[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXIX. GERMANIUM MONOHYDRIDE[1]

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RECEIVED MARCH 8, 1930 PUBLISHED JUNE 6, 1930

The hydrides of the type RH_4 of carbon, silicon, germanium, tin and lead elements in the fourth group of the Periodic Table are known. Higher homologs of the type R_nH_{2n+2} of carbon, silicon and germanium have also been prepared. Carbon alone of these five elements has yielded hydrides of the type R_nH_{2n}.

Of the hydrides of the type R_nH_n, acetylene is familiar, and analogous hydrides of silicon,[2] tin[3] and lead[4] have been announced, although each deserves further study. Bradley and Weeks give for the three compounds the formulas Si_2H_2, Sn_2H_2 and Pb_2H_2 but, since no determinations of the molecular weights were made, they should for the present be represented by the general formula $(RH)_x$.

When an alloy of germanium and magnesium is treated with dilute hydrochloric acid, the chief products[5] are germanium hydrides of the type Ge_nH_{2n+2}.

Haller took up in the Cornell Laboratory some three years ago the study of the product obtained by treating an alloy of calcium and germanium with hydrochloric acid. He obtained a powder which spontaneously dissociated. No detailed study was made of it at that time.

Experimental

With the thought that an alloy of an alkali metal with germanium might yield unsaturated germanium hydrides more readily than a calcium–germanium alloy, a mixture of powdered germanium and small pieces of sodium in equi-atomic proportions was heated to 1000° in a small, special steel crucible provided with a steel cover which made an air-tight seal when bolted into place. When the cooled crucible was opened, it was found to be filled with a dense, hard, pyrophoric product, analysis and microscopic examination of which showed it to be a homogeneous alloy of the composition NaGe. *Anal.* Calcd. for NaGe: Na, 24.06; Ge, 75.94. Found: Na, 24.08; Ge, 75.94.

Sodium Germanide

The alloy is slowly acted upon by moist air, and consequently it must be kept in a tightly closed receptacle or under a dry, inert gas.

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by N. A. Skow in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bradley, *Chem. News*, **82**, 149 (1900).

[3] Weeks, *Rec. trav. chim.*, **45**, 201 (1926).

[4] Weeks, *J. Chem. Soc.*, **127**, 2845 (1925).

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

When this sodium germanide was added to cold water, or to dilute or concentrated hydrochloric acid, a dark brown powder was formed.

When this was collected on a filter and washed with water, it decomposed with a puff but without detonation, when dried in the air. When water was removed from it by washing it on the filter first with alcohol and then with ether, it exploded with slight detonation as soon as the ether had run through the funnel.

After somewhat extensive experimentation, the analysis of the product was successfully accomplished in the following manner.

The sodium germanide was carefully ground to a fine powder in a dry agate mortar, and then was added in small portions to cold water to avoid rise of temperature during the reaction. The brown powder was then collected on a filter, washed first with water, then with alcohol and finally with ether, and, keeping it moist with ether, was rinsed with a jet of ether into B of the double U-bulb A, Fig. 1, which had previously been weighed while evacuated. The bulb-tube was attached to the chain by the ground joints as shown, and with M closed and R open, pure, dry carbon dioxide was passed over the sample until the ether was removed. D was closed and both B and C were evacuated through the two-way stopcock E, which was then closed. A was then detached and weighed. It was afterwards found that the substance slowly dissociates in a vacuum at room temperature, but as the products of the decomposition could not escape from A, this partial disintegration had no effect upon the weight of the sample.

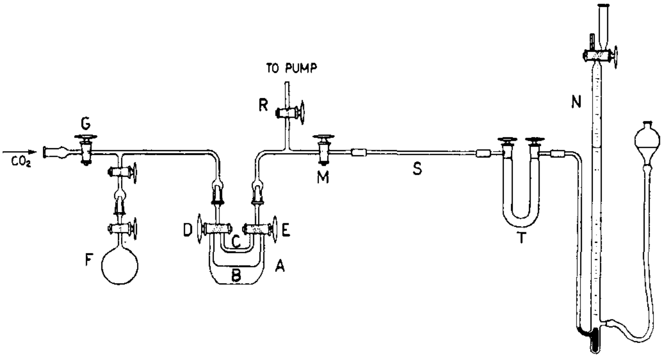

Fig. 1.

A was now again attached to the chain, and all air in the connecting tubes and other parts of the apparatus was swept out by passing carbon dioxide through C and the remainder of the chain into the Schiff nitrometer N, which contained a concentrated solution of potassium hydroxide. When complete absorption of the gas in N showed that air had been removed, the stopcocks D and E were closed, and a glycerin-bath was brought up around B, which contained the sample. The bath was heated to 165°, at which temperature the substance dissociated with an explosive puff, filling the bulb with finely divided germanium and liberating hydrogen. The bath was removed, D and E were turned to communicate with B, and carbon dioxide was slowly passed through the bulb, sweeping out all gases through S and T into N. S was a thin-walled tube of quartz which was heated by a gas flame during the passage of the gases: any germanium escaping from B as a hydride was decomposed, depositing germanium on the walls of S, and liberating hydrogen, which passed on into N. T was a U-tube containing pumice and sulfuric acid for absorption of any water that the sample might still have contained.

S and T were now detached and weighed, and A was evacuated and then weighed. The hydrogen in N was measured, and its purity was then ascertained by combustion in a Dennis–Hopkins combustion pipet.

Anal. Subs., 0.1847: found, Ge (in B and S), 0.1699; H, 0.0029; H_2O, 0.0119. Subtracting from the weight of the sample the weight of water found, the results of the analysis were: Subs., 0.1728: Ge, 0.1699; H, 0.0029. Calcd. for $(GeH)_x$: Ge, 0.1699 = 98.63; H, 0.0029 = 1.37. Found: Ge, 0.1699 = 98.63; H, 0.0029 = 1.37. The results of two other analyses, calculated on the dry sample as before, were: *Anal.* Subs., 0.1566, 0.1004: Calcd. for $(GeH)_x$: Ge, 0.1544, 0.0990; H, 0.0021, 0.00137. Found: Ge, 0.1543 = 98.53, 0.0990 = 98.63; H, 0.0021 = 1.37; 0.00137 = 1.37.

The analyses show the substance to be germanium monohydride.

Germanium Monohydride

Prepared in the manner above described, the compound is a dark brown powder that decomposes with an explosive puff when dried in the air. In an inert gas or in a vacuum the substance dissociates only very slowly at room temperature, but when warmed to about 165° it suddenly breaks down with a slight detonation, yielding hydrogen and germanium.

Qualitative tests showed that the substance is not soluble without change in any of the usual inorganic or organic solvents. Dilute or concentrated nitric acid rapidly oxidizes the germanium to the dioxide. Concentrated solutions of alkali hydroxides are without action. Hydrogen peroxide readily oxidizes it with solution of the resulting germanium dioxide.

The following experiments were made with samples of the compound that had been freed entirely from moisture; this was accomplished by holding it for two hours at 140° in a current of carbon dioxide. Analysis of the residue showed it to be anhydrous $(GeH)_x$ of high purity.

Hydrogen chloride was without appreciable action upon the germanium monohydride at temperatures below that at which the compound dissociated.

A solution of potassium permanganate acidulated with sulfuric acid quantitatively oxidized the substance.

$$2GeH + 2KMnO_4 + 3H_2SO_4 = 2GeO_2 + K_2SO_4 + 2MnSO_4 + 4H_2O$$

Dry fluorine instantly attacked the compound with a burst of flame and the formation of germanium tetrafluoride and hydrogen fluoride.

The reaction between germanium monohydride and dry chlorine was studied in the following manner. A sample of the hydride was collected and dried in B and both B and C were then evacuated and A was weighed. The amount of chlorine called for by the equation

$$2GeH + 5Cl_2 = 2GeCl_4 + 2HCl$$

was brought into the bulb F, the chlorine was frozen by means of liquid air, and the air in the tube was pumped out through C and R. The refrigerant from around F was then removed, D was opened and chlorine was admitted in small portions into B. The monohydride reacted energetically with chlorine and disappeared when all of the gas had been admitted. If the reaction proceeds according to the equation given above, 0.0606 g. of hydrogen chloride, and 0.3566 g. of $GeCl_4$ should have been formed. The amounts found were 0.0609 g. of hydrogen chloride and 0.3562 g. of $GeCl_4$. The purity of the latter was shown by its vapor tension at 0°, 24.4 mm. The experiment was repeated, introducing smaller amounts of chlorine than were called for in the above equation, to ascertain whether lower chlorides of germanium would be formed. In each case only a portion of the monohydride was acted upon, and only $GeCl_4$ was produced.

The reaction with bromine was similar to that with chlorine, only pure $GeBr_4$ being formed even when the germanium monohydride was present in excess.

Vapor of iodine acted slowly upon the monohydride to form GeI_4.

Summary

When sodium germanide, NaGe, reacts with water, germanium monohydride $(GeH)_x$ is formed. This is a brown solid which instantly dissociates with an explosive puff when the dry, or nearly dry, substance is brought into contact with the air. When in an inert gas or a vacuum the compound dissociates only slowly. The monohydride is a strong reducing agent, and unites with the free halogens to form compounds of the type GeX_4.

The preparation of $(GeH)_x$ completes the series of hydrides of the type R_nH_n in the group carbon to lead.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 247]

THE ELECTRODE POTENTIAL OF INDIUM AGAINST INDIUM CHLORIDE SOLUTIONS

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RECEIVED MARCH 10, 1930 PUBLISHED JUNE 6, 1930

Upon the electrode potential of metallic indium there exist only the early inexact investigations of Erhard[1] and Thiel.[2] Later, Richards and Wilson[3] determined with great precision the electromotive forces of cells containing indium amalgams of various concentrations, but they did not measure the pure metal in relation to these amalgams.

This investigation was therefore undertaken for the purpose of obtaining accurate values of the electrode potential of metallic indium against solu-

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[1] Erhard, *Z. anorg. Chem.*, **39**, 119 (1904).

[2] Thiel, *Wied. Ann.*, **14**, 504 (1881).

[3] Richards and Wilson, *Z. physik. Chem.*, **72**, 129 (1910).