838. *The Chemistry of Bivalent Germanium Compounds. Part IV.* Formation of Germanous Salts by Reduction by Hypophosphorous Acid.*

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By reducing an acid solution of germanium dioxide with the minimum amount of hypophosphorous acid, a complex iodo-hypophosphite, $3Ge(H_2PO_2)_2,GeI_2$, germanous phosphite, $GeHPO_3$, and a germanous phosphate, $Ge_3(PO_4)_2,2GeHPO_4$, have been isolated. Only compounds derived from the halogen acids or oxyacids of phosphorus can be obtained by this method. In the course of this work germanic di(hydrogen phosphate) has been isolated, and evidence obtained of the existence of germanic hypophosphite. Although the Ge^{++} ion probably occurs in crystalline germanous salts, it is doubtful if this ion can occur in solution.

By reducing a solution of quadrivalent germanium in excess of halogen acid with hypophosphorous acid, germanous iodide (*Inorg. Synth.*, **3**, 63) and the complex salts $Ge(H_2PO_2)_2,GeCl_2$ and $3Ge(H_2PO_2)_2,GeBr_2$ (Part II, *J.*, 1952, 1670) have been isolated. The following work was undertaken to establish how far this procedure was applicable as a general method for the preparation of germanous salts in the presence of acids other than the halogen acids, particularly as the simple process of making these salts by dissolving hydrous germanous oxide in the required acid was not satisfactory. This was due both to the ease of oxidation of the oxide and to the low solubility of its more deeply coloured forms (Latimer and Jolly, *J. Amer. Chem. Soc.*, 1952, **74**, 5751), hydrous germanous oxide always containing a proportion of these coloured, less active, forms.

There were three main requirements for this method. First, the acid used must be resistant to reduction by hypophosphorous acid or bivalent germanium; secondly, it must be sufficiently strong to prevent hydrolysis to hydrous germanous oxide; thirdly, it must not form stable complexes with quadrivalent germanium. For example, citric, oxalic, and tartaric acids, which do form such complexes, prevent reduction of quadrivalent germanium with hypophosphorous acid unless a large excess of hydrochloric or hypophosphorous acid is present. These three conditions restricted the choice to the oxyacids of phosphorus and to the already established halogen acids.

In all the work described below an inert atmosphere was not found essential, although contact of bivalent germanium solutions with the air must be kept to a minimum.

Halogen Acids.—With hydrochloric or hydrobromic acid attempts to prepare the simple halides failed; $Ge(H_2PO_2)_2,GeCl_2$ and $3Ge(H_2PO_2)_2,GeBr_2$, the only products obtained, are apparently less soluble than the simple halides. With hydriodic acid, germanous iodide was obtained unless the amount of hydriodic acid was limited, whereupon the new complex salt $3Ge(H_2PO_2)_2,GeI_2$ (m. p. 120°) was formed. As with the bromo-compound, no 1 : 1 double salt was isolated. The conditions expected to favour its formation resulted in precipitation of germanous iodide. The properties and reactions of $3Ge(H_2PO_2)_2,GeI_2$ closely resembled those of $3Ge(H_2PO_2)_2,GeBr_2$.

Phosphorous Acid.—By reducing germanium dioxide with hypophosphorous acid in excess of phosphorous acid, germanous phosphite, $GeHPO_3$, was obtained. The compound $Ge(H_2PO_3)_2$ was not formed, even with a large excess of phosphorous acid. Germanous phosphite was also isolated on carrying out reduction in a mixture of phosphorous and 2N-halogen acids; no double salts between germanous phosphite and the germanous halides were obtained. The formation of $Ge(H_2PO_2)_2,GeCl_2$ and of $3Ge(H_2PO_2)_2,GeBr_2$ in the latter experiments was precluded by using the minimum stoicheiometric amount of hypophosphorous acid for reduction.

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* Part III, *J.*, 1953, 660.

The reduction of germanium dioxide with hypophosphorous acid can be formulated as $GeO_2 + H_3PO_2 = GeHPO_3 + H_2O$, phosphorous acid not reducing quadrivalent germanium. As this equation indicates, germanous phosphite could also be isolated from the solutions formed by heating germanium dioxide alone with hypophosphorous acid, precipitation being slow and incomplete. This reaction sometimes resulted in formation of germanous phosphite during the preparation of other germanous salts by the present method.

Germanous phosphite was soluble in warm dilute or concentrated halogen acids, hypophosphorous or phosphoric acid, but was sparingly soluble in phosphorous acid. It was insoluble in dilute sulphuric acid, glacial acetic acid, formic acid, and organic solvents. Decomposition to germanium dioxide occurred with warm concentrated sulphuric or nitric acids, and alkalies caused hydrolysis to hydrous germanous oxide. When heated in an open capillary tube it decomposed, without melting, at approximately 230°, and blackening occurred above 300°. In all these properties germanous phosphite closely resembled stannous phosphite, $SnHPO_3$; *e.g.*, stannous phosphite was insoluble in water or organic solvents, soluble in mineral acids, hydrolysed by alkali to stannous oxide, and decomposed at approximately 320—330°, leaving a black residue (Everest and Rich, unpublished work).

Phosphoric Acid.—A mixed germanous monohydrogen tertiary phosphate, $Ge_3(PO_4)_2,2GeHPO_4$, has been obtained by addition of alkali to a hot phosphoric acid solution of bivalent germanium freshly reduced with hypophosphorous acid. This was the only compound isolated even when the rate of addition of alkali, the temperature of precipitation, or the concentration of the phosphoric acid was varied. Precipitation of $Ge_3(PO_4)_2,2GeHPO_4$ was always incomplete but was favoured by high temperatures. This resembled the behaviour of the manganous monohydrogen tertiary phosphate (pentamanganous dihydrogen tetraphosphate), $Mn_3(PO_4)_2,2MnHPO_4,5H_2O$, which only crystallised from phosphoric acid at temperatures above 50° (Salmon and Terrey, *J.*, 1950, 2813). If excess of alkali was added to these incompletely precipitated germanous phosphate solutions, hydrous germanous oxide was only slowly precipitated. This was similar to the behaviour observed with solutions of the complex tartrate of bivalent germanium (Robinson, *Ann. Reports*, 1944, **41**, 112) and indicated that germanous phosphate was complex in phosphoric acid solution.

$Ge_3(PO_4)_2,2GeHPO_4$ was insoluble in, and slowly hydrolysed by, water; with alkali, rapid hydrolysis to hydrous germanous oxide occurred. It dissolved readily in halogen, hypophosphorous, and phosphoric acids. If dry, it was stable in air, one sample showing no appreciable oxidation after 72 hr. in dry air. In all these properties it resembled the stannous orthophosphates (Jablczynski and Wieckowski, *Z. anorg. Chem.*, 1926, **152**, 207). On heating, $Ge_3(PO_4)_2,2GeHPO_4$ melted at a dull red heat.

Salts of Quadrivalent Germanium.—During this work germanic di(hydrogen phosphate) was obtained as an anhydrous crystalline precipitate by dissolving activated germanium dioxide in phosphoric acid, $GeO_2 + 2H_3PO_4 \rightleftharpoons Ge(HPO_4)_2 + 2H_2O$. It was easily hydrolysed, being decomposed on washing, and it was not possible to isolate a completely pure specimen. Germanic di(hydrogen phosphate) dissolved completely in hot water, hydrolysis being complete; it was easily soluble in phosphoric acid, and in hypophosphorous acid with reduction. Germanic di(hydrogen phosphate) was usually obtained as an intermediate during the preparation of germanous phosphate.

An impure sample of germanic hypophosphite, $Ge(H_2PO_2)_4$, has been obtained by prolonged heating of germanous iodide with 90% hypophosphorous acid in good contact with the air so that oxidation could freely take place. The chief impurity appeared to be germanic phosphite resulting from the oxidation of hypophosphorous to phosphorous acid, this oxidation being catalysed by the cyclic reduction and oxidation of the germanium present. Like the phosphate, germanic hypophosphite was readily hydrolysed by water. Germanic hypophosphite decomposed at *ca.* 170—180°.

If activated germanium dioxide was dissolved in 35% phosphorous acid a heavy white precipitate quickly separated. This precipitate was not further investigated, but it indicated the probable existence of germanic phosphite.

EXPERIMENTAL

Analytical Procedures.—Total germanium. This was determined iodometrically as previously described (Part II, *loc. cit.*). For accurate results three additional precautions should be taken. First, the hydrochloric acid solution of quadrivalent germanium must not be rapidly heated initially, otherwise germanium tetrachloride may be volatilised. Secondly, the amount of hypophosphorous acid must be strictly controlled (not above 0·3—0·35N); thirdly, the solution must be under 20° when titrated, otherwise the iodine and the hypophosphorous acid interact.

Reduction equivalent and bivalent germanium. In the absence of halogens, bivalent germanium and lower oxyacids of phosphorus were determined by titration with potassium permanganate (Everest, *J.*, 1951, 2903).

Phosphorus. The sample was dissolved in sodium hydroxide–hydrogen peroxide mixture, and the resulting solution acidified with nitric acid; the phosphate was then determined gravimetrically with ammonium molybdate. Germanium did not interfere, presumably owing to the high solubility of germanomolybidic acid (Schwarz and Giese, *Ber.*, 1930, **63**, 2428). With hypophosphites, the sample was dissolved in hydrochloric acid and the hypophosphite oxidised to phosphate with bromine; hydrochloric acid was then evaporated off.

Halogen. This was determined as previously described (Part II, *loc. cit.*).

Activated Germanium Dioxide.—This was prepared by dissolving the normal oxide in 10N-sodium hydroxide, diluting ten-fold, acidifying with the same acid as used in the subsequent reaction, and finally neutralising with ammonia. The solution was left for 2—3 hr. to complete precipitation, and the activated oxide filtered off, washed with water, and air-dried.

Double Salt, $3Ge(H_2PO_2)_2,GeI_2$.—This *salt* (m. p. 120°) was prepared by heating activated germanium dioxide (0·5 g.) with 30% hypophosphorous acid (10 ml.) under reflux for 1 hr.; 57% hydriodic acid (1·5 ml.), decolorised by warm 15% hypophosphorous acid (1·5 ml.), was then added; on cooling, crystals separated. Alternatively, germanous iodide (2·0 g.) was dissolved in 30% hypophosphorous acid (9 ml.); on cooling, crystals separated. These were washed with dilute hypophosphorous acid, absolute alcohol, and ether, and dried in a vacuum at room temperature [Found: Ge (total), 31·2; I, 27·6; P, 20·5. $3Ge(H_2PO_2)_2,GeI_2$ requires Ge, 31·1; I, 27·2; P, 19·9%].

Germanous Phosphite.—Activated germanium dioxide (0·4—1·0 g.) was dissolved in a warm solution of phosphorous acid (1·5 g.), 50% hypophosphorous acid (0·5—1·5 ml., to maintain an equimolecular ratio of germanium dioxide to hypophosphorous acid), and water to a total volume of 5 ml.; these quantities gave a variable ratio of germanium to phosphorous acid. After any insoluble material had been filtered off, the solution was heated to 100° for 90 min.; a crystalline precipitate was formed together with a yellowish-green mother-liquor. With the lower germanium concentrations, precipitation occurred only on cooling. The *germanous phosphite* crystals were washed with a little water and absolute alcohol and dried in a vacuum at room temperature [Found: Ge (total), 47·6%; reduction equiv., 37·6. $GeHPO_3$ requires Ge, 47·6%; reduction equiv., 38·15]. The experiments with halogen acids were conducted similarly, with use of activated germanium dioxide (0·5 g.), 2N-hydrochloric or -hydrobromic acid (4·5 ml.), phosphorous acid (1·5 g.), and 50% hypophosphorous acid (0·6 ml.) [Found: Ge (total), 47·7%].

Germanium Dioxide–Hypophosphorous Acid Reaction.—Activated germanium dioxide (0·6 g.) was heated with 25% hypophosphorous acid (5 ml.) for 90 min., and a yellowish-green solution was formed; on cooling for 12 hr., 0·08 g. of crystals separated [Found: Ge (total), 47·5%]. This solid had the reactions and properties of germanous phosphite.

Germanous Phosphate, $Ge_3(PO_4)_2,2GeHPO_4$.—This *salt* was prepared by heating activated germanium dioxide (0·5 g.) with 4·5—7·5M-phosphoric acid (10 ml.) and 50% hypophosphorous acid (1·5—2·5 ml.) under reflux for 30 min.; 3N-sodium hydroxide (4—8 ml.) was then added, with stirring, to the hot solution (temperature varied, 50—100°), whereupon a precipitate formed. Typical results were:

H_3PO_4, M	Wash liquid	Ge(II), %	PO_4, %	Ge : PO_4
4·5	—	46·3	51·05	1 : 0·84
4·5 *	5 Ml. EtOH	48·1	52·1	1 : 0·83
7·5 *	1 Ml. H_2O, 5 ml. each EtOH and Et_2O	48·7 †	50·9	1 : 0·80

$Ge_3(PO_4)_2,2GeHPO_4$ requires Ge, 48·7; PO_4, 51·0%.

* Dried *in vacuo*. † Total germanium estimated.

Germanic Di(hydrogen Phosphate).—This *salt* was obtained by dissolving activated germanium dioxide (0·5 g.) in 4·5—5M-phosphoric acid (10 ml.) and heating under reflux for 5 min.; the crystals which separated were sucked as dry as possible, rapidly washed with alcohol and ether (5 ml. each), and dried *in vacuo*. Results were :

H_3PO_4, M	Ge, %	PO_4, %	Ge : PO_4	H_3PO_4, M	Ge, %	PO_4, %	Ge : PO_4
3	27·1	68·0	1 : 1·92	5	28·4	68·8	1 : 1·85 *
4·5	27·1	69·0	1 : 1·95	7	27·1	—	—
4·5	26·4	67·4	1 : 1·95				

$Ge(HPO_4)_2$ requires Ge, 27·4; PO_4, 71·8%.

* Washed with 2 ml. of water in addition to alcohol and ether. These results illustrate the ease of hydrolysis of this phosphate.

Germanic Hypophosphite.—Germanous iodide (1·0 g.) was heated for 2 hr. at 100° with 90% hypophosphorous acid (10 ml.) in a shallow basin with stirring; this ensured good contact with the air. After cooling, *germanic hypophosphite* was precipitated with alcohol [Found : Ge, 21·0%; reduction equiv., 22·9. $Ge(H_2PO_2)_4$ requires Ge, 21·8%; reduction equiv., 20·8].

DISCUSSION

Bivalent Germanium.—Evidence that the Ge^{++} ion can occur in the solid state has been adduced by Powell and Brewer (*J.*, 1938, 197), who observed that germanous iodide had the cadmium iodide crystal structure. It seems probable that the Ge^{++} ion can also occur in other crystalline germanous salts such as the phosphite, which is similar to the salt-like stannous phosphite, and germanous phosphate, which resembles not only the stannous phosphates, but the manganous phosphates also. However, as observed in Part II (*loc. cit.*), there is no evidence for the existence of the uncomplexed Ge^{++} ion in solution. The only aqueous solvents known for bivalent germanium compounds are the halogen acids, hypophosphorous and phosphoric acids; in all these solvent bivalent germanium complexes are known to be present (Parts II and III, *locc. cit.*; present paper, p. 4118). The Ge^{++} ion does, however, appear as an intermediate in the oxidation or reduction of bivalent germanium at the dropping mercury electrode in hydrochloric or hypophosphorous acids (Part III). Latimer (" Oxidation Potentials," 2nd. edn., p. 147) has suggested that the uncomplexed Ge^{++} ion would spontaneously disproportionate in aqueous solution. The existence of bivalent germanium in solution probably depends, therefore, upon the germanium's being in complex form.

Quadrivalent Germanium.—The only oxy-salts of quadrivalent germanium known hitherto were the sulphate (Schwarz, Schenk, and Giess, *Ber.*, 1931, **64**, 362) and the acetate (Schmidt, Blohm, and Jander, *Angew. Chem.*, 1947, **59**, 233); they could be made only under anhydrous conditions and were completely hydrolysed by water. It appears that germanium dioxide is too weak a base for its salts to exist in aqueous solution. This is illustrated by Pugh's solubility measurements (*J.*, 1929, 1537) which showed no combination between germanium dioxide and sulphuric acid up to 16N. That germanic monohydrogen phosphate and hypophosphite can be prepared from aqueous solution is due to their insolubility and/or the probable complex nature of their solutions in excess phosphoric or hypophosphorous acids. The solubility of germanium dioxide in halogen acids is due to formation of complex anions $GeHal_5^-$ and $GeHal_6^{--}$, simple halides only resulting on breaking down these complexes by volatilisation or crystallisation.

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