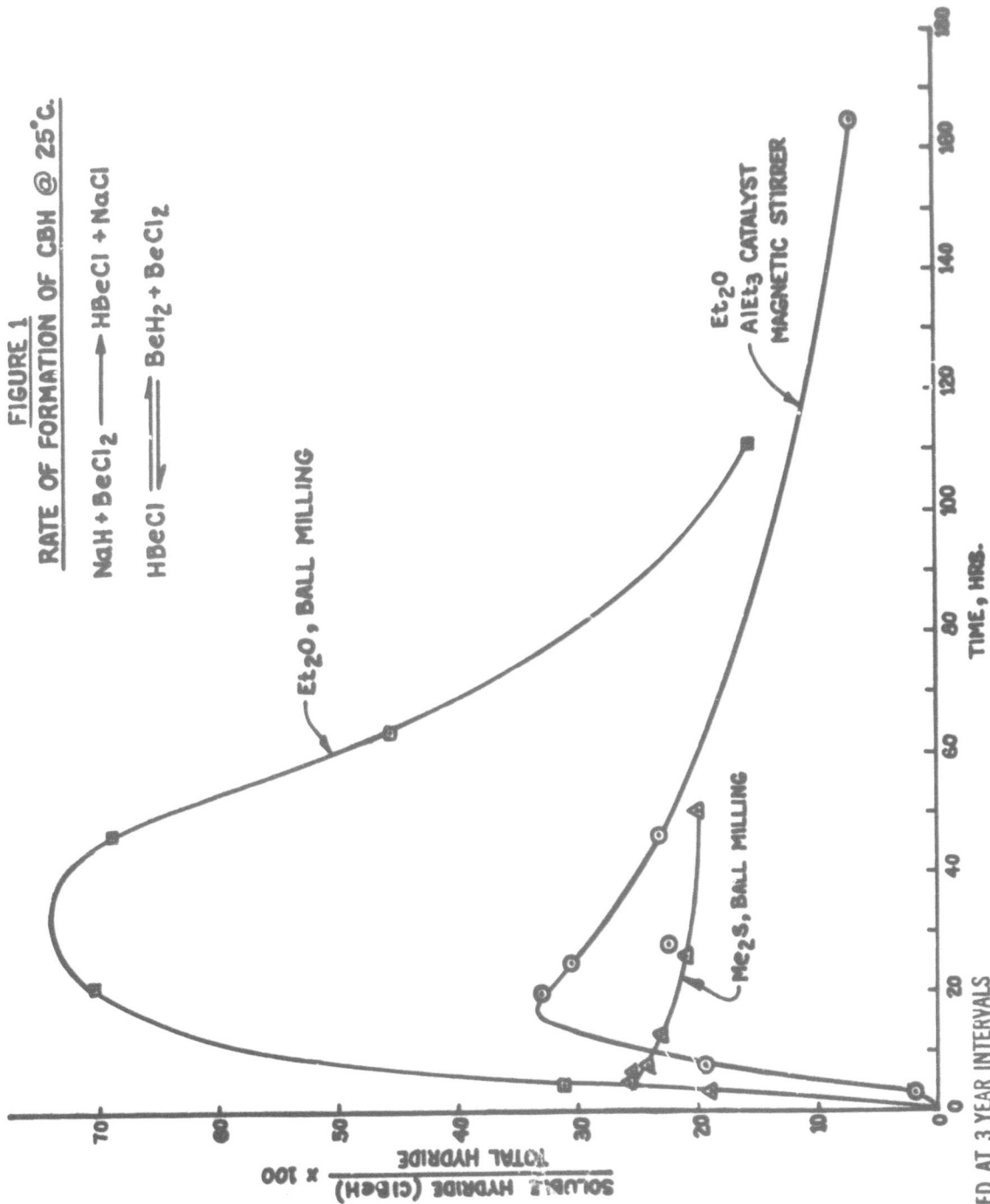
(c) Based on BeCl₂.

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FIGURE 1
RATE OF FORMATION OF CBH @ 25°C.



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The data of Table II shows that some of the hydride (column 9) was unaccounted for and presumably deposited as insoluble beryllium hydride. This was confirmed by precipitation of a chloride-free, ether-insoluble, white solid by allowing a sodium-free, clear solution to stand at room temperature. The solid product exhibited an infrared absorption band at 5.8 μ , in contrast to a Be-H absorption near 5.9 μ^1 . The solid generated hydrogen on treatment with aqueous acids. Since it is free of sodium the source of hydrogen must be BeH₂. It is important to note that in the Et₂O experiments the unaccounted for hydride is much less than in DMS (column 9), making Et₂O the solvent of choice for carrying out step 1 at ambient temperature.

Concentration of BeCl₂: The conversion of BeCl₂ to CBH in ether solutions increased with increasing initial concentration of BeCl₂ as shown in Table III.

TABLE III

Effect of Concentration of BeCl₂ in Ether on
its Conversion to Chloroberyllium Hydride

(Temperature = 25°C., Reaction Time = 17.5 hrs., Ball-mill Attrition.)

Expt. No.	Concn. of BeCl ₂ g. mole/1000 g. Et ₂ O	Ratio NaH/ BeCl ₂	% Conv. to ClBeH	% Hydride Unaccounted for
952-114	0.595	1.03	61.2	22.0
946-28	0.650	0.93	68.5	-
952-113	0.935	1.03	77.2	5.7

These results (Table III) indicate that the disproportionation of CBH was repressed by increasing the concentration of BeCl₂ in Et₂O. A decrease in the unaccounted for hydride, from 22.0% to 5.7% (column 5), reflected an increase in conversion to 77.2% of soluble CBH. This is consistent with the reversal of the equilibrium reaction of Eq. 2.

(1) CPFA, Specialized Fuel Meeting, (u) Sept. 17-18, 1963, page 6, Ethyl Corp., Baton Rouge, Louisiana.

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Molar Ratio NaH/BeCl₂: The data presented in Table II (Expts. 952-71, and 952-67) show that 69.4% conversion to CBH was obtained at a molar ratio of NaH/BeCl₂ = 1.795 in contrast to 60.30% obtained at a ratio of 0.987. Although higher conversions can be obtained by employing higher ratios of NaH/BeCl₂, this would lead to coating of excess NaH by NaCl by-product. Recycle of excess hydride would be cumbersome.

Type of Mixing: Magnetic stirring was found to be suitable in dilute ethereal solutions of BeCl₂. In concentrated solutions, however, BeCl₂ forms two phases of etherates. The lower phase, being a heavy oil, prevents intimate mixing of reagents. In such cases ball-milling is preferred. Ultrasonic agitation did not give faster reaction rates than ball-mill attrition.

Catalysts: Attempts to catalyze the reaction by using BEt₃ to solubilize NaH, resulted only in a minor change in the conversion (Table II). Use of AlEt₃ (Fig. 1, Curve 3) lowered both the rate of formation of CBH and its subsequent transformation to insoluble Be-H bonds. Use of these alkyls was discouraged by the possibility of introducing undesirable impurities to BeH₂.

Factors Affecting the Rate of Reduction of BeCl₂:2Et₂O with NaH in Aromatic Solvents

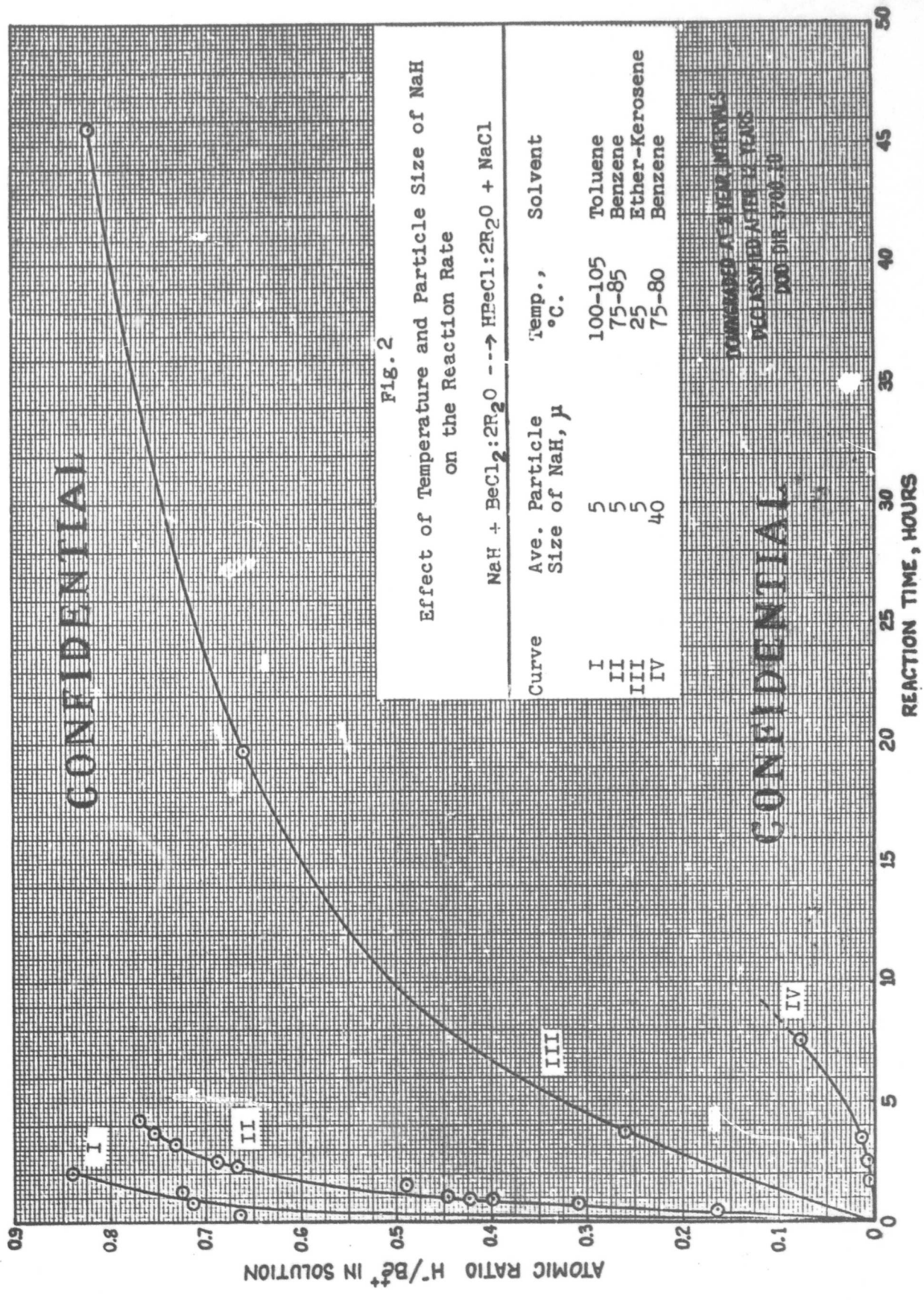
Variables such as temperature, particle size of NaH, concentration, and type of complexing ether were found to be the most important factors influencing the rate of CBH formation. These are discussed below:

Effect of Temperature on the Reduction Rate: It is known that aromatic solvents dissolve BeCl₂-etherates. Consequently they were chosen as reaction media for the reduction of BeCl₂ with NaH at above ambient temperatures.

In toluene at 100-105° reaction (1) yielded a solution in which the atomic ratio of H⁻/Be⁺⁺ was 0.84 obtained in about 2 hours of reaction time (see Fig. 2, Curve 1). In benzene at 75-80°C. a ratio of 0.77 was obtained in 4.2 hrs. (Curve II). However, at room temperature in the ether-kerosene system a ratio of 0.66 was obtained in 19.7 hrs. and 0.82 in 45.7 hrs. (Curve III). Thus, reducing BeCl₂:2Et₂O with NaH in benzene and in toluene at reflux temperatures decreased the reaction time from days to hours.

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Effect of Particle Size of NaH on the Reaction Rate:
 Reduction of $\text{BeCl}_2 \cdot 2\text{Et}_2\text{O}$ with NaH of different particle size was carried out under controlled conditions (Table IV). The results showed that using NaH of an average particle size of about 5.0μ gave 33-fold faster reaction rate than that obtained with 40μ . The rate data are shown in Fig 2 Curve IV for comparison.

TABLE IV

Effect of Particle Size of NaH on the Rate of Formation of ClBeH

NaH Particle Size, μ	Temp., °C.	Solvent	Reaction Time, hrs.	Ratio $\text{H}^-/\text{Be}^{++}$ ^c
40 ^a	80	Benzene	7.5	0.07
5 ^b	80	Benzene	2.25	0.71

- (a) Commercial sample obtained from Metal Hydrides Inc.
- (b) Made by US. Industrial Chemicals Co.
- (c) Ratio of hydride to beryllium in solution.

Effect of BeCl_2 Concentration on the Reaction Rate:
 The rate of formation of CBH from the reaction of $\text{BeCl}_2 \cdot 2\text{Et}_2\text{O}$ with NaH in benzene was found to increase with increasing initial concentration of the dietherate. The trend is shown in Fig. 3. After 60-80% completion, the concentration of CBH did not increase, presumably due to coating of NaH by solid by-product NaCl.

Examination of the data of Fig. 3 indicated that about 80% conversion was obtained at 70-80°C. in 4 hrs. and 87.5% in 8 hrs. by employing an initial concentration of $\text{BeCl}_2 \cdot 2\text{Et}_2\text{O}$ of 1.37 mmoles per 1000 grams of solution and a ratio of NaH/BeCl_2 of 1/1. At a concentration of 0.85 molal the conversion was about 65% in 2 hrs. and 73% in 7 hrs. at 65-70°C. Decreasing the concentration to 0.45 molal, the conversion decreased to 46.7% in 2 hrs. at 70-80°C. In these experiments the concentration of soluble Be^{++} remained essentially constant indicating that the intermediate $\text{ClBeH} \cdot 2\text{Et}_2\text{O}$ was stable under the conditions of its formation.

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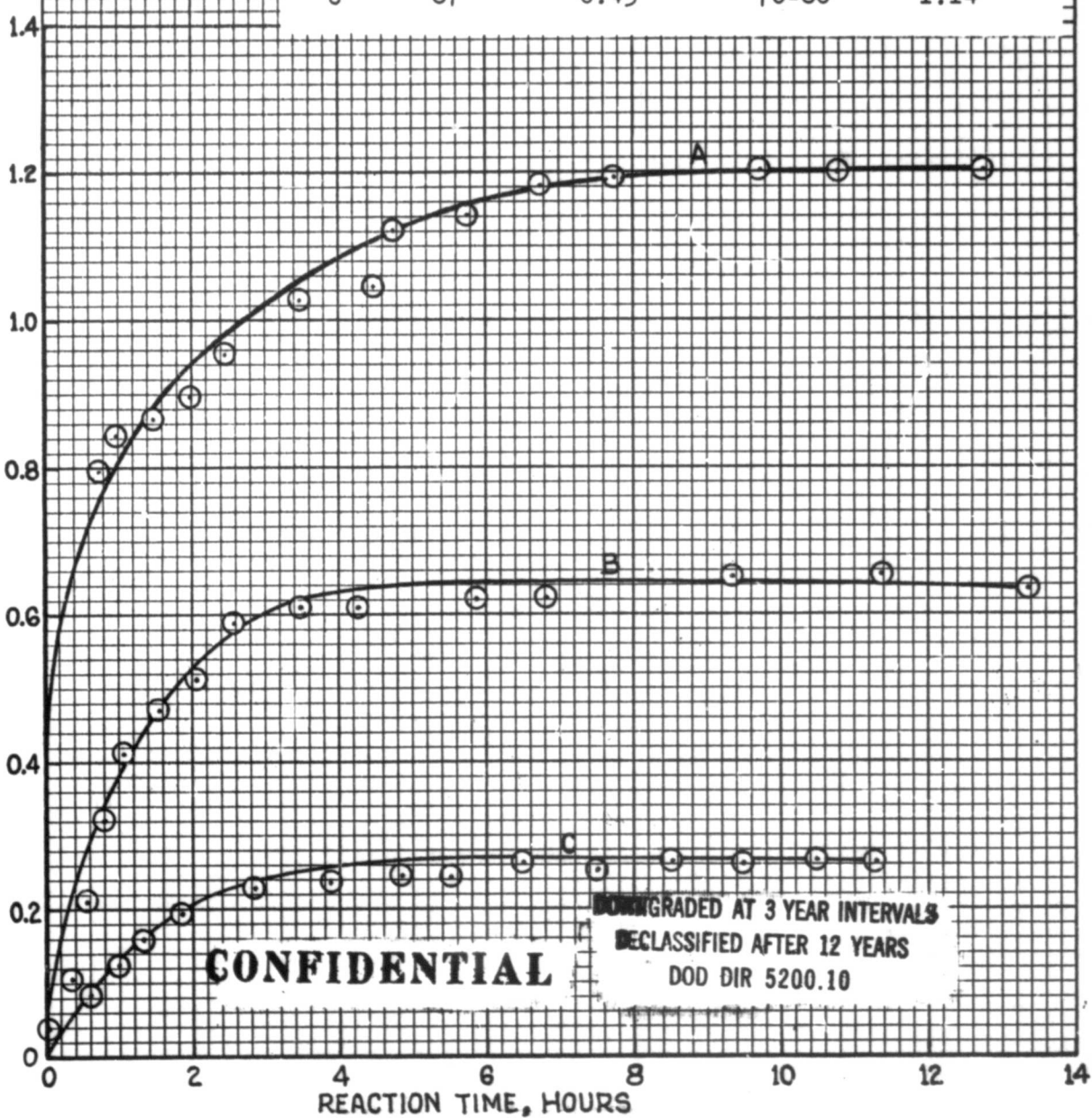
Fig. 3

Effect of Initial Concentration of $\text{BeCl}_2:2\text{Et}_2\text{O}$ on the Reaction Rate in Benzene Solution



Curve	Expt. No.	Initial Concn. $\text{BeCl}_2:2\text{Et}_2\text{O}$ Moles/1000g. Solution	Temp. °C.	Molar Ratio NaH/BeCl_2
A	93	1.37	70-80	1.06
B	78	0.85	65-70	1.02
C	87	0.45	70-80	1.14

CONCENTRATION OF ClBeH IN MOLES PER 1000 GRAMS OF SOLUTION



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Effect of Incremental Addition of NaH on the Atomic Ratio H^-/Be^{++} : In order to increase the ratio of H^-/Be^{++} in solution, additional NaH was added to the reaction mixture (Step 1) after the concentration of CBH reached a constant value. The results are shown in Fig. 4. Curve A describes the variation H^-/Be^{++} ratio with time. When the ratio reached a constant level of 0.84, introduction of 33% additional NaH resulted in an increase to 0.95 approaching the theoretical value 1.00 to $ClBeH$. Curve B describes the results of a second experiment where an addition of 48% excess of NaH increased the H^-/Be^{++} ratio from 0.58 to 0.89.

Effect of Complexing Ether on the Reaction Rate: Comparative study of the reduction of $BeCl_2:2Et_2O$, $BeCl_2:2Me_2S$, $BeCl_2:2Me_2O$ with NaH in benzene solution at 65-95°C. showed that the use of Et_2O gave soluble ratios of H:Be of up to 0.90. When Me_2S or Me_2O were used low values were obtained, 0.41 and 0.44 respectively. The intermediate $HBeCl:2Et_2O$ seemed to undergo little or no side reaction during its formation in benzene solution, shown by an increase in the soluble hydride concentration with time while the beryllium content remained practically unchanged. The results of a typical experiment are plotted in Figure 5.

However, the dimethyl sulfide adduct $ClBeH:2Me_2S$, appeared to undergo side reaction as shown by simultaneous diminution of hydride and beryllium concentrations as shown in Fig. 6. The dimethyl sulfide probably promotes side reactions which consume the hydride.

In the case of dimethyl ether difficulties were encountered due to the low solubility of $BeCl_2:2OMe_2$ in benzene (about 0.16% at 25°C.). Crystallization of the solute as it cools upon sampling led to clogging of the passages resulting in unreliable analytical results. This difficulty was overcome by operating at 90-95°C. A ratio of H^-/Be^{++} of 0.44 was obtained after 4 hours of reaction time. A decrease in the concentration of soluble hydride and of soluble beryllium was observed during the course of the reaction. This indicates the occurrence of side reactions by which soluble Be-H bonds are rendered insoluble. This was confirmed by the presence of beryllium in the solid phase. This amount of the insoluble beryllium was 26% of the total. Thus, dimethyl ether appears to promote undesirable side reactions which consume CBH. This behavior is analogous to that of tetrahydrofuran and of diglyme observed earlier (Table II).

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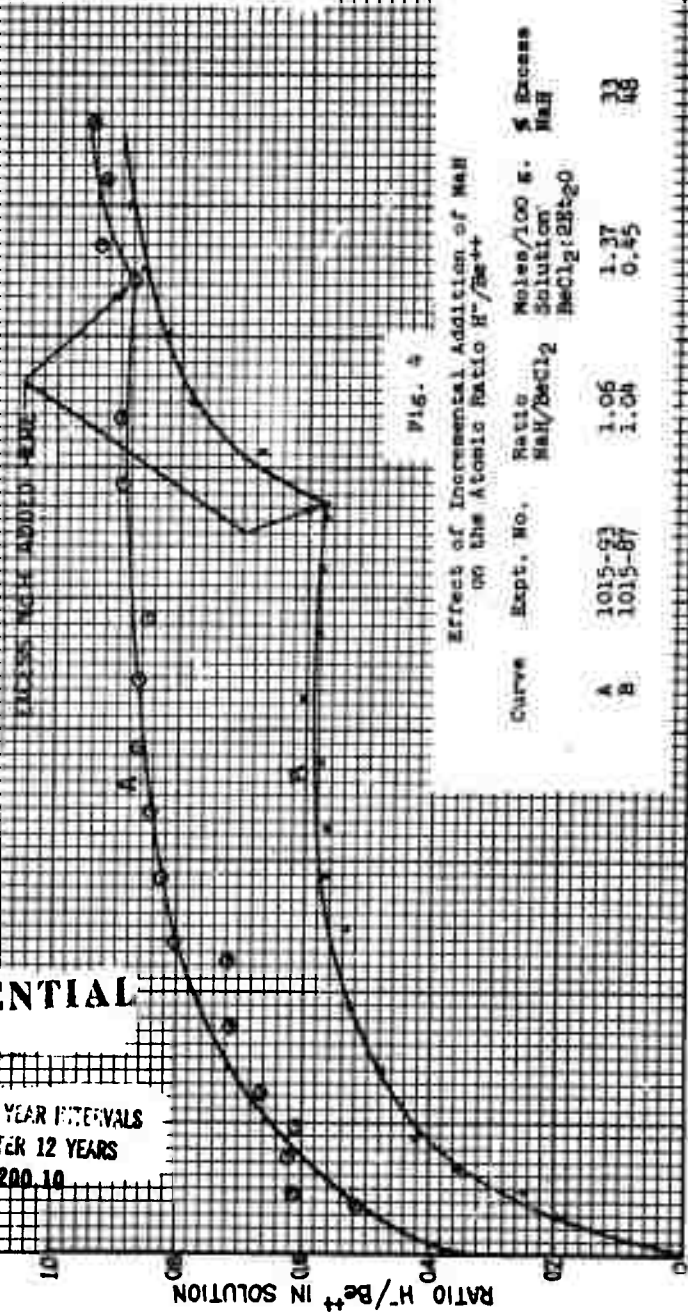
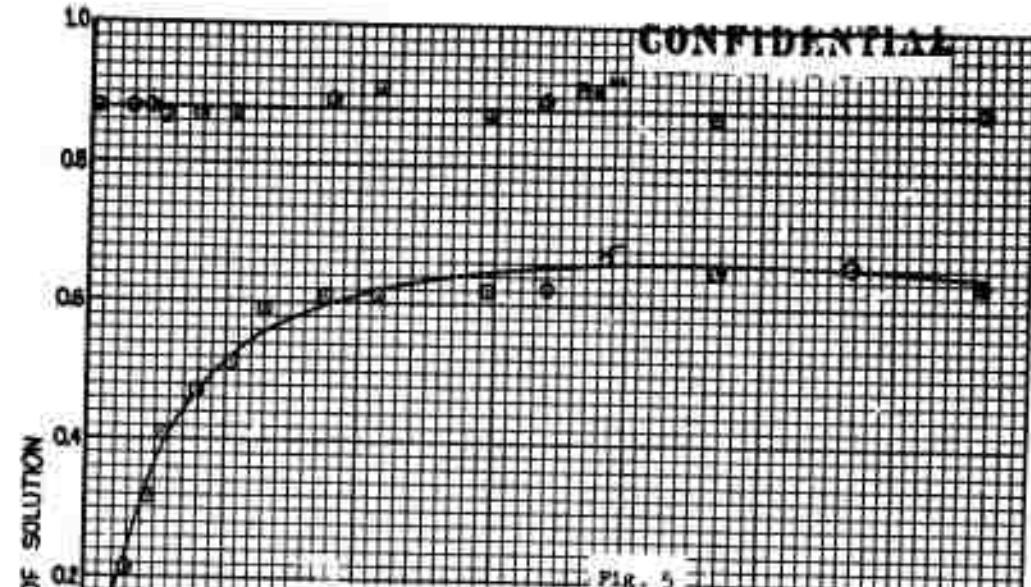


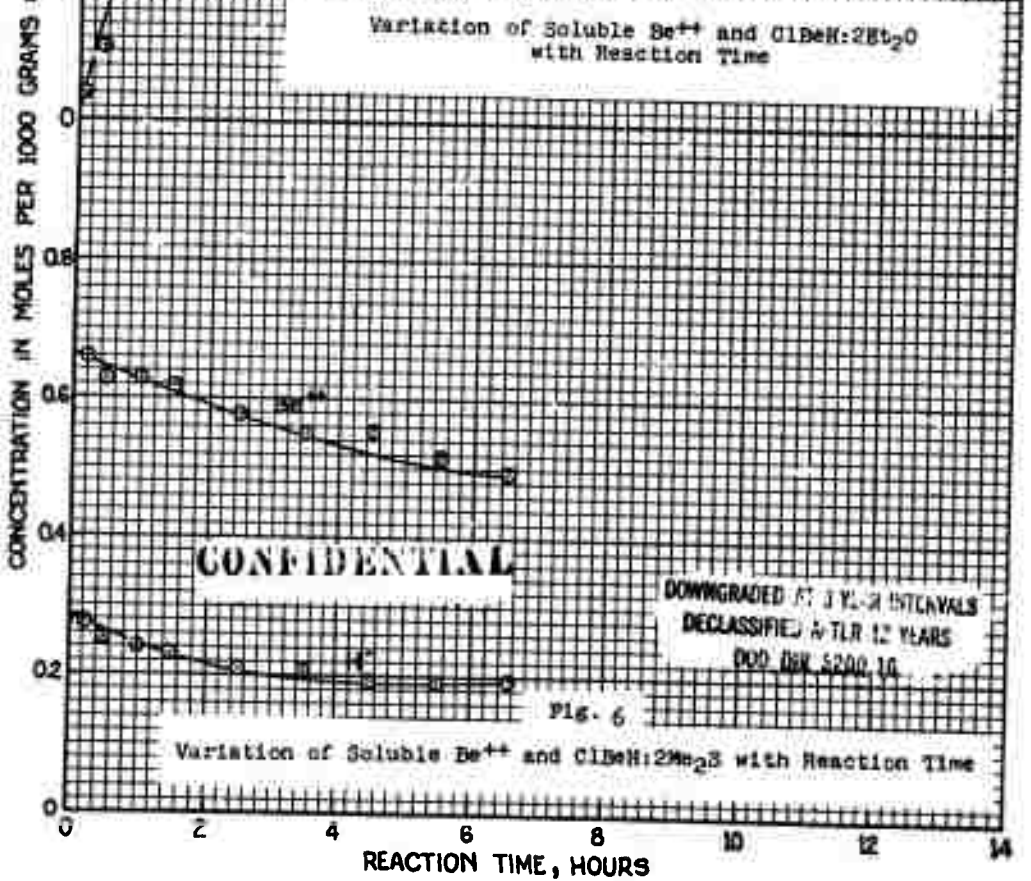
FIG. 4
 Effect of Incremental Addition of H⁻
 on the Atomic Ratio H⁻/Be⁺⁺

REACTION TIME, HOURS

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Variation of Soluble Be^{++} and $ClBeH \cdot 2Be_2O$ with Reaction Time



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Variation of Soluble Be^{++} and $ClBeH \cdot 2Be_2S$ with Reaction Time

REACTION TIME, HOURS

Purification Methods of Chloroberyllium Hydride

The intermediate CBH isolated from the reaction mixture of (Step 1) was always contaminated by small amounts of unreacted BeCl_2 -etherate. It can be upgraded by two methods:

1. Fractional crystallization of unreacted $\text{BeCl}_2\text{:OEt}_2$:
 The liquid phase isolated from the reaction mixture ($\text{NaH} + \text{BeCl}_2$) after vacuum removal of the solvent was seeded with preformed $\text{BeCl}_2\text{:OEt}_2$. This resulted in the deposition of a crystalline solid and a liquid having the following atomic ratios:

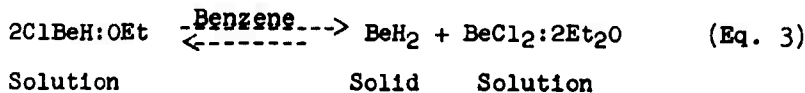
	Atomic Ratios		
	Be ⁺⁺	H ⁻	Cl ⁻
Found:	1.00	1.037	1.005
	1.00	0.978	1.015
Theory for ClBeH :	1.00	1.00	1.00

The solid phase was not analyzed.

2. Reduction of Unreacted $\text{BeCl}_2\text{:OEt}_2$ with NaH: Incremental addition of NaH to the reaction mixture of Step 1 afforded a convenient route to upgraded CBH in one step. Reduction of beryllium chloride with 20-30% excess sodium hydride over that required by Eq. 1 gave a product with an atomic ratio of Cl/Be of 1.04/1.00 approaching the theoretical values 1/1 for ClBeH . This result confirms other observations that incremental addition of excess of NaH to the reaction mixture of step 1 afforded a soluble ratio of $\text{H}^-/\text{Be}^{++}$ of 0.95/1.00 (Fig. 4).

Properties of Purified CBH-Etherate

Molecular weight of CBH: Having isolated $\text{CBH}\text{-OEt}_2$ in essentially pure form, determination of its molecular weight was desirable. An attempt to determine its degree of association in benzene solution was hampered by the deposition of a white solid, presumably due to formation of BeH_2 according to the equilibrium:



Other solvents such as dichloromethane and chlorobenzene in which CBH does not undergo disproportionation should be used as media for molecular weight determination.

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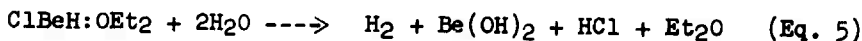
Reaction of CBH with Iodine: Iodine (I_2) reacted instantaneously and quantitatively with 2 moles of chloroberyllium hydride with release of one mole of gaseous hydrogen (H_2) as described below:

$$2ClBeH + I_2 \text{ -----} \rightarrow 2ClBeI + H_2 \quad (\text{Eq. 4})$$

Theory (mmoles)	2.00	1.00	-	1.00
Found (mmoles)	2.04	1.00	-	0.97

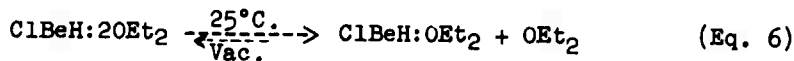
Oxidation of CBH with iodine* provides a convenient and rapid method for its quantitative determination. The procedure is simple. It involves titrating a solution of CBH in Et_2O with a standard solution of I_2 in toluene or other inert solvents. The end point is taken when a yellow color persists due to slight excess of iodine. The accuracy of the method depends on absolute exclusion of moisture from reagents and equipment.

Reaction of CBH with Protonic Hydrogen: Like other active hydrides, CBH-etherates undergo protonolysis generating gaseous hydrogen and hydrogen chloride.



This reaction is violent and accompanied by heat evolution.

Etherates of CBH: Like beryllium chloride, $ClBeH$ forms di- and monoetherates. The dietherate, $ClBeH:2OEt_2$ can be isolated from its ether or benzene solution by pumping in high vacuum at $0^\circ C$. to remove unbound ether. The ratio of bound ether to beryllium was 2/1. The dietherate upon pumping at $25^\circ C$. loses one mole of ether per mole of adduct to form the monoetherate according to the equation



* We wish to thank Dr. D. Horvitz of this laboratory for suggesting use of iodine as an oxidizing agent for chloroberyllium hydride.

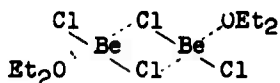
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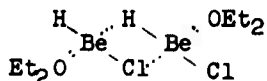
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The dimeric nature of beryllium chloride monoetherate ²



suggests a dimeric structure for ClBeH:OEt_2



which accounts for the formation of BeH_2 on disproportionation.

Behavior of CBH toward NaH: Synthesis of CBH at room temperature in the presence of a large excess of NaH indicated that this intermediate undergoes little or no reaction with NaH. At a stoichiometry of 1.795 NaH to 1.0 BeCl_2 , the conversion of BeCl_2 to CBH was 69.4%, higher than the 60.3% obtained at the ratio of 0.987 to 1.0 (Table II), Expts. No. 752-71, -67).

The behavior of CBH:2OEt_2 toward NaH was also examined in benzene solution at 70-80°C. (Figs. 3 and 4). Increasing the molar ratio of NaH/ BeCl_2 from 1.06 to 1.33 increased the soluble ratio of H/Be from 0.84 to 0.95 without an observed diminution in the beryllium concentration. These observations indicate that even at these temperatures the CBH intermediate is remarkably stable toward NaH.

Infrared Absorption of CBH: An IR spectrum of ClBeH -etherate exhibited a band at 5.6 μ , close to 5.63 μ observed for $i\text{-PrBeH}$ ³.

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- (2) NAVWEPS Report No. 7227, page 6, 1962.
(3) LPIA Abstracts, C61-403, 1961.

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Disproportionation of Chloroberyllium Hydride

Two methods for the preparation of beryllium hydride from CBH were investigated: (1) vacuum disproportionation in the absence of solvents and (2) disproportionation in various solvents at atmospheric pressure. Factors studied include:

- (1) Temperature of disproportionation
- (2) Type of solvent used for extracting $\text{BeCl}_2 \cdot \text{OEt}_2$ (Eq. 7)
- (3) Effect of temperature on removal of solvents from the final product.
- (4) Treatment of BeH_2 with hydride reagents to remove residual chloride and retained ether.
- (5) Nature of complexing agents for the CBH intermediate, e.g., Et_2O , Me_2S , Me_2O and NMe_3
- (6) Type of disproportionation media e.g., ether, dimethylsulfide, diphenyl sulfide, benzene, toluene, dichloromethane, 1,2-dichloroethane, 1,1-dichloroethane, chlorobenzene, cyclohexane and kerosene.

To date, all methods examined for the disproportionation of CBH, except that in which 1,2-dichloroethane was used as a solvent, gave products amorphous to X-ray with purities ranging from 23 to 85 wt. % BeH_2 . In the case of 1,2-dichloroethane the disproportionation products exhibited crystalline structure to X-ray. However, the purity was 31 wt. % BeH_2 (or 76.6 mole % based on total Be). This result was somewhat encouraging in view of the fact that the other products with comparable purity were totally amorphous to X-ray. It is not certain whether the observed diffraction lines are related to crystalline species of BeH_2 or to unknown impurities. Therefore, judgement on the crystallinity awaits preparation of pure BeH_2 .

In order to establish the chemistry involved in the disproportionation step most of the work was carried out under vacuum in the absence of solvents to avoid possible complication by solvent effects. The details are described below:

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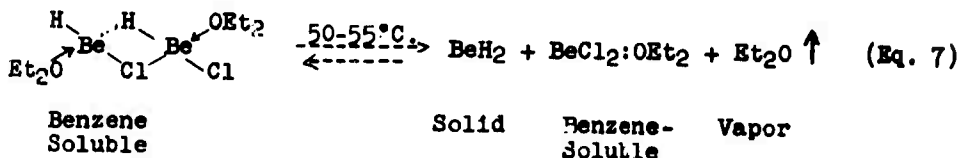
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Vacuum Disproportionation of CBH

Subjecting ClBeH:OEt_2 to vacuum heating with distillation of the ether as soon as formed yielded BeH_2 in conversions up to 63.9% based on initial CBH:



The beryllium hydride produced was a white solid having extreme sensitivity toward atmospheric conditions. When freshly isolated, it sparked and glowed on exposure to moist air with enormous evolution of heat. The major impurities were attributed to Be-O and residual Be-Cl bonds. The source of the oxide contaminant was most likely due to the incomplete exclusion of air and moisture during handling of the solid.

Ether cleavage was not observed during the disproportionation of the CBH-etherate, indicating that the oxide impurity was not derived from ether cleavage.

Evidence for $\text{BeCl}_2\text{:OEt}_2$ as By-Product in the CBH Disproportionation: While investigating the thermal stability of CBH-etherate in a closed system, a crystalline material sublimed and deposited above the heated zone. Beryllium and chlorine content in the sublimate corresponded closely to that of beryllium chloride-monoetherate, $\text{BeCl}_2\text{-Et}_2\text{O}$. Anal: Calculated for $\text{BeCl}_2\text{O}(\text{C}_2\text{H}_5)_2$: Be, 5.85%; Cl, 46.0%. Found: Be, 5.78%; Cl, 44.78%.

Factors Governing the Disproportionation of CBH in Vacuum: The disproportionation of CBH to BeH_2 and BeCl_2 was found to depend on several factors: (a) presence of excess ether, (b) effect of temperature, and (c) type of solvents.

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Use of $AlEt_3$ as the ether acceptor was discouraged by the possibility of inducing ethyl-hydride exchange between aluminum and beryllium.

Effect of Temperature on the Extent of Disproportionation: Thermal dissociation of CBH-etherate under vacuum also resulted in the disproportionation to BeH_2 and $BeCl_2$ monoetherate. The disproportionation product exhibited improved H/Be ratio with increasing temperature. The percent conversion of CBH to BeH_2 and the percent purity were improved with higher temperatures. These trends are shown in Table V.

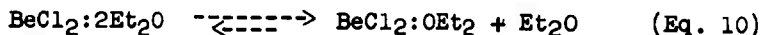
TABLE V

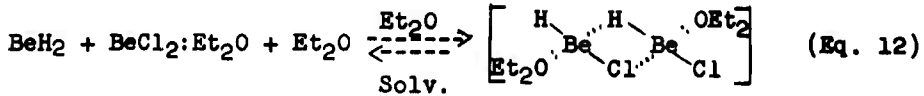
Effect of Temperature on the Extent of Disproportionation of CBH Under Vacuum

Expt. No.	Temp. of Disproportionation, °C.	Ratio ^a H/Be	Ratio ^a H/Cl	% Conversion of CBH to BeH_2	Purity, Wt. % as BeH_2
952-164	25	1.52	-	20.6	49.9
237	55.5	1.68	6.75	31.4	--
238	80	1.74	14.25	58.2	--
134	85	--	--	63.9	69.2
212	95	1.86	15.05	--	--

(a) Aqueous acetic acid solutions were used in the hydrolysis.

Formation of the monoetherate during the disproportionation step is consistent with previous findings² describing the dissociation of beryllium chloride-dietherate to the monoetherate and ether.





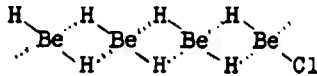
Solid Solution

Solution

In the absence of free Et_2O or Me_2S using benzene as the extracting solvent, $\text{BeCl}_2 \cdot \text{OEt}_2$ can be mostly washed away from BeH_2 without dissolution of the latter. For this reason, the conversion of CBH to BeH_2 is higher than in dimethyl sulfide (Table VI). These results showed that benzene is preferred for the initial removal of $\text{BeCl}_2 \cdot \text{OEt}_2$ from BeH_2 . Residual Be-Cl bonds may be minimized by additional extraction with ether or thioether.

Purity of the Disproportionation Product: The purity of the product appeared to depend on several factors: (a) Effect of solvent. (b) Inertness of atmosphere under which the product is handled. (c) Temperature of disproportionation.

Effect of Solvent on the Purity of BeH_2 :
Although BeCl_2 -monoetherate was extracted from BeH_2 by benzene, some Be-Cl bonds were retained in the solid. This indicated that some residual Be-Cl bonds were either physically occluded in the solid or chemically bound in the structure, postulated as:



The effect of solvents on the removal of retained Be-Cl bonds and on the purity of produced BeH_2 is shown in Table VII.

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TABLE VII

Analytical Data on the Effect of Solvents on the
Removal of Residual Be-Cl Bonds and on the Purity of BeH₂

Extraction Solvent	Sample Wt., mg.	Composition, mmoles			Ratio H ⁻ /Cl ⁻	Purity of BeH ₂ , Wt. %
		H ⁻	Be ⁺⁺	Cl ⁻		
Benzene ^a	48.4	1.42	1.70	0.35	4.0	16.1 ^c
Et ₂ O ^b	187.0	20.88	11.59	0.85	25.2	61.4 ^c
Me ₂ S ^b	117.2	12.92	7.64	0.30	43.2	60.4 ^c
Me ₂ S ^b	56.4	7.66	4.25	0.15	51.2	74.7 ^d
Me ₂ S + Benzene ^e	14.5	11.53	6.11	0.16	72.2	85.1 ^d
Me ₂ S ^b	63.4	8.33	4.67	0.12	69.4	72.3 ^d

- (a) Washing with benzene until filtrate is free of soluble chloride.
- (b) Soxhlet extraction.
- (c) Handled in a polyethylene bag filled with nitrogen.
- (d) Handled in a dry box filled with nitrogen.
- (e) Washed with Me₂S followed by extraction with benzene.

These results show that the observed beryllium content in the final product was always larger than that required to combine with total hydride and chloride ions. This indicated the presence of beryllium compounds other than BeH₂ and BeCl₂. The major impurity appeared to consist of beryllium oxide or Be(OH)₂ resulting from exposure of the product to atmospheric conditions during handling. This point was demonstrated by an observed decrease in the purity with continued manipulation of the product as shown below.

Effect of Exposure to Atmospheric Conditions:

Handling and weighing of the solid in a dry box, using nitrogen, gave higher purities (Table VII) than obtained with plastic bags filled with nitrogen. Continued handling of the solid resulted in diminution of the active hydride and chloride content of the product with corresponding increase in Be(OH)₂. This trend is shown in Table VIII.

TABLE VIII

Data on the Decrease in Purity of BeH₂ with Further Handling

Extraction Solvent	Extraction Time, hrs.	Distribution of Be Mole %			Purity of BeH ₂ Wt. %	
		BeH ₂	BeCl ₂	Be(OH) ₂ ^b	Calc. ^c	Obs. ^d
Et ₂ O	16	90.10	3.65	6.25	63.5	61.4
Me ₂ S	16 ^a	-	-	-	-	54.1
Me ₂ S	16 ^a	82.60	3.20	14.20	50.8	50.3

- (a) Duplicate samples analyzed 24 hrs. apart.
- (b) Obtained by difference from beryllium balance.
- (c) Based on BeCl₂ and Be(OH)₂ as the only impurities.
- (d) Heated at 100°C. with pumping (10⁻⁵ mm. Hg.) to remove residual solvents.

The results presented in Table VIII show that further manipulation of the solid led to a decrease of 7.5% in the molar content of BeH₂ and a 0.45% decrease in BeCl₂ with a corresponding increase of 7.95% in Be(OH)₂. It is significant to note that the percent purity calculated on the basis of BeCl₂ and Be(OH)₂, being the only contaminants, is in good agreement with the observed purity based on sample weight. This indicated that other impurities derived from ether cleavage or solvent retention were negligible. It is therefore essential to maintain absolutely moisture- and oxygen-free conditions during handling (isolation, transfer, and weighing) of the solid.

Effect of Disproportionation Temperature on the Purity of BeH₂: The possibility of ether cleavage under the conditions of CBH disproportionation was studied. Cleavage of Et₂O was not observed when the disproportionation step was carried out at 75°C. for a period of 1 hr. However, when the reaction mixture was pumped at 85°C for 20 hrs. ethyl chloride was detected (Eq. 13). Sublimation of BeCl₂-monoetherate and generation of free ether were also observed. No trace of ethane was found. The latter substance would be present if ether were cleaved by Be-H bonds.

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The residual Cl^- content in EeH_2 was found to be a function of disproportionation temperature. The results are compiled in Table IX.

TABLE IX

Effect of Disproportionation Temperature on the Purity of BeH_2 and on the Retention of Residual Cl^- Ions



Disproportionation Temperature, °C.	Atomic Ratio		Purity of BeH_2 , Wt. %
	$\text{H}^-/\text{Cl}^-^{\text{c}}$	H/Be^{++}	
125	20.0	1.97	43.3
80	39.5	1.88	70.9
74	51.0	1.80	74.7
60	107.5	1.94	77.8
58	72.2	1.89	85.1
45	37.6	1.91	61.7

- (a) Extracted with solvents such as toluene, benzene and/or dimethyl sulfide
- (b) Removed by vacuum distillation.
- (c) Atomic ratio of active H^- to residual Cl^- in final product.

These data (Table IX) show that the atomic ratio of active H^- to residual Cl^- increases with decreasing temperature reaching a maximum value of 107.5 at 60°C. At a lower disproportionation temperature (45°C.) the ratio decreased to 37.6. These observations indicate existence of an optimum temperature at which residual Be-Cl bonds are at minimum.

In view of the increase in residual chloride content at the high temperatures, and the report of Turova et al.⁴

(4) Turova et al., Russian J. Inorg. Chem. 8, 275-7 (1963).

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on the thermal decomposition of $\text{BeCl}_2:20\text{Et}_2\text{O}$ to form polymeric ethoxyberyllium chloride, ethyl chloride, and ether



without formation of BeCl_2 -monoetherate, it was suspected that cleavage of ether might contribute to the chloride impurity. Accordingly, the thermal behavior of $\text{BeCl}_2:2\text{Et}_2\text{O}$ was investigated under the conditions of the disproportionation of CBH.

Dissociation of $\text{BeCl}_2:2\text{Et}_2\text{O}$ with removal of Et_2O as soon as it is formed gave one mole of Et_2O per mole of adduct according to (Eq. 10) without formation of EtCl . However, when the decomposition was carried out in a closed system at up to 113°C . (without ether removal) ethyl chloride formation was observed. Consequently, the decomposition was studied at various temperatures to determine the lowest temperature at which the monoetherate can be formed without inducing ether cleavage. Thus, the dietherate was heated at different temperatures, trapping the volatiles at -196°C ., and examining the condensates for the presence of EtCl . The results are shown in Table IX.

TABLE IX

Data on Thermal Stability of $\text{BeCl}_2:20\text{Et}_2\text{O}$ (Initial $\text{BeCl}_2:20\text{Et}_2\text{O} = 12.5$ mmoles)

Heating Temp., $^\circ\text{C}$.	Heating Time, hrs.	Et_2O Evolved ^a mmoles	Ratio ^b $\text{Et}_2\text{O}/\text{BeCl}_2$
25.8	1.00	3.54	1.72
30.5	1.00	5.77	1.25
49.0	1.16	2.85	1.03

- (a) No trace of EtCl was found by mass spectra
 (b) Molar ratio $\text{Et}_2\text{O}/\text{BeCl}_2$ in the residue

These data indicate that even at 49°C. the adduct $\text{BeCl}_2:2\text{Et}_2\text{O}$ readily loses ether to form the monoetherate without elimination of EtCl . Additional heating of the residue ($\text{BeCl}_2:\text{Et}_2\text{O}$) at 74°C. for 1.0 hr. gave no sign of cleavage. However, continued heating at 76°C. for long periods of time (24 hrs.) resulted in considerable amounts of EtCl elimination. This is in agreement with the previous finding on the formation of ethyl chloride when CBH -etherate was heated at 85°C. (p.28). Thus, the disproportionation under vacuum should be conducted at temperatures lower than 75°C.

Disproportionation of Chloroberyllium Hydride in Solution

Solvent Effect on the Disproportionation: The study of the disproportionation of CBH in solution was encouraging because the product exhibited improved properties over those obtained by vacuum-heating. The disproportionation in solution rendered the product BeH_2 less reactive, more compact and readily filtrable and hence easier to handle than observed previously.

Etherates of ClBeH and BeCl_2 dissolve in ether, diphenylsulfide, benzene, toluene, chlorobenzene, 1,2-dichloroethane and dichloromethane. Consequently, the disproportionation was carried out in these solvents with the objective of obtaining crystalline BeH_2 .

Heating a solution of CBH in Et_2O produced an ether-insoluble white solid. Infrared spectra of the solid in Nujol mulls exhibited a Be-H absorption band between 5.60 and 5.75 μ . The disproportionation product was found to be sensitive to atmospheric conditions. An infrared spectrum of its KBr pellet made under atmospheric conditions resulted in disappearance of this band and appearance of an O-H absorption band. This spectrum was identical to that of $\text{Be}(\text{OH})_2$ indicating that the solid hydride had hydrolyzed to hydroxide. This was confirmed by evolution of gaseous hydrogen on treatment of the solid with dilute aqueous acids.

Analysis of another sample, after Soxhlet extraction with ether, gave a product analyzing 71.3 wt.% BeH_2 with a ratio of H^- to residual Cl^- of 90.5/1.0. These results indicate that dimeric CBH undergoes facile disproportionation in liquid media which dissolve the by-product $\text{BeCl}_2:\text{OEt}_2$. The conversion of $\text{ClBeH}:2\text{OEt}_2$ to the dimeric form $(\text{ClBeH}:\text{OEt}_2)_2$ was found to be a prerequisite for the disproportionation (Eq. 7).

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The disproportionation reaction in Et_2O is slow. Only 9.5% of the active soluble hydride was rendered insoluble on heating at reflux for 16 hrs. Chloride concentration remained constant indicating that the disproportionation step proceeded as anticipated. The product was X-ray amorphous.

In diphenylsulfide the disproportionation gave gelatinous products difficult to filter, wash and process. However, treatment with polar solvents such as diethyl ether and dimethyl sulfide resulted in transformation from a gel to a powder with discrete particles which could be readily filtered, extracted and transferred. Although, the Et_2O -treated products had better flow characteristics than the gelatinous materials, they exhibited amorphous structure toward X-ray.

Disproportionation of CBH:OEt_2 in benzene and toluene with or without small amount of biphenyl also produced amorphous products.

When the disproportionation was carried out in 1,2-dichloroethane solvent the product exhibited considerable amount of crystallinity toward X-ray. Analysis of a sample, kept for several weeks in a glass container stoppered with a serum cap, gave a purity of 31 wt.% BeH_2 . It is not certain whether the X-ray lines are derived from crystalline BeH_2 or from contaminants. The role of 1,2-dichloroethane needs to be clarified.

Use of 1,1-dichloroethane as a disproportionation medium was explored and found to give a product totally amorphous to X-ray in contrast to the crystalline product obtained in 1,2-dichloroethane.

Other solvents tried were β,β' -dichloroethyl ether and diisopropyl ether. In the former disproportionation of CBH could not be effected to give solid products even upon heating at 112°C . At this temperature darkening of solvent was observed. In the case of diisopropyl ether the disproportionation of CBH gave a solid product highly rich in chloride content presumably forming insoluble BeCl_2 -isopropyl etherates.

In chlorobenzene solvent, no evidence of CBH disproportionation was observed as shown by lack of solid formation even upon heating at 75°C . for 8 hrs. At reflux temperature (132°C .) only an insignificant amount of solid was formed. This indicated that chlorobenzene is a good solvent for CBH:OEt_2 and that it should provide a good medium for

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molecular weight determination of the adduct. Another solvent in which the disproportionation could not be effected was found to be dichloromethane which should also be a good medium for determining the degree of association of $\text{CBH}:\text{OEt}_2$.

In non-solvent media such as cyclohexane and kerosene, the disproportionation led to solid products. Soxhlet extraction with benzene left insoluble amorphous BeH_2 with extreme reactivity toward moisture similar to that exhibited by the product obtained from vacuum-disproportionation.

These results point to the specific effects of various solvents on the course of CBH disproportionation as well as the nature of product.

Effect of Temperature and Time of Disproportionation on the Purity of BeH_2 : In addition to the effect of solvents, other variables such as temperature and time of disproportionation seemed to influence the purity of the product as shown in Table X. The product obtained in benzene solution at $80-83^\circ\text{C}$. after 16.8 hrs. of reaction time had a maximum purity of 75.3 wt. % BeH_2 , compared to 48.4% obtained in 0.9 hrs. By contrast the vacuum-disproportionation gave 70.9% at 80°C . and 85.1% at 58°C . Attempts to increase the purity by conducting the disproportionation in benzene solution at a lower temperature, 54°C ., under reduced pressure, gave 23.1 wt.% BeH_2 with a ratio of H/Cl^- of 6.55.

The data of Table X showed that the atomic beryllium distribution in the isolated products reached up to 96 mole % BeH_2 , 3.22 mole % BeCl_2 and 0.78 mole % of Be^{++} bound to anions other than Cl^- . It was observed that the product retained Et_2O as evidenced by mass spectral analysis conducted on the gaseous products resulting from hydrolysis. Ethane was also detected indicating cleavage of the ether by the heat generated during acid hydrolysis. This result implied that the ether underwent cleavage by Be-H bonds rather than by Be-Cl bonds. Efforts were directed to remove the residual Be-Cl impurity which, most likely, provides the sites for ether coordination.

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TABLE X

Data on the Disproportionation of CBH in Refluxing Benzene



Solution Solid Solution Vapor

Expt. No.	Disproportionation Time, hrs.	Vacuum Heating of Solid		Time, hrs.	Be Distribution			Purity d Wt. % BeH ₂
		Temp., °C.	Temp., °C.		BeH ₂	BeCl ₂	Be + c	
966-163 e	0.9	140		16	78.18 f	3.42	18.40	48.4 h
157	3.3	122		16	77.20 g	3.18	19.60	54.2 i
151	3.3	96		1.3	96.00 g	3.22	0.78	55.2 i
134	16.8	25		16.0	93.84 f	2.65	3.51	61.0 i
131	16.8	160		12	93.20 f	2.42	4.38	75.3 i

(a) Ether distilled off at a reflux ratio of 30/1.

(b) To remove residual solvents.

(c) Beryllium impurity other than BeCl₂, possibly Be(OH)₂ or Be-OEt bonds derived from ether cleavage.

(d) Ether detected in the hydrolysis products.

(e) CBH-etherate added dropwise to refluxing benzene with simultaneous distillation of Et₂O (reflux ratio 10/1).

(f) Soxhlet-extracted with benzene.

(g) Soxhlet-extracted with Me₂S followed by benzene.

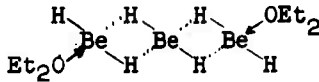
(h) Electrostatic with extreme hydrolytic activity.

(i) Non-electrostatic, readily filtrable with low activity toward water.

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Removal of Retained Ether: The retained ether probably coordinates with the hydride at terminal positions, thereby preventing build-up of long chains of polymeric beryllium hydride.



In view of the fact that linear high polymers are generally crystalline materials, it is likely that long linear chains of $(\text{BeH}_2)_n$ will assume crystalline structure. Accordingly methods were sought to remove the ether thereby permitting linear chain growth.

Two methods for the removal of the ether were investigated: (a) Thermal dissociation, and (b) Chemical displacement with hydride reagents.

Thermal Dissociation: In order to remove ether, the thermal behavior of the linkages $\text{BeH}_2:\text{OEt}_2$ (retained ether) and $\text{Et}_2\text{O}:\text{BeHCl}$ (residual Cl^-) was studied by subjecting the products to pumping at various temperatures ($97-177^\circ\text{C}$.). The study showed that the extent of ether removal depends on the temperature and time of heating. The results are shown in Table XI.

The data of Expt. 198 show that subjecting a sample of BeH_2 to pumping at 100°C . for 4 hrs. left a hydride residue with 72 wt. % BeH_2 , and an ether content of 4.47 wt. % Et_2O (evolved on hydrolysis). Heating another sample at 97° for 16 hrs. under vacuum (Expt. 194) removed considerable amount of the ether leaving a product with 1.46 wt. % Et_2O but decreased the purity to 68.8% BeH_2 . This result was traced to side reaction involving ether-cleavage producing involatile $\text{Be}-\text{OEt}$ bonds with liberation of ethane and small amount of ethyl chloride (Expt. 199). These vapors including ether and benzene were condensed in traps cooled by liquid N_2 and finally analyzed by mass spectra.

In Expt. 201 a product obtained from CBH disproportionation at 54°C . in benzene solution suffered considerable cleavage reaction when vacuum-heated for 47 hrs. at 104°C . as shown by an increase in the percentage of ethane and ethyl chloride and a decrease in the purity to 23.1% BeH_2 . Thus, it is evident that the product could not be freed from retained ether by thermal means, since the involatile cleavage

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TABLE XI

Data on the Removal of Residual Chloride and Ether from the CBH Disproportionation Product
Effect of Temperature on Cleavage of Retained Ether

Expt.	Vacuum-Heating Time,	Temp., h	Residual Cl ⁻ , Wt.-%	Retained Et ₂ O, Wt.-% ^a	Atomic Ratio H ⁻ /Cl ⁻	Purity BeH ₂ , Wt.-%	Condensables Evolved g on Heating, mole %	
							Et ₂ O	EtCl
996-198	4	100	3.6 ^b	4.5	130.0	72.0	-	-
194	16	97	3.2 ^b	1.5	137.5	68.8	-	-
199	17	107	3.6 ^b	1.4	113.2	64.5	6.7	2.3
201	47	104	22.8 ^c	2.80	6.55	23.1	57.8	20.4
177	17.5	142	15.1 ^d	0.5 ^e	19.8	46.2	59.0	32.0
192	18.5	177	12.9 ^d	0.3 ^f	43.3	80.0	(H ₂)	

- (a) Ether evolved on hydrolysis, based on weight of solid hydrolyzed
- (b) Disproportionation of CBH carried out under vacuum at 45-55°C.
- (c) Disproportionation of CBH carried out in benzene solution at 54°C.
- (d) Disproportionation of CBH carried out in benzene solution at reflux (80-82°C.).
- (e) Product treated with LiBH₄ at 25°C.
- (f) Product treated with LiBH₄ at 52°C.
- (g) Percent of total condensables including benzene.
- (h) To remove solvents.

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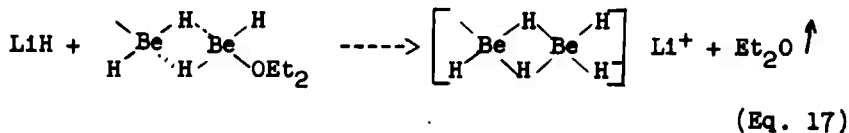
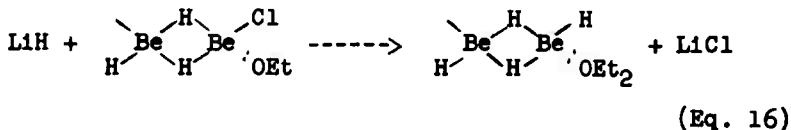
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products, Be-OEt bonds, render the hydride impure. Consequently chemical means were investigated to displace the ether and residual chloride.

Chemical Displacement of Ether with Hydride Reagents: It is known that hydride reagents displace ligands such as Et₂O and NMe₃ from their adducts.⁵



Therefore, the action of hydride reagents was explored as a means to remove chloride and ether impurities in accordance with the following equations:



Reduction with ether-soluble hydrides such as LiBH₄ and LiAlH₄ was briefly examined

(5) Bell, N.A., and Coates, G. E., J. Chem. Soc., 692 (1965)

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Reaction with Lithium Borohydride: Preliminary results with LiBH_4 indicated incorporation of BH_3 groups to the BeH_2 structure without retention of Li^+ ions. Treatment of an impure product, 55.2 wt. % BeH_2 , with LiBH_4 in Et_2O increased the purity to 80.0 wt. % based on BeH_2 (as 100%). Its atomic ratio of H/Be was 2.28 indicating a composition $(\text{BeH}_2)_{21} \cdot \text{B}_2\text{H}_6$. The residual chloride content decreased from an initial value of 26.7 to 12.9 wt. % Cl. The retained ether amounted to 0.3 wt. % $(\text{C}_2\text{H}_5)_2\text{O}$.

The experimental results are presented in Table XI for comparison. Expt. 192 shows results obtained with a product treated with LiBH_4 at 52°C . followed by Soxhlet extraction with ether. Heating of the product at 177°C . in a closed system for 18.5 hrs. decomposed the hydride to metallic beryllium and gaseous hydrogen. The pyrolytic H_2 was measured and the solid was hydrolyzed to release hydrolytic H_2 . About 46.5% of the initial hydride underwent decomposition showing that hydride was unstable at 177°C . The data of Expt. 177 (Table XI) show results related to the reaction of LiBH_4 with a sample of BeH_2 (prepared from CBH disproportionation in refluxing benzene at $80-81^\circ\text{C}$.). In this experiment the product was treated with an ether solution of LiBH_4 at 25°C ., Soxhlet-extracted with ether, pumped at 25°C . to remove most of the solvent and finally heated at 142°C . for 17.5 hrs. The volatile gases were condensed at -196°C . and measured. The -196 condensate consisted of 59.0% Et_2O , 32.0% C_2H_6 and 0.2 $\text{C}_2\text{H}_5\text{Cl}$ pointing to ether cleavage at 146°C . forming EtO-Be bonds which account for the observed low purity of 46.2 wt. % BeH_2 . The chloride and ether contents were 15.1 wt. % Cl and 0.5 wt. % $(\text{C}_2\text{H}_5)_2\text{O}$.

In view of incorporating BH_3 groups as well as imparting thermal instability to the final product, use of LiBH_4 as a reagent for removing ether and chloride impurities was suspended.

Action of Lithium Aluminum Hydride: Treatment of the CBH disproportionation product with LiAlH_4 in ether solutions diminished both the residual chloride and ether with little or no retention of lithium and aluminum ions. This treatment led to an increase in the atomic ratio H/Cl from 107/1 to 142/1 and a decrease in the ether content from 9.16 to 0.86 wt. % $\text{C}_2\text{H}_5\text{O}$.

In this experiment, a product having a purity of 77.7 wt. % BeH_2 was treated with LiAlH_4 in ether solution in a sealed bulb at 54°C . (bath temperature) for 16 hrs. The solid residue was extracted with ether to remove soluble

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chloride. The ether solvent was vacuum-distilled at room temperature and the solid was finally heated under vacuum at 130°C. for 12 hours. The product was then weighed in a dry box for analysis. Comparative results obtained with and without LiAlH_4 are given in Table XII.

TABLE XII

Effect of LiAlH_4 on the Residual Chloride Content in BeH_2 Obtained from the Disproportionation of CBH

Expt. No. 1054-	Sample Wt., mg.	Weight Percent				Atomic Ratios		
		BeH_2	BeCl_2	$\text{Be}(\text{OH})_2$	Et_2O	H/Be	H/Cl	(H+Cl)/Be
11 ^a	73.0	77.70	5.47	7.67	9.16 ^c	1.94	107.5	1.96
12 ^b	35.0	69.3 ^e	3.44	27.10	0.86 ^d	1.82	142.2	1.89

- (a) Before treatment with LiAlH_4 .
- (b) After treatment with LiAlH_4 at 54°C.
- (c) Determined by difference.
- (d) Determined by vapor phase chromatography on the hydrolysate.
- (e) The solid contained undetectable amount of Li^+ and small amount of Al^{+3} (0.4 mg.) as shown by spectrographic analysis.

Although a decrease in the ether and chloride was observed (Table XII), the purity suffered a decrease from 77.7 to 69.3 wt. % BeH_2 . This was attributed to possible attack by moisture during work-up, isolation and sampling of the final product as shown by a decrease in the atomic ratio of H/Be from 1.94 to 1.82 and of (H+Cl)/Be from 1.96 to 1.89. This is in contrast to the theoretical value 2.00 for (H+Cl)/Be if exposure to moisture is avoided. From these observations it was not certain whether the decrease in ether content was related to displacement by hydride ions (H^-) or to hydrolysis.

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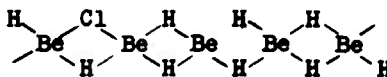
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It was surprising to note that treatment with LiAlH_4 led to diminution in both residual chloride and ether without retention of lithium ions. Displacement of ether from the BeH_2 product was expected to result in the incorporation of lithium hydride as represented by Eq. 17. The absence of lithium ions in the product indicates that the ether lost was not due to displacement by lithium hydride. Displacement of the ether via formation of new hydrogen bonds with concomitant increase in molecular weight of the $(\text{BeH}_2)_n$ polymer provides an alternate explanation which fits the observations. It might also be possible that the lithium content was too small to detect.

It is recommended that the action of LiAlH_4 should be further investigated toward obtaining chloride- and ether-free BeH_2 .

Effect of 1,2-Dichloroethane: Of all the solvents tried (p. 30-31) for the disproportionation of CBH only 1,2-dichloroethane gave a crystalline product toward X-ray. Initial experiments with 1,2-dichloroethane gave a product containing high residual chloride content ($\text{H/Cl} = 8.6$). This ratio was improved to 51/1 by treating the product with LiAlH_4 in ether solvent at 55-60°C. The purity however, was 34.1 wt. % BeH_2 . Some of the impurities were identified to be Et_2O (by vapor phase chromatography) and LiCl (by X-ray diffraction). Retention of the latter in this sample may be due to incomplete extraction with Et_2O . The X-ray diffraction pattern exhibited a number of lines in addition to those attributed to LiCl . In efforts to determine the origin of these lines it was suspected that $\text{BeCl}_2:\text{OEt}_2$, a by-product in the CBH disproportionation step (Eq. 2) could be insoluble in 1,2-dichloroethane and hence it would constitute a crystalline contaminant. However, it was found that $\text{BeCl}_2:\text{OEt}_2$ was completely soluble in 1,2-dichloroethane under the conditions of CBH disproportionation and that the X-ray pattern of the product excludes presence of $\text{BeCl}_2:\text{OEt}_2$. Other suspected impurities such as $\text{BeCl}_2:2\text{Et}_2\text{O}$, $\text{Be}(\text{OH})_2$, $\text{BeCO}_3:4\text{H}_2\text{O}$ and BeO have been excluded from the X-ray lines. These observations are encouraging in that the observed X-ray lines might be related to crystalline BeH_2 .

It is also possible that the observed X-ray diffraction might be related to residual Be-Cl bonds incorporated in a crystalline structure:



It was hoped that treatment with LiAlH_4 might transform the residual Be-Cl bonds to the corresponding Be-H bonds without alteration in the basic structure of the polymer. Thus, it was observed that treatment of the product resulting from CBH disproportionation in 1,2-dichloroethane with LiAlH_4 gave a different X-ray diffraction pattern than that obtained without LiAlH_4 .

Further work is necessary to determine the effect of 1,2-dichloroethane on the course of disproportionation and of LiAlH_4 on the nature of the final product.

Effect of Nucleation with Crystalline BeH_2 on the Nature of the CBH Disproportionation Product

CBH disproportionation was carried out in benzene, toluene, diphenyl sulfide, chlorobenzene, chloromethane, 1,2-dichloroethane in the presence of a few nuclei of crystalline BeH_2 (obtained from Ethyl Corporation). Thus far, the disproportionation in the presence of a few seeds of phase 378 gave amorphous products with the exception of 1,2-dichloroethane. In this solvent with or without seeding the products had similar X-ray diffraction patterns. It seems that seeding had no effect on the nature of the product.

Nature of Complexing Agents for CBH: A study of complexing ClBeH with Lewis bases of different coordination strength toward the central Be atom might lead to a disproportionation system to produce crystalline beryllium hydride.



Benzene
Soluble

Benzene-
Insoluble

Benzene-
Soluble

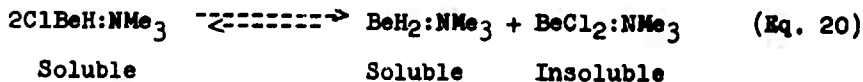
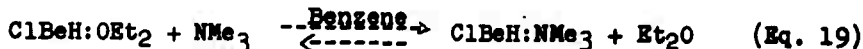
where $\text{Z} = \text{Et}_2\text{O}, \text{Me}_2\text{S}, \text{Me}_2\text{O}, \text{Me}_3\text{N}$.

The products obtained from the disproportionation of $\text{ClBeH}:\text{OEt}_2$, $\text{ClBeH}:\text{SMe}_2$, and $\text{ClBeH}:\text{OMe}_2$ under vacuum were all amorphous to X-ray. This indicated that coordination of ClBeH with different ligands such as Et_2O , Me_2S , and Me_2O did not alter the nature of the disproportionation product.

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The behavior of ClBeH:OEt_2 toward trimethylamine was investigated in benzene solution with the hope of displacing ether by the amine with simultaneous disproportionation to soluble $\text{BeH}_2:\text{NMe}_3$ and slightly soluble $\text{BeCl}_2:\text{NMe}_3$.⁶



To test this hypothesis, a benzene solution containing ClBeH:OEt_2 in admixture with some $\text{BeCl}_2:\text{OEt}_2$ was treated with trimethyl amine. In a preliminary experiment the displacement proceeded at room temperature to the extent of 87% based on the ether evolved. After removal of the ether and cooling of the benzene solution to 10°C. a small amount of a crystalline solid deposited which gave no hydrogen on hydrolysis, but the hydrolysate contained Be^{++} and Cl^- ions. The benzene solution contained both Be-H and Be-Cl bonds indicating that the intermediate, ClBeH:NMe_3 , if formed, did not undergo disproportionation as expected.

Attempted transformation of Amorphous to Crystalline BeH_2

Other areas related to possible transformation of amorphous BeH_2 to crystalline product were briefly examined. These are:

- (1) Solubilizing agents for BeH_2 , e.g., $\text{BeCl}_2:2\text{OEt}_2$, ClBeH:2OEt_2 , ClBeH:2SMe_2 and $\text{BeH}_2:\text{NMe}_3$.
- (2) Dissociation of $\text{BeH}_2:\text{NMe}_3$ in the presence of sodium hydride.
- (3) High shear extrusion of amorphous BeH_2 suspended in molten polystyrene.

Effect of Solubilizing Agents: Digestion of amorphous BeH_2 in mixed benzene-ether solvents containing

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- (6) Ethyl Corp., Quarterly Progress Report No. 2, contract AF 04(611)-9888, p. 5, August-October 1964.

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small amounts of solubilizing agents such as $\text{BeCl}_2:\text{OEt}_2$, $\text{HBeCl}:\text{SMe}_2$, $\text{HBeCl}:\text{OEt}_2$ or $\text{BeH}_2:\text{NMe}_3$ did not effect a noticeable change even after heating at 100°C . for several weeks.

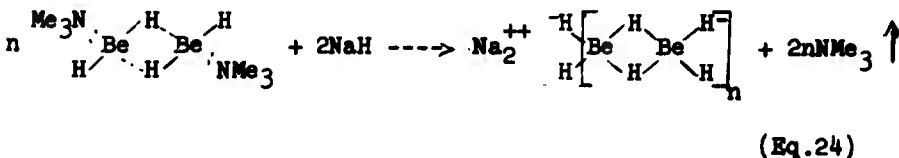
Dissociation of $\text{BeH}_2:\text{NMe}_3$ in the Presence of Hydride Reagents: Dissociation of $\text{BeH}_2:\text{NMe}_3$ is known to proceed according to the equilibrium,⁷



and since hydride reagents are known to displace ligands such as NMe_3 and Et_2O from their adducts e.g.,



it was hoped that use of catalytic amounts of NaH or LiAlH_4 as initiators for the displacement of NMe_3 from the adduct $\text{Me}_3\text{N}:\text{BeH}_2$ might produce ionic sites which might polymerize BeH_2



It is hoped that the ionic sites could propagate linear polymerization of BeH_2 chains with crystalline structure. Thus, the dissociation of $\text{BeH}_2:\text{NMe}_3$ (obtained from Ethyl Corporation) was studied in benzene solution in the

- (7) Ethyl Corporation, Annual Technical Summary Report No. 2 Contract AF 04(611)9376, page 44, June 1965.
 (8) J. K. Ruff and M. F. Hawthorne, J. Amer. Chem. Soc., 83, 535 (1961).

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presence of NaH. Only small amounts of solid were obtained at room temperature. However, carrying out the dissociation at reflux temperatures increased the amount of solid. Unfortunately, the product was amorphous to X-ray except for diffraction lines attributed to possible impurities in the hydride reagent used. It is of interest to note that $\text{BeH}_2\text{:NMe}_3$ underwent dissociation into its components in ether solution at reflux even in the absence of hydride reagents. The latter type of reaction to produce amorphous BeH_2 may have proceeded instead of the desired ionic growth reaction.

High Shear Extrusion

The amorphous nature of the hydride polymer may be due to the short chain lengths or to branching. Since linear high polymers are generally crystalline materials, it is likely that linear chains of $(\text{BeH}_2)_n$ will assume crystalline structure. Accordingly, an attempt was made to linearize the hydride product by stretching it through a small orifice at 180°C ., hoping to attain a crystalline structure. At this temperature crystallization of the hydride was not realized. High shear extrusion at higher temperatures may be required to effect the desired transformation.

STATUS

This effort is being continued under Air Force Contract AF04(611)-11402.

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EXPERIMENTAL

Materials: Two sources of BeCl_2 were used: (a) BeCl_2 -etherate prepared by reacting metallic beryllium with hydrogen chloride in anhydrous ether according to the known reaction.



The product had a ratio of $\text{Cl}/\text{Be} = 1.955$. (b) Beryllium chloride obtained from Brush Beryllium with 99.8% purity. Sodium hydride suspensions in heptane or in kerosene (18.15% NaH) was prepared in this laboratory with ratios of H/Na of 0.95 to 1.00.

Synthesis of CBH in Diethyl Ether Solvent: In a typical experiment, a solution of 49.4 mmoles of BeCl_2 in 106.6 g. of ether was treated with a suspension of 47.3 mmoles of NaH in kerosene. The reaction mixture was stirred with a magnetic stirrer at room temperature for 15.75 hrs. It was then filtered, and the solid phase was washed twice with fresh ether, and the filtered washings combined with the main filtrate. The volatile materials were distilled off under high vacuum leaving a clear residue, consisting of two colorless liquid layers with the upper layer being kerosene. Hydrolytic analysis of the bottom layer gave 32.58 mmoles of hydrogen,* 44.70 mmoles Be , 58.67 mmoles Cl and no sodium. These data show that the ether solution consisted of 32.58 mmoles CBH and 6.07 mmoles of unchanged BeCl_2 . Thus, the conversion to CBH was 68.9% based on initial NaH . The ratio of $(\text{Cl} + \text{H})/\text{Be}$ was 2.04 in close agreement with the theoretical value 2.00 for a mixture of ClBeH and BeCl_2 .

Analysis of the solid phase disclosed presence of 9.59 mmoles of unreacted NaH and 40.10 mmoles of NaCl . The hydride balance showed that 5.13 mmoles of hydride (or 10.8% of total hydride) was unaccounted for and presumably deposited as BeH_2 during step 1.

* Passed through 4 U-tubes held in liquid N_2 , collected by a Toepler pump into a flask of calibrated volume and measured. The H_2 was identified by combustion with CuO at 275-300°C. to give H_2O .

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Rate of CBH Formation from the Reaction of NaH with BeCl₂ in Diethyl Ether: In this study a mixture of sodium hydride and beryllium chloride in ether was attrited with steel balls in a glass reactor for specified intervals of time. The reaction mixture was allowed to stand for a few minutes to permit settling of the solid phase. A sample of the clear liquid phase was withdrawn periodically for analysis of soluble active hydride and chloride. After all of the liquid fractions were withdrawn, the solid phase was filtered and extracted with fresh ether. The ether extract was also analyzed. The results of a typical experiment are presented in Table XIII.

TABLE XIII

Rate Study of the Formation of Chloroberyllium Hydride from the Reaction of Beryllium Chloride with Sodium Hydride in Diethyl Ether at Room Temperature. (Initial amounts: BeCl₂, 66.7 mmoles, NaH, 62.8 mmoles. Solvent: Et₂O, 104.1 g.; kerosene, 6.8 g.)

Time, hrs.	Wt. of Filtrate grams	Mmoles		Atomic Ratio H ⁻ /Cl ⁻
		H ⁻	Cl ⁻	
3.75	19.09	3.87	14.12	0.203
19.75	18.80	7.48	14.07	0.532
45.42	29.13	13.50	19.64	0.693
62.42	19.17	8.60	12.96	0.664
110.42	Ether extract	9.86	15.14	0.652

The ratio H⁻/Cl⁻ in solution increased with time reaching a maximum value of 0.693 at an interval of 45.4 hrs. The ratio decreased to 0.652 after an interval of 110.4 hrs. It is evident that CBH undergoes very slow change over extended periods of time at room temperature in diethyl ether.

Composition of the Solid Phase: Hydrolytic analysis showed that the ether-insoluble solid contained 8.88 moles of unreacted NaH (14.1% of initial NaH), 54.33 mmoles of NaCl and 6.64 mmoles of Be. The ratio of undetected hydride (11.61 mmoles by total hydride balance) to the Be was 1.75, indicating, again, formation of BeH₂ during step (1). Infrared spectra on the solid before hydrolysis had a Be-H absorption of 5.8 μ.

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Rate of Formation of CBH from the Reaction of NaH with BeCl₂:2OEt₂ in Aromatic Solvents: Two types of apparatus were used - a) A 250 ml. 4-neck Morton flask provided with an electric stirrer fitted with a Teflon sleeve, a water cooled condenser, a thermometer, and a serum cap for sample withdrawal. (b) A 2-liter stainless steel reactor (Parr bomb) equipped with 2-inch diameter Cowles dispersator, a dip tube for sample removal, a thermocouple well and a heating mantle.

In this study a suspension of sodium hydride in kerosene was added to a stirred solution of BeCl₂-etherate in benzene, toluene or ether at a certain temperature. Samples of the reaction mixture were withdrawn periodically, weighed, filtered, and the clear filtrates analyzed for soluble active hydride and beryllium. The hydride content was determined by iodimetric titration and the beryllium by the conventional precipitation as Be(OH)₂ and ignited to the oxide. The ratios of soluble hydride to beryllium were then plotted vs. time (Fig. 2). Experimental details are given in Table XIV.

Rate of Formation of CBH in Me₂S: In this study a mixture of NaH and BeCl₂ was stirred with steel balls in a glass reactor for specified intervals of time. Samples of the reaction mixture were withdrawn periodically, filtered and the clear liquid phase was analyzed for soluble active hydride content. The data of a typical experiment is shown in Table XV.

TABLE XV

Rate of Formation of CBH in Dimethyl Sulfide

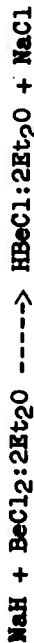
	BeCl ₂ + NaH $\xrightarrow{\text{Me}_2\text{S}}$ HBeCl + NaCl							
Time, hrs.	3.42	4.25	5.42	7.08	12.58	25.80	50.33	
% Conversion to HBeCl	17.80	25.50	25.20	24.15	23.00	21.10	20.15	

These data are plotted in Fig. 1. The shape of the curve obtained from plotting % conversion vs. time indicates occurrence of two consecutive reactions. The first portion of the curve represents rate of formation of CBH, and the

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TABLE XIV

Experimental Details on the Rate of CBH Formation in Aromatic Solvents



Expt.	Reaction Time, hrs.	Temp. °C.	Solvent	Molar Ratio		Conc. BeCl_2	Ratio H/Be^{++} c
				$\text{Et}_2\text{O}/\text{BeCl}_2$	BeCl_2/NaH a		
1005-							
65	4.0	65-80	Toluene	4.58	1.02	2.16	0.55
91	3.5	96-100	Toluene	2.57	0.90	1.31	0.62
84	2.0	100-105	Toluene	2.00	1.02	1.09	0.84
96	3.3	78-80	Benzene	2.01	0.87	0.96	0.70
1015-							
48	7.50	80	Toluene	2.2	1.0 d	0.7	0.07
41	1.25	100-103	Toluene	1.0 e	1.0	1.0	0.41
52	4.57	65-84	Benzene	2.02	1.0	0.9	0.72
60	4.2	73-80	Benzene	3.3	0.96	1.55	0.77

- (a) Average particle size of NaH = 5 u, with kerosene carrier
- (b) Moles per 1000 grams of solvent.
- (c) Ratio of hydride to beryllium in solution.
- (d) Average particle size of NaH = 40 u.
- (e) Dimethyl ether as complexing agent.

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last represents rate of consumption of CBH due to either disproportionation to insoluble BeH_2 or further reaction of CBH with NaH. A similar peaked curve occurs when Et_2O is the solvent although at higher conversion level. In Me_2S the maximum conversion of NaH to CBH is 25.5% at 4.25 hours, in contrast to 74% obtained in Et_2O at 30 hours. This indicates that Me_2S solvent is unsuitable for CBH production but it would be more suitable for extracting $\text{BeCl}_2:\text{OEt}_2$.

Preparation of $\text{ClBeH}:\text{OEt}_2$: Solutions of $\text{ClBeH}:\text{2OEt}_2$ were prepared routinely from the reaction of NaH (suspended in benzene) with solution of $\text{BeCl}_2:\text{2OEt}_2$ (1 molar) in benzene at $50\text{--}60^\circ\text{C}$. The reaction mixture was filtered and the clear filtrate vacuum-distilled at room temperature to strip the solvent and any ether of dissociation. This leaves a slightly viscous liquid consisting of $\text{ClBeH}:\text{OEt}_2$ with small amounts of unconverted $\text{BeCl}_2:\text{OEt}_2$, as shown below.

Evidence for the Existence of CBH-Dietherate: An ether solution, 49 g., containing 31.3 mmoles of chloroberyllium hydride and 16.0 mmoles of beryllium chloride, was cooled to -78°C . and pumped for 17 hrs. to remove unbound ether. The residue was then pumped at $0^\circ\text{C}/10^{-2}$ mm.Hg. for 1.0 hr. The weight of the final residue was 9.72 g. in close agreement with 9.44 g. calculated for 31.3 mmoles $\text{ClBeH}:\text{2Et}_2\text{O}$ and 16 mmoles $\text{BeCl}_2:\text{2Et}_2\text{O}$,

Evidence for the Existence of ClBeH -Monoetherate: Evidence for the existence of ClBeH -monoetherate has similarly been substantiated. A benzene solution containing known amounts of $\text{ClBeH}:\text{2Et}_2\text{O}$ (23.25 mmoles) and $\text{BeCl}_2:\text{2Et}_2\text{O}$ (5.65 mmoles) was slowly pumped at 25°C . under high vacuum (10^{-4} mm Hg) to remove the solvent and any ether of dissociation. The weight of the residue was found to be (3.68 g.) in good agreement with the total weight calculated (3.65 g.) for the monoetherates, i.e., 23.25 mmoles of $\text{ClBeH}:\text{OEt}_2$ and 5.65 mmoles of $\text{BeCl}_2:\text{OEt}_2$. The molar ratio of $\text{Et}_2\text{O}/\text{Be}$ was 1.02 in contrast to the theoretical value 1.00 for the monoetherates.

Upgrading of $\text{ClBeH}:\text{OEt}_2$: The viscous liquid obtained above was seeded with preformed $\text{BeCl}_2:\text{OEt}_2$ and cooled to 0°C . depositing a crystalline solid which can be readily centrifuged. Analysis of the supernatant liquid gave ratios of $\text{Cl}:\text{Be}:\text{H}$ of 1.01:1.00:1.04 and 1.02:1.00:0.98 in contrast to theoretical values 1:1:1 for ClBeH . Composition of the solid phase was not determined.

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Disproportionation of ClBeH:OEt_2 Under Vacuum: Solutions of $\text{ClBeH:2Et}_2\text{O}$ in various solvents such as ether, benzene or toluene were vacuum-distilled at room temperature to strip the solvents and any ether of dissociation. Two colorless liquid layers were obtained. The upper phase was found to be kerosene. The bottom phase consisted of a mixture of monoetherates, ClBeH:OEt_2 and unconverted $\text{BeCl}_2:\text{OEt}_2$. The monoetherates, freed from kerosene by decantation, were subjected to various disproportionation temperatures under high vacuum to give white solid products. The products were then digested with various solvents, e.g., toluene, benzene and/or dimethyl sulfide. The insoluble solids were filtered and washed with fresh solvents or subjected to Soxhlet extractions. Residual solvents were removed by vacuum-heating at 100 to 125°C . The final products were analyzed for active hydrogen, beryllium and residual chloride. Results of representative experiments are recorded in Tables V to VII.

Disproportionation of ClBeH:OEt_2 in Solution: Samples of CBH:OEt_2 were added to various solvent and nonsolvent media (benzene, toluene, chlorobenzene, diphenyl sulfide, dichloromethane, 1,2-dichloroethane, cyclohexane, kerosene). The reaction mixtures were then slowly subjected to fractional distillation at one atmosphere to partially remove coordinated ether. The distillations were terminated when evolution of ether had ceased. The solid products were filtered and Soxhlet-extracted with benzene, ether and/or dimethyl sulfide until free of soluble chloride ions. Removal of residual solvents was carried out by vacuum-heating at 110° to 130°C . overnight. The products were finally transferred to a dry-box filled with nitrogen (6-15 ppm moisture) for loading into capillary tubes for X-ray diffraction and for chemical analysis.

The samples were mounted in a Debye Scherrer camera and exposed to nickel-filtered copper radiation for 6 hrs. The spectrographic settings were 45 kv, 15 ma. The capillaries were rotated during the entire exposure time. All diffraction patterns contained an amorphous halo at 4.13°A with the exception of the disproportionation product obtained in 1,2-dichloroethane solvent. This product exhibited a number of diffraction lines in addition to a faint halo at 4.13°A . This experiment was repeated and the product gave the same X-ray diffraction pattern. Origin of the X-ray lines has not yet been determined.

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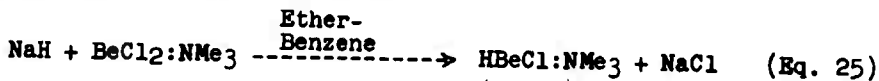
Dissociation of $\text{BeH}_2:\text{NMe}_3^*$ in the Presence of NaH: To 1.05 g. sample of $\text{BeH}_2:\text{NMe}_3$ (15 mmoles) dissolved in benzene solution was added 0.14 mmoles of NaH suspended in heptane. The reaction mixture was heated in a distillation apparatus under argon. The distillation was stopped when the head temperature reached 78°C . The reaction mixture was filtered and the solid was extracted with benzene for 16-1/2 hrs. X-ray analysis of the solid showed a halo at a d spacing of 4.130°A .

Dissociation of the amine adduct in the absence of NaH in refluxing ether solution also gave an amorphous product.

When catalytic amount of LiAlH_4 was used as the hydride reagent, only a small amount of solid was formed.

Displacement of Et_2O from $\text{CBH}:\text{OEt}_2$ with Trimethyl Amine: A 25.8 g. benzene solution containing 62.9 mmoles of $\text{HBeCl}:\text{OEt}_2$ and 7.1 mmoles of $\text{BeCl}_2:\text{OEt}_2$ was cooled to -196°C . and evacuated. Onto the frozen mixture was condensed 75.5 mmoles of trimethyl amine. The reaction mixture was warmed under vacuum and stirred at room temperature overnight. The volatile materials were removed by condensation at -80°C . leaving a solid residue. The -80°C . condensate contained 61.0 mmoles of Et_2O (by vapor phase chromatography) indicating displacement of 87% of total coordinated ether. The solid residue was redissolved in benzene and cooled to 10°C . depositing a crystalline solid which was filtered and washed with benzene at 10°C . Hydrolysis of the solid disclosed absence of active hydride indicating that hydride remained in solution which contained both active H^- and Cl^- ions. Exact composition of the solution was not determined.

Reaction of NaH with $\text{BeCl}_2:\text{NMe}_3$: The reaction of NaH with $\text{BeCl}_2:\text{NMe}_3$ was attempted in benzene by Ethyl Corp.⁶ to produce $\text{BeH}_2:\text{NMe}_3$ directly. The desired product $\text{BeH}_2:\text{NMe}_3$ was not obtained since no soluble hydride was isolated. The difficulty was attributed to the insolubility of the reactants in the reaction solvent. During the course of investigating the behavior of ClBeH toward NMe_3 we observed that the adduct $\text{BeCl}_2:\text{NMe}_3$ dissolves readily in a mixed ether-benzene solvent. Consequently its reaction with NaH was carried out to produce $\text{ClBeH}:\text{NMe}_3$ according to the equation



* Obtained from Ethyl Corp.

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To 8.00 g. of BeCl_2 (100 mmoles) suspended in 82.3 g. of dry benzene was added 5.54 g. of NMe_3 (94 mmoles). To this mixture dry ether (155.5 g.) was added. The solid went into solution except for slight cloudiness. The mixture was filtered under dry N_2 and charged into a ball-mill. To this mixture 2.45 g. of sodium hydride (102 mmoles suspended in 22.5 g. of benzene) was added and ball-milling was applied at room temperature. Samples of the reaction mixture were withdrawn at certain intervals, filtered and both the filtrate and the solid phase analyzed for H, Be, Cl and Na, the latter in solid phase only. The analysis indicated that after 18.5 hrs. of reaction time 24.1% of the initial $\text{BeCl}_2:\text{NMe}_3$ underwent transformation to soluble hydride presumably $\text{HBeCl}:\text{NMe}_3$. After 33 hrs. the conversion of soluble hydride was 33.5% and increased to 40.7% after 75.0 hrs. Most of the beryllium remained in solution except for a small amount which was not completely washed out from the solid phase consisting of by-product NaCl and unconsumed NaH .

Dissociation of $\text{BeCl}_2:2\text{Et}_2\text{O}$: A sample of 12.5 mmoles of $\text{BeCl}_2:2\text{Et}_2\text{O}$ was heated under vacuum at different temperatures: 25.8°, 36.5° and 49.0°C. for a period of 1 hour each. The volatile materials were removed from the heating zone and condensed in a trap held at -196°C. Mass spectral analysis of the condensates disclosed presence of pure ether. Ethyl chloride was not detected. The cumulative amount of Et_2O evolved was 12.16 mmoles leaving a molar ratio of $\text{Et}_2\text{O}/\text{BeCl}_2$ of 1.03 in the residual adduct.

Decomposition Pressure of $\text{BeCl}_2:2\text{Et}_2\text{O}$: A sample of the dietherate was prepared in a closed system provided with a mercury manometer. The solid etherate having a ratio of $\text{Et}_2\text{O}/\text{BeCl}_2 = 1.97$ was heated at various temperatures and decomposition pressures developed were recorded (Table XV).

TABLE XV

Decomposition Pressure of Beryllium Chloride-Dietherate

($\text{BeCl}_2:2\text{Et}_2\text{O} = 6.13$ mmoles, Vapor Space = 526.1 cc.)

t, °C.	31	32	41	45	49	55	61	65	72	86	89
P, mm.Hg.	3	4	6	9	13	14.5	20	22.5	32	45	49
t, °C.	90	93	94	98	100	104	105	108	111	113	
P, mm.Hg.	52	56	60	66	70	78	81	90	95	100	

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Upon cooling to room temperature the pressure decreased to 12 mm., indicating presence of a volatile material other than Et_2O . The vapor phase was removed while the solid was reheated to 88°C . Analysis by mass spectra showed that the vapor consisted of 2.5 mole % ethyl chloride and 97.5 mole % Et_2O .

The molar ratio of $\text{Et}_2\text{O}/\text{BeCl}_2$ left in the solid residue was 0.95, in contrast to the theoretical value 1.00 for the monoetherate, $\text{BeCl}_2:\text{Et}_2\text{O}$.

High Shear Extrusion of Beane Product: 1-2 g. Beane product (obtained from Ethyl Corp.) was suspended in 110 g. solution of 9% polystyrene in toluene. After evaporation of the toluene the polymer (containing BeH_2) was forced through an orifice of 0.6 mm. diameter and 8.3 cm. length at 180°C . and at a rate of 2.5 cm/min. The pressure delivered to a 1/2 in. diameter ram was in the range of 2500-3000 pounds. The polystyrene was finally Soxhlet-extracted with toluene leaving solid BeH_2 . The solid was amorphous to X-ray.

STATUS

This effort is being continued under Air Force Contract AFO4(611)-11402.

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DOCUMENT CONTROL DATA - R&D		
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1. ORIGINATING ACTIVITY (Corporate author) U.S. Industrial Chemicals Company Division of National Distillers & Chemical Corporation, Cincinnati, Ohio		2a. REPORT SECURITY CLASSIFICATION CONFIDENTIAL
		2b. GROUP 4
3. REPORT TITLE SYNTHESIS OF LMH-2 (UNCLASSIFIED TITLE)		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report, January 15, 1964 - October 15, 1965		
5. AUTHOR(S) (Last name, first name, initial) Murib, Jawad H.,		
6. REPORT DATE October 15, 1965	7a. TOTAL NO. OF PAGES 58	7b. NO. OF REFS 8
8a. CONTRACT OR GRANT NO AF04(611)-9700	9a. ORIGINATOR'S REPORT NUMBER(S) AFRPL-TR-66-15	
b. PROJECT NO. AFSC Project No. 3148		
c. Program Structure No. 7500	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) Monitor Report No. AFRPL-TR-66	
d.		
10. AVAILABILITY/LIMITATION NOTICES .1*		
11. SUPPLEMENTARY NOTES None	12. SPONSORING MILITARY ACTIVITY AFRPL (RPCS) Edwards Air Force Base, Calif. 93523	
13. ABSTRACT <p>Preparation of chloroberyllium hydride (CBH) from beryllium chloride-etherate and sodium hydride was achieved in conversions up to 95.3% based on initial beryllium chloride (C).</p> <p>Disproportionation of the CBH intermediate was demonstrated to give beryllium hydride in purities up to 85.1 wt.% BeH₂. The product was amorphous with residual Be-Cl bonds, retained ether, and Be-O bonds as the major contaminants. The atomic ratio of active hydride to residual chloride (H⁻/Cl⁻) in some samples of the final product reached up to 137/1 corresponding to an impurity of 5.0 wt. % BeCl₂ (C).</p>		

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14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
		Complex compounds, Metal Hydrides, Metal Chlorides, Disproportionation, Synthesis, Benzene, 1,2-Dichloroethane, Ethers, Thioethers.					

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