

PREPARATION OF BERYLLIUM HYDRIDE BY AN IMPROVED PYROLYSIS TECHNIQUE

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Summary

Beryllium hydride has been produced in purities of 90–98 wt% by the controlled pyrolysis of di-*t*-butylberyllium etherate in hot oil. It was obtained as an amorphous solid, remarkably stable at elevated temperatures and resistant to attack by water and common organic solvents. The source of residual impurities was shown by deuterium labeling to be derived largely from incomplete pyrolysis and ether cleavage. A series of alkylberyllium homologs was subjected to the pyrolysis reaction; of these $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$ gave the highest purity BeH_2 .

Introduction

Various methods for preparation of beryllium hydride have been reported since its discovery in 1933 [1]. At the time our work was undertaken only two routes were considered to be practical for producing it both in quantity and in reasonably high purity. In 1951 Schlesinger and coworkers [2] reported a procedure for the synthesis of BeH_2 in 50 wt% purity by reaction of LiAlH_4 with Me_2Be in diethyl ether. Holley and Lemons [3] obtained products containing about 60 wt% BeH_2 by the same method.

In 1954 Coates and Glockling [4] reported that BeH_2 could be prepared in about 70 wt% purity by the thermal decomposition of di-*t*-butylberyllium etherate at temperatures of 150–210°C. Holley and coworkers [5] repeated the work using a modified procedure, and obtained 80 wt% BeH_2 . Ether-free di-*t*-butylberyllium was also prepared and the pyrolysis product again contained about 80 wt% BeH_2 .

The present paper reports a technique for synthesis of BeH_2 , based on a modification of the Coates [4] and Holley [5] procedures, which routinely gives product purities of 90–95 wt%.

Results and discussion

High-purity BeH_2 was prepared by the addition of $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$ to well-stirred hot mineral oil (termed solution pyrolysis in this paper). The key to high purity lies in the pyrolysis technique, although it is essential that the highest quality reactants be used.

Di-t-butylberyllium etherate

The reaction of $\text{BeCl}_2 \cdot 2 \text{Et}_2\text{O}$ with the *t*-butyl-Grignard reagent was studied in detail. Large excesses of the Grignard reagent were found to promote Wurtz reactions; however, a small excess (10–15%) was needed to ensure that chloride did not contaminate the product. The properties of $t\text{-BuBeCl} \cdot \text{Et}_2\text{O}$ * are such that it should be expected to codistill with $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$.

Gel formation often occurred during the addition of $\text{BeCl}_2 \cdot 2 \text{Et}_2\text{O}$ to the Grignard reagent. This problem was particularly difficult to deal with when the reaction was scaled-up. Inverse addition was tested unsuccessfully. It was established that gelation of the reaction mixture could be related to the crystalline form of $\text{MgCl}_2 \cdot \text{Et}_2\text{O}$ produced. One type of $\text{MgCl}_2 \cdot \text{Et}_2\text{O}$, made up of fine, matted acicular crystals, always predominated when gelling occurred. A second type, characterized by small, granular irregularly shaped crystals, was present under non-gelling conditions. Both types analyzed as the MgCl_2 monoetherate, but gave significantly different X-ray diffraction patterns, as shown in Table 1. The factors controlling formation of one or the other types were never conclusively identified, although gelation usually could be prevented by adding a heel of the granular material to the reaction mixture.

Because of the low molecular weight of BeH_2 , almost any contaminant exerts an unusually large effect on purity. For example, considering only the by-products associated with the pyrolysis reaction (free metal, oxide, alkoxides, alkyls and chloride), a BeH_2 purity of 95 mol% is equivalent to only about 80 wt%. Therefore, once at the stage of $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$ distillation, air and moisture must be rigorously excluded.

Solution pyrolysis of $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$

For optimum purity, a pyrolysis temperature of $200 \pm 5^\circ\text{C}$ is crucial. BeH_2 purity drops significantly if the temperature is allowed to fall to only 185°C and overpyrolysis to free Be metal occurs at temperatures exceeding 210°C . For this reason, hydrocarbons with boiling points just above 200°C are desirable as reaction media. This allows additional temperature control by the refluxing oil as well as efficient isobutene and ether by-product removal.

Beryllium hydride of 90–95 wt% purity was prepared consistently in laboratory glassware by the solution pyrolysis method. Scale-up to larger equipment (5 and 25 gallon reactors) gave BeH_2 of 95–98 wt% purity. The analysis of material typically produced by this method, as well as that of the best sample obtained from a series of more than a hundred runs, is given in Table 2. Calculated on a mole basis, the typical product contained 97.8% BeH_2 , and the best

* Colorless platelets, m.p. $86\text{--}88^\circ\text{C}$, subl. 60°C at 0.15 mmHg (ref. 5, m.p. 50°C , subl. $<50^\circ\text{C}$ under vacuum).

TABLE 1
X-RAY POWDER DIFFRACTION DATA FOR $\text{MgCl}_2 \cdot \text{Et}_2\text{O}$

Granular form		Fibrous form	
d (Å)	I/I_0	d (Å)	I/I_0
7.60	s	10.8	s
7.13	s	3.46	m
5.18	m	3.07	m
3.49	m	2.51	w
3.24	w		
3.08	w		
2.85	w		
2.70	w		

product at least 99%. The impurities resulting from incomplete pyrolysis, reaction with air or moisture, and ether cleavage were identified as beryllium alkyls (containing ethyl, propyl and isobutyl groups) and alkoxides (principally ethoxy, isopropoxy and isobutoxy). Beryllium oxide and hydroxide accounted for most of the remaining impurities.

The neat pyrolysis procedure described by Coates and Glockling [4] and Holley and coworkers [5] was included in the present investigation, and we too were unable to achieve BeH_2 impurities above about 80 wt%. The problem with this technique lies in the physical behavior of the reaction mass. The neat pyrolysis is best done slowly, first at atmospheric pressure and then under vacuum. The reaction mass becomes a voluminous, porous solid with poor heat transfer characteristics. Even interrupting the process and crushing the solid to powder form affords little improvement in product purity. The solution pyrolysis method completely overcomes this problem.

Properties of pyrolytic BeH_2

Unlike the material obtained by metathesis reactions [2,3,6], BeH_2 prepared by solution pyrolysis is surprisingly stable at elevated temperature and is resistant to attack by water (pH 6–8) and common organic solvents [4]. Thermal stability tests indicate a decomposition rate of about 2.5% per year at 100°C. Differential thermal analysis (Fig. 1) of the two types of BeH_2 clearly shows the

TABLE 2
COMPOSITION OF BeH_2 PREPARED BY SOLUTION PYROLYSIS OF $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$

	Weight (%)	
	Typical product	Best product
BeH_2	94.3	98.4
Be metal	1.5	— ^b
BeCl_2 ^a	0.2	0.03
Be alkyls ^a	2.7	1.7
Be alkoxides ^a	0.2	0.04

^a Calculated as such. There is no evidence that the simple compound is present. ^b Below the detection limit, which is <1%.

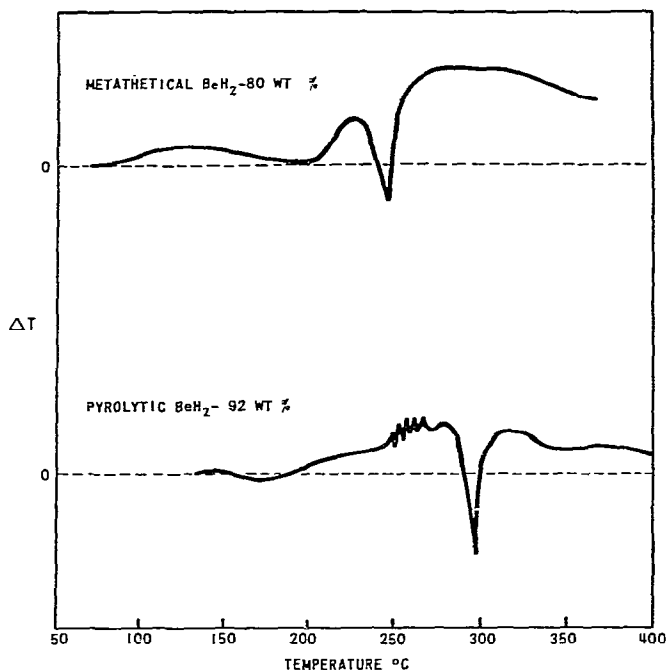


Fig. 1. DTA curves for beryllium hydride ($10^{\circ}\text{C}/\text{min}$, N_2 atmosphere).

greater thermal stability of BeH_2 prepared by solution pyrolysis. The major decomposition endotherm for pyrolytic BeH_2 initiates at about 275°C and peaks at 300°C , whereas decomposition of the sample prepared by metathesis* begins at the lower temperature of 235°C and peaks at 255°C . Analysis of the evolved gases by mass spectrometry showed that the exotherms at $250\text{--}275^{\circ}\text{C}$ in pyrolytic BeH_2 result from decomposition of small amounts of incompletely pyrolyzed alkylberyllium impurities.

Pyrolytic BeH_2 is a white to grey powder having an average particle size of $40\text{--}60\ \mu$. These particles are agglomerates of smaller ones 5 to $20\ \mu$ in size. The density averages $0.62\text{--}0.65\ \text{g}/\text{cm}^3$. At ambient conditions pyrolytic BeH_2 is resistant to attack by many of the common solvents, including protic ones. It reacts readily with mineral acids; hydrolysis is rapid below pH 4. A listing of the chemical reactivity of pyrolytic BeH_2 with a variety of solvents is given in Table 3. In some instances, e.g., with tap water or propionic acid, the BeH_2 surface appears to become passivated to further reaction after an initial contact period. On the other hand, if fresh surfaces are exposed by grinding, it will react with complexing solvents at room temperature [7].

Because it is nonvolatile and insoluble in solvents with which it does not react, molecular weight data for BeH_2 could not be obtained. Its properties conform to that for a chain polymer structure having bridging hydrogen atoms and relatively few terminal $\text{Be}\text{--}\text{H}$ groups [3]. It is amorphous (by X-ray diffrac-

* Prepared by reaction of Et_2AlH with $\text{BeCl}_2 \cdot 2\ \text{Et}_2\text{O}$.

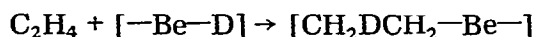
TABLE 3
STABILITY OF PYROLYTIC BeH₂ TO SOLVENTS

No reaction at room temperature	Reacts at room temperature	Reacts at elevated temperature
Tap water	Mineral acids	Distilled water
Hydrocarbons	Strong alkali	Alcohols
Alcohols	Ammonia	Organic acids
Ethers	Hydrazine	Tertiary amines
Organic acids		Be alkyls
Tertiary amines		B alkyls
		Al alkyls

tion) and gives an infrared spectrum (KBr disc) characterized by a broad absorption band at 1200–1500 cm⁻¹, assigned to a BeH₂Be stretching mode [8], and a broad weak band at 2780–3200 cm⁻¹.

Source of pyrolysis by-products

Incompletely pyrolyzed alkylberyllium compounds and free metal constitute most of the impurities. The ethyl- and butylberyllium species predominate, as might be expected from the composition of the starting material. Di-*t*-butylberyllium-*d*₁₈ etherate was pyrolyzed to 92–96 wt% BeD₂ and the beryllium alkyls remaining in the product were determined by hydrolysis with dilute HCl, followed by mass spectrometric analysis of the evolved gases. These gases consisted of (mol %): ethane (38), propane (3) and isobutane (58). The ethane fraction contained over 90% CH₃CH₂D, which indicates that ether cleavage was the source of the Et–Be moiety. Furthermore, it suggests that a CH₂DCH₂–Be species was formed during pyrolysis, probably by reaction of ethylene (produced by ether cleavage similarly to the “Schorigin type” of metal alkyl cleavage cited in ref. 9) with a transitory Be–D group:



This also would account for the ethoxide found in the pyrolysis product.

Analysis of the isobutane fraction showed it to consist almost completely of isobutane-*d*₉ with the structure (CD₃)₂CDCHD₂. The position of the tertiary deuterium atom indicates that the butylberyllium groups remaining after pyrolysis were present largely as isobutyl rather than *t*-butyl. In this case, isomerization of the butylberyllium could occur by addition of isobutene to BeD₂ or by thermal rearrangement of the *t*-butyl group after loss of ether from the complex. Ether-free *t*-Bu₂Be was found to isomerize almost completely to *i*-BuBe-*t*-Bu in 3 h at 68°C, although *t*-Bu₂Be · Et₂O was unchanged after many months storage at room temperature.

Because of the small size of the propane sample, attempts to determine the position of labeling in this fraction gave inconclusive results.

Pyrolysis of other beryllium alkyls

Several additional alkylberyllium compounds were synthesized and subjected

TABLE 4
SOLUTION PYROLYSIS OF ALKYLBERYLLIUM COMPOUNDS AND THEIR ETHERATES

Compound	Pyrolysis temp. (°C)	BeH ₂ in product (wt. %)
(n-Bu) ₂ Be	200	61
(i-Bu) ₂ Be	195	64
(i-Bu) ₂ Be · Et ₂ O	195	84
(t-Bu) ₂ Be	200	77
(i-Bu)Be(t-Bu)	200	70
(neo-C ₅ H ₁₁) ₂ Be · Et ₂ O	195—230	— ^a

^a Me₂Be was obtained, but no BeH₂.

to solution pyrolysis conditions similar to those used for t-Bu₂Be · Et₂O. A summary of the best BeH₂ product purities obtained is given in Table 4. None of the compounds gave BeH₂ of the purity found using t-Bu₂Be · Et₂O. The presence of diethyl ether appears to be beneficial, based on results with the iso-butyl and t-butyl compounds. Dineopentylberyllium was found to give a stable monoetherate, like di-t-butylberyllium. However, it thermally decomposed to dimethylberyllium at temperatures above 200°C.

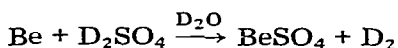
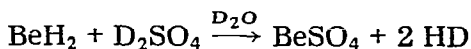
Experimental

All operations were conducted either in a glove box or with conventional glassware using a purge of dry nitrogen. Diethyl ether was distilled over lithium aluminium hydride before use; dodecane was used as received. All solvents and reagents were obtained from commercial sources and in reagent grade where possible.

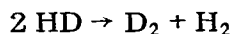
Infrared spectra were obtained using a Perkin—Elmer Model 21 spectrophotometer. X-ray powder data were collected on a Philips Norelco X-ray unit using a 114.6 mm camera with Ni-filtered Cu-K_α radiation. DTA data were obtained under nitrogen with a Tempress closed-system unit.

Analytical procedures

Beryllium hydride purities were determined in two ways: (1) by combustion analysis and (2) by hydrolysis on a vacuum line equipped with a Toepler pump. A Brinkmann—Heraeus Model B-H microcombustion furnace with a cupric oxide/silver wool combustion tube packing was used for the combustion method. Hydride hydrogen was calculated by subtracting the hydrocarbon hydrogen from the total hydrogen content. Hydrocarbon hydrogen was derived from residual alkyl and alkoxide groups and averaged 19% of the carbon present. The hydrolysis method employed sulfuric acid-d₂, which allowed a correction to be made for free beryllium metal in the sample:



Corrections were made for isotopic purity and for the small amount of disproportionation which occurred during hydrolysis or in the mass spectrometer:



Beryllium hydride purities found by the two methods usually agreed within 1%.

On hydrolysis, incompletely pyrolyzed alkylberyllium compounds (containing ethyl, propyl and butyl groups) gave the corresponding alkanes. These were condensed at liquid N_2 temperature and analyzed by gas chromatography (GC) on a dibenzyl ether column. Beryllium alkoxides similarly were liberated by hydrolysis. The resultant alcohols were separated from the reaction mixture by distillation and analyzed by GC on a Carbowax 200 column. Aliquots of the hydrolysis residue were analyzed for chloride by a modified Volhard method and for total beryllium by precipitation with 8-hydroxyquinoline [10].

Preparation of $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$

Di-*t*-butylberyllium etherate was prepared by the method of Coates and Glockling [4] with modification. To 850 ml of anhydrous diethyl ether were charged 36.5 g (1.5 mol) of magnesium turnings, 12.0 g (0.13 mol) of *t*-butylchloride and 10 ml of previously prepared 1.3 *M* *t*-butylmagnesium chloride (used as initiator). Then 126.8 g (1.37 mol) of *t*-butylchloride was added to the well-stirred mixture over a period of several hours and the ether solution refluxed for an additional hour. The resulting Grignard solution was 1.3–1.35 *M* (85–90% yield).

A solution containing 50.5 g (0.63 mol) of anhydrous BeCl_2 in 200 ml ether was added rapidly to the well stirred Grignard reagent over a period of 2 min or less. It was important that the BeCl_2 solution be added very quickly, otherwise gelation often occurred, which interfered with stirring and reaction completion. The mixture was then stirred at gentle reflux for 2 h. Granular MgCl_2 precipitated and was removed by filtration. Alternatively, the slurry could be used directly in the distillation step.

The ether was removed by distillation at atmospheric pressure and the di-*t*-butylberyllium etherate fraction collected at 55–65°C/1.0 mmHg in a yield of 65–75 g (55–65%). Anal. Found: 1.00/1.92/0.82. Calcd. for $t\text{-Bu}_2\text{Be} \cdot \text{Et}_2\text{O}$: $\text{Be}/i\text{-C}_4\text{H}_{10}$ (upon hydrolysis)/ Et_2O , 1.0/2.0/1.0. The vapor pressure-temperature relationship over the range 30–70°C can be expressed by

$$\log P = 3.390 - \frac{522.9}{T^\circ\text{C} + 100}$$

Preparation of BeH_2

To a nitrogen-purged 3-neck reaction flask fitted with stirrer, reflux condenser vented through an oil bubbler, and dropping funnel was charged 200 g of dodecane. The dodecane was heated to 200°C and the temperature maintained at $200 \pm 5^\circ\text{C}$ throughout the experiment. Stirring speed was increased to a high rate and 50 g of di-*t*-butylberyllium etherate was added to the dodecane over a period of about 15 min. After addition was completed, gas evolution slowed rapidly and essentially ceased after another 5–10 min. Then stirring was stopped

and the hot slurry filtered immediately through a glass frit. The filter cake was washed with 200–300 ml of dry petroleum ether and freed of residual solvent by heating at 100°C in vacuo. The yield of BeH₂ was essentially quantitative when transfer losses were considered. It was recovered as a white, fine granular solid (*d* 0.63–0.66 g/cm³). Anal. found: C, 3.23; H, 18.00; Be, 77.60 (94.9 wt% BeH₂). BeH₂ calcd.: C, 0.00; H, 18.28; Be, 81.72%.

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