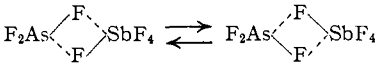
more resonances indicated that fluorine exchange was taking place in this system. (Exchange phenomena of sufficiently high frequency have been shown capable of collapsing a two-line spectrum into a single, concentration-dependent resonance.[4]) The exchange rate was too fast to be "frozen out" by cooling the solutions. It was therefore not possible to establish whether F^- or AsF_4^- is the major conducting species in arsenic trifluoride solution.[5]

The F^{19} magnetic resonance spectrum of a melt of $KAsF_4$ consisted of a single rather broad resonance at +940 c.p.s. The tetrafluoroarsenite anion is isoelectronic with selenium tetrafluoride and thus may be expected to have a trigonal bipyramid structure. The absence of structure in the spectrum of the melt is due to fluorine exchange. The exchange mechanism may be simply described by a dissociation of the fluoroarsenite into AsF_3 and MF. This dissociation was demonstrated tensimetrically at temperatures below the melting points. The dissociation pressures at 100° ranged from 0.18 atm. for $KAsF_4$ to 0.07 atm. for $CsAsF_4$. Equilibria were attained slowly. Because of slight etching of the glass equipment by the fluoroarsenites at 100°, the dissociation pressures are considered to be approximate values.

Covalent Fluorides.—Nuclear magnetic resonance spectra of binary systems of covalent fluorides and arsenic trifluoride were examined in an attempt to gain structural information. Samples were prepared by condensing the fluorides in 5 mm. o.d. Pyrex tubes which were then sealed. Approximately equimolar quantities of the fluorides were used except where excess arsenic trifluoride was necessary to prevent solid formation.

Although boron trifluoride slightly increases the conductivity of arsenic trifluoride, no evidence for interaction of these two liquids was obtained at temperatures up to ~ − 10° or between liquid arsenic trifluoride and gaseous boron trifluoride up to 30°. The characteristic resonances of the components were observed. Woolf and Greenwood[1] have suggested the possibility of an unstable $AsF_2^+BF_4^-$ compound in such mixtures but the n-m-r data give no support to this suggestion.[6]

The F^{19} magnetic spectrum of arsenic trifluoride–antimony pentafluoride consisted of a single resonance peak. The position of the peak was between the resonance positions of the pure fluorides and was concentration dependent. Any type of compound formed between the antimony and arsenic fluorides would have non-equivalent fluorines and would present two or more peaks in the fluorine spectrum. Absence of structure in the spectrum is attributed to a rapid fluorine exchange (low temperature did not slow the rate sufficiently to permit a structural analysis). Although lacking conclusive evidence, a bridge-type structure is suggested for this system in the liquid state since such a structure provides a simple mechanism for fluorine exchange



A bridge structure is supported by related data. Bridge-type structures have been cited as intermediates for fluorine exchange in halogen fluorides.[7] Antimony pentafluoride appears to have bridge-bonding[8] and a bridge intermediate has been proposed for chlorine exchange between antimony (III) and antimony(V).[9] It should be noted that a simple coördination complex $F_5Sb{-}AsF_3$ is not acceptable as an intermediate for exchange since dissociation of such a complex would not involve cleavage of As–F or Sb–F bonds.

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[4] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[5] Although the fluoroarsenites are undoubtedly composed of M^+ and AsF_4^- aggregates in the solid state, it does not necessarily follow that the tetrafluoroarsenite anion is the major anion in AsF_3 solution. The equilibrium for $AsF_4^-(\text{soln}) \rightleftarrows AsF_3 + F^-(\text{soln})$ may be far to the right.

[6] It should be noted that an $AsF_2^+BF_4^-$ intermediate could be present to concentrations involving approximately 5% of the total fluorine and not be detected. However, if this intermediate is present, rapid equilibration between the components and the intermediate does not occur. Rapid equilibration would yield a single F^{19} resonance rather than the observed, non-perturbed resonances of the components.

[7] E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **79**, 322 (1957).

[8] E. L. Muetterties and W. D. Phillips, manuscript in preparation.

[9] H. M. Neumann and H. Brown, THIS JOURNAL, **78**, 1843 (1956).

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Di-*t*-butylberyllium and Beryllium Hydride[1]

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Methods are described for the preparation of pure di-*t*-butylberyllium and for the preparation of beryllium hydride (approx. 80 wt. %) by the pyrolysis of both pure di-*t*-butylberyllium and its etherate. Pure di-*t*-butylberyllium is a clear, colorless, mobile liquid with a density of 0.65 g./cc. and a freezing point of −16°. When freshly prepared it has a vapor pressure of about 35 mm. at 25°; on standing it undergoes slow decomposition at room temperature with the evolution of isobutene. Beryllium hydride prepared by pyrolysis of di-*t*-butylberyllium has a density of about 0.57 g./cc., evolves hydrogen slowly at 190 to 200° and rapidly at 220°, is relatively inert to laboratory air, and reacts slowly with water and rapidly with acid. It was analyzed by chemical and microscopic methods. It gave no X-ray pattern.

Introduction

The preparation of beryllium hydride has been announced by a number of workers. In view of the apparently tenuous nature of some of the published results, the present authors, with others,[2] have investigated these procedures in considerable detail. Attempts to prepare beryllium hydride by heating beryllium in atomic hydrogen by the method of Pietsch[3] were unsuccessful. A surface reaction between excess lithium hydride and beryllium chloride in ether solution was observed as described by Wiberg and Bauer,[4] but separation of the product, which contained organic material, from the excess lithium hydride could not be accomplished and analysis was not possible. There seems to be little direct evidence for identifying this material as beryllium hydride.

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[1] This work was done under the auspices of the Atomic Energy Commission.

[2] Some 30 staff members of this Laboratory have contributed to the program to a greater or lesser extent. In addition to procedures mentioned here, preparation of beryllium hydride was attempted by many other methods, including direct combination of the elements under various conditions, reduction of inorganic salts and reduction of beryllium alkyls with various reducing agents. Los Alamos Scientific Laboratory report LA-1660, "The Preparation of the Hydrides of Magnesium and Beryllium," by C. E. Holley, Jr., and J. F. Lemons, April 1, 1954.

[3] E. Pietsch, *Z. Elektrochem.*, **39**, 577 (1933).

[4] E. Wiberg and R. Bauer, *Z. Naturforsch.*, **6b**, 171 (1951).

Experiments on the reaction between lithium aluminum hydride and dimethylberyllium in diethyl ether essentially confirm the results of Schlesinger and co-workers.[5] Our best product, out of some 30 preparations, contained 60+% BeH_2,[6] and was contaminated with several per cent. each of lithium hydride and aluminum hydride, or possibly lithium aluminum hydride, and ether, which was the major impurity.

Recently Coates and Glockling[7] reported the preparation of beryllium hydride by the pyrolysis of di-*t*-butylberyllium etherate to give a product containing 71% BeH_2 (96.5 mole %). These experiments have been repeated, essentially confirming the results of Coates and Glockling, and by modifications of the procedure a purer product was obtained. Also, a method for the preparation of ether-free di-*t*-butylberyllium has been developed. These latter experiments are described below along with the results of the determination of some of the properties of the beryllium hydride thus obtained.

Preparation of Di-*t*-butylberyllium Etherate.—The di-*t*-butylberyllium etherate was prepared from *t*-butylmagnesium chloride and beryllium chloride in diethyl ether solution following the directions of Coates and Glockling[7] as closely as possible. The product was analyzed by hydrolysis and found to contain 51 to 52 mole % di-*t*-butylberyllium, the remainder being ether, as compared to 55.4 mole % obtained by Coates and Glockling.

Preparation of Ether-free Di-*t*-butylberyllium.—Attempts to increase the di-*t*-butylberyllium content to higher values according to the directions of Coates and Glockling were unsuccessful. An investigation was then made of the effect on the etherate of etherphilic substances such as $AlCl_3$, BF_3 and $BeCl_2$. The first two gave complicated reactions but treatment with anhydrous beryllium chloride was successful in giving pure di-*t*-butylberyllium. A typical preparation is described below.

In an inert atmosphere (N_2), approximately 7.5 g. of anhydrous $BeCl_2$ and a glass-enclosed iron stirring bar were put into a reaction flask fitted with a stopcock and ground joint for attaching to the vacuum line, and a seal-off constriction and ground joint for introducing the di-*t*-butylberyllium etherate, the latter joint plugged with a rubber stopper. After connecting the flask to the vacuum line, the rubber stopper was removed and the ground joint on the end of a glass ampoule containing approximately 24 g. of di-*t*-butylberyllium etherate (15 g. di-*t*-butylberyllium) was inserted. (These quantities correspond to a 50% excess of $BeCl_2$ if each $BeCl_2$ molecule accepts two ether molecules.) The flask was then evacuated, the stopcock closed, the break-off seal in the end of the ampoule broken, and the di-*t*-butylberyllium allowed to drain into the flask onto the beryllium chloride, the last portion being driven into the reaction flask by heating the ampule with a hair dryer. Upon completion of the transfer the flask was cooled with liquid nitrogen and the ampule and ground joint removed by sealing at the seal-off. This procedure permitted a transfer without exposure to the atmosphere with the possibility of weighing by difference the amount of di-*t*-butylberyllium etherate used.

The contents of the flask were stirred magnetically for several hours at room temperature, usually overnight, after which the stopcock was opened and the contents exposed at room temperature to a −80° trap followed by a −195° trap to collect the volatile constituents. In addition to di-*t*-butylberyllium, some isobutane and isobutene were formed, which were soluble in it but which could be separated from it and collected in the −195° trap by alternate freezing and thawing. Some of this gas may have been present in the original di-*t*-butylberyllium etherate, but some probably was formed during the reaction with beryllium chloride or by subsequent slow decomposition of the ether-free di-*t*-butylberyllium.

The yield of ether-free di-*t*-butylberyllium was about 40% of the amount expected on the basis of the di-*t*-butylberyllium content of the starting material.

A by-product of the treatment with beryllium chloride was a volatile white solid which melted at about 50° and sublimed under vacuum at temperatures just below this. From analysis it was apparently *t*-butylberyllium chloride etherate but it was not otherwise characterized.

Some Properties of Di-*t*-butylberyllium and its Etherate.—Di-*t*-butylberyllium etherate containing 51 to 52 mole % of di-*t*-butylberyllium is a clear, colorless liquid with a density of 0.78 g./cc. Its vapor pressure is a few millimeters at room temperature, and it gave no evidence of decomposition.

The freshly prepared ether-free material is a clear, colorless, mobile liquid with a density of 0.65 g./cc.; and a freezing point of −16°. The freshly prepared material had a vapor pressure of about 35 mm. at 25°. A reliable figure could not be obtained since at room temperature the compound decomposed slowly with the liberation of isobutene and apparently with the polymerization of the remaining liquid. After standing for seven weeks under its own vapor, it could not be distilled quantitatively.

Pyrolysis of Di-*t*-butylberyllium and its Etherate.—When the pyrolysis of di-*t*-butylberyllium etherate was carried out as described by Coates and Glockling,[7] using a closed vessel up to a temperature of 150° and a vacuum at higher temperatures, considerable amounts of ethane were formed and a product containing only 40% BeH_2 was obtained. The pyrolysis was repeated using a vessel equipped with a cold finger maintained at −20°. The di-*t*-butylberyllium was refluxed under vacuum by means of an oil-bath which was slowly raised to 200°. The volatile decomposition products were collected in a liquid nitrogen cold trap and thus prevented from possible reaction with beryllium hydride. The product analyzed 80% BeH_2, the remainder being mostly ether. This is equivalent to 97 mole %, assuming ether to be the only impurity. Between 190 and 200° the loss of hydrogen from the product was detectable, but negligible in 1 hr.; at 220° the hydrogen loss was rapid.

Pyrolysis of ether-free di-*t*-butylberyllium could not be carried out in this apparatus because of its high volatility. Since no ether was present to react with the beryllium hydride, it could be pyrolyzed, first in a closed system until its volatility became negligible, and then under vacuum. In this way a product was obtained which again contained about 80% BeH_2, the impurity probably being unreacted *t*-butyl groups, however, instead of ether.

Vapor phase pyrolysis of pure di-*t*-butylberyllium was attempted by passing it repeatedly through a hot tube. This was not successful. At temperatures between 150 and 210° most of the material passed through the tube and condensed as a liquid of low volatility, and above 210° the beryllium hydride decomposed rapidly.

Analyses.—Samples of di-*t*-butylberyllium and its pyrolysis products were hydrolyzed, and the resulting gases were measured and analyzed with the mass spectrometer. The solutions from the hydrolyses were analyzed for beryllium and chlorine and in the case of the di-*t*-butylberyllium etherate, for magnesium also. A combustion analysis for carbon and hydrogen also was carried out on some of the pyrolysis products using the method of Head and Holley.[8]

Some typical analytical results with a possible interpretation follow.

1. **Hydrolysis of Di-*t*-butylberyllium Etherate.**—A typical sample (weighing approximately 0.6 g.) on hydrolysis was found to contain 36.1% ether, and isobutane and isobutene (4:1 molar ratio) equivalent to 61.7% di-*t*-butylberyllium, or a total of 97.8% of the original sample.

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[5] G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **73**, 4585 (1951).

[6] All percentages in this paper refer to per cent. by weight unless otherwise stated.

[7] G. E. Coates and F. Glockling, *J. Chem. Soc.*, 2526 (1954).

[8] E. L. Head and C. E. Holley, Jr., *Anal. Chem.*, **28**, 1172 (1956).

Analysis of the hydrolysis solution showed beryllium equivalent to 66.6% di-*t*-butylberyllium or, including the ether, a total of 102.7% of the original sample. On a molar basis the sample was about 51% di-*t*-butylberyllium.

Several points deserve comment. First, isobutene was always evolved on hydrolysis. If its origin is the decomposition of di-*t*-butylberyllium, a corresponding amount of hydrogen should be observed. Although hydrogen was occasionally found, it was not observed in this instance. Second, the discrepancies in material balance are probably within experimental error, since the individual analyses are accurate, at best, to only 1%. It was observed in each of five different preparations that the ether content was slightly less than 50 mole %.

2. **Hydrolysis of Beryllium Hydride Prepared by the Pyrolysis of Di-*t*-butylberyllium Etherate.**—A sample (approximate weight 19 mg.) of the best preparation of beryllium hydride from di-*t*-butylberyllium etherate was found on hydrolysis to liberate hydrogen equivalent to 81% BeH_2. Analysis of the hydrolysis solution showed beryllium equivalent to 79% BeH_2. The check between the beryllium found and the hydrogen observed is within the expected analytical error, so the major impurity is not a beryllium compound and is probably ether. In this sample the hydrolysis gases were not analyzed for ether and isobutane. In other samples both ether and isobutane in varying ratios were found in addition to the hydrogen. The purity of most preparations was between 76 and 80%.

3. **Combustion Analysis of Beryllium Hydride Prepared by the Pyrolysis of Di-*t*-butylberyllium Etherate.**—A sample (weight 33 mg.) on combustion gave CO_2 equivalent to an ether content of 21%. The hydrogen (determined as water) in excess of the stoichiometric amount required for ether corresponded to a BeH_2 content of 76%. Analysis of this material by the hydrolysis procedure also indicated a BeH_2 content of 76%. The ether and BeH_2 calculated in this manner account for 97% of the original sample weight.

4. **Hydrolysis of Di-*t*-butylberyllium.**—Hydrolysis of a sample of the best di-*t*-butylberyllium (weight 225.2 mg.) gave isobutane and isobutene (molar ratio 60:1) equivalent to 101% di-*t*-butylberyllium. (Half as much hydrogen was observed as isobutene.) Analysis of the hydrolysis solution showed an equivalent amount of beryllium (17.5 mg. found, 16.8 mg. expected).

5. **Hydrolysis of Beryllium Hydride Prepared by Pyrolysis of Di-*t*-butylberyllium.**—A sample weighing 17.9 mg. gave, on hydrolysis, hydrogen equivalent to 80.5% BeH_2 and isobutane equivalent to 17.8% di-*t*-butylberyllium, giving a total of 98.3% of the sample. Analysis of the hydrolysis solution showed beryllium equivalent to 99% of the beryllium calculated from the gas analysis (the di-*t*-butylberyllium contributes a minor amount of beryllium to the solution). This is the best sample of beryllium hydride prepared by pyrolysis of ether-free di-*t*-butylberyllium.

Properties of Beryllium Hydride.—The density of the product was estimated from the fact that it sank in liquid ethane at −110°, but floated at lower temperatures. The density of ethane is 0.561 g./cc. at −100°,[9] and the density of the product is estimated to be 0.57 ± 0.02 g./cc. at −110°. Since the product is 97 mole % BeH_2, it is probable that the density of pure BeH_2 would not differ significantly.

Beryllium hydride prepared by pyrolysis is relatively inert to laboratory air. A 26-mg. sample containing 76% BeH_2 gained 0.8 mg. on exposure to laboratory air for eight days and the BeH_2 content decreased to 72%. The product reacts slowly with water but vigorously with dilute mineral acid.

The product prepared from ether-free reagent was not altered by treatment with ethereal $LiAlH_4$.

A microscopic examination of the product prepared from the etherate showed it to be heterogeneous, consisting of optically isotropic grains, with refringence near 1.58, which contained optically anisotropic inclusions with much lower refringence, densely but non-uniformly distributed. The grain size of the inclusions was several tenths of a micron. The two constituents appeared to be present in approximately equal amounts.

X-Ray examination of the product prepared from di-*t*-butylberyllium gave no lines attributable to BeH_2.

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(9) "Handbook of Chemistry and Physics," 30th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1948, p. 790.

Los Alamos, N. M.

[Contribution from the National Research Council of Canada]

Electrolyte Catalysis. III. The Cleavage of Benzyl Phenyl Ether by Hydrogen Bromide in Nitrobenzene, Chloroform and Carbon Tetrachloride

By A. Y. Drummond and A. M. Eastham

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The kinetics of the cleavage of benzyl phenyl ether by hydrogen bromide in nitrobenzene and chloroform have been determined and the effects of five substituted ammonium bromides on the rate of reaction in these solvents examined. The rate of cleavage in carbon tetrachloride solution is negligibly small but is subject to heterogeneous catalysis by several solid salts. Mechanisms are suggested for the cleavage and its catalysis by electrolytes.

Earlier work in this Laboratory[1,2] showed that several reactions involving the cleavage of a C–O bond were catalyzed by electrolytes in non-aqueous solvents. The salts had considerable specificity in their catalytic powers and it was suggested that the electrolyte facilitated the charge transfers which occurred during the reaction.

In order to obtain more information about this type of catalysis, the cleavage of ethers by hydrogen bromide has now been studied. Walvekar, *et al.*,[3] have reported that this reaction is catalyzed by amine salts in carbon tetrachloride and *n*-hexane. It was first necessary to establish the kinetics of the uncatalyzed reaction for, although the similar cleavage by hydrogen iodide is widely used, little work has been done on the mechanism of this type of reaction.[4]

Since cleavage of ethers by hydrogen bromide is much slower than that by hydrogen iodide, benzyl

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(4) R. L. Burwell, *Chem. Revs.*, **54**, 689 (1954).