

was thus obtained in the cold trap 60.2 g. of low boiling material which by mass spectrometer analysis was shown to contain mostly methyl iodide and small amounts of trimethylborane plus a trace of trimethyl borate. Upon precision distillation of the liquid product, there was obtained 16 g. (97% yield and conversion) of trimethylborane boiling at  $-20^{\circ}$  at atmospheric pressure.<sup>14</sup>

In the same manner as above, except that the  $-78^{\circ}$  cold trap was omitted, 120 g. of ethyl iodide was added dropwise over a period of 1.5 hours to 36 g. of trimethyl borate and 30 g. of 8- to 20-mesh aluminum. At the end of the addition, the reaction mixture was heated at reflux for 1.5 hours. The reactor then was cooled to about  $-70^{\circ}$  and the system evacuated. An evacuated stainless steel cylinder then was connected to the system and the reactor warmed slowly to about  $50^{\circ}$ . The volatile reaction products distilled over into the cylinder. There was thus obtained 24 g. of volatile reaction products which by mass spectrometer analysis were shown to contain mainly triethylborane and ethyl iodide.

A stainless steel-lined pressure vessel was charged with 21

(14) E. L. Muetterties, U. S. Patent 2,840,590 (1958).

g. of trimethyl borate, 40 g. of 8- to 20-mesh aluminum, 5 g. of aluminum powder and 0.5 g. of iodine. The reactor was closed, evacuated, charged with 41 g. of methyl chloride and then heated under autogenous pressure for 3 hours at  $130^{\circ}$ . After cooling to room temperature, there was obtained by distillation into a stainless steel cylinder, cooled in a liquid nitrogen bath, 35 g. of volatile products which by mass spectrometry were shown to contain 85–88% of methyl chloride, 10–11% of trimethylborane and 1.8–2.0% of trimethyl borate. The amount of trimethylborane obtained corresponds to a 30% conversion based on the ester.

**Hydrogenation of Alkylboranes.**—A stainless steel-lined pressure vessel was charged with 20 g. of Al powder, 30 g. of  $\text{BCl}_3$ , 50 g. of  $\text{CH}_3\text{I}$  and 1 g. of  $\text{AlCl}_3$ , heated to  $80^{\circ}$  and then pressured with hydrogen to about 800 atm. After 2 hours at  $80^{\circ}$  and 3 hours at  $160^{\circ}$ , the vessel was cooled and bled through a trap cooled to collect condensables. The condensables were methane and methylated diboranes. This mixture was distilled. Two high boiling fractions,  $-1$  to  $1^{\circ}$  ( $\sim 70\%$ ) and  $58$ – $64^{\circ}$  ( $\sim 30\%$ ) were obtained and mass spectrographic analysis indicated they were  $\text{B}_2\text{H}_2(\text{CH}_3)_4$  (reported b.p.,  $-2.6^{\circ}$ ) and unsymmetrical  $\text{B}_2\text{H}_4(\text{CH}_3)_2$  (reported b.p.,  $68.6^{\circ}$ ), respectively.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

## Dimethylgermanium Oxide and Dimethylgermanium Sulfide

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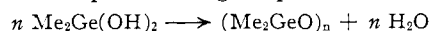
Trimeric, tetrameric and high-polymeric forms of dimethylgermanium oxide have been prepared and characterized. At room temperature the high-polymeric form is the most stable and the trimeric form the least stable. At elevated temperatures the vapors of dimethylgermanium oxide and dimethylgermanium sulfide are trimeric.

Although the polysiloxanes  $(\text{Me}_2\text{SiO})_n$  (where  $n$  is three or more<sup>2</sup>) have been well characterized and studied, the corresponding dialkylgermanium oxides  $\text{R}_2\text{GeO}$  (where R is methyl,<sup>3</sup> ethyl,<sup>4,5</sup>  $n$ -propyl,<sup>6</sup> isopropyl<sup>7</sup> or phenyl<sup>8</sup>) have not received as much attention. The present paper examines more closely dimethylgermanium oxide and dimethylgermanium sulfide.<sup>3</sup>

We find that dimethylgermanium oxide is most conveniently prepared and purified as the tetramer, which is easily obtained in 67% yield by hydrolysis of dimethyldichlorogermane with aqueous sodium hydroxide, followed by extraction with petroleum ether and subsequent crystallization. The well-defined colorless crystals (m.p.  $92^{\circ}$ ) were identified as tetrameric  $(\text{Me}_2\text{GeO})_4$  by cryoscopic measurements in benzene, in which they are readily soluble. By analogy with octamethylcyclotetrasiloxane, an eight-membered ring structure is assumed for this tetramer.

Unlike its silicon analog, the tetramer is very soluble in water, although the rate of solution is somewhat slow. Cryoscopic measurements on a dilute aqueous solution give a molecular weight corresponding to one  $\text{Me}_2\text{GeO}$  unit. We assume

hydration to form the diol  $\text{Me}_2\text{Ge}(\text{OH})_2$ , already postulated as a hydrolysis product of dimethyldichlorogermane.<sup>9</sup> On allowing an aqueous solution of dimethylgermanium oxide to evaporate, a white fibrous material,  $(\text{Me}_2\text{GeO})_n$ , is obtained, with the same melting point ( $132$ – $133^{\circ}$ ) as the material previously obtained by distillation.<sup>3</sup> This material does not sublime in a high vacuum until its melting point is reached and then gives a sublimate which melts over a large range; the tetramer readily sublimates unchanged at about  $45^{\circ}$ . This behavior suggests a high-polymeric structure which breaks down on melting. The insolubility in organic solvents such as cyclohexane, benzene and carbon tetrachloride and the fibrous nature of the material are also in accordance with a high-polymeric structure. It may be assumed that a condensation reaction takes place during evaporation of the water



The reaction is reversible, since the polymer can be dissolved in water (although the rate of solubility is very slow). A dilute solution again contains only monomeric units. Only a trace of water is necessary to catalyze this over-all change of tetramer to high-polymer, but in the absence of moisture the tetramer is stable for months at room temperature.

Tensimetric experiments (described below) show that, at temperatures of about  $160$  to  $250^{\circ}$  and in the vapor phase at pressures of about 100 mm., dimethylgermanium oxide exists as the trimer  $(\text{Me}_2\text{GeO})_3$ . However, as the tensimeter cools to room temperature a heterogeneous solid with a large melting range is obtained, probably a mixture of

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(2) M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *THIS JOURNAL*, **68**, 667 (1946).

(3) E. G. Rochow, *ibid.*, **70**, 1801 (1948).

(4) E. A. Flood, *ibid.*, **64**, 1663 (1932).

(5) H. H. Anderson, *ibid.*, **72**, 194 (1950).

(6) H. H. Anderson, *ibid.*, **74**, 2370 (1952).

(7) H. H. Anderson, *ibid.*, **75**, 814 (1953).

(8) (a) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925); (b) C. A. Kraus and C. L. Brown, *THIS JOURNAL*, **52**, 3690 (1930).

(9) E. G. Rochow and A. L. Allred, *ibid.*, **77**, 4489 (1955).

polymers formed by decomposition of the trimer at intermediate temperatures. Rapid cooling of a silica tube containing dimethylgermanium oxide vapor at  $210^\circ$  gives unstable, fern-like crystals which have a molecular weight corresponding to that of the trimer, according to cryoscopic measurements in benzene. The crystals are soluble in organic solvents and soon undergo transformation to the high-polymer; indeed, samples cannot be kept in air for more than thirty minutes or so without transformation. Before melting, the substance changes phase over a wide range and only the infrared spectrum proves that it is a definite compound and not a mixture (for example, one containing the tetramer) which might also have the same properties.

The spectrum repeatedly obtained from samples of trimer pressed into discs with KBr appears to be that of a mixture of tetramer and high-polymer, probably formed by catalytic decomposition of the trimer by water unavoidably present in the KBr. However, after several attempts a stable solution of the trimer in freshly dried and distilled carbon disulfide was obtained, and a good spectrum was obtained in the  $700$  to  $950\text{ cm.}^{-1}$  region, which is the region of most characteristic absorptions of the individual dimethylgermanium oxides. Figure 1 shows that the spectrum of the trimer is sufficiently different to distinguish it from that of the tetramer (also in carbon disulfide) and the high-polymer (in a pressed KBr disc, since it is insoluble in carbon disulfide). These absorptions are assigned to the methyl-rocking and the germanium-oxygen vibrations.<sup>10</sup>

**Tensimetric Measurements.**—The results for dimethylgermanium oxide shown in Table I, obtained from Runs 1 and 2 for which a mercury tensimeter was used, show that the apparent degree of polymerization  $n$  at pressures of about 100 mm. is close to three and that there is a slight, but nevertheless real, decrease from 3.16 at  $165^\circ$  ( $20^\circ$  above saturation point) to an average value of 2.98 at  $200^\circ$ . The latter temperature of  $200^\circ$  is about the upper limit for a mercury tensimeter, and to determine  $n$  at higher temperatures (where, if the steady decrease continued, values smaller than 3 would be encountered, indicating the existence of a dimer) a tensimeter fitted with a quartz spiral gauge was used. However, Table I shows that between  $200$  and  $250^\circ$   $n$  remains 3, with an estimated experimental error of within 1.5%. The tensimetric measurements were all made at pressures of the order of 100 mm., but that dimethylgermanium oxide is trimeric even at a pressure of about one atmosphere is shown by the sealed-tube experiments where from the weight of the sample and volume of the tube the pressure is calculated to be 500 to 1,000 mm. of mercury.

The results of a run carried out on dimethylgermanium sulfide are shown in Table II. The quartz spiral tensimeter was used for this experiment. It is concluded from these results that this compound, like dimethylgermanium oxide, is trimeric in the vapor phase. The sulfide is also trimeric in benzene solution according to cryoscopic measurements.

(10) More details of the infrared spectra of these and related compounds will be published shortly.

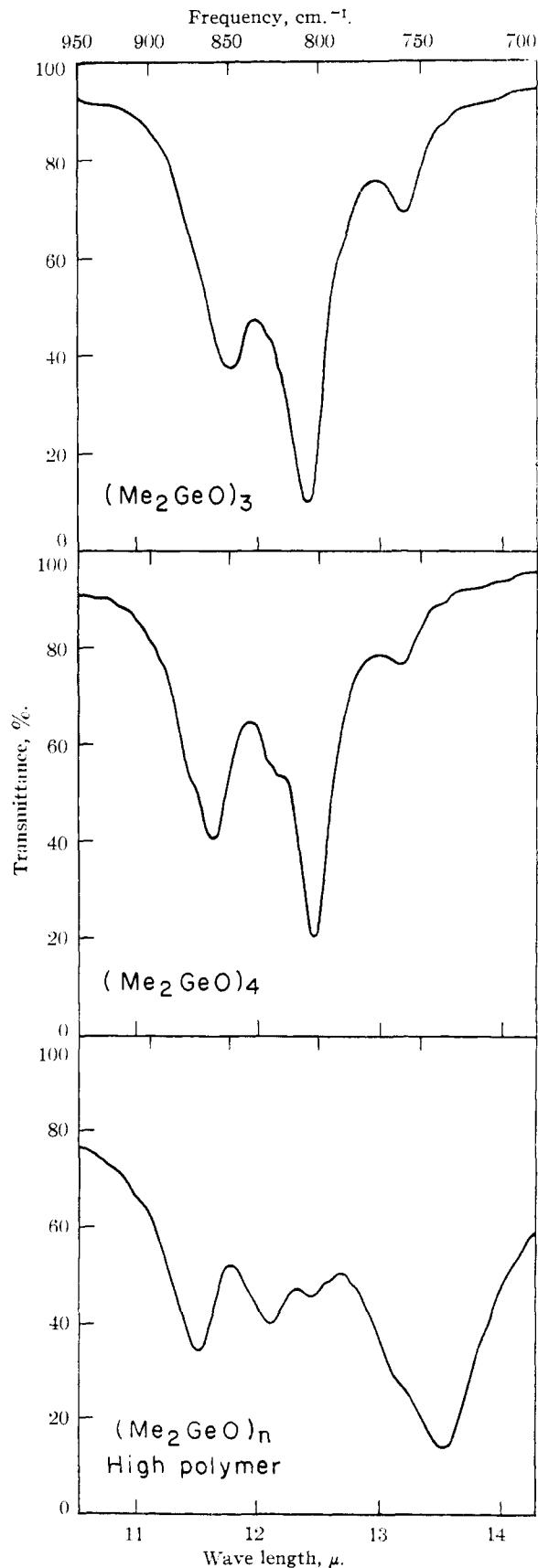


Fig. 1.—Infrared spectra between  $700$  and  $900\text{ cm.}^{-1}$  of dimethylgermanium oxide polymers.

Experimental<sup>11</sup>

**Preparation of Tetrameric Dimethylgermanium Oxide.**—Dimethyldichlorogermane<sup>12</sup> (21.8 g.) was hydrolyzed in aq. NaOH (9.85 g. in 10 cc. water), petroleum ether (30 cc., b.p. 30–60°) was added, and the mixture was refluxed for 4 hr. The organic layer was separated and the remainder extracted four times with more petroleum ether. After drying the combined ether portions with anhydrous CaSO<sub>4</sub>, petroleum ether was evaporated from the solution in a current of dry nitrogen and crude tetramer (10.0 g., 67% yield), m.p. 88–92° was obtained. Recrystallization gave pure material, m.p. 91–92°. Cryoscopic measurements in benzene were: subs., 0.2993, 0.6597 g.; benzene, 21.89 g.; *T*, 0.146, 0.320°; mol. wt., found, 468, 471. Calcd. for (Me<sub>2</sub>GeO)<sub>4</sub>, 475.

*Anal.* Calcd. for C<sub>2</sub>H<sub>6</sub>GeO: C, 20.24; H, 5.10. Found: C, 20.09; H, 4.90.

**Preparation of High-Polymeric Dimethylgermanium Oxide.**—An aqueous solution of Me<sub>2</sub>GeO (0.97 g. in 2.0 cc. water) was allowed to evaporate at room temperature for 48 hr., yielding a fibrous solid (Me<sub>2</sub>GeO)<sub>x</sub>, m.p. 132–133°.

*Anal.* Found: C, 20.35; H, 4.90.

This material was insoluble in benzene, cyclohexane and carbon tetrachloride but was readily soluble in ethanol and glacial acetic acid. Cryoscopic measurements in water were: subs., 0.1891, 0.3633 g.; water, 20.0 g.; *T*, 0.162, 0.295°; mol. wt., found, 108, 114; calcd. for Me<sub>2</sub>GeO, 118.7.

**Preparation of Trimeric Dimethylgermanium Oxide.**—A sample (approximately 0.2 g.) of tetramer or high-polymer was placed in a silica tube (i.d. 15 mm., length 200 mm., sealed at one end and connected to smaller bore tubing at the other) previously "flamed out" *in vacuo*. The tube was evacuated, sealed off and heated at 210–220° for at least 24 hr. On quenching in cold water, unstable crystals were obtained. The results of immediate cryoscopic measurements on samples from two different tubes were: subs., 0.1828, 0.3094 g.; benzene, 17.36 g.; *T*, 0.142, 0.249°; mol. wt. found, 371, 358; calcd. for (Me<sub>2</sub>GeO)<sub>3</sub>, 356.

**Dimethylgermanium sulfide** was prepared as previously described.<sup>3</sup> It had a sharp m.p. of 55°.

*Anal.* Calcd. for C<sub>2</sub>H<sub>6</sub>GeS: C, 17.83; H, 4.49; S, 23.80. Found: C, 17.89; H, 4.46; S, 23.51.

The results of cryoscopic measurements in benzene were: subs., 0.3519, 0.2019 g.; benzene, 17.36 g.; *T*, 0.249, 0.404°; mol. wt. found, 407, 395. Calcd. for (Me<sub>2</sub>GeS)<sub>3</sub>, 404.

**Tensimetric Measurements.**—The samples of tetrameric Me<sub>2</sub>GeO and Me<sub>2</sub>GeS were freshly sublimed and had sharp melting points. The mercury tensimeter consisted of a glass bulb (200 cc.) connected to one limb of a short mercury manometer of wide bore, the other limb of which was connected to a vacuum line. The tensimeter was evacuated through the empty manometer tube and was degassed by heating it in a silicone oil bath at 250° for 3 hr. and then was allowed to cool. Dry nitrogen was admitted and the sample quickly introduced *via* a vertical tube attached to the bulb and fitted with a ground joint and stopper (which projected above the oil level during the degassing procedure). The stopper was replaced, the tensimeter evacuated and the vertical limb sealed off. Finally the manometer was filled with mercury from a bulb attached by a ground joint to the vacuum line side of the manometer. The volume of the tensimeter in relation to the level of mercury in the manom-

(11) Melting points are uncorrected. Carbon and hydrogen analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(12) Prepared by the direct reaction of methyl chloride with germanium. See E. G. Rochow, *THIS JOURNAL*, **69**, 1729 (1947).

TABLE I

THE DEGREE OF POLYMERIZATION OF DIMETHYLGERMANIUM OXIDE VAPOR FROM TENSIMETRIC MEASUREMENTS

Run no.	(Me <sub>2</sub> GeO) <sub>4</sub> , g.	Temp., °C.	Press., cm. at 0°C.	Vol., cc.	Apparent degree of polymerization <sup>a</sup>
1	0.2505	165	7.158	255.2	3.16
1	.2505	180	7.524	255.6	3.10
1	.2505	200	8.258	256.6	2.94
2	.2821	180	8.375	256.6	3.13
2	.2821	200	9.040	257.6	3.01
3	.2886	205	10.64	229.1	2.97
3	.2886	250	11.74	229.1	2.95

<sup>a</sup> Estimated error within ± 0.55.

TABLE II

THE DEGREE OF POLYMERIZATION OF DIMETHYLGERMANIUM SULFIDE VAPOR FROM TENSIMETRIC MEASUREMENTS

Sample, g.	Temp., °C. <sup>a</sup>	Press., cm. at 0°C.	Vol., cc.	Apparent degree of polymerization
0.2590	224	8.55	229.1	3.04
.2590	234	8.83	229.1	3.00
.2590	245	9.42	229.1	2.88
.2590	256	9.64	229.1	2.87

<sup>a</sup> The saturation point for this run was between 212 and 224°.

eter was known from calibrations with known amounts of CO<sub>2</sub>.

For each run it was necessary to attach a vertical tube and, after introducing the sample, to seal again at the same point. The error in volume thus introduced was estimated as under 0.5 cc., or 0.2%.

A series of measurements made both at 165 and 200° showed that the pressure did not reach a steady value until after 24 hr. of heating at a constant temperature. Therefore the readings reported in Table I were obtained after maintaining the temperature indicated, to within ± 1°, for at least 24 hr. Presumably the reaction



requires a considerable time for completion under the conditions studied. It seems reasonable to suppose that it takes place on the walls of the tensimeter. As a final check at the end of every run, a reading at the lowest temperature was taken, and in every case this was identical (within experimental error) with that first obtained.

The tensimeter used for dimethylgermanium oxide at higher temperatures (Run 3), and for dimethylgermanium sulfide, had a quartz spiral in place of the mercury manometer. The pressure inside the tensimeter was measured by a null method whereby the long glass pointer attached to the spiral was brought back to its original position, corresponding to zero pressure, by a known external pressure of nitrogen. The pressure could only be determined to the nearest mm. (representing an error of about 1%), but the spiral could withstand a pressure difference of one atmosphere. This tensimeter was evacuated as before, and the sample introduced in the same way.

**Infrared Measurements.**—The spectrophotometer was a Perkin Elmer (Model 21).

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