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PREPARATION OF PURE DIMETHYLBERYLLIUM, INCLUDING A SURVEY OF THE LITERATURE

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PREPARATION OF PURE DIMETHYLBERYLLIUM, INCLUDING A SURVEY OF THE LITERATURE

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ABSTRACT

The preparation and purification of dimethylberyllium together with the physical and chemical properties of this compound are described in detail. Relevant literature references pertaining to dimethylberyllium are included. Analytical results are presented which indicate that essentially pure dimethylberyllium free of diethyl ether can be prepared by making use of the reaction between dimethylmercury and beryllium metal. Some precautions which must be observed in the preparation and handling of this reactive material are given.

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1. Introduction

In the course of an investigation of possible methods for synthesizing certain inorganic beryllium compounds it was necessary to make dimethylberyllium as an intermediate. Although this compound is well known, and there is a considerable body of literature concerning it, certain experimental difficulties are encountered in its preparation and use. The preparation of gram quantities of dimethylberyllium completely free of ether or mercury as contaminants has not hitherto been reported.

This report describes the preparation and purification of dimethylberyllium as carried out in this laboratory. A comprehensive literature survey of dimethylberyllium is also included.

2. Preparation of Dimethylberyllium

The preparation of dimethylberyllium was first announced by Lavroff[1] in 1884 by the method of heating beryllium metal and dimethylmercury in a sealed tube at 130°C. This method has been used also by Schulze[2] (1933), Burg and Schlesinger[3] (1940), and Coates, Glockling, and Huck[4] (1952). The latter authors refluxed dimethylmercury with beryllium metal under dry nitrogen at slightly above atmospheric pressure for 36 hr. The advantage of this method is that a product free of ether is obtained. The disadvantages are that dimethylmercury must be prepared and the final product is contaminated with mercury.

In 1923 Krause and Wendt[5] reported that dialkylberyllium compounds could be prepared from the corresponding organomagnesium halides and beryllium chloride or bromide. These reactions were carefully investigated by Gilman and Schulze[6] in 1927, who announced the preparation of dimethylberyllium by the reaction of methylmagnesium iodide with beryllium chloride in diethyl ether under an inert atmosphere. This method of preparation has also been used by Schulze[2], Rundle and Snow[7] (1950), and Coates, Glockling and Huck.[4] The latter authors found that dimethylberyllium prepared in this manner could not be obtained entirely free of ether, as judged by its vapor pressure. A large scale preparation of dimethylberyllium by this method has been developed by Wood and Brenner.[8]

In addition to the above methods of preparation, Gilman and Schulze[6] say: "It is possible to prepare beryllium dialkyls by heating beryllium with the appropriate alkyl halides, an alkylberyllium halide being an intermediate product." However, no detailed report of dimethylberyllium having been prepared in this was found in the literature.

The first preparations of dimethylberyllium in this laboratory were by the Grignard method using a modification of the apparatus of Gilman and Schulze.[6] Later, dimethylberyllium free of ether was desired and preparations were made by the dimethylmercury method.

2.1. Preparation from Methylmagnesium Iodide and Beryllium Chloride

The method of Gilman and Schulze,[6] with minor variations, was used, with results essentially as described by them.

In some of the preparations the beryllium chloride was added as the dry powder instead of in ether solution, which had the advantage of simplicity. However, preparations made in this way were always contaminated with halogen, the cause of which was never certainly determined. A sublimation of the product would probably free it of beryllium halide.

Analysis of the products showed that they contained more beryllium than could be accounted for from the methane evolved on hydrolysis, even when no halogen was present. The cause of this excess beryllium was not investigated because the Grignard method was set aside at this time in favor of the dimethylmercury-beryllium reaction which was found to yield an ether-free product of high purity.

2.2. Preparation from Dimethylmercury

2.2.1. Preparation of Dimethylmercury. The dimethylmercury was made by the reaction between CH_3MgI and $HgCl_2$ following the directions of Marvel.[9] The reaction was carried out in a hood with good ventilation using closed apparatus as much as possible. These precautions are necessary for two reasons. In the initial stages of the reaction, the Grignard reagent must be protected from exposure to air or moisture. In the final stages of the reaction the product, dimethylmercury, while not sensitive to air or water, is quite volatile (v.p. $\cong$ 50 mm. at 25°C.), has an objectionable odor, and is quite toxic both as a vapor and as a liquid in contact with the skin. Therefore, rubber gloves and a supplied-air gas mask were worn during the final manipulations in the preparation. The product was stored in glass stoppered flasks.

2.2.2. Reaction between Dimethylmercury and Dimethylberyllium. For the preparation of dimethylberyllium from dimethylmercury use was made of the reaction

$$Be + (CH_3)_2Hg \longrightarrow (CH_3)_2Be + Hg$$

which takes place at about 115 to 130°C. Since this is above the boiling point of dimethylmercury, the reaction must be carried out under pressure.

An entirely satisfactory method makes use of the apparatus shown in Fig. 1. Two grams of beryllium powder or fine turnings were placed in the bottom of the tube which was then evacuated while being heated at 400°C. for a few hours to drive off any moisture. About 8 ml. of dimethylmercury were then distilled into the tube from a storage vessel, the contents were frozen with liquid nitrogen, and the tube evacuated and sealed off at the constriction. The sealed tube was placed in an oil bath at 115 to 130°C. and left until the reaction appeared to be complete as judged by the disappearance of the liquid dimethylmercury. This usually

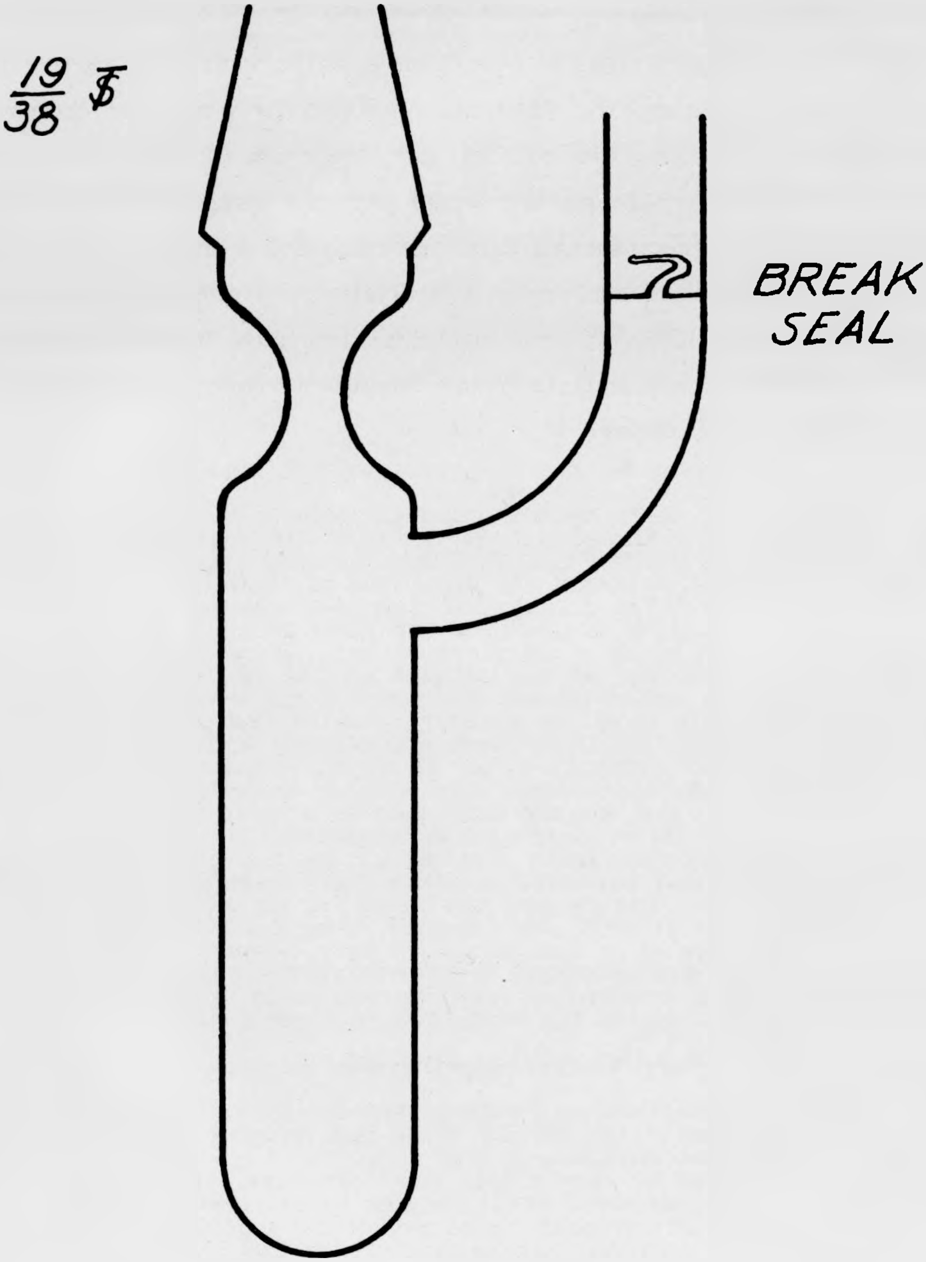


Fig. 1 Reaction tube for preparation of dimethylberyllium.

occurred within 24 hr. If the reaction did not occur within a reasonable time, it could usually be made to take place by distilling the dimethylmercury into a new reaction tube with fresh beryllium. In one case when this was not done, and the reaction tube was allowed to stand in the oil bath with little evidence of reaction for over a week, an explosion occurred which completely shattered the reaction tube. The theoretical yield, based on the dimethylmercury, is about 4 gm. of dimethylberyllium. Although the actual yield was not determined, the reaction is believed, on the basis of visual inspection, to go essentially to completion.

2.2.3. Purification of the Dimethylberyllium. The product of this reaction consisted of about 4 gm. of dimethylberyllium mixed with mercury and the excess beryllium metal. A sublimation will separate the dimethylberyllium from the beryllium metal but still leaves the sublimate contaminated with mercury. The method developed for removing the mercury was as follows, making use of the apparatus of Fig. 2.

The tube, A, containing the reaction products, was sealed onto a bulb, B, as shown in the figure. Above bulb B there were a glass wool plug, some strips of gold foil, and a coarse frit. The apparatus was attached to the vacuum line and evacuated, and the break seal broken with the magnetic striker. The dimethylberyllium was sublimed into bulb B with a free flame. If this was done carefully much of the mercury was left behind in A with the excess beryllium metal. Tube A was then sealed off at constriction 1 and the bulb B immersed in an oil bath at 65°C. so that the top of the oil bath was at the level of the glass wool plug. Under these conditions the mercury was appreciably more volatile than the dimethylberyllium. After several hours the gold would be covered with amalgam. The apparatus was then sealed off at constriction 2 and taken into an inert box where the dimethylberyllium was transferred to another flask. The whole process was repeated, using fresh or regenerated gold, as many times (two or three) as was necessary to remove all the mercury. The dimethylberyllium resulting from this process was in the form of very white needlelike crystals.

If the presence of ether was not objectionable, the separation from the mercury was carried out by leaching the reaction products with dry ether followed by filtration on a medium frit and then a sublimation through a coarse frit.

Several of these preparations were analyzed by hydrolysis followed by chemical analysis of the solution and mass spectroscopic analysis of the gas. In addition, carbon and hydrogen were determined by combustion on one sample. The results are shown in Table 1. From the results it can be concluded that within the limits of analytical error, pure dimethylberyllium may be prepared in this way.

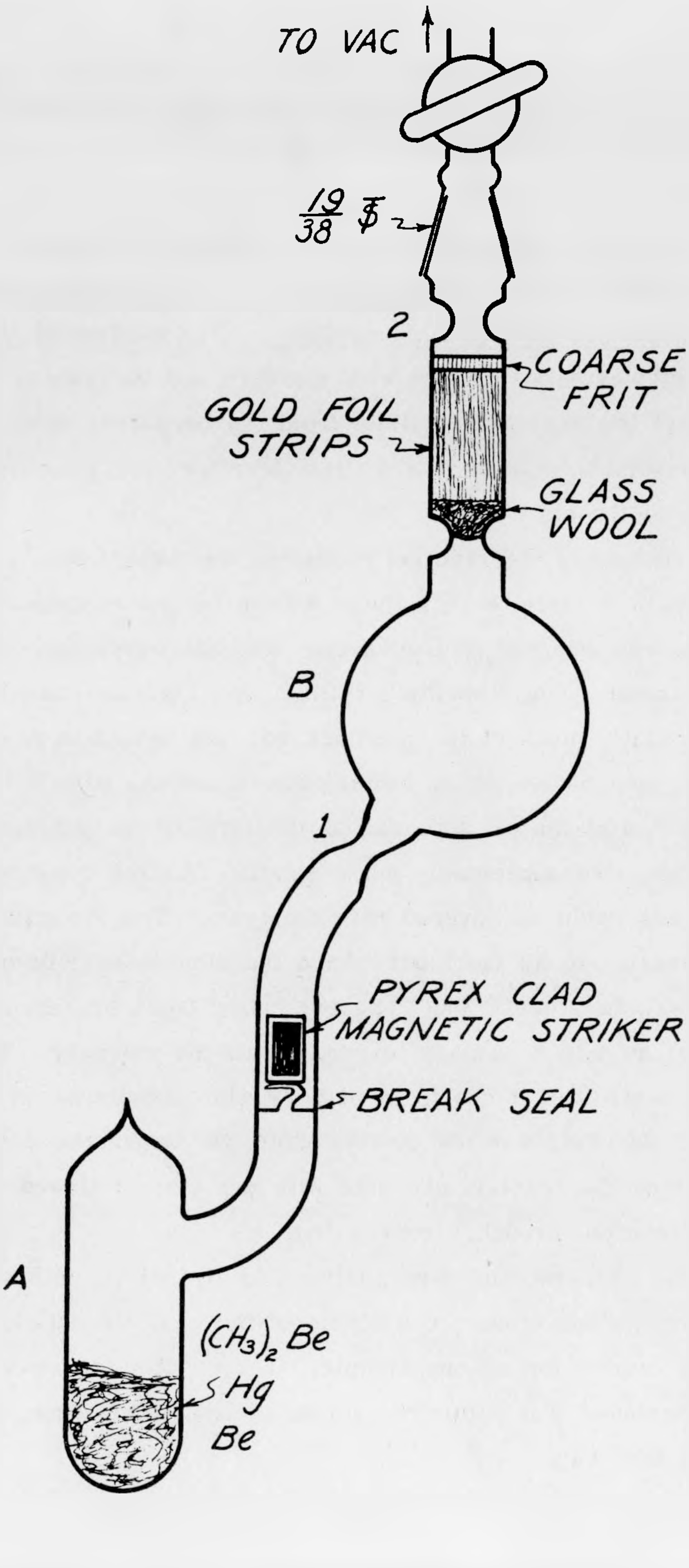


Fig. 2 Sublimation apparatus for purification of dimethylberyllium.

TABLE 1

ANALYTICAL RESULTS ON DIMETHYLBERYLLIUM

(based on 100-mg. samples)

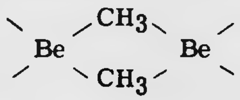
Sample No.	CH_4, mmoles	Be, mmoles	CO_2, mg.	H_2O, mg.	Purity
Theoretical	5.12	2.56	224.9	138.1	
MA-$BeMe_2$-1	4.33	2.14	-	-	84% (contained Hg)
MA-$BeMe_2$-2	5.07	-	-	-	99% $(CH_3)_2Be$
MA-$BeMe_2$-3	4.98	2.59	223.8	137.8	97.4% based on CH_4 101 % based on Be 99.5% based on C 99.7% based on H

3. Physical Properties of Dimethylberyllium

3.1. Crystal Structure

The crystal structure has been determined by Snow and Rundle.[10] Their product was prepared by the Grignard method and the ether was removed by repeated distillation. The first sublimation led to apparently isotropic crystals, with triangular and square faces, which transformed to another form on standing. The first form could not be retained long enough to study with X-rays. The stable form consisted of fibrous needles with a density of 0.88 ± 0.1 gm./cc. as determined by the flotation method using cyclohexane (ρ = 0.78) and chlorocyclohexane (ρ = 0.98).

Single crystals were grown in an evacuated capillary by sublimation under a temperature gradient.

The crystal structure was found to be body-centered orthorhombic, with $a_0 = 6.13$, $b_0 = 11.53$, and $c_0 = 4.18$ A, the structure being similar to SiS_2. In the  chain the C - Be - C angle within the 4-membered ring is somewhat greater than tetrahedral, and the Be - C - Be angle is only 66°. The electron-deficient Be - C bonds are 1.93 A in length.

X-ray examination of dimethylberyllium carried out at this laboratory confirms the results reported by Snow and Rundle.

3.2. Vapor Pressure

The vapor pressure of dimethylberyllium has been measured by Coates, Glockling, and Huck.[4] They used material prepared from dimethylmercury which could be obtained free of ether. They found that over the range studied, 100 to 180°C., the plot of log P vs. the reciprocal of the temperature was not quite linear, but that the observed vapor pressures could be represented closely by two linear equations:

$$100 \text{ to } 155^{\circ}\text{C.}: \quad \log_{10} P_{mm} = 12.530 - 4771/T$$

$$155 \text{ to } 180^{\circ}\text{C.}: \quad \log_{10} P_{mm} = 13.292 - 5100/T$$

From their measurements they found evidence for the existence of dimers, trimers, and higher polymers, as well as monomers. If the dissociation constants for the dimer and trimer are defined as $K_D = P_{dimer}/P^2_{monomer}$ and $K_T = P_{trimer}/P^3_{monomer}$, then the values found were $\log_{10} K_D = 10.92 - 5325/T$ and $\log_{10} K_T = 20.3 - 9770/T$. The heat of sublimation to the monomer was found to be ΔH_S (heat of sublimation to monomer) = 23.5 ± 1 kcal.

No vapor pressure studies of dimethylberyllium have been made at this laboratory.

4. Chemical Properties of Dimethylberyllium

4.1. Reactivity

The dialkylberyllium compounds are less reactive than the corresponding dialkylmagnesium compounds according to Gilman and Woods.[11] Nonetheless, they are very reactive. Dimethylberyllium is spontaneously inflammable in air and concentrated ethereal solutions are inflammable in moist air.[6] It burns in air with a luminous flame, evolving dense white fumes of beryllium oxide. It reacts violently with water. It reacts with carbon dioxide to give acetic acid.[6]

Dimethylberyllium forms addition compounds with trimethylamine, trimethylphosphine, dimethyl ether, and diethyl ether, but not with trimethylarsine or dimethyl sulfide.[4]

Its reactions with various organic reagents have been investigated by Gilman and Schulze[6,12] and Coates, Glockling, and Huck.[4]

4.2. Toxicity

Because of its high reactivity, the toxicity of dimethylberyllium as such probably cannot be studied. However, the products of its reaction with air or water have toxic properties which have been extensively investigated.[13-15] Considerable care must be exercised in the handling of dimethylberyllium.

5. The Handling of Dimethylberyllium

The very reactive nature of dimethylberyllium and its solutions in ether make it necessary that it be handled either under vacuum or in an inert atmosphere. Solid dimethylberyllium will fume in any but the very best inert dry-box atmospheres. The fact that it is volatile makes possible a considerable amount of manipulation in completely closed and evacuated glass systems.

However, because of the wide explosion limits of air-ether mixtures and the presence of the dimethylberyllium as an igniter, great care must be used in handling ether solutions of dimethylberyllium to see that all air is excluded in order to avoid an explosion. These requirements on the handling due to reactivity also mean that health requirements are met. The only additional safety requirement is that the apparatus or equipment being used with dimethylberyllium be in a good hood or other place where accidental breakage with the resultant fire will not cause a hazard.

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