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Ethylgermanium Formates, Acetates and Mercaptoacetate

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Previous investigations on germanium revealed the relatively low stability of germanium chlorobromides,[1] the comparatively remarkable stability of ethylgermanium isocyanates[2] and two ethylgermanium sulfates,[3] $(Et_3Ge)_2SO_4$ and $(Et_2GeSO_4)_2$.

This report describes the products of the reaction of bis-(triethylgermanium) oxide and tetrameric (or trimeric) diethylgermanium oxide with formic acid, acetic anhydride and mercaptoacetic acid—in the last case with the former oxide only.

Preparation of New Germanium Compounds.—This research was possible with the availability of germanium tetrachloride prepared by the author at Harvard University,[1] and of pure diethylgermanium dichloride kindly furnished by Professor Eugene G. Rochow of Harvard University. Following the procedure of Flood,[4] 37 g. of pure, center fraction tetraethylgermanium and 9.3 ml. of bromine were mixed, and after standing for only 40 hours at 32° gave a mixture containing only 0.3 volume-per cent. of free bromine according to color; after hydrolysis and washing, drying and distillation, a center fraction boiling at 254–256° was obtained. Nearly 20 g. resulted; the purest material yielded the following new data for bis-(triethylgermanium) oxide: $d^{20}{}_4$ 1.147; refractive index at 20°, 1.461_4; hence, molar refraction, 80.3_1 ml. Only the best material was used in the preparations described below.

Diethylgermanium dichloride (and some diethylgermanium diisocyanate which was on hand) upon hydrolysis with aqueous alkali, extraction, washing, drying and upon distillation of the resultant $(Et_2GeO)_4$ at 128.5–129.0° under 3 mm. pressure yielded a very pure oxide. Used in the preparations below, this oxide had a refractive index of 1.471_1 on supercooled liquid at 20°, had a density at 31° of 1.358_2, and melted at approximately 29° (98% liquid, 2% solid); the molar refraction of the structural unit Et_2GeO was 30.11 ml.

TABLE I

PROPERTIES OF NEW COMPOUNDS

Compound	B. p., °C.	$d^{20}{}_4$	n^{20}	R, ml.	Mol. wt. (camphor) Calcd.	Mol. wt. (camphor) Found	Neut. equiv., g. Calcd.	Neut. equiv., g. Found	Distillation range, °C.	Mm.
$Et_3Ge(HCOO)$	185.7	1.167_2	1.443_6	46.6	204.8	216	204.8	202.0, 202.0	185.5–186.5	768
$Et_2Ge(HCOO)_2$	210	1.366[5]	1.445_4	43.0	220.6	218	110.4	111.8, 111.0	59–60	3
$Et_3Ge(CH_3COO)$	190.5	1.129_9	1.441_3	51.2	218.8	225	218.8	216.4, 216.4	190–191	766
$Et_2Ge(CH_3COO)_2$	217	1.260	1.440_4	52.0	248.8	257	124.4	125.2, 126.0	134–135	51
$Et_3Ge(SCH_2COO)GeEt_3$	326	1.222_4	1.499_3	98.5	409.7	425	409.7	388[6]	158.5–159.5	4

Triethylgermanium formate ensued in a 90% yield upon combining 2.2 ml. of bis-(triethylgermanium) oxide and 2.6 ml. of 90% formic acid, whereupon the temperature rose approximately 10°; after an hour of reflux the excess formic acid was distilled off. (Special small distilling equipment with ground joints not in the direct line of reflux served in the five preparations; micro transfer methods were indispensable. After the distillation of the excess of acid or acid anhydride, the residual liquid was transferred to smaller equipment.) A yield of 2.4 ml. of product, distilled under the conditions in Table I, served for all measurements.

Diethylgermanium diformate was present in a yield of only 30% after a total of five hours of reflux of 2.2 ml. of tetrameric (trimeric) diethylgermanium oxide and 3.3 ml. of at least 96% formic acid–90% acid treated with phosphorus pentoxide, followed by distillation, with measurement of refractive index. After distillation of formic acid at 200 mm., the product was transferred to smaller equipment and distilled at 59–61° under 3 mm. pressure, amounting to 1.0 g. as pure compound and 0.4 g. in the residue of chiefly unchanged organogermanium oxide.

Triethylgermanium acetate, after a two-hour reflux of 6.4 g. of bis-(triethylgermanium) oxide with 4.2 g. of acetic anhydride, constituted a yield of over 90%; after distillation of the excess anhydride, the product was distilled, taking the center fraction for measurements. Very little, if any, unchanged organogermanium oxide remained.

Diethylgermanium diacetate was the product of a five-hour reflux of 3.8 g. of the diethylgermanium oxide and 6.0 g. of acetic anhydride. Following distillation of excess anhydride, the resultant diacetate was best distilled under reduced pressure—with a yield of over 90%.

Triethylgermanium S-triethylgermanium mercaptoacetate resulted through mixing of 4.3 g. of bis-(triethylgermanium) oxide with 2.0 g. of anhydrous mercaptoacetic acid, $HSCH_2COOH$, which was prepared through low-pressure evaporation of the water in a commercial 80% product. This mixture warmed up approximately 30° of its own accord; after fifteen minutes at 100°, 0.1 ml. of water was distilled at 50° under 80 mm. pressure. Then a fraction without a definitely sharp boiling point distilled, consisting of unchanged organogermanium oxide, unchanged acid, probably decomposition products of mercaptoacetic acid, and possibly even some $Et_3GeCOOCH_2SH$, yet unknown but not easily separable (presumably boiling at approximately 240°, according to a method of calculation being developed). Finally, the highest-boiling constituent was distilled first at 208° under 12 mm. and later at 158.5–159.5° under 4 mm. pressure. A yield of 2.7 g. of a clear, light-yellow liquid corresponded to 56% of the theoretical.

Bis-(ethylgermanoso) oxide and acetic anhydride did not react; $[(EtGeO)_2O]_n$—from water and the momentarily available $EtGe(NCO)_3$—and acetic anhydride were subjected to a 20-minute reflux. Upon cooling the polymeric ethylgermanium oxide crystallized out. Further experiments at a later date will use a metallic acetate and $EtGeCl_3$, when the latter is available.

Physical Properties, see Table I.—All were colorless liquids save the light-yellow mercaptoacetate. All were of low viscosity at 30°, save the mercaptoacetate, which was somewhat more viscous than is carbon tetrachloride. Triethylgermanium formate had a primarily camphoraceous odor, but with the bitterness of an acid; diethyl-

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(1) Forbes and Anderson, THIS JOURNAL, **66**, 931 (1944).

(2) Anderson, *ibid.*, **71**, 1799 (1949).

(3) Anderson, *ibid.*, **72**, 194 (1950).

(4) Flood, *ibid.*, **54**, 1663 (1932).

(5) Calculated from $d^{31}{}_4$, 1.351.

(6) Also, using iodine in KI, found S, 7.6; calcd. S, 7.8.

germanium diformate smelled like a weak acid; triethylgermanium acetate was essentially camphoraceous; diethylgermanium diacetate smelled like acetic acid, except weaker. All the boiling points were measured on the day of purification using calibrated thermometers.

Chemical Properties.—All the compounds hydrolyze rapidly enough to permit titration with ethanolic sodium hydroxide solution if five minutes elapse before the final endpoint. The mercaptoacetate is easily soluble in cyclohexane, acetone and carbon tetrachloride at 30°; the other four compounds may be assumed to be quite soluble in organic solvents.

In the system $2Et_3Ge(CH_3COO) + H_2O \rightleftarrows (Et_3Ge)_2O + 2CH_3COOH$, 12 *N* acid produces one phase, and evidently shifts the equilibrium to the left, favoring the organogermanium acetate.

A concentration of 70% formic acid produces one phase in the system $2Et_3Ge(HCOO) + H_2O \rightleftarrows (Et_3Ge)_2O + 2HCOOH$.

In contrast, only 30% acetic acid is needed to produce one phase in the system $4Et_2Ge(CH_3COO)_2 + 4H_2O \rightleftarrows (Et_2GeO)_4 + 8CH_3COOH$. With the corresponding formate a comparably dilute acid sufficed for production of one phase. Whenever the acid is weaker than these specified concentrations, then two liquid phases exist. It is noteworthy that the triethylgermanium systems require more acid than do diethylgermanium systems.

Analysis consisted of molecular weights in camphor; the determination of sulfur in the sulfhydryl group using iodine in potassium iodide, after alcoholysis of the one ethylgermanium mercaptoacetate; the titration of the acid obtained after treatment with 90% of the theoretical equivalence of 95% ethanolic sodium hydroxide solution. With the formates the indicator was brom phenol blue; with the acetates, phenolphthalein; with the one mercaptoacetate the best indicator, as determined with pure mercaptoacetic acid, was phenol red. In view of the straightforward methods of preparation these analyses are considered sufficient to establish the identity of the compounds.

Discussion

1. In mercaptoacetic acid, $HSCH_2COOH$, the sulfhydryl hydrogen has a dissociation constant of approximately 10^{-11} and the carboxyl hydrogen a constant approximately 10^{-4} [7]; the formation of $Et_3GeSCH_2COOGeEt_3$ indicates that $Et_3GeOGeEt_3$ is fairly basic.

2. A 90% yield of $Et_3Ge(HCOO)$ as compared to a 30% yield of $Et_2Ge(HCOO)_2$ is consistent with a relatively weaker basicity of $(Et_2GeO)_{3-4}$. The failure of $[(EtGeO)_2O]_n$ to react with acetic anhydride is no surprise, since this organogermanium oxide is acidic. Moreover, a similar tendency exists in related silicon compounds: the relatively more basic $(CH_3)_3SiOSi(CH_3)_3$ reacts with sulfuric acid,[8] while $[(CH_3)_2SiO]_{3-8}$ does not react with sulfuric acid.

3. Herein germanium is seen to be definitely at least a metalloid, or even a metal with some non-metallic properties. This is in accord with the relatively low stability of mixed halides of germanium.[1] In the series carbon, silicon, germanium, tin (and lead) the basicity increases with increasing atomic volume.

4. There is a definite progressive decrease in basicity as the oxygen content increases among the oxides $Et_3GeOGeEt_3$, $(Et_2GeO)_4$ and $[(EtGeO)_2O]_n$.

Summary

1. Bis-(triethylgermanium) oxide, $(Et_3Ge)_2O$, and tetrameric (or trimeric) diethylgermanium oxide, $(Et_2GeO)_4$, react with the appropriate aliphatic organic acids and acetic anhydride to yield new compounds boiling as follows: triethylgermanium formate, $Et_3Ge(HCOO)$, 185.7°; diethylgermaium diformate, $Et_2Ge(HCOO)_2$, 210°; triethylgermanium acetate, $Et_3Ge(CH_3COO)$, 190.5°; diethylgermanium diacetate, $Et_2Ge(CH_3COO)_2$, 217°; triethylgermanium S-triethylgermaniummercaptoacetate, $Et_3GeSCH_2COOGeEt_3$, 326°, with slight decomposition—or undecomposed at 159° under 4 mm. pressure.

2. Indices of refraction, densities, molar refractions, and other details, both for the five new compounds and for the two ethylgermanium oxides, are in the text.

3. These preparations agree well with the concept of a progressive decrease in basicity of the oxides: from $(Et_3Ge)_2O$, which replaces even a sulfhydryl hydrogen (dissociation constant, 10^{-11}) and gives a practically quantitative yield with 90% formic acid; through the tetrameric (or trimeric) $(Et_2GeO)_4$ which gives a 30% yield with 96% formic acid; down to the acidic $[(EtGeO)_2O]_n$ which merely recrystallized from acetic anhydride, and which is soluble in water. In the ethylgermanium oxides an increase in oxygen content is linked with an increase in acidity.

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(7) Larsson, *Z. anorg. Chem.*, **172**, 380 (1928).

(8) Sommer, *et al.*, THIS JOURNAL, **68**, 156 (1946); **70**, 445 (1948).