[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Nitrogen Compounds of Germanium. IV. The Action of Ammonia and Amines on Germanium Tetraiodide

BY WARREN C. JOHNSON AND ALBERT E. SIDWELL

Germanium tetrachloride has been shown by several workers[1,2,3] to be completely ammonolyzed in liquid ammonia solution to germanic imide, $Ge(NH)_2$ and ammonium chloride. Germanous iodide has been recently found to behave similarly in ammonia to produce germanous imide, GeNH, and ammonium iodide.[4] Thomas and Southwood[5] found germanium tetrachloride to undergo *aminolysis* with ethylamine and with diethylamine but no reaction was observed with tertiary amines.

Recently, Karantassis and Capatos[6] have reported reactions of germanium tetraiodide with ammonia and amines in carbon tetrachloride solutions. They conclude from their experiments that in each instance an addition compound is formed, namely, $GeI_4 \cdot 8NH_3$, $GeI_4 \cdot 6C_2H_5NH_2$, $GeI_4 \cdot 10(C_2H_5)_2NH$, $GeI_4 \cdot 5(C_2H_5)_3N$, $GeI_4 \cdot 4C_6H_5NH_2$, $GeI_4 \cdot 6CH_3C_6H_4NH_2$ and $GeI_4 \cdot 10C_9H_7N$. Analyses of the products are reported only for germanium and iodine; in addition, these writers were apparently unaware of the previous work with germanium tetrachloride. On the basis of the results obtained with germanous iodide and ammonia,[4] one would expect germanic iodide to undergo ammonolysis readily since the germanous ion is derived from a stronger base than is the germanic ion.

In view of these facts and the unusual results of Karantassis and Capatos, the following described work was undertaken. The results of the investigation, with the exception of those found for triethylamine, do not give any indication of the formation of addition compounds. On the other hand, they demonstrate germanic iodide to be ammonolyzed and aminolyzed in ammonia and amine solutions, respectively, and to be entirely in accord with the results of the earlier experiments with germanic chloride.

Experimental

Preparation of Material

Germanic Iodide.—Two methods of preparation were used here. (A) In the preparation of germanous iodide from germanous sulfide as previously described,[4] considerable quantities of germanic iodide are obtained due to the oxidation of the former salt. It was separated from germanous iodide with benzene, then recrystallized and finally dried and analyzed. For the germanium analysis, the iodide was treated with nitric acid to form germanic oxide. The Volhard method was used for the iodine determination.

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(1) Schwarz and Schenk, *Ber.*, **63**, 296 (1930).

(2) Johnson, Thesis, Brown University, 1929.

(3) Thomas and Pugh, *J. Chem. Soc.*, 1051 (1926); 60 (1931).

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

(5) Thomas and Southwood, *J. Chem. Soc.*, 2083 (1931).

(6) Karantassis and Capatos, *Compt. rend.*, **193**, 1187 (1931).

Anal. Calcd. for GeI_4: Ge, 12.53; I, 87.47. Found: Ge, 12.44, 12.45; I, 87.03, 87.05.

(B) The procedure described by Laubengayer and Brandt[7] was found very satisfactory for this preparation. Approximately 85 g. of the iodide was prepared by this method.

Anal. Found: Ge, 12.51, 12.49; I, 87.50.

Solvents.—Anhydrous ammonia of commerce was siphoned from its container into small steel cylinders containing metallic sodium as a dehydrating agent. The ammonia was allowed to escape as a gas into the vacuum apparatus used for the experiments.

The amines were obtained from the Eastman Kodak Company as the purest, anhydrous products available. They were treated with metallic lithium in a vacuum apparatus to remove traces of moisture.

Carbon tetrachloride (C. P.) was purified by repeated distillation.

Apparatus and Procedure.—Two different procedures were followed to study the action of ammonia and amines on germanic iodide. In the first method, germanic iodide was treated directly with these solvents at low temperatures, −33.5°. The apparatus used here was essentially the same as that previously described in the study of germanous iodide in liquid ammonia.[4] It is so designed that it may be easily weighed on an ordinary analytical balance and thus any changes in weight accompanying a given reaction may be readily detected. In addition, the products of the reaction may be washed with liquid ammonia or amine and the solution eliminated through the glass filter in order to separate the soluble from the insoluble products.

In the second procedure, germanic iodide was dissolved in carbon tetrachloride at room temperature and ammonia gas or amine vapor was allowed to pass through the solution contained in the apparatus indicated above.

Since the purpose of the investigation was to show that germanic iodide is ammonolyzed and aminolyzed in ammonia and amines, respectively, a separation of the products of the reactions was not attempted in all cases. Such a separation was made in the ammonia experiments in order to obtain germanic imide in a pure state; on the other hand, the detailed studies of Thomas and Southwood,[5] who worked with germanic chloride and amines, permitted us to demonstrate merely the nature of the reactions that proceed between germanic iodide and amines. Evidence for the latter was obtained by a treatment of the products of the reactions with metallic lithium in the liquid amine. If an aminolytic reaction were to proceed, the alkylammonium iodide produced would react with metallic lithium with the liberation of hydrogen; on the other hand, an addition compound between germanic iodide and an amine would not liberate hydrogen in the presence of metallic lithium (alkylamines show little tendency to react with metallic lithium at low temperatures).

Results

Small amounts of germanic iodide (1–2 g.) were treated with these solvents according to the two procedures described above. At the completion of a reaction, the greater part of the solvent was allowed to evaporate and finally the last traces were removed by the vacuum pumps at room temperature. This procedure was repeated until the reaction tube and its contents showed no change in weight. The results are shown in Table I.

The ammonium iodide formed in experiments 1, 2 and 4 was separated from the germanic imide quantitatively by several washings with liquid ammonia. This separation was found to be efficient due to the low solubility of the imide and the relatively high solubility of the ammonium salt. These washings on evaporation yielded 2.2701,

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[7] Laubengayer and Brandt, THIS JOURNAL, 54, 621 (1932).

TABLE I

THE ACTION OF AMMONIA AND AMINES ON GERMANIC IODIDE

A. Ammonia

Expt.	Solvent	GeI_4, g.	NH_3 reacted, g.	Ratio NH_3/GeI_4
1	NH_3	2.2662	0.3972	5.98
2	NH_3	2.0658	.3637	6.00
3	CCl_4	1.7809	.3142	6.01
4	CCl_4	1.6433	.2896	6.00

B. Amines

Expt.	Solvent	GeI_4, g.	Amine reacted, g.	Ratio amine/GeI_4
5	$C_2H_5NH_2$	1.2894	0.6062	6.05
6	$C_2H_5NH_2$	1.2175	.5642	5.97
7	$C_2H_5NH_2$ in CCl_4	1.6184	.7569	6.02
8	$(C_2H_5)_3N$ in CCl_4	0.8021	.6907	4.95
9	$(C_2H_5)_3N$ in CCl_4	.8941	.7747	4.98

2.0678 and 1.6418 g. of ammonium iodide, respectively; the calculated amounts are 2.2645, 2.0639 and 1.6421 g. on the basis of the equation

$$GeI_4 + 6NH_3 = Ge(NH)_2 + 4NH_4I \quad (1)$$

The product left in the reaction chamber, germanic imide, was shaken into small tubes attached to the apparatus. These were sealed off and weighed and then the contents were subjected to analysis for germanium and ammonia according to the usual procedures.

Anal. Calcd. for $Ge(NH)_2$: Ge, 70.74; N, 27.30. Found: Ge, 70.76, 70.65, 70.78; N, 27.30, 27.24, 27.26.

The above data and experiments show that germanic iodide is ammonolyzed according to equation (1). The same reaction takes place in carbon tetrachloride solution as in pure liquid ammonia.

In order to show the nature of the reaction between germanic iodide and ethylamine, the products were treated in liquid ethylamine solution with metallic lithium. Hydrogen gas was liberated immediately due to the presence of ethylammonium iodide. The products of the reactions, designated in Table I as experiments 6 and 7, gave in the presence of excess lithium 93.9 and 120.0 cc. of hydrogen, respectively; the calculated amounts based on equations (2) and (3) are 94.0 and 125.0 cc.

Germanic iodide was also subjected to liquid diethylamine. The increase in weight was found to vary from 5.0 to 5.3 moles of the amine per mole of the iodide. When the products of the reaction were treated with metallic lithium in liquid diethylamine solution, hydrogen gas was liberated in an amount more than sufficient to account for the complete aminolysis of germanic iodide. The excess hydrogen (5–8%) was due to an appreciable reaction that proceeds between metallic lithium and diethylamine.

In the case of the reactions with triethylamine (Expts. 8 and 9) only five moles of the amine are involved. The products obtained from this reaction failed to yield any hydrogen in the presence of metallic lithium in liquid triethylamine solution.

Discussion

The results obtained from the reactions studied with germanic iodide and ammonia are in complete agreement with those found by Schwarz and Schenk and Thomas and Pugh for germanic chloride and ammonia. On the other hand, the results are not in accord with those reported by Karantassis and Capatos. The latter workers conclude that eight moles of ammonia react with one mole of germanic iodide to form an ammonate. Our results clearly demonstrate the reaction to be one of ammonolysis and not of ammonation; at the same time, we find only six moles of ammonia to react with one mole of germanic iodide. Karantassis and Capatos analyzed the products of the reaction for germanium and iodine; they made no attempt to determine the ammonia content directly. It is quite evident that such a procedure is faulty when one considers the weights of the constituents involved in the reaction. Germanic iodide has a molecular weight of about 580; six moles of ammonia account for a weight of 102. Two moles of ammonia, 34 in weight, are equivalent to about 5% of the total weight of germanic iodide and ammonia. The germanium analysis reported by Karantassis and Capatos is about 4% low calculated on the basis of the addition of eight moles of ammonia per mole of germanic iodide. The iodide analysis is about 1% high on this same basis.

Karantassis and Capatos do not describe any procedure for the separation of the reaction products from carbon tetrachloride so as to exclude moisture. Germanic imide is known to react readily with moisture to give ammonia and germanic oxide. Extreme care must be taken to prevent even traces of moisture in the preparation of a pure product. Analyses of the products of the reactions for only germanium and iodine would not give any indication of the presence or absence of germanic imide; complete hydrolysis of germanic imide would yield germanic oxide, while the ammonium iodide would remain unchanged. The difference in weight between germanic oxide (104.6) and germanic imide (102.6) is inappreciable in comparison with the total weight of the reaction products.

The apparatus and procedure employed in our experiments permits of a complete separation of ammonium iodide in the absence of air and moisture, and the subsequent isolation of germanic imide in a very pure state. The amount of ammonium iodide obtained in each experiment agrees well with the value calculated on the basis of the ammonolysis of germanic iodide. The same results are obtained when the reaction is carried out in carbon tetrachloride solution.

When germanic iodide is subjected to ethylamine in the amine solution or in carbon tetrachloride, a reaction is found to take place which involves six moles of the amine per mole of the iodide. This result is in agreement with those of all former workers. The nature of this reaction is shown as one of aminolysis and may be represented by the following equation

$$GeI_4 + 6C_2H_5NH_2 = Ge(NC_2H_5)_2 + 4C_2H_5NH_3I \qquad (2)$$

The evidence presented for the course of this reaction, as described in the experimental procedure, is readily obtained from the equation

$$C_2H_5NH_3I + Li = C_2H_5NH_2 + LiI + {}^1/_2H_2 \qquad (3)$$

Equation (2) is entirely in accord with the results of Thomas and Southwood; Karantassis and Capatos do not consider the possibility of the aminolysis of germanic iodide. Thomas and Southwood also found germanic chloride to react with four moles of ethylamine under certain conditions; however, the conditions of our experiments were such, with excess ethylamine, as to eliminate the chance for this reaction to occur. It would be difficult to explain such a reaction on the basis of aminolysis of the germanic halide unless only a part of the total number of halogen atoms were found to react, or a hydrochloride of germanium diethyldiimide were formed as has been suggested by Thomas and Southwood.

Our results of germanic iodide with diethylamine are not as well defined as those with ammonia and ethylamine. However, they agree with those of Thomas and Southwood as regards the nature of the reaction, namely, that it is one of aminolysis. Karantassis and Capatos found ten moles of the amine to react with one mole of germanic iodide, while Thomas and Southwood observed a ratio of 5 to 1 with the chloride. The description of the experiments given by the latter workers serves to explain the ratios we obtained which were as high as 5.3 to 1. These workers also obtained ratios between 5 to 1 and 6 to 1 when the products of the reactions were not heated and thoroughly pumped at temperatures as high as 90°.

It is evident that there is no opportunity for aminolysis to occur in the case of a tertiary amine since the latter lacks a direct nitrogen–hydrogen linkage. Thomas and Southwood did not detect any reaction between germanic chloride and diethylaniline, a tertiary amine. Our experiments with triethylamine show five moles of the amine to react with one mole of germanic iodide; the same result was observed by Karantassis and Capatos. When this product was subjected to the action of metallic lithium in liquid triethylamine, no reaction between the constituents could be detected nor was any hydrogen gas eliminated. It must be concluded that triethylamine forms an addition compound, aminate, with germanic iodide.

Studies are under way in this Laboratory to obtain more definite information than is now at our disposal in regard to the nature of reactions between germanous as well as germanic halides and amines.

Summary

Germanic iodide is found to react with six moles of ammonia in liquid ammonia or in carbon tetrachloride solution with the formation of ammonium iodide and germanic imide. The latter compound has been obtained in a high state of purity. This result agrees with previous work with germanic chloride and ammonia but is not in accord with the results of Karantassis and Capatos, who worked with germanic iodide.

Ethylamine and diethylamine are found to react with germanic iodide in the amine as well as in carbon tetrachloride solutions. Evidence is presented to demonstrate the nature of these reactions as that of aminolysis.

Triethylamine forms an addition compound, aminate, with germanic iodide in which five moles of the former are combined with 1 mole of the iodide.

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The Complex Ions Formed by Iodine Cyanide with Cyanide and Iodide Ions. The Vapor Pressure, Free Energy and Dissociation of Iodine Cyanide

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Introduction

Former investigations[1] of the equilibria involving iodine cyanide had as their object the determination of the free energy of formation of cyanogen. Since the results led to a negative value for the entropy of this substance, which would be a contradiction of the third law, it was considered of importance to reinvestigate some of the reactions involved.

One of the reversible [2,1] reactions employed was

$$ICN + H^+ + I^- = I_2 + HCN \qquad (1)$$

but the measurements indicated that it was complicated by the formation of the complex ions I_2CN^- and $I(CN)_2^-$. By means of distribution experiments we have determined the stabilities of these ions and estimated their effect on reaction (1).

Another reaction previously studied[3] was the dissociation of solid iodine cyanide into iodine and cyanogen

$$ICN(s) = \tfrac{1}{2}I_2(g) + \tfrac{1}{2}C_2N_2(g) \qquad (2)$$

In this case we have considered it better to redetermine the dissociation with all substances present as gases than to have a solid phase present with its possible catalytic effect on the formation of paracyanogen.

In this paper are presented the results of measurements (1) on the stabilities of the ions $I(CN)_2^-$ and I_2CN^-, (2) on the vapor pressures and solubility of iodine cyanide, and (3) on the dissociation of the latter into iodine and cyanogen. There are also presented the free energy calculations made by combining our results with those of other investigators.

Preparation of the Materials and Experimental Methods

The iodine cyanide was prepared by adding iodine to a moderately concentrated solution of potassium cyanide, and extracting the resulting mixture with ether after

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 591.

[2] Laura Kovach, *Z. physik. Chem.*, **80**, 107 (1912).

[3] Ref. 1, p. 592.