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

Nitrogen Compounds of Germanium. V. Germanous Nitride

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Germanic nitride has been prepared by two methods: (I) through the action of gaseous ammonia on metallic germanium at high temperatures,[1] and (II) by the thermal decomposition of germanic imide, $Ge(NH)_2$.[2] By means of a study of the equilibrium relations among the constituents of reaction (I), it has been shown[3] that it is not possible to form germanic nitride from its elements.

A study of reaction (I) over a wide range of conditions was found to produce only germanic nitride. Accordingly, there appear three methods of approach to the preparation of germanous nitride, namely, (A) the thermal decomposition of germanic nitride, (B) the direct combination of germanium with nitrogen and (C) the thermal decomposition of germanous imide. Of these possible reactions, only (C) was found to produce germanous nitride, Ge_3N_2.

Experimental

(A) The Thermal Decomposition of Germanic Nitride.—Schwarz and Schenk[2] found germanic nitride to decompose at high temperatures into its elements. However, it was decided to be advisable to study this reaction under different conditions, since it might lead to an intermediate stage with germanous nitride as the product.

Germanic nitride was prepared and analyzed as previously described.[1] It was placed in a small quartz tube which was provided with a small Pyrex stopcock by means of an intermediate graded seal. This apparatus was sufficiently small to be weighed conveniently on an ordinary analytical balance.

In the first series of experiments (Expts. I, II and III) the nitrogen liberated in the decomposition was removed from the apparatus with the vacuum pumps as fast as it appeared. At 825° there appeared an appreciable loss in weight of the tube and its contents; however, it was found necessary to increase the temperature to 900° and above before the rate of decomposition became sufficiently high to allow for the completion of an experiment with approximately 0.5 g. of Ge_3N_4 over a period of ten to twelve hours. In the second series of experiments (Expts. IV and V) the volume of liberated nitrogen was measured and kept in contact with the solid phases in a closed system. The results are shown in Table I.

TABLE I

THE DISSOCIATION OF GERMANIC NITRIDE

Expt.	Ge_3N_4, g.	Loss N_2, g.	Loss N_2, cc.	Loss N_2, calcd. g.	cc.
I	0.5981	0.1228		0.1225	
II	.1490	.0302		.0305	
III	.1572	.0322		.0322	
IV	.1386	.0272	22.2	.0283	22.6
V	.1774	.0358	28.6	.0363	29.0

The residue in the quartz tube was identified as germanium. It failed to liberate any ammonia when subjected to hydrogen at 700° (both nitrides of germanium liberate ammonia under these conditions); however, in the presence of oxygen at 800° it was converted to germanic oxide. (0.1180, 0.0236 g. residue gave 0.1687, 0.0336 g. GeO_2. Calcd. GeO_2: 0.1700, 0.0340.) Several samples of the residue were heated at 700° in a stream of ammonia gas to form germanic nitride. (0.1380, 0.3616 g. residue gave 0.1728, 0.4536 g. Ge_3N_4. Calcd. Ge_3N_4: 0.1734, 0.4545.)

These results clearly demonstrate that germanic nitride dissociates at high temperatures to germanium and nitrogen without the intermediate formation of germanous nitride.

(B) The Action of Nitrogen on Germanium.—In the second series of experiments described under (A) the nitrogen obtained from the dissociation of the nitride was allowed to remain in contact with the germanium for several hours at 900°; however, no change was observed which would indicate the formation of a new product. In order to substantiate this result nitrogen gas was passed over gray germanium powder in a quartz tube for ten days at temperatures ranging from 600 to 1200°. A few mg. of a brown powder was found to collect in the cooler regions of the tube, but an examination of the substance disclosed the formation of germanous oxide. Hydrogen gas was passed over the residue left in the tube, over the material which had distilled to the walls, and the brown powder, with the exit gases leading through a known volume of standard hydrochloric acid solution, but no indication of the presence of ammonia in the solution was found.

The material remaining in the boat and on the walls of the quartz tube was identified as germanium. The germanous oxide (brown powder) may be explained by the failure to remove completely the oxygen from the nitrogen; with the partial pressure of oxygen being extremely low, one would expect germanous oxide rather than germanic oxide as the product. In addition, it is well known that at these high temperatures germanic oxide is reduced readily to germanous oxide by metallic germanium. The above experiment was repeated several times with the same results.[4,5]

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(1) Johnson, THIS JOURNAL, **52**, 5160 (1930).

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

(3) Morey and Johnson, THIS JOURNAL, **54**, 3603 (1932).

(4) We are indebted to Mr. Glen H. Morey for the assistance rendered in carrying out these experiments.

(5) In an earlier article of this series (Ref. 1) it was stated that germanium powder combines directly with nitrogen at 700° to give germanous nitride. The above experiments show this statement to be incorrect. We were at first misled by the formation of the brown powder described above which, upon closer examination, was found to be due to oxygen.

(C) The Thermal Decomposition of Germanous Imide.—Germanous imide was prepared as previously described[6] by allowing germanous iodide to react with ammonia. The increase in weight due to the formation of ammonium iodide corresponds to 3 moles of ammonia as expressed by the equation

$$GeI_2 + 3NH_3 = GeNH + 2NH_4I \qquad (1)$$

(GeI_2: 1.0105, 2.5044. Weight increase: 0.1530, 0.3857. Ratio, moles NH_3/mole GeI_2: 2.92, 2.96.) The ammonium iodide was removed from the germanous imide by washing the mixture with liquid ammonia in the absence of air and moisture. (GeI_2: 1.0105, 0.6095, 0.6299. GeNH found: 0.2757, 0.1643, 0.1676. GeNH calcd.: 0.2712, 0.1635, 0.1688.)

The imide appeared as a light yellow powder. It was shaken into a small side-tube of the apparatus in which it was prepared and then a small electric furnace was placed about this tube which was finally heated at 250–300° for several hours. Since the tube was connected to a system of known volume, including a manometer, it was possible to follow qualitatively the rate as well as the extent of dissociation at a given temperature.

Dissociation of the imide was found to proceed as follows

$$3GeNH = Ge_3N_2 + NH_3 \qquad (2)$$

The results of several experiments are given in Table II.

TABLE II

THE DISSOCIATION OF GERMANOUS IMIDE

	Ge_3N_2, g.		NH_3 gas, cc.	
GeNH, g.	Found	Calcd.	Found	Calcd.
0.3950	0.3694	0.3685	33.3	33.7
.4274	.3997	.3997	36.9	36.4
.1496	.1393	.1398	12.7	12.7
.1527	.1443	.1428	12.2	13.0

The ammonia gas was identified through its molecular weight as determined by the vapor density method. *Mol. wt.* Vol. of gas: 15.14, 23.32, 23.67 cc. Wt. of gas: 0.0117, 0.0174, 0.0176 g. Mol. wt.: 17.3, 16.7, 16.7.

The germanous nitride was left in the tube as a finely-divided, dark brown powder. Although reaction (2) is not reversible at pressures of ammonia as high as one atmosphere, the nitride was found to adsorb appreciable amounts of ammonia gas. In order to remove all of the ammonia from the product, it was found necessary to keep the temperature of the nitride at about 300° while the ammonia was being condensed in an auxiliary tube at liquid nitrogen temperatures. The volume of ammonia reported above was thus obtained by allowing the gas to expand into a system of known volume which was not in contact with the nitride.

Several experiments were carried out to identify the nitride. Hydrogen gas was passed over several different samples at 500–600° and the exit gases were allowed to bubble through a known volume of standard hydrochloric acid solution. A reaction was found to proceed in accordance with the equation

$$Ge_3N_2 + 3H_2 = 3Ge + 2NH_3 \qquad (3)$$

The amount of ammonia and germanium obtained in this experiment was slightly less than that calculated, due to a reaction of the nitride with moisture of the atmosphere during the preparation and weighing of the samples. Upon exposure to air the nitride liberates ammonia and is accompanied by an increase in weight, probably due to the formation of germanous hydroxide and subsequently germanic oxide. In this respect germanous nitride differs markedly from germanic nitride, the latter being highly stable even under the influence of hot, concentrated sodium hydroxide solution.

In order to obtain the nitrogen content of germanous nitride, it was allowed to hydrolyze in dilute sodium hydroxide solution and the liberated ammonia was distilled and collected in standard hydrochloric acid solution. The alkaline solution which remained was neutralized and then made 6 *N* with respect to sulfuric acid. Hydrogen sulfide gas was passed through this solution to precipitate germanic sulfide. The latter was collected on a filter, washed and then ignited and weighed as germanic oxide. (Ge_3N_2, 0.1443. Found: Ge, 0.1236; N, 0.0157; ratio Ge/N, 1.52. Calcd.: Ge, 0.1278; N, 0.1064; ratio Ge/N, 1.50.)

Further evidence for the existence of the nitride was obtained through a study of the products resulting from its decomposition at high temperatures. The nitride was shaken into a small quartz tube which was attached to the apparatus used for its preparation. When heated, a slow evolution of gas was observed at 500° whereas at 850° the rate of gas formation was fairly high. The molecular weight of the gas was determined by the vapor density method (18.75 cc. of gas weighed 0.0216 g. Mol. wt. found, 26; calcd. for N_2, 28). The volume of gas together with the weight of germanium obtained supports a reaction which may be expressed as

$$Ge_3N_2 = 3Ge + N_2 \qquad (4)$$

(Ge_3N_2, 0.3491. Found: Ge, 0.3120; N, 32.8 cc.; ratio Ge/N, 1.47. Calcd.: Ge, 0.3093; N, 31.9 cc.; ratio Ge/N, 1.50.) From these data it is evident that germanous nitride dissociates directly into its elements. In this respect it resembles germanic nitride at high temperatures. Since it was found impractical to prepare germanous nitride from germanium and nitrogen under ordinary conditions, it is to be expected that reaction (4) would be noticeably reversible only at high pressures of nitrogen.

The method used here for the preparation of germanous nitride is the same as that employed formerly by Bergstrom[7] for the preparation of stannous nitride. Like germanium, other possible methods have failed to produce stannous nitride.[8] These two nitrides represent the only combinations known of the outer fourth group elements, in the lower valence state, with nitrogen. It appears that the indirect method used above for the preparation of a nitride may lead to a more extensive chemistry of inorganic nitrogen compounds than heretofore anticipated.

Summary

Germanous nitride has been prepared by the thermal decomposition of germanous imide. Other attempts of preparation, namely, the ther-

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

(7) Bergstrom, *J. Phys. Chem.*, **32**, 433 (1928).

(8) Observations made in this Laboratory.

mal decomposition of germanic nitride and the direct combination of germanium with nitrogen, were unsuccessful.

The nitride is obtained as a finely divided, dark brown powder, which is slowly hydrolyzed by moisture, when exposed to air, and readily hydrolyzed in solutions of alkali, with the liberation of ammonia. At high temperatures it dissociates to give germanium and nitrogen.

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NOTES

Molecular Changes Accompanying the Radioactive Transformation of Radium D

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The introduction of radioactive elements into volatile organic compounds, for example, radium D tetramethyl into lead tetramethyl, affords an opportunity to investigate molecular changes accompanying radioactive transformations. The expulsion of an electron from the radioactive nucleus of such a molecule not only leaves the molecule an ion, but the resultant recoil of the nucleus as well as its change in atomic number involve relatively large energy changes and raise the question as to whether the molecule is completely decomposed or merely adjusts itself to the new valence conditions.

The transformation of radium D into radium E and then into radium F (polonium) is essentially a change of an atom of lead into bismuth and then polonium. Lead tetramethyl is well known. Bismuth trimethyl has been prepared,[1] and is fairly stable in an inert atmosphere. Diffusion experiments indicate that polonium is bivalent,[2] and as tellurium forms alkyl derivatives, it is probable that polonium could form a dimethyl compound.

In view of the fact that radium D emits only beta rays which are too feeble to produce an appreciable effect on the electroscope, while radium E and F possess strong beta and alpha activity, respectively, it should be possible by an examination of the vapor above radioactive lead tetramethyl to detect volatile compounds of radium E and F, if present. Lead tetramethyl containing a small amount of radium D tetramethyl was synthesized by means of methylmagnesium bromide from radioactive lead chloride which had been crystallized from a solution of ordinary lead chloride plus a small amount of radium D chloride. This lead tetramethyl was placed in a small flask and allowed to stand for about thirty days, during which time appreciable quantities of radium E and F were formed. At the end of this period the vapor over the lead tetramethyl was allowed to pass at 25° into a fused silica cell, and was condensed therein at −80°. Up to this point the system was sealed from the atmosphere. The silica cell was then detached from the system, and filled with octane to dissolve the contents. The solution was transferred to a porcelain dish, an excess of bromine added, and the mixture evaporated to dryness in vacuum. The residue was tested immediately, and showed strong *initial* alpha and beta ray activity, demonstrating the presence in the vapor of volatile compounds of both radium E and F.

Blank experiments indicated that no non-volatile radioactive residue was formed when radium D tetramethyl was allowed to stand for a short time. Exposure of the vapor containing radium D, E and F compounds to ultraviolet radiation (2537 Å.) resulted in the decomposition of all three, the radioactive elements going into a non-volatile residue, which was soluble in nitric acid. An exposure which was sufficient to decompose 99% of the volatile radium E compound decomposed only 22% of the radium D tetramethyl and 7% of the radium F compound.

From the above evidence we must conclude that the radioactive transformation of radium D tetramethyl proceeds entirely to the formation of volatile compounds of radium E and F, presumably radium E (bismuth) trimethyl and polonium dimethyl. This indicates that the molecule of radium D tetramethyl is not completely broken down by the radioactive transformation, but adjusts itself to the new valence conditions by the loss of a methyl group and the completion of the electron pair by the acquisition of an electron from its surroundings, *i. e.*

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[1] Schaefer and Hein, *Z. anorg. allgem. Chem.*, **100**, 297 (1917).

[2] G. v. Hevesy, *Physik. Z.*, **14**, 49 (1913).