[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Compounds of Germanium and Hydrogen: Some of their Reactions and Derivatives. I. Preparation of Monogermane. II. Sodium Trihydrogermanides

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Aside from carbon, germanium is the only element forming non-polar compounds with hydrogen that are stable under ordinary conditions. The silicanes, while more stable than the germanes toward thermal decomposition, are much more reactive toward oxygen and water. The germanes, therefore, are well suited for the study of what might be called the "hydranes," more commonly called "hydrides." The latter term is objectionable since the "ide" ending has long been employed to indicate a salt or electropolar compound.

Excepting derivatives of carbon, our knowledge of non-polar hydranes is very limited. It is only the elements of the fourth and third groups that form compounds of this type and, of these, the hydranes of tin are unstable even at room temperatures while those of boron are extremely reactive toward oxygen as well as other substances. The silicanes, while quite stable thermally, are reactive toward oxygen. The result has been that, while numerous hydranes of these various elements are known, comparatively little is known regarding their general chemical behavior. The chemistry of monogermanes has not been studied extensively. Indeed, it is only recently that the germanes have been obtained in considerable quantity. A study of the hydranes is of interest not only because of its bearing on the chemistry of the central element of the compounds in question, but also because it may yield an insight into the chemistry of hydrogen.

In the present paper there are described an improved method for the preparation of monogermane, a method for the preparation of sodium trihydrogermanide, and some of the properties and reactions of this interesting compound.

I. Preparation of Monogermane

Monogermane, GeH_4, has been prepared by Voegeln,[1] Paneth and Schmid-Hebbel,[2] Schenck,[3] and Dennis, Corey and Moore.[4] Previously, the most successful method of preparation has been to treat magnesium germanide with hydrochloric acid. By means of this method, Dennis, Corey and Moore obtained a yield of 22% of mixed germanes, in which the monogermane predominated. We have employed substantially the same method except that, in place of treating magnesium germanide with hydrochloric acid in aqueous solution, we have treated it with ammonium bromide in liquid ammonia. By this method, yields ranging from 60 to 70%, and even higher, have been obtained.

Preparation of Magnesium Germanide.—The yield of germanes is greatly influenced by the condition of the alloy. The best results are obtained when the alloy consists of a fine powder; if the alloy is sintered, the yield is lowered.

The alloy is prepared by heating germanium powder—as obtained by reduction of the oxide—with magnesium filings in an atmosphere of hydrogen. The metals are placed in an iron boat which is placed in an iron tube, and this tube, in turn, is placed in a Vitreosil tube, which may be exhausted and filled with hydrogen. The hydrogen is purified by diffusion through a palladium tube. The boat is heated in an electric furnace to about 800°, approximately thirty-five minutes being required in raising the alloy to that temperature. The temperature is then maintained at about 800° for fifteen minutes, when the furnace is cooled rapidly. An excess of several per cent. of magnesium is employed.

Reaction of Magnesium Germanide with Ammonium Bromide.—The reaction between the alloy and ammonium bromide is carried out in a tube as illustrated in Fig. 1. The alloy is introduced into the reaction tube A and ammonium bromide (50% excess) is introduced into the addition tube B. The apparatus is connected with a vacuum pump, and the stirring tube C is connected with a cylinder containing pure ammonia (not shown in the figure). The exit tube D is connected with a collecting tube E through a mercury trap F. Ammonia is introduced through the stirring tube and condensed in the reaction tube until it is approximately two-thirds full. With a slow stream of ammonia passing through the tube for purposes of stirring, ammonium bromide is gradually introduced from the addition tube B by turning the latter on its axis in the ground joints G. Reaction between the ammonium bromide and the alloy takes place promptly with evolution of germanes. The gases pass out through the mercury trap under a pressure of about 25 cm. and are collected over water in E. The water can be changed by means of bulbs I, J. Toward the end, when the reaction slows down, the remaining ammonium bromide is added. Reaction proceeds over a period of several hours and may continue even longer. The ammonia is allowed

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[1] Voegeln, *Z. anorg. Chem.*, **30**, 325 (1902).

[2] Paneth and Schmid-Hebbel, *Ber.*, **55**, 2615 (1922).

[3] Schenck, *Rec. trav. chim.*, **41**, 569 (1922).

[4] Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

to boil away, being absorbed in water in the collecting tube and, finally, the reaction tube is heated, in which process some further gases are evolved. From the collecting tube, the gases are carried through a tube K containing phosphorus pentoxide which absorbs both water and ammonia vapors. Thence the gases are transferred by means of a Toepler pump L to the collecting tube M, where they are stored.

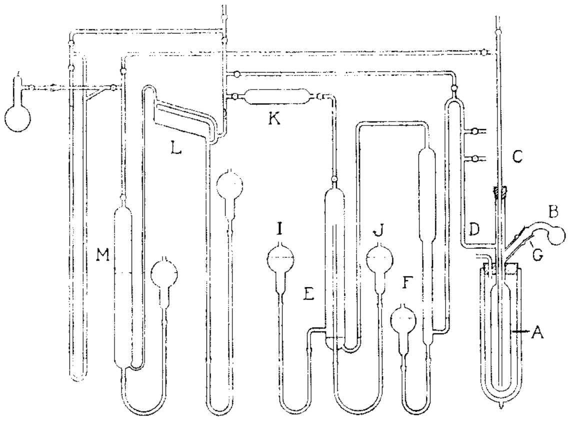

Fig. 1.—Apparatus for preparation of germanes.

The yield of mixed germanes, based on the germanium used, ordinarily averaged between 60 and 70 per cent., occasionally it was higher.

Purification.—The gases as collected contain from 30 to 40% of hydrogen; the remainder consists of mixed germanes in which monogermane predominates. These gases may be purified by means of liquid air as described by Dennis, Corey and Moore.[4] Purification may also be accomplished by passing the gases through a solution of sodium in liquid ammonia. In this process, the monogermane reacts with sodium to form sodium trihydrogermanide with evolution of hydrogen. Presumably, the digermane is directly reduced to sodium trihydrogermanide, while the higher germanes are reduced with the formation of sodium trihydrogermanide and disodium dihydrogermanide. The resulting compounds are all very soluble in liquid ammonia and are converted to monogermane on addition of ammonium bromide.

The reaction tube employed for this purpose is similar to that already described except that it is provided with two addition tubes, one for sodium, the other for ammonium bromide. The crude gases are bubbled slowly through the sodium solution under a pressure of about 25 cm. above that of the atmosphere. The hydrogen formed in the reaction, as well as that originally present in the mixture, passes out through the mercury trap and is collected over water. This hydrogen carries several per cent. of germanes which are best recovered by means of liquid air.

The mixed germanes are passed through the solution until all the sodium has been used up. After removing extraneous gases by means of a stream of ammonia vapor, ammonium bromide is slowly added to the liquid ammonia solution of the trihydrogermanide salts. Reaction takes place immediately with the evolution of monogermane, which passes through the mercury trap and is collected over water. The gas is dried and transferred as already described. Except for traces of impurities that may be introduced through the water, which is not readily kept entirely free from air, the final product is pure monogermane. We have thus obtained monogermane of 99.7% purity as determined from its density. Further purification is best carried out by means of liquid air. The above method is very convenient in that it converts the higher germanes to monogermane.

II. Sodium Trihydrogermanide, $NaGeH_3$

Preparation.—When monogermane is passed slowly through a solution of sodium in liquid ammonia, reaction takes place quantitatively according to the equation.

$$GeH_4 + Na = NaGeH_3 + {}^1/_2H_2 \qquad (1)$$

The preparation is carried out in a tube of the type illustrated in Fig. 2, which is attached to the system illustrated in Fig. 1. Ammonia is condensed in the reaction tube A and sodium is introduced into the addition tube B through C, a stream of ammonia being kept issuing through C at the time. The sodium is contained in weighed tubes of about 1.5 mm. internal diameter and 10 cm. length. These tubes are prepared by closing one end and drawing down the other end to a fine capillary of about 1 cm. length. A number of such tubes are suspended by means of a suitable holder, capillary ends down, in a larger tube containing sodium. After exhausting the tube, the sodium is melted and nitrogen is introduced under a pressure of approximately one atmosphere, thus filling the tubes with sodium. After allowing the apparatus to cool, the larger tube is opened, paraffin is added, the sodium is melted under the paraffin and the small tubes are removed. In the process of removal, a film of paraffin adheres to the tips of the capillaries, sealing them against the atmosphere. The tubes are then weighed with the paraffin adhering to the tips. Just before using, the tip is broken off, the tube is cut in the middle and the two halves are introduced into the addition tube through C as described. The paraffin tips are weighed back, which gives the necessary data for calculating the exact weight of sodium in the tubes.

The tube method of handling the alkali metals has the advantage that the tubes can be calibrated previously and any desired weight of metal closely approximated. They are also handled conveniently in the addition tube and may be added to the ammonia solution as required.

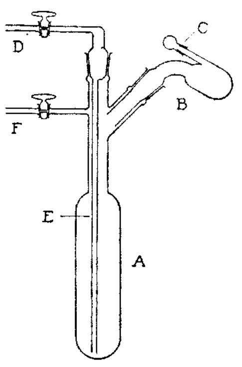

Fig. 2.—Reaction tube for preparation of sodiumtrihydrogermanide.

After introducing the metal into the addition tube B, the ammonia in A is saturated with monogermane under a pressure of 25 cm. of mercury. In some cases the bath surrounding the reaction tube was boiled under reduced pressure, which made it possible to correspondingly increase the partial pressure of germane in the reaction tube.

With monogermane entering through the stirring tube DE and passing out through F, the sodium tubes are dropped into A. Care should be taken to have the tubes in the ammonia open end up, otherwise the metal will not dissolve readily out of the tubes, since the solution is lighter than the pure solvent.

The original purpose of adding the metal in this way was to avoid an excess of sodium in the solution and thus to prevent the possible reduction of the germane below $NaGeH_3$. It has since been found, however, that this precaution is unnecessary. Nevertheless, if quantitative experiments are to be carried out with the resulting salt, the method described above is to be recommended.

Hydrogen is evolved as reaction proceeds and this, together with some unreacted germane, passes out through the mercury trap and is collected over water. When the reaction is completed, all excess gases are blown out of the reaction tube by means of a stream of ammonia vapor.

Sodium Trihydrogermanide.—The composition of the compound formed in the above described reaction was determined by weighing the products of reaction in the tube. The ammonia was slowly withdrawn by boiling the solution under slightly reduced pressure at liquid ammonia temperatures. The last traces of ammonia were removed by means of a high vacuum pump. The tube was then detached from the system and weighed. Following are the results of several determinations: Na, 0.1205, 0.1304; product, 0.5177, 0.5553; calcd. for $NaGeH_3$, 0.5167, 0.5591.

Sodium trihydrogermanide is a white solid which is very soluble in liquid ammonia and is insoluble in ethylamine. It reacts very readily with oxygen. It decomposes slowly at liquid ammonia temperatures, becoming slightly yellow in the course of twenty-four hours. At room temperatures, decomposition takes place more rapidly, the product turning brown in the course of several hours. In the presence of ammonia, the rate of decomposition is greatly accelerated.

Thermal Decomposition of Sodium Trihydrogermanide.—With rising temperature, sodium trihydrogermanide decomposes rapidly according to the equation

$$NaGeH_3 = NaGe + 1.5H_2 \qquad (2)$$

The rate of evolution of hydrogen is greatest in the neighborhood of 125°, although hydrogen is slowly evolved at temperatures up to 360°. The hydrogen was collected by means of a Toepler pump and its volume and density were determined. The following results were obtained: m. atoms Na, 5.24, 5.67; cc. H_2 found (N. T. P.), 166.5, 179.3; m. moles H_2 found, 7.43, 8.00; calcd. for Eq. (2), 7.86, 8.51; deficiency, 5.5, 6.0%; mol. wt. gas found, 1.87, 2.16.

The reaction tube was weighed back to determine the weight of residual alloy; the results follow: Na, 0.1205, 0.1304; wt. $NaGeH_3$ found, 0.5177, 0.5553; wt. residue, 0.5022, 0.5386; calcd. for NaGe, 0.5008, 0.5421; weight loss due to H_2 found, 0.0166, 0.0167; calcd., 0.0159, 0.0170.

The residue corresponds to an alloy of composition NaGe; it is evidently identical with the alloy prepared by Dennis and Skow[5] by direct interaction of the two metals at elevated temperatures. The hydrogen as determined is approximately 5% short. It is not improbable that some hydrogen remains in the alloy even after heating to 360°. The residual alloy is generally somewhat soluble in liquid ammonia, the solution being colored red. The solubility is the lower, the higher the temperature to which the alloy has previously been heated.

Germanium Monohydride.—To determine the nature of the alloy left after decomposition of sodium trihydrogermanide, it was treated with ammonium bromide in liquid ammonia. Dissolved material reacted immediately, while the solid adhering to the walls reacted more slowly, a brownish colored solid being formed as the reaction proceeded. No gas was evolved.

On heating the brown solid, after evaporating the ammonia, hydrogen was evolved at 100° and above. While most of the hydrogen was given off between 100 and 200°, smaller quantities were evolved at temperatures up to 500°. The evolved gas was collected by means of a Toepler pump and its volume and density were determined. The mean molecular weight of the gas, after removing a trace of ammonia, was 2.5, which identified it as hydrogen. Its volume, however, was about 25% below that required for the reaction

$$(GeH)_x = xGe + x/2H_2 \qquad (3)$$

The brown solid is unstable and decomposes readily under shock, metallic germanium and hydrogen being formed. The compound was evidently germane monohydride (perhaps somewhat impure), described by Dennis and Skow.[5]

Oxidation of Sodium Trihydrogermanide.—When oxygen is introduced into a solution of sodium trihydrogermanide in liquid ammonia, reaction takes place immediately with the formation of a white, solid precipitate. No gas is evolved.

A known weight of sodium trihydrogermanide was treated with oxygen until no further reaction occurred. The solvent was evaporated at liquid ammonia temperatures and the reaction tube was exhausted to a pressure of 0.15 mm. On warming up to room temperature, the presence of water vapor was made evident by the pressure in the system, which corresponded to that of water. Some water vapor was lost in the connecting tubes. The tube was weighed with results as follows: Na, 0.1184; $NaGeH_3$ (calcd.), 0.5077; final product found, 0.8126; O_2 absorbed, 0.3049; atoms O per atom Na, 3.7.

Even without taking into account the water vapor lost, 3.7 atoms of oxygen per atom of germanium were present in the final product as weighed. This indicates that the sodium trihydrogermanide was completely oxidized according to the equation

$$NaGeH_3 + 2O_2 = NaOGe(OH)_3 \qquad (4)$$

The orthogermanate formed evidently loses water at room temperature.

Ammonia was condensed on the product in the reaction tube and ammonium bromide was added. The solvent was evaporated and the tube was exhausted and weighed. A loss in weight of 0.1374 g. took place, due in part to the reaction of ammonium bromide with sodium orthogermanate (0.0876) and in part to the loss of water (0.0498). On heating the tube to 100°, water vapor was given off and, on cooling, this was reabsorbed. The tube was now heated to 85° and the water vapor was absorbed in phosphorus pentoxide. Finally the tube was exhausted with a high vacuum pump. The results were: product

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[5] Dennis and Skow THIS JOURNAL, **52**, 2369 (1930).

after dehydration, 1.1254; NH_4Br + NaBr, 0.5476; compound, 0.5778; GeO_2 (calcd.), 0.5385; H_2O absorbed in P_2O_5, 0.0384; H_2O retained by oxide, 0.0393. It is evident that, on treating the sodium orthogermanate with ammonium bromide, a hydrated germanium oxide is formed. It is an interesting fact that the dehydration of the oxide was reversible. However, the oxide could not be dehydrated completely by exhausting at 85°. The oxide resulting from the above experiment dissolved completely in 100 cc. of water.

III. Phase Relations in the System NH_3–$NaGeH_3$

Sodium trihydrogermanide crystallizes from liquid ammonia with six molecules of ammonia of crystallization, which are lost in several stages. Altogether, in passing from a dilute ammonia solution to pure $NaGeH_3$, there are five monovariant equilibria. In determining the composition of the solid phases, the pressures of the various monovariant equilibria were first determined by approaching the equilibria from both sides. The amount of ammonia in the system was then adjusted to a point where a solid phase was in equilibrium with the vapor and a new phase was just appearing. Correction was made for ammonia in the vapor phase. The ammonia evolved in the various transformations was absorbed in a weighed bulb containing moist phosphorus pentoxide. In this way, the ammonia associated with the various solid phases was determined.

The transformations involved are indicated in Table I.

TABLE I

TRANSFORMATIONS IN THE SYSTEM $NaGeH_3$-NH_3

Number	Pressure, mm.	Phases	Transformation
1	416	S_1, L_1, G	$L_1 \longrightarrow S_1 + G$
2	315	S_1, S_2, G	$S_1 \longrightarrow S_2 + G$
3	24	S_2, L_2, G	$S_2 \longrightarrow L_2 + G$
4	23	S_3, L_2^1, G	$L_2^1 \longrightarrow S_3 + G$
5	3	S_3, S_4, G	$S_3 \longrightarrow S_4 + G$

G = vapor phase, L_1, L_2, L_2^1 = liquid phases
S_1 = $NaGeH_3 \cdot 6NH_3$, S_2 = $NaGeH_3 \cdot 4.5NH_3$
S_3 = $NaGeH_3 \cdot 2NH_3$, S_4 = $NaGeH_3$

The data relating to the various transformations are given in Table II.

TABLE II

AMMONIA EVOLVED IN TRANSFORMATION OF SOLID PHASES (EXPT. 1, 5.24 M. ATOMS Na; EXPT. 2, 5.67 M. ATOMS Na)

Transformation	1a	1b	2a	2b	Theory
$S_1 \longrightarrow S_2$	1.48	1.81	1.52	1.41	1.5
$S_2 \longrightarrow S_3$	..	2.14	2.47	2.50	2.5
$S_1 \longrightarrow S_3$	..	3.95	3.99	3.91	4.0
$S_3 \longrightarrow S_4$	..	2.00	2.05	2.09	2.0
$S_1 \longrightarrow S_4$	..	5.95	6.04	6.00	6.0

In some instances it was difficult to obtain an exact adjustment to the composition of a pure phase. This was not, in general, the case with the first phase, $NaGeH_3 \cdot 6NH_3$. However, in the transformation $S_1 \longrightarrow S_2$, in experiment 1b, the amount of ammonia obtained, 1.81, was much too high. This was due to the fact that in the course of the operation the pressure was reduced below the equilibrium pressure of the transformation in question. It will be noted that, in the case of experiment 1b, the amount of ammonia involved in the transformation $S_2 \longrightarrow S_3$ is correspondingly low. In three experiments, the total amount of ammonia as determined for $S_1 \longrightarrow S_3$ is 3.95, 3.99 and 3.91 which is close to the value 4.0. The ammonia found in the transformation $S_1 \longrightarrow S_4$, 5.95, 6.04 and 6.00 moles, respectively, per atom of germanium, is in close agreement with the value 6.0.

The solid phase $S_2(NaGeH_3 \cdot 4.5NH_3)$ breaks down under a pressure of 24 mm. to form the liquid phase L_2 and vapor. The next transformation, $L_2^1 \longrightarrow S_3 + G$, takes place at a pressure of 23 mm., only 1 mm. below that of the preceding transformation. In obtaining S_2, great care must be exercised not to lower the pressure too far, otherwise the phase S_3 is formed. By careful removal of ammonia, the liquid phase L_2 may be carried to pressures as low as 12 mm. in the metastable region. By tapping the tube, crystallization may be induced, the solid phase S_3 appears, and the pressure rises to 23 mm. It is evident that phases S_2 and S_3 do not have a transition point at the pressure of the above experiments. All the above equilibria are at −33°, the boiling point of liquid ammonia.

IV. Summary

A method of preparing germanes is described which gives yields of between 60 and 70% of mixed germanes. A method for the conversion of higher germanes to monogermane is likewise described.

By the action of sodium on monogermane in liquid ammonia, sodium trihydrogermanide, $NaGeH_3$, has been prepared. Some of the properties and reactions of this compound are described.

The phase relations in the system NH_3–$NaGeH_3$ at −33° have been investigated. There are formed four solid phases: $NaGeH_3 \cdot 6NH_3$, $NaGeH_3 \cdot 4.5NH_3$, $NaGeH_3 \cdot 2NH_3$ and $NaGeH_3$.

PROVIDENCE, R. I. RECEIVED APRIL 21, 1933