NITROGEN COMPOUNDS OF GERMANIUM. III. GERMANOUS IMIDE

BY WARREN C. JOHNSON, GLEN H. MOREY AND ARTHUR E. KOTT

The ammonolysis of germanium tetrachloride has been studied[1,2] in liquid ammonia solution. The results clearly demonstrate germanic imide and ammonium chloride as the only two products of the reaction. A separation of these products was accomplished in ammonia through the low solubility of the imide and the relatively high solubility of the ammonium salt. However, in no instance was it found possible to obtain the imide of a purity greater than 97.2%. More recently, Karantassis and Capatos[3] passed dry ammonia gas into a solution of germanium tetraiodide in carbon tetrachloride. A white product was precipitated from the solution to which upon analysis the formula $GeI_4 \cdot 8NH_3$ is assigned. However, the analytical data given for this product are not sufficient to warrant the existence of this ammonate. Germanic iodide would not be expected to behave differently from germanic chloride in its reactions with ammonia.

According to the literature no studies have been made with solutions of germanous salts in liquid ammonia. One would predict a germanous salt to exhibit a greater stability toward ammonolysis than a germanic compound since the former is derived from a stronger base. The following report shows, however, that germanous iodide is completely ammonolyzed in liquid ammonia to germanous imide and ammonium iodide. The procedure employed in the investigation affords a convenient method for the study of this type of reaction, which necessitates the complete exclusion of air and moisture.

Experimental

The Preparation of Germanous Iodide.—Dennis and Hance[4] prepared germanous iodide by a reaction between germanium and iodine and also by the dissociation of germanium tetraiodide at temperatures above 440°. They found both of these methods impractical since small yields were obtained. Our attempts in this direction bear out their results.

Brewer and Dennis[5] found later that, when an excess of a mixture of the two hydrated oxides of germanium was allowed to react with concentrated hydriodic acid solution at low temperatures, below 40°, germanous iodide was obtained from the solution

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

[2] Thomas and Pugh, *J. Chem. Soc.*, 60 (1931).

[3] Karantassis and Capatos, *Compt. rend.*, **193**, 1187 (1931).

[4] Dennis and Hance, THIS JOURNAL, **44**, 2854 (1922).

[5] Brewer and Dennis, *J. Phys. Chem.*, **31**, 1526 (1927).

on cooling. In our preparations germanous sulfide[6] was used in place of the hydrated oxides since it was available in considerable quantities.

Crystalline germanous sulfide was pulverized and then added to concentrated hydriodic acid, sp. gr. 1.7, at room temperature. The reaction was found to proceed slowly with the evolution of hydrogen sulfide. After several hours the reaction became sluggish due to saturation of the hydrogen iodide solution with germanous iodide. The temperature of the solution was increased to 50° in order to ensure complete solution of the product, then the supernatant liquid was decanted from the unreacted germanous sulfide and finally filtered. When this solution was cooled to −80° with a solid carbon dioxide–acetone mixture, an appreciable amount of germanous iodide separated as bright yellow crystals. The yields were found to be much smaller when the cooling was carried out with a hydrochloric acid–ice mixture. The crystals of the salt were collected on a Buchner funnel in an atmosphere of nitrogen to prevent any oxidation of the germanous compound. The filtrate, which contained some germanous iodide in the hydrogen iodide solution, was returned to the germanous sulfide crystals for further reaction. This procedure was repeated several times until the greater part of the hydrogen iodide had reacted with the sulfide. The combined lots of germanous iodide crystals were then washed with benzene to remove any germanic iodide and the product was finally dried over phosphorus pentoxide with the aid of a Hy-Vac pump.

Several different preparations of the iodide were analyzed for germanium by oxidation with nitric acid to germanic oxide.

Anal. Germanium, subs., 0.4502, 0.5921, 0.3631: GeO_2, 0.1441, 0.1902, 0.1162. Calcd. for GeI_2: Ge, 22.24. Found: 22.22, 22.29, 22.21.

The Volhard method for the determination of iodine was found impractical for germanous iodide.[7] This method invariably gives high results for iodine due to reduction of silver ion to metallic silver by germanous ion. No satisfactory method was found for the preferential oxidation of germanous ion in the presence of iodide ion. The iodine content of this salt was successfully determined by a procedure to be described later in this paper.
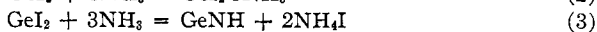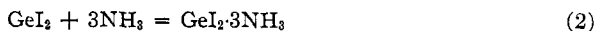
The Ammonolysis of Germanous Iodide.—Schwarz and Schenk[1]

found germanium tetrachloride to be completely ammonolyzed in liquid ammonia to germanic imide

$$GeCl_4 + 6NH_3 = Ge(NH)_2 + 4NH_4Cl \qquad (1)$$
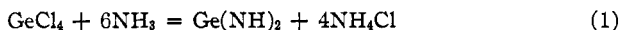
One would predict a germanous salt to possess a greater stability in ammonia than a germanic salt as regards ammonolysis. If the germanous ion is assumed to have a coördination number of four, it would be predicted that, in the formation of an ammonate, four molecules of ammonia would combine with one molecule of the germanous salt. However, experiments showed an increase in weight corresponding to only three molecules of ammonia when germanous iodide was subjected to liquid ammonia. This result allows for two possibilities, namely, the addition of three molecules of ammonia or the ammonolysis of the salt to germanous imide as expressed by the equations

[6] The germanium used in this investigation was obtained as germanous sulfide from germanite ore. For abstract of the process, see Kraus and Johnson, paper given before the Swampscott Meeting of the American Chemical Society, September, 1928.

[7] The authors are indebted to Mr. I. Aarons for the results of these studies, which were carried out in the quantitative laboratories.

$$GeI_2 + 3NH_3 = GeI_2 \cdot 3NH_3 \tag{2}$$
$$GeI_2 + 3NH_3 = GeNH + 2NH_4I \tag{3}$$

Subsequent experiments showed the reaction to proceed quantitatively according to equation (3).

The apparatus shown in Fig. 1 was used to study the ammonolysis of germanous iodide. Approximately 1 g. of the iodide was introduced into the reaction tube at E so as to assume the position indicated by H. When ammonia gas was allowed to enter at A through stopcock B to come in contact with the iodide at room temperature, reaction between the constituents took place immediately with the liberation of sufficient heat to decompose the unused germanous iodide to germanic iodide and finely divided germanium. This was quite evident according to the increase in temperature of the bulb and the appearance of the products of decomposition. Similar difficulties were experienced when liquid ammonia was allowed to come in contact with the iodide at $-33.5°$. In order to eliminate this decomposition, oxygen-free, dry nitrogen gas was first introduced into the reaction chamber at a pressure of one atmosphere and a temperature of $-33.5°$, the boiling point of liquid ammonia. Then ammonia gas was allowed to diffuse through the nitrogen at a pressure of about 85 cm. to reduce its concentration in the region of the iodide. As the reaction progressed, the concentration of the nitrogen was reduced to about one-half atmosphere; however, at no time during this procedure was any ammonia condensed upon the iodide. When the reaction was completed, as shown by the disappearance in color due to the iodide, ammonia was condensed in the reaction chamber and the contents of the tube were agitated to ensure uniformity of the products. Finally the ammonia was removed by evaporation and the entire system was thoroughly evacuated at room temperature until no change in weight could be observed. The apparatus shown in Fig. 1 was sufficiently small to weigh on an ordinary analytical balance. The following results were obtained with several different preparations.

TABLE I

THE ACTION OF AMMONIA ON GERMANOUS IODIDE

GeI_2, g.	NH_3 added, g.	Ratio moles NH_3/mole GeI_2
1.1723	0.1814	2.97
0.8178	.1276	2.99
0.8712	.1367	3.01
4.7771	.7434	2.99
1.9310	.3000	2.98
1.6961	.2643	2.99

The values given in the above table show that three gram molecules of ammonia are involved in the reaction with one gram molecule of germanous iodide. If the reaction proceeds according to equation (3), the products would consist of one gram molecule of germanous imide and two gram molecules of ammonium iodide. The presence of ammonium iodide in liquid ammonia may be readily detected by a strongly electropositive element, e. g., sodium, which reacts with the acid to liberate hydrogen gas

$$2NH_4I + 2Na = 2NaI + 2NH_3 + H_2 \tag{4}$$

Several such experiments were carried out at $-33.5°$ in which the hydrogen was collected and measured over water in an apparatus similar to that

previously described.[8,9]   The results of these experiments are given in Table II.

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TABLE II

THE ACTION OF SODIUM ON THE PRODUCTS OBTAINED FROM GERMANOUS IODIDE IN LIQUID AMMONIA

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GeI₂, g.	H₂ (found), cc.	H₂ (calcd.), cc.
1.2509	83.0	85.8
0.7560	52.5	51.9
.7777	54.3	53.4
.9855	70.1	67.6

The values given for hydrogen in column 3, Table II, are calculated on the assumption that the reaction proceeds according to equation (3) with the formation of ammonium iodide which, upon the addition of metallic sodium, follows equation (4).   No consideration is given in these calculations to the possibility of a reaction occurring between germanous imide and sodium in liquid ammonia.   However, it will be noted that the values found for hydrogen (column 2, Table II) agree well with those calculated on the above assumption.   From this standpoint it may be assumed that the imide does not react appreciably with sodium to form a sodium salt, GeNNa, with the liberation of hydrogen.   Further observations bear out this conclusion.   When sodium was added to the solution, a vigorous reaction followed until the solution became permanently blue, due to the presence of an excess of the metal.   The solution was allowed to stand for an hour or more, during which time only an inappreciable amount of hydrogen was liberated;   practically all of the hydrogen collected in a given experiment was discharged from the solution before the characteristic blue color appeared.   It is not possible to state whether the hydrogen liberated after the solution became blue was due to a reaction between the imide and sodium or to a reaction between ammonia and sodium. If the former were taking place, the rate of the reaction must be exceedingly low under the conditions of the experiment, namely, small concentration of sodium and of germanous imide and low temperature, $-33.5°$.   Ammono bases of the type corresponding to germanous imide are known to be amphoteric;   for example, stannous imide reacts with potassium amide in liquid ammonia to form potassium ammono stannite, SnNK.[10]   Germanous imide would be expected to behave similarly;   its apparent inactivity with sodium may be accounted for by its extreme insolubility.

Germanous Imide.—The experiments described above show that germanous iodide is completely ammonolyzed in liquid ammonia to germanous imide.   In order to obtain the imide in a pure condition, it is

[8] Kraus and Brown, THIS JOURNAL, **52**, 4031 (1930).

[9] Johnson and Fernelius, J. Chem. Ed., **4**, 441 (1929).

[10] Bergstrom, J. Phys. Chem., **32**, 433 (1928).

necessary to remove completely the ammonium iodide which accompanies it in solution. The apparatus shown in Fig. 1 was designed to accomplish this separation. Preliminary experiments indicated germanous imide to be practically insoluble in liquid ammonia. Ammonium iodide is known to be highly soluble in this medium.

After the germanous iodide had reacted with ammonia, in a manner previously described to prevent decomposition, additional ammonia was condensed in the bulb of the reaction chamber until the liquid assumed the position indicated by I. The imide was allowed to settle and then the solution above was siphoned through the Jena glass filter C with stopcock D open. (The Jena glass filter was attached to the Pyrex apparatus by means of an intermediate seal of G702P glass.) Ammonia was again condensed into the bulb through stopcock B, the solution was agitated through boiling with the Dewar flask removed, and finally the supernatant liquid was siphoned through D. This procedure was repeated until the discarded solution failed to give a test for the iodide ion. Finally, the ammonia remaining in the bulb was eliminated by means
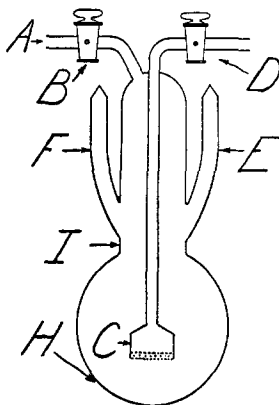

Fig. 1.

of the pumps. The imide appeared as a canary yellow powder. Samples for analysis were shaken into tubes E and F, which were then sealed from the reaction chamber.

It was found necessary to exercise considerable care in the exclusion of air and moisture from the germanous imide in the processes described above. Small amounts of water in the ammonia or the glass line are sufficient to destroy the imide as follows

$$GeNH + 2H_2O = Ge(OH)_2 + NH_3 \tag{5}$$
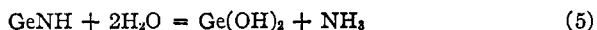
Dry oxygen reacts vigorously with the imide with the liberation of sufficient heat to cause the material to glow brightly. Germanic oxide appears to be one of the products of this reaction.

In two preparations of the imide the amount of ammonium iodide separated from the mixture was determined quantitatively. The ammonium iodide solution was allowed to evaporate and then the salt was collected and weighed in the absence of moisture after being heated to 100°. The results are given in Table III.

TABLE III

THE AMOUNT OF AMMONIUM IODIDE SEPARATED FROM GERMANOUS IMIDE

GeI_2, g.	NH_4I (found), g.	NH_4I (calcd.), g.
1.1723	1.0340	1.0400
5.7299	5.1070	5.0810

For the germanium analysis, germanous imide was oxidized to germanic oxide with nitric acid. It was found necessary to allow the imide to react first with water and then to treat the germanous hydroxide, suspended in water, with nitric acid. If the imide is exposed to air, a violent reaction takes place with oxygen with the liberation of considerable heat. Accordingly, a part of the unreacted imide is thermally decomposed to a black substance, presumably germanous nitride, which resists the action of nitric acid. Table IV records the results of the oxidation process.

TABLE IV

THE OXIDATION OF GERMANOUS IMIDE

GeNH, g.	GeO₂ (found), g.	GeO₂ (calcd.), g.
0.0836	0.0992	0.0998
.2456	.2937	.2932
.1904	.2268	.2273

The Kjeldahl method was employed to determine the nitrogen content of germanous imide. A small tube containing a sample was broken and then dropped into a flask of dilute sodium hydroxide solution. The distillate was collected in a known quantity of standard acid solution. It was found difficult to obtain consistent results in this procedure due to the inability to exclude all traces of oxygen during the transfer processes. However, these results, together with those for the germanium analyses, are sufficient to demonstrate the existence of germanous imide in a fairly high state of purity.

TABLE V

THE HYDROLYSIS OF GERMANOUS IMIDE

GeNH, g.	NH₃ (found), g.	NH₃ (calcd.), g.
0.1364	0.0279	0.0265
.1793	.0342	.0348
.1402	.0255	.0272

Properties.—Germanous imide, as prepared by the ammonolysis of germanous iodide in liquid ammonia solution, appears as a light yellow powder. It is insoluble in liquid ammonia. It reacts readily with water or dilute alkali to give germanous hydroxide and ammonia. The imide reacts violently with oxygen with the liberation of considerable quantities of heat. Germanic oxide appears as one product of this oxidation. It is readily oxidized by nitric acid.

Summary

A new method is given for the preparation of germanous iodide, which consists of a reaction between germanous sulfide and concentrated hydrogen iodide solution.

Germanous imide is prepared by the action of ammonia on germanous iodide. A convenient apparatus is described for this preparation and the

separation of ammonium iodide to obtain the imide in a fairly high state of purity.

Some of the properties of germanous imide are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATE OF THE FOURTH ORDER REACTION BETWEEN BROMIC AND HYDROBROMIC ACIDS.   THE KINETIC SALT EFFECT

BY HERBERT A. YOUNG AND WILLIAM C. BRAY

Introduction

While reactions of high order are not common, the reduction in acid solution of bromate or chlorate by a halide,[1] and that of iodate by iodide at very low concentration of iodide,[2] are of the fourth order. Their rates are represented by differential equations of the form

$$-d(XO_3^-)/dt = k(XO_3^-)(Y^-)(H^+)^2$$

According to Brönsted,[3] k should decrease rapidly with increasing ionic strength, and the function $k\gamma_n/\gamma_{HXO_3}^2\gamma_{HY}^2$ should be constant at low ionic strengths. Since γ_n, the activity coefficient of a neutral substance, differs but little from unity, the kinetic salt effect may be represented by the equation

$$k/\gamma_{HXO_3}^2\gamma_{HY}^2 = \chi \tag{1}$$

where χ is a true constant.

To study this kinetic salt effect, an investigation of the reduction of bromic acid by hydrobromic acid was undertaken. The reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \tag{2}$$
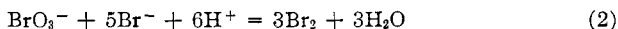
was first studied by Judson and Walker,[4] and their conclusion that its rate might be represented by an equation of the above form was later confirmed by Skrabal and Weberitsch.[5] Still later, Bray and Davis[6] investigated the autocatalytic reduction of bromate ion by hydrogen peroxide

$$BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + 3H_2O \tag{3}$$
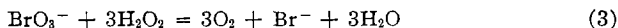
[1] Skrabal, Z. Elektrochem., 30, 123 (1924); "International Critical Tables," Vol. VII, p. 149.

[2] Abel and Hilferding, Z. physik. Chem., 136, 186 (1928).

[3] J. N. Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, 1927.

[4] Judson and Walker, J. Chem. Soc., 73, 418 (1898).

[5] Skrabal and Weberitsch, Monatsh., 36, 211 (1915).

[6] Bray and Davis, THIS JOURNAL, 52, 1427 (1930).