GERMANIUM. XXXV. GERMANIUM MONOXIDE. GERMANIUM MONOSULFIDE[1]

BY L. M. DENNIS AND R. E. HULSE

Germanium Monoxide

Indications of the existence of this compound were observed by Winkler[2] but he was unable to purify the product for analysis. Consequently his statement that it is germanous oxide lacked experimental confirmation. Isolated details have since then appeared in the literature,[3] but none of the investigators made a systematic study of the compound. To extend our knowledge of this substance and possibly to open the way to the general study of the compounds of divalent germanium, about which comparatively little is known at present, this investigation was taken up.

Experimental

Preparation of Hydrous[4] Germanium Monoxide.—Germanium dioxide was dissolved in a slight excess of a 5 N solution of potassium hydroxide, hydrochloric acid was added in amount necessary to make the solution about 5 N in respect to HCl,[5] an excess of a 30% solution of hypophosphorous acid was then added, and the solution was held at 95° for two hours.

Since the hydrous germanium monoxide is quickly oxidized by air, it was necessary to precipitate and wash the compound in an inert atmosphere. This was accomplished with the apparatus shown in Fig. 1.

The reduced solution was placed in the cylinder A which was surrounded by a jacket through which hot water was kept circulating. Through the rubber stopper in the top of A were inserted a tube carrying a small separatory funnel and a branch M, a glass hand-stirrer B which passed loosely through a short piece of glass tubing, and a siphon tube D.

The air above the solution in A was displaced by hydrogen which entered through M and escaped around the glass rod B. This passage of hydrogen was continued throughout the operation.

Germanous hydroxide was now precipitated by adding dilute ammonium hydroxide through C. The contents of A was then held at about 90.° for one hour by the hot water rising from the flask and filling the jacket around A. The precipitate was then allowed

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by R. E. Hulse in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Winkler, *J. prakt. Chem.*, **142**, 177 (1886).

[3] Biltz, *Z. anorg. Chem.*, **72**, 313 (1911); Dennis, *ibid.*, **174**, 107 (1928); Hantzsch, *ibid.*, **30**, 289 (1902); Bardet and Tchakirian, *Compt. rend.*, **186**, 637 (1928).

[4] This term was introduced by Weiser to distinguish precipitated oxides that contain varying amounts of water, from hydrates in which water is chemically combined in definite stoichiometric proportions. See Weiser, "The Hydrous Oxides," **1926**.

[5] When the solution is acidified, some germanium dioxide is precipitated, but this dissolves during the reduction.

to settle, the supernatant liquid was drawn off through D, hot water that had been boiled to free it from air was run in through C, and the mixture was stirred by moving B up and down and turning it. The precipitate was again allowed to settle, the supernatant liquid was drawn off, and the operations of washing were repeated until most of the soluble salts had been removed, which was shown by the tendency of the precipitate to become co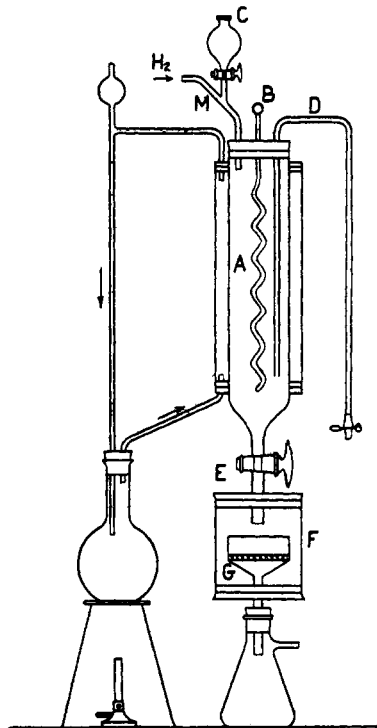lloidal. Precipitate and liquid were then run into F by opening E and the precipitate was collected on a filter paper in the Büchner funnel G. Contact with the air was here avoided by surrounding G with the glass cylinder F which was closed at top and bottom with large rubber stoppers. The precipitate was washed until free from chloride, and was then quickly transferred to a boat of porcelain or alundum. This was inserted into a combustion tube and the precipitate was dried by heating it in a current of pure nitrogen to the desired temperature.

Freshly precipitated hydrous germanium monoxide varies in color from yellow to red, depending upon the conditions of precipitation. It is readily soluble in the halogen acids. Sulfuric acid, 6 N, changes its color to dark brown (partial dehydration) and slowly dissolves it. It is only slightly soluble in fixed alkalies, but forms red colloidal solutions.

When dried by heating *in vacuo*, water was steadily removed, and no evidence of the formation of definite hydrates was obtained. As the temperature of drying is raised, the oxide changes in color from red to brown to black, with decrease in solubility. Examination under the microscope showed that the particle size increases as the color becomes darker, which indicates that the color change is not due to tautomerism as Hantzsch supposed, but is dependent upon the size of the particles and the amount of water associated with the oxide.

Fig. 1.

Anhydrous Germanium Monoxide.—Hydrous germanium monoxide is completely dehydrated when heated in nitrogen to 650°, and jet-black crystalline germanium monoxide, GeO, results. It was analyzed by oxidizing it with pure hydrogen peroxide, evaporating the solution to dryness, heating the residue to 800° and weighing the resulting GeO₂.

   Anal. Subs., 0.1401, 0.1515. Calcd. for GeO: Ge, 0.1143, 0.1248 = 81.94%. Found: Ge, 0.1147 = 81.87%, 0.1240 = 81.81%.

Properties.—Anhydrous germanium monoxide is not acted upon by moisture or atmospheric oxygen at room temperature, is attacked very slightly, if at all, by hydrochloric or sulfuric acid or solutions of fixed alkali hydroxides, but is slowly oxidized by fuming nitric acid, potassium permanganate or chlorine water. It is rather readily oxidized by hydrogen

peroxide in the presence of ammonium hydroxide. Oxidation in dry air begins at 550°. When heated in a closed apparatus in pure nitrogen, the oxide sublimes at 710°.

When heated in nitrogen in a boat of platinum or nickel to a temperature above 500°, germanium monoxide yields germanium dioxide and metallic germanium, the latter forming an alloy with the metal of the boat. When heated in boats of siliceous material the monoxide reacts above 800° to form yellow glazes.

Germanium monoxide is rapidly attacked by hydrogen chloride at about 175° with the formation of germanium chloroform and water. Chlorine attacks the oxide at 250°, forming $GeCl_4$ and GeO_2. No evidence of the formation of the oxychloride $GeOCl_2$, was obtained. The action of bromine is similar to that of chlorine.

Germanium Monosulfide

Germanium monosulfide was first described by Winkler,[2] and a study of its preparation by reduction of GeS_2 in hydrogen was made by Dennis and Joseph.[6] To obtain further information concerning the formation of GeS by precipitation of a solution of a germanous compound, and the properties of the resulting product, the present investigation was undertaken.

Experimental

Preparation of Germanium Monosulfide.—A solution of germanous chloride was prepared in the manner described under Germanium Monoxide. Hydrogen sulfide was passed into the hot solution and continued until the solution had cooled to room temperature. The precipitate under these conditions is dark red in color and granular. Precipitated from cold solution, the sulfide is light yellow and gelatinous. The red precipitate can readily be filtered and washed, and is quite stable toward oxygen at room temperature. Upon heating it to about 300° in pure nitrogen, all water was removed.

Analysis.—Germanium was determined by dissolving a sample in dilute ammonium hydroxide and 3% hydrogen peroxide that had been redistilled to free it from residue, evaporating the solution to dryness and carefully igniting the resultant GeO_2.

Sulfur was determined by the method of Popoff and Newman.[7]

Anal. Subs., 0.0970, 0.1340. Calcd. for GeS: Ge, 0.0673, 0.0930 = 69.37%. Found: Ge, 0.0671 = 69.22%; 0.0929 = 69.30%. Subs., 0.2236, 0.2571. Calcd. for GeS: S, 0.0685, 0.0788 = 30.63%. Found: S, 0.0684 = 30.59%; 0.0786 = 30.56%.

Properties.—Germanium monosulfide, thus prepared, is a dark red, amorphous substance; specific gravity, d_4^{20} 3.31. It is readily soluble in dilute hydrochloric acid, but is only slowly attacked by sulfuric, phosphoric or organic acids. It is rapidly oxidized by hot dilute nitric acid, and by aqueous solutions of hydrogen peroxide, potassium permanganate, chlorine or bromine.

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[6] Dennis and Joseph, *J. Phys. Chem.*, **31**, 1716 (1927).

[7] Popoff and Newman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 45 (1930).

The red sulfide is readily soluble in solutions of alkali hydroxides or sulfides, forming deep red solutions, from which the addition of alcohol causes the separation of red, viscous liquids. The sulfide is slowly oxidized in air at 350°, and rapidly at higher temperatures, forming GeO_2 and SO_2. When heated to about 150° in hydrogen chloride, germanium chloroform and hydrogen sulfide are formed. Chlorine attacks the sulfide at room temperature forming $GeCl_4$ and chlorides of sulfur.

Crystalline Germanium Monosulfide.—When red, amorphous germanium monosulfide is held at 450° in an atmosphere of nitrogen, it changes in a few hours to the black crystalline form described by Dennis and Joseph.[6] The substance is slowly oxidized by an ammoniacal solution of hydrogen peroxide and also by chlorine water or potassium permanganate. It begins to sublime in nitrogen at 430°, and melts at 625°. Its specific gravity is d_4^{20} 3.78.

Summary

This article describes the preparation and properties of hydrous and anhydrous germanium monoxide, and of amorphous and crystalline germanium monosulfide.

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THE EFFECTS OF SUBSTITUENTS ON QUANTUM EFFICIENCY IN THE QUINONE–ALCOHOL REACTION

BY PHILIP A. LEIGHTON AND WILLIAM F. DRESIA

The average of over twenty determinations[1] of quantum efficiency for the photochemical reaction between benzoquinone and ethyl alcohol in the wave length region λ4350–2537 Å. yields the figure 0.502. In other words, for every quinone molecule decomposed, two quanta are absorbed. The nearness of this ratio to one-half immediately raises interest as to its source.

Weigert and Brodmann[2] explained a quantum efficiency of one-half in the nitrobenzaldehyde photolysis as due to the different possible orientations of the absorbing molecules with respect to the electric vector of the incident light, by which statistically only one-half of the absorbed light could be effective in producing activation and subsequent chemical change.

By assuming a superoxide structure for quinone, the same explanation can be applied to the observed quantum efficiency in the quinone reaction. However, as was pointed out, the results can also be explained by assuming that every absorbed quantum is effective in producing activation, and that a 50% efficient secondary reaction is responsible for the observed yields.

[1] Leighton and Forbes, THIS JOURNAL, **51**, 3549 (1929).

[2] Weigert and Brodmann, *Trans. Faraday Soc.*, **21**, 453 (1925).