[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Dimethylgermanium Sulfide and Dimethylgermanium Oxide

BY EUGENE G. ROCHOW*

Organogermanium oxides of varying degree of complexity have been prepared,[1,2,3] some of them closely analogous to the organosilicon condensation products prepared by Kipping.[4] The ready availability of dimethylgermanium dichloride[5] suggests the preparation of dimethylgermanium oxide to determine whether it has polymeric forms and whether such forms resemble the corresponding methylpolysiloxanes or silicones.

It also is of interest to note that aqueous solutions of germanium dioxide and related inorganic compounds of germanium have been shown to stimulate the production of red blood cells in mammals.[6] New organogermanium oxides or related compounds may provide more suitable reagents for such studies.

Experimental

Preliminary.—Methyl silicones may be prepared by hydrolyzing the corresponding chlorosilanes, separating the water-insoluble methyl siloxane, and processing it to produce the desired polymer. It soon was found that the behavior of the germanium analogs was entirely different. Dimethylgermanium dichloride did not produce a water-repellent film on solids as does dimethyldichlorosilane[7]; instead it dissolved completely in 100 volumes of water. When this solution was evaporated to dryness, no residue was left. When the dimethylgermanium dichloride was hydrolyzed in dilute ammonium hydroxide and the resulting clear solution was evaporated, only ammonium chloride remained. This behavior suggests either volatile hydrolysis products or a readily reversible reaction

$$(CH_3)_2GeCl_2 + 2H_2O \rightleftarrows (CH_3)_2Ge(OH)_2 + 2HCl$$

4.44 g. of dimethylgermanium dichloride was refluxed with two equivalents (0.92 g.) of water for fifteen minutes and allowed to stand overnight. Samples of the aqueous layer then were withdrawn and titrated, and were found to be 3.19 N to hydrochloric acid, showing that the reaction equilibrium was far to the left.

Other techniques of direct hydrolysis, including repeated extraction of the dichloride with small portions of cold water, produced some resinous products in poor yield but were ineffective in producing a pure dimethylgermanium oxide. A pure preparation was achieved only by conversion of the sulfide.

Dimethylgermanium Sulfide.—When dimethylgermanium dichloride was dissolved in 6 N sulfuric acid and treated with hydrogen sulfide as in the determination of germanium,[8] there was precipitated a waxy white solid which was soluble in acetone (which GeS_2 is not) and insoluble in dilute ammonium hydroxide (which dissolves GeS_2). This precipitate was found to be dimethylgermanium sulfide, $(CH_3)_2GeS$.

100 g. of dimethylgermanium dichloride was stirred with 1000 g. of water[9] and treated with hydrogen sulfide over a period of several days. The precipitate was washed, dissolved in 100 ml. of warm alcohol, and reprecipitated by the addition of four volumes of cold water.[10] The mixture was chilled and saturated with hydrogen sulfide to prevent hydrolysis, and then filtered with suction. The crystals were washed on the filter with water containing hydrogen sulfide, and dried in a desiccator; yield, 73.4 g., or 94.5% of theoretical.

Anal. Calcd.: C, 17.83; H, 4.49; Ge, 53.9; S, 23.80. Found: C, 17.92, 17.77; H, 4.52, 4.46; Ge, 51.6, 52.0[11]; S, 23.42, 24.07, 23.80.[12]

The dimethylgermanium sulfide so prepared crystallizes in flat plates which melt at 55.5° and boil at 302°. These have a peculiar pepper-and-onions odor, and hydrolyze very slowly in moist air to liberate hydrogen sulfide. Hydrolysis also is slow in boiling water, but more rapid in dilute acids or dilute solutions of hydrogen peroxide.

Dimethylgermanium Oxide.—The hydrolysis of dimethylgermanium sulfide in a 10% aqueous solution of hydrogen peroxide yields a clear water solution of methylgermanium oxides or hydroxides, from which resinous and crystalline substances may be obtained upon evaporation. If the original dimethylgermanium dichloride contained some methylgermanium trichloride, or if the treatment with hydrogen peroxide is sufficiently vigorous to oxidize a minor fraction of the methyl groups, there is obtained a sirupy mass which becomes resinous when chilled. The resin is soluble in hot water, in benzene, and in alcohol. Upon long standing, white crystals (presumably of hydroxide) slowly grow in the mass but dissolve upon reheating. A resinous sample which had an average of but 1.2 methyl groups per germanium atom by analysis did not crystallize on standing and was found to be infusible though slightly soluble in water.

The effect of hydrogen peroxide in accelerating the hydrolysis of dimethylgermanium sulfide might be interpreted as the oxidation of a small amount of sulfide ion to sulfate, following by acid hydrolysis of the remainder of the organogermanium sulfide. If so, dilute sulfuric acid would be preferable to hydrogen peroxide as a hydrolytic

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(1) Orndorff, Tabern and Dennis, THIS JOURNAL, **49**, 2512 (1927).

(2) Kraus and Brown, *ibid.*, **52**, 3690 (1930).

(3) Burschkies, *Ber.*, **65**, 956 (1932).

(4) See Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

(5) Rochow, THIS JOURNAL, **69**, 1729 (1947).

(6) Beard, Myers, Baker and Rafferty, *J. Biol. Chem.*, **94**, 71 (1931), and *J. Am. Med. Assn.*, **93**, 1210 (1929); Hueper, *Am. J. Med. Sci.*, **181**, 820 (1931); Parr, *Trans. Ill. Acad. Sci.*, **21**, 194 (1928) and U. S. Patent 1,909,070; Lenker, *Penn. Med. J.*, **26**, 86 (1922); Kast, Croll and Schmitz, *J. Lab. Clin. Med.*, **7**, 643 (1922); Harrold, Meek and McCord, *Ind. Med.*, **23**, 236 (1944).

(7) Patnode, U. S. Patent 2,306,222; Norton, *Gen. Elec. Rev.*, **47**, No. 8, p. 6 (1944).

(8) Johnson and Dennis, THIS JOURNAL, **47**, 790 (1925).

(9) Six normal sulfuric acid was used in the preliminary experiments because the initial observation came out of attempts to analyze dimethylgermanium dichloride. Later experiments showed that the same crystalline sulfide is precipitated from a water solution or suspension of the dichloride. The products from water and 6 N H_2SO_4 had the same melting point and the same mixed melting point. Lacking an investigation of the crystal structure, it is not known whether the structural units are monomeric $(CH_3)_2GeS$ or some association of several monomeric units.

(10) Well-formed crystals may be obtained merely by cooling the alcohol, but better separation from residual chlorine is obtained by precipitating tiny crystals by the water dilution method.

(11) Germanium was determined by wet oxidation with fuming nitric acid and ammonium persulfate (THIS JOURNAL, **69**, 1730, (1947)), but volatilization of GeO was encountered repeatedly at the beginning of ignition of the residues. Oxidation in a Parr bomb followed by precipitation of the germanium as GeS_2 is being studied.

(12) Sulfur was determined by Dr. L. P. Pepkowitz, using a new method which he has developed for the analysis of microgram samples.

medium for making a pure dimethylgermanium oxide because it has been shown that it does not affect the methyl groups. Accordingly, 7.63 g. of pure distilled $(CH_3)_2GeS$ was refluxed with 20 ml. of water and 0.5 ml. of concentrated sulfuric acid for seven hours, or until there no longer was a rapid evolution of hydrogen sulfide. A solution of barium hydroxide then was added dropwise until the solution was just alkaline to phenolphthalein, and the barium sulfate was filtered off.[13] The clear filtrated was evaporated under reduced pressure to a sirup. The remaining water was distilled off, along with some volatile dimethylgermanium oxide or hydroxide, in the range 100 to 105°, and then the boiling point rose rapidly to over 200° and a polymer of dimethylgermanium oxide distilled. The empirical composition was shown to correspond to $(CH_3)_2GeO$.

Anal. Calcd.: C, 20.24; H, 5.10; Ge, 61.2. Found: C, 20.34, 20.52; H, 5.25, 5.16; Ge, 60.96, 60.28.

The dimethylgermanium oxide so prepared melts at 133.4°[14] and boils at 211°. It does not dissolve readily in water, benzene or cyclohexane. It dissolves in alcohol, and upon addition of water is not precipitated but reverts to the water-soluble form encountered during the preparation. Cryoscopic determinations of the molecular weight of the solid in cyclohexane were inconclusive, probably because of the very limited solubility of the substance. Camphor was found to be a good solvent, however, and determinations of molecular weight (found, 491; calcd. for $(CH_3)_2GeO$, 118.7) indicate that the substance is a tetramer.[15] However, upon repeated melting of the camphor solutions in sealed tubes the depression of the freezing point was found to increase in a way that suggests an (as yet unknown) alteration of the polymeric state of the oxide.

Summary

1. The hydrolysis of dimethylgermanium dichloride is shown to be reversible to an extent which makes impractical the preparation of dimethylgermanium oxide by the techniques used for preparing silicones.

2. Dimethylgermanium sulfide (m. p. 55.5°, b. p. 302°) has been prepared.

3. Dimethylgermanium oxide has been obtained in a crystalline polymeric form (m. p. 133.4°, b. p. 211°) by hydrolysis of the sulfide.

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(13) The weight of dried barium sulfate was slightly under the weight expected from the amount of sulfuric acid originally used, showing that there was no oxidation of sulfide to sulfate during the hydrolysis.

(14) Melted samples solidify to a glassy phase which then melts at about 125°.

(15) Probably cyclic, see related tetramer of $(C_6H_5)_2GeO$ in Morgan and Drew, ref. 4.

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Alcoholysis of Ethyl Phosphate. The Preparation of Mixed Ethyl Butyl Phosphates

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Examples of the alcoholysis of esters derived from inorganic acids are not nearly so plentiful in the chemical literature as are those of the organic acid esters. Recently, the alcoholysis of alkyl silicates was studied by Peppard, Brown and Johnson,[1] who found that in some cases the alcoholysis of silicates proceeded without the addition of catalysts to yield mixed silicic acid esters, while, in other instances, hydrogen chloride or silicon tetrachloride was needed to catalyze the reaction. A similar transalkylation reaction between butyl silicate and ethyl silicate under the catalytic influence of aluminum chloride or the alkoxides of aluminum, antimony or magnesium was also found by these same authors[2] to produce mixed alkyl silicates.

Morel and Friedel[3] have shown that under the influence of sodium ethylate, a mixture of ethanol and phenyl phosphate will yield mixed ethyl phenyl phosphates as well as phenetole. The latter property of alkylation is an interesting feature in this reaction and has been extended by Noller and Dutton.[4] Toy[5] has found that methyl alkyl ethers can be prepared by refluxing a mixture of trimethyl phosphate and alcohols whose boiling points are greater than 160°. The residue products in this reaction are described by Toy to be alkali soluble mixtures of alkyl acid phosphates.

The reaction between *n*-butanol and ethyl phosphate was studied in this Laboratory with the view of obtaining diethyl *n*-butyl and ethyl di-*n*-butyl phosphates. It was observed that an equimolar mixture of ethyl phosphate and *n*-butanol would not undergo appreciable reaction even at temperatures of about 160°. In the presence of small amounts of sodium butylate, however, alcoholysis proceeded rapidly at temperatures between 90 and 120°. In Table I, it can be seen that the relative amounts of diethyl *n*-butyl phosphate and ethyl di-*n*-butyl phosphate depend upon the relative amounts of sodium butylate present in the reaction mixture and also upon the mole ratio of ethyl phosphate to *n*-butanol. Some physical properties of the mixed esters are presented in Table II.

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(1) Peppard, Brown and Johnson, This Journal, **68**, 73 (1946).

(2) Peppard, Brown and Johnson, *ibid.*, **68**, 77 (1946).

(3) Morel and Friedel, *Compt. rend.*, **128**, 507 (1899).

(4) Noller and Dutton, This Journal, **55**, 424 (1933).

(5) Toy, *ibid.*, **66**, 409 (1944).