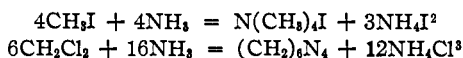


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## Germanium. XL. Action of Ammonia upon Monochloromonogermane and Dichloromonogermane. Action of Water upon Monochloromonogermane<sup>1</sup>

BY L. M. DENNIS AND R. W. WORK

**Introduction.**—The action of anhydrous ammonia upon the mono-, di-, and trihalogen derivatives of methane and monosilane has been studied by various investigators. They may briefly be summarized as follows



$\text{CHCl}_3$  (in sealed tube with ammonia and absolute alcohol).—Chief product  $\text{NH}_4\text{CN}$ .<sup>4</sup>

$\text{SiH}_3\text{Cl} + \text{NH}_3$ .—Stock and Somieski found<sup>5</sup> that, with excess of ammonia, the compound at once lost all of its chlorine to form ammonium chloride, and that the silicon retained its three atoms of hydrogen, forming nitrogen-containing derivatives of monosilane such as the volatile  $(\text{SiH}_3)_2\text{NH}$ .

They give the reaction of dichloromonosilane with excess of ammonia as  $\text{SiH}_2\text{Cl}_2 + 3\text{NH}_3 = \text{SiH}_2(\text{NH}) + 2\text{NH}_4\text{Cl}$ , the silicon compound forming at once a solid, non-volatile polymer.

With excess of ammonia,  $\text{SiHCl}_3$  forms<sup>6</sup>  $(\text{SiH}\cdot\text{NH})_2\text{NH}$ .

No halogenated derivatives of the normal hydrides of tin and lead are as yet known, but since such compounds of germanium are available,<sup>7</sup> the study of their behavior when treated with an excess of ammonia, with a view to ascertaining to what extent the reactions were analogous to those of the corresponding compounds of carbon and silicon, was taken up.

### Experimental

Monochloromonogermane,  $\text{GeH}_3\text{Cl}$ , and dichloromonogermane,  $\text{GeH}_2\text{Cl}_2$ , were prepared from pure monogermane by the method of Dennis and Judy.<sup>7</sup> The purity was checked by determinations of molecular weight. Calcd. for  $\text{GeH}_3\text{Cl}$ , 111.1; found, 110.8, 109.9. Calcd. for  $\text{GeH}_2\text{Cl}_2$ , 145.5; found, 145.6.

**Reaction of Monochloromonogermane with Ammonia.**—The experiments were carried out in the vacuum fractionation apparatus, as modified by Laubengayer and Corey,<sup>8</sup> but all of the bulbs were provided with stopcocks and normal, interchangeable, ground joints, which made it possible to disconnect them and attach them at any desired points on the apparatus.

(1) This article is based upon the thesis presented to the Graduate School of Cornell University by Robert W. Work in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Chablay, *Ann. chim.*, [9] 1, 477 (1914).

(3) Höland, *Ann.*, 240, 225 (1887).

(4) Heintz, *Ann. physik Chem.*, 174, 263 (1856).

(5) Stock and Somieski, *Ber.*, 54, 740 (1921).

(6) Stock and Zeidler, *ibid.*, 56, 986 (1923).

(7) Dennis and Judy, *THIS JOURNAL*, 51, 2321 (1929).

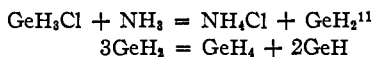
(8) Laubengayer and Corey, *J. Phys. Chem.*, 30, 1043 (1926).

A sample of  $\text{GeH}_3\text{Cl}$  was distilled into a weighed bulb on the apparatus, the stop-cock of the bulb was closed, and the bulb was detached and weighed. The bulb was again attached, and ammonia was distilled upon the sample and was allowed to act for two hours at  $-78$  to  $-50^\circ$ . There appeared in the bulb a yellowish substance.

The bulb was held at  $-50^\circ$  and the excess of ammonia was distilled into a second bulb by surrounding the latter with liquid air. The residue was now clearly seen to be a mixture of a white, crystalline compound and an amorphous powder. The first bulb was found to have lost weight, which showed that a volatile product had been removed with the ammonia. To ascertain its nature, the distillate in the second bulb was held at  $-78^\circ$  and the ammonia was distilled over into a third bulb. Nothing remained in the second bulb. The distillate was then surrounded by a bath at  $-110^\circ$  at which temperature ammonia has a vapor tension of only 1 mm.<sup>9</sup> Manometric readings disclosed the presence of a substance condensable with liquid air, but having an appreciable vapor tension at  $-135^\circ$ . This was carefully distilled off at  $-135^\circ$  and was further fractionally distilled to separate the gas from traces of ammonia and its volume was measured. Molecular weight, calcd. for  $\text{GeH}_4$ , 76.6; found, 76.2.

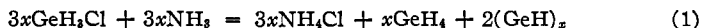
Ammonium chloride was undoubtedly formed in the reaction of the ammonia on the  $\text{GeH}_3\text{Cl}$ , and its amount in the reaction bulb was ascertained by utilizing the fact that it forms a triammonate,  $\text{NH}_4\text{Cl}\cdot 3\text{NH}_3$ , for which the dissociation pressure-temperature curve is known. This indirect method of determining ammonium chloride was used by Pugh and Thomas,<sup>10</sup> who kept the pressure constant and varied the temperature of the bath. We departed from this procedure and kept the material at constant temperature,  $-5^\circ$ , removing volumes of ammonia stepwise and thus lowering the decomposition pressure of the ammonate. The amount of ammonium chloride may be calculated from the volume of ammonia evolved between two points of equal pressure in the system before and after the  $\text{NH}_4\text{Cl}\cdot 3\text{NH}_3$  has been decomposed.

It having thus been ascertained that all of the chlorine in the  $\text{GeH}_3\text{Cl}$  is removed by the ammonia to form ammonium chloride, and that monogermane is simultaneously produced, there remained some hydrogen still to be accounted for. The presence of  $\text{GeH}_4$  in the reaction products rendered it probable that an unsaturated hydride of germanium might first be formed and that this then dissociated with the production of  $\text{GeH}_4$  and a lower hydride, thus



Germanium monohydride,  $(\text{GeH})_x$ , was found by Dennis and Skow<sup>12</sup> to break down into metallic germanium and hydrogen when slightly heated. To learn whether the solid residue in the reaction bulb contained  $(\text{GeH})_x$ , the bulb was touched with the flame of a Bunsen burner. There was instant formation of a black mirror on the wall of the bulb, and a rise of gas pressure in the apparatus. The gas, which was noncondensable by liquid air, was pumped off, measured and analyzed by combustion. It was found to be pure hydrogen.

The various data thus obtained indicate that the reaction proceeds according to the equation



and this is confirmed by the analytical results.

*Anal.* Sample of  $\text{GeH}_3\text{Cl}$ , 0.2342 g.  $\text{NH}_4\text{Cl}$  formed, calcd. 0.1128 g., found 0.1127 g.

(9) Karwat, *Z. physik. Chem.*, **112**, 487 (1924).

(10) Pugh and Thomas, *J. Chem. Soc.*, 60 (1931).

(11)  $\text{GeH}_3$  has recently been isolated by Royen and Schwarz, *Z. anorg. allgem. chem.*, **211**, 412 (1933).

(12) Dennis and Skow, *THIS JOURNAL*, **52**, 2369 (1930).

H<sub>2</sub> produced, calcd. for 2GeH, 0.001418 g., found, 0.001416 g. Sample of GeH<sub>3</sub>Cl, 0.2831 g. GeH<sub>4</sub> formed, calcd., 0.0645 g., found, 0.0647 g.

The correctness of equation (1) is thus established.

**Reaction of Monochloromonogermane with Water.**—Upon treatment of monochloromonosilane with water, there is formed the volatile compound disiloxane,<sup>13</sup> b. p.  $-15.2^{\circ}$ .  $2\text{SiH}_3\text{Cl} + \text{H}_2\text{O} = (\text{SiH}_3)_2\text{O} + 2\text{HCl}$ .

To ascertain whether an analogous compound of germanium is produced, water was distilled into a bulb containing GeH<sub>3</sub>Cl. There was formed at once a white solid which gradually became light yellow in color. No evidence of the formation of a volatile compound of germanium was obtained.

**Reaction of Dichloromonogermane with Ammonia.**—Anhydrous ammonia was distilled in the fractionation chain upon a sample of GeH<sub>2</sub>Cl<sub>2</sub> of known weight, the ammonia being first condensed by liquid air and then allowed to rise to  $-78^{\circ}$ . At that temperature reaction took place at once, with the formation of a brown solid that became black in a few seconds. The bulb was allowed to come to room temperature and the excess of ammonia was then removed. No volatile substance other than ammonia was present. The reaction bulb was again weighed, and the weight of the ammonia that took part in the reaction was thus ascertained. Millimoles of NH<sub>3</sub>, 4.682; of GeH<sub>2</sub>Cl<sub>2</sub>, 2.435. Ratio NH<sub>3</sub>:GeH<sub>2</sub>Cl<sub>2</sub> = 1.997:1.000.

The experiment was repeated with another sample, except that the reaction bulb was held at  $-27^{\circ}$  and the ammonia was introduced very slowly. The reaction product was at first white, then changed to yellow and finally became black. The ratio NH<sub>3</sub>:GeH<sub>2</sub>Cl<sub>2</sub> was again determined and was found to be 2.067:1.000.

The residue in the reaction bulb was extracted with water, and crystals from the solution were identified as ammonium chloride under the microscope. The black powder was found to be insoluble in hydrochloric acid, both dilute and concentrated, in dilute sulfuric acid and in hydrofluoric acid. It was not attacked by 6 *N* sodium hydroxide, but when hydrogen peroxide was added, it quickly dissolved yielding a solution that contained germanium. These reactions identified it as free germanium.<sup>14</sup>

The experimental results show that when an excess of anhydrous ammonia acts upon dichloromonogermane, it does so in the ratio 2NH<sub>3</sub>:GeH<sub>2</sub>Cl<sub>2</sub>, that ammonium chloride is formed and germanium is simultaneously set free, and that no volatile substance is produced. The reaction is, therefore,  $\text{GeH}_2\text{Cl}_2 + 2\text{NH}_3 = \text{Ge} + 2\text{NH}_4\text{Cl}$ .

The elements in the fourth group show decreasing affinity for hydrogen with rise of atomic weight, methane being very stable, SiH<sub>4</sub> being decomposed into its elements at about  $400^{\circ}$ , GeH<sub>4</sub> at  $285^{\circ}$ , and the hydrides of tin and lead dissociating spontaneously.

The halogenated derivatives of methane react less readily with ammonia than do the analogous compounds of silicon and germanium, which may be explained by the fact that both the normal and maximum valencies of carbon are four, and that it forms stable compounds with both hydrogen and the halogens.

If the next element in the group, silicon, is considered to have a maximum valency of six,<sup>15</sup> then ammonia, with a lone pair of valency electrons, can act as a *donor*, and can form coördinate linkages with the silicon atom, with subsequent breakdown of the complex to form new molecules. The

(13) Stock, Somieski and Wintgen, *Ber.*, **50**, 1754 (1917); Stock and Somieski, *ibid.*, **56**, 132 (1923).

(14) See Dennis, Tressler and Hance, *THIS JOURNAL*, **45**, 2033 (1923).

(15) Sidgwick, "The Electronic Theory of Valency," Oxford, 1927, p. 152.

investigations of Stock and his co-workers have shown that when the mono-, di-, and trichloro derivatives of monosilane are treated with ammonia, the affinity of the silicon for hydrogen is such that it retains, in the first reaction, all of the hydrogen atoms that it possessed before treatment with the ammonia, the chlorine being removed as a negative ion.

Germanium, standing below silicon in the group, has weaker affinity for hydrogen, and, when caused to react with ammonia, the chlorinated derivatives of monogermane,  $\text{GeH}_2\text{Cl}$  and  $\text{GeH}_2\text{Cl}_2$ , lose all of the halogen, and a part or all of the hydrogen.

The study, not as yet completed, of the action of ammonia upon trichloromonogermane indicates that there is first formed a diammonate,  $\text{GeHCl}_3 \cdot 2\text{NH}_3$ , and that this, upon further treatment with ammonia, is converted to germanous imide,  $\text{GeNH}$ .<sup>16</sup>

### Summary

1. The reaction between monochloromonogermane and an excess of liquid ammonia is,  $3x\text{GeH}_3\text{Cl} + 3x\text{NH}_3 = 3x\text{NH}_4\text{Cl} + x\text{GeH}_4 + 2(\text{GeH})_x$ .

2. The reaction between dichloromonogermane and an excess of liquid ammonia is  $\text{GeH}_2\text{Cl}_2 + 2\text{NH}_3 = \text{Ge} + 2\text{NH}_4\text{Cl}$ .

3. The reaction between monochloromonogermane and an excess of water produces neither hydrogen nor the hypothetical compound  $(\text{GeH}_3)_3\text{O}$ .

(16) Johnson, Morey and Kott, *THIS JOURNAL*, **54**, 4278 (1932).

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## The Thermodynamic Constants of Iodine Monochloride, Iodine Monobromide and Bromine Monochloride in Carbon Tetrachloride Solutions

BY CHARLES M. BLAIR, JR., AND DON M. YOST

### Introduction

The changes in free energy, heat content and entropy of most reactions have been determined for only a single environment. In order to facilitate future studies on the relations between reactions taking place both in the gas phase and in solutions the determination of the thermodynamic constants of iodine monochloride, iodine monobromide and bromine monochloride in carbon tetrachloride was undertaken. The solvent, carbon tetrachloride, was chosen so that the resulting solutions would be as nearly perfect as possible. The constants for iodine monochloride,<sup>1</sup> iodine mono-

(1) McMorris and Yost, *THIS JOURNAL*, **54**, 2247 (1932).