TABLE II

| Temp., °C. | Vapor pressure, mm. Before equil. shift | After equil. shift |
|---|---|---|
| −80 | 8.5 | 53 |
| −63 | 29 | 74 |
| −45 | 80 | 127 |
| −23 | 158–226 | 254 |

## Discussion and Conclusions

Boron trichloride and diborane react to form chloroboranes without change in the number of moles of gas present. This may be explained by equilibria such as

$$BCl_3 + B_2H_6 \rightleftarrows B_2H_5Cl + BHCl_2$$

Of the possible reactions which may be written, this involves the simplest mechanism. One molecule of boron trichloride and one molecule of diborane come together and exchange a chlorine atom for a hydrogen atom. The reaction products of this interaction are monochlorodiborane and dichloroborane. These have been identified in the infrared spectrum. One may view this equilibria as a sort of gaseous ion exchange where hydrogen and chlorine are continuously being exchanged at the boron exchange site.

Monochlorodiborane and dichloroborane are relatively stable in the product equilibrium mixture. They do not spontaneously disproportionate, but instead they interact with the other species present in the reaction mixture by exchange of hydrogen and chlorine atoms until equilibrium is established. Previous reports of the instability of monochlorodiborane and dichloroborane may have been observations of reaction product mixtures containing these compounds trying to attain equilibrium. If one of the equilibrium components is removed by fractionation, the remainder of the equilibrium mixture will then react until a new equilibrium mixture is formed.

One would expect that pure monochlorodiborane would have a stability similar to diborane in an environment of diborane. Dichloroborane would also be fairly stable in an environment of boron trichloride since the proposed equilibria would permit only small concentrations of diborane and monochlorodiborane at equilibrium.

Some diborane syntheses may produce reaction products which are rich in boron–hydrogen bonding and others produce reaction products which contain a large quantity of boron–chlorine bonding. This could explain the differences of opinion in the literature. Reaction product mixtures which are mostly diborane and monochlorodiborane can have only small concentrations of boron trichloride and dichloroborane present in the equilibrium mixture. In like manner, reaction products rich in boron–chlorine bonding would have low concentrations of diborane and monochlorodiborane at equilibrium. Fractionation or distillation would yield the desired diborane product by shifting the equilibrium.

The exchange of hydrogen and chlorine atoms may be similar to that observed by Keller and his coworkers[10] for the interaction of boron trichloride and boron tribromide and by Porter, *et al.*,[11] for boron trichloride and boron trifluoride.

The interaction of boron trichloride with silane reported by Edwards and Pearson[12] may proceed through a similar hydrogen–chlorine exchange. They found that when a 4:1 excess of boron trichloride was used, the disproportionation of dichloroborane was inhibited so that most of the hydrogen bonding remained as dichloroborane. Conceivably, a large excess of silane would yield monochlorodiborane and diborane and little dichloroborane and boron trichloride.

If a chemical species is added which interacts with and removes one or more of the equilibrium components, the remaining components interact to set up new equilibria until the reaction has gone to completion. Examples of this may be found in the work of Brown and Tierney,[13] Onak, Landesman, and Shapiro,[14] and others.

Perhaps current methods of infrared analysis should be evaluated in the light of these findings.

It is hoped that these observations may prove useful in catalysis reactions involving boron and similar compounds.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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# Reactions of Alkylgermanium Alkanesulfonates[1]

BY HERBERT H. ANDERSON

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Triphenylgermanium benzenesulfonate, b.p. 160° (1.3 mm.), white needles of m.p. 38°, the only previously known organogermanium compound with a sulfonate group, is the product of a 6-hr. reflux of triphenylgermane with benzenesulfonic acid in toluene[2] solution.

A rapid transesterification such as $2R_3GeOCOR' + H_2SO_4 = [R_3Ge]_2SO_4 + 2HOCOR'$, involving a distillation for 15 min. in equipment of at least five theoretical plates, is adequate in the preparation of $[(n\text{-}C_3H_7)_3Ge]_2SO_4$, b.p. 370°,[3] $[(i\text{-}C_3H_7)_3Ge]_2SO_4$, b.p. 380°,[4] $[(i\text{-}C_3H_7)_2GeSO_4]_2$, m.p. 115° dec.,[3] and $[(C_2H_5)_3Si]_2SO_4$, b.p. 278°.[5] This procedure offers many advantages

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TABLE I

PROPERTIES OF NEW COMPOUNDS

| Compound | B.p., °C. | $d^{20}_4$ | $n^{20}$[a] | Mol. refr. Calcd.[b] | Mol. refr. Found | $OSO_2R$ Calcd. | $OSO_2R$ Found[c] | Mol. wt. Calcd. | Mol. wt. Found[d] | Distilled at B.p., °C. | Distilled at mm. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $(C_2H_5)_3GeSO_3CH_3$ | 280 | 1.286 | $1.465_0$ | 54.77 | 54.78 | 37.3 | 37.4 | 255 | 246 | 116–117 | 1 |
| $(C_2H_5)_3GeSO_3C_2H_5$ | 289 | 1.253 | $1.465_1$ | 59.41 | 59.34 | 40.6 | 40.7 | 269 | 260 | 125–126 | 1 |
| $(i\text{-}C_3H_7)_2Ge(SO_3CH_3)_2$ | 379[e] | 1.426 | $1.477_0$ | 67.92 | 69.15 | 53.3 | 53.9 | 349 | 380 | 180–182 | 1 |
| $(n\text{-}C_4H_9)_3GeSO_3CH_3$ | 330 | 1.131 | $1.464_1$ | 82.65 | 82.74 | 28.0 | 28.1 | 328[f] | 339 | 150–152 | 1 |
| $(n\text{-}C_4H_9)_3GeSO_3C_2H_5$ | 337 | 1.117 | $1.465_4$ | 87.30 | 87.29 | 30.9 | 31.1 | 344[g] | 353 | 149–151 | 1 |

[a] In white light, ±0.0010. All compounds are colorless. [b] Taking the combination Ge–O and $OSO_2-$ as 11.56 ± 0.05. [c] Titration with standard ethanolic sodium hydroxide solution; two determinations, with blue color of brom thymol blue indicator. [d] Molecular weights in camphor, except for diisopropylgermanium bis(methanesulfonate), which required naphthalene. [e] Decomposed during measurement of normal boiling point. [f] Calcd.: Ge, 21.4. Found: Ge, 21.2. [g] Calcd.: Ge, 20.56. Found: Ge, 20.3.

TABLE II

REACTIONS OF ALKYLGERMANIUM ALKANESULFONATES, 0.60 G./RUN, IN 10-MIN. REFLUX

| Starting materials | | | Reaction products | | | | |
|---|---|---|---|---|---|---|---|
| Compound | Compound | Wt., g. | Chief product | B.p., °C. | Wt., g. | Yield, % | Other products |
| $(C_2H_5)_3GeSO_3CH_3$ | $(C_5H_5)_2TiCl_2$ | 0.62 | $(C_2H_5)_3GeCl$[a] | 173 | 0.44 | 96 | $(C_5H_5)_2Ti(SO_3CH_3)_2$ |
| $(C_2H_5)_3GeSO_3CH_3$ | $HgCl_2$ | 1.08 | $(C_2H_5)_3GeCl$ | 174 | 0.39 | 85 | $Hg(SO_3CH_3)_2$ |
| $(C_2H_5)_3GeSO_3CH_3$ | $(n\text{-}C_4H_9)_2GeBr_2$ | 0.82 | $(C_2H_5)_3GeBr$ | 192 | 0.50 | 88 | $(n\text{-}C_4H_9)_2Ge(SO_3CH_3)_2$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | $(C_2H_5)_3SnF$ | 1.37 | $(C_2H_5)_3GeF$ | 151 | 0.37 | 91 | $(C_2H_5)_3SnSO_3C_2H_5$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | $(C_6H_5)_2SnCl_2$ | 0.76 | $(C_2H_5)_3GeCl$ | 174 | 0.43 | 98 | $(C_6H_5)_2Sn(SO_3C_2H_5)_2$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | AgCl[b] | 2.25 | $(C_2H_5)_3GeCl$ | 175 | 0.28 | 64 | $AgSO_3C_2H_5$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | $HgBr_2$ | 1.22 | $(C_2H_5)_3GeBr$ | 190 | 0.38 | 71 | $Hg(SO_3C_2H_5)_2$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | KI | 1.63 | $(C_2H_5)_3GeI$ | 212 | 0.64 | 99 | $KSO_3C_2H_5$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | KCN | 1.06 | $(C_2H_5)_3GeCN$ | 211 | 0.40 | 96 | $KSO_3C_2H_5$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | $(C_6H_5)_3SiNCO$ | 1.92 | $(C_2H_5)_3GeNCO$ | 199 | 0.37 | 82 | $(C_6H_5)_3SiSO_2C_2H_5$ |
| $(C_2H_5)_3GeSO_3C_2H_5$ | KSCN | 1.55 | $(C_2H_5)_3GeNCS$ | 250 | 0.42 | 86 | $KSO_3C_2H_5$ |
| $(i\text{-}C_3H_7)_2Ge(SO_3CH_3)_2$ | $ZnCl_2$ | 0.74 | $(i\text{-}C_3H_7)_2GeCl_2$ | 202 | 0.30 | 76 | $Zn(SO_3CH_3)_2$ |
| $(n\text{-}C_4H_9)_3GeSO_3CH_3$ | $SbF_3$ | 0.26 | $(n\text{-}C_4H_9)_3GeF$ | 247 | 0.42 | 90 | $Sb(SO_3CH_3)_3$ |
| $(n\text{-}C_4H_9)_3GeSO_3CH_3$ | $PbCl_2$ | 2.08 | $(n\text{-}C_4H_9)_3GeCl$ | 270 | 0.46 | 93 | $Pb(SO_3CH_3)_2$ |
| $(n\text{-}C_4H_9)_3GeSO_3CH_3$ | $Na_2SO_3$ | 1.77 | $(n\text{-}C_4H_9)_6Ge_2O$ | 352 | 0.32 | 72 | $NaSO_3CH_3$, $SO_2$ |
| $(n\text{-}C_4H_9)_3GeSO_3C_2H_5$ | NaCl | 0.68 | $(n\text{-}C_4H_9)_3GeCl$ | 269 | 0.40 | 84 | $NaSO_3C_2H_5$ |
| $(n\text{-}C_4H_9)_3GeSO_3C_2H_5$ | $KOCOCH_3$ | 1.07 | $(n\text{-}C_4H_9)_3GeOCOCH_3$ | 273 | 0.40 | 78 | $KSO_3C_2H_5$ |

[a] Identification of each chief product included a qualitative test, density or refractive index. [b] With silver chloride there were two refluxes of 30 min. each, with two distillations.

over the reaction of sulfuric acid[6] with $[(C_2H_5)_3Ge]_2O$ to form $[(C_2H_5)_3Ge]_2SO_4$, b.p. 342°. Further transesterifications furnish five new alkylgermanium alkanesulfonates in the present publication.

These five new alkylgermanium alkanesulfonates are all colorless liquids; all except diisopropylgermanium bis(methanesulfonate) are relatively stable at their normal boiling points. Strong infrared absorptions for asymmetric sulfonate stretch are typical of these compounds. Molar refractions in Table I use the value 11.56 ± 0.05 for the combination Ge–O and $OSO_2-$ (this excludes the less pure bis(methanesulfonate) from the average), which is lower than the total of 12.57 obtained from 2.47[7] for Ge–O and 10.10[8] for $OSO_2-$. This addition neglects the mutual effect of Ge–O and $OSO_2-$ upon each other.

Other evidence indicates that the alkylgermanium alkanesulfonates are essentially covalent compounds. All the compounds are easily soluble in the covalent solvents camphor, carbon tetrachloride, and petroleum ether. For 0.60 *F* tri-*n*-butylgermanium ethanesulfonate in 99.7% acetic acid the molar conductance is only $8 \times 10^{-3}$ cm.$^2$ ohm$^{-1}$ mole$^{-1}$. In 0.031 *F* tri-*n*-butylgermanium ethanesulfonate in 59% aqueous ethanol approximately 40% hydrolysis occurs. All the compounds are colorless liquids.

A general comparison of dialkyltin bis(alkanesulfonates)[9] and the trialkylgermanium alkanesulfonates herein clearly shows the alkylgermanium compounds are relatively more covalent, because the germanium compounds have lower molar conductance, a greater solubility in covalent organic solvents, high stability at the boiling point, a greater degree of hydrolysis, much lower melting points, and also greater resistance to dealkylation with an alkanesulfonic acid.

Seventeen exchange reactions in Table II, bearing some resemblance to previous exchange reactions in volatile isocyanates and isothiocyanates of silicon, germanium, and phosphorus,[10] have a median yield of 86%. These seventeen exchange reactions show replacement of $OSO_2R$ attached to germanium by fluoride, chloride, bromide, iodide, cyanide, isocyanate, isothiocyanate, acetate, and oxide—the last one undoubtedly through decomposition of an alkylgermanium sulfite. Although unproven, neucleophilic attack by $X^-$ ion could explain the majority of these reactions.

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## Experimental

**Materials.**—Triethylgermanium acetate,[6] diisopropylgermanium diacetate,[3] and tri-*n*-butylgermanium trifluoroacetate[11] served in the preparation of new alkylgermanium alkanesulfonates. In Table II di-*n*-butylgermanium dibromide,[11] triethyltin fluoride,[12] triphenylisocyanatosilane,[13] and antimony(III) fluoride were special preparations; some commercial products required drying or dehydration.

**Triethylgermanium Methanesulfonate, Triethylgermanium Ethanesulfonate, Diisopropylgermanium Bis(methanesulfonate), Tri-*n*-butylgermanium Methanesulfonate, and Tri-*n*-butylgermanium Ethanesulfonate.**—Typically, 5.70 g. or 15.9 mmoles of tri-*n*-butylgermanium trifluoroacetate and 1.39 g. or 14.5 mmoles of methanesulfonic acid in a 10-min. reflux with distillation furnished approximately 1.36 g. or 12.0 mmoles of trifluoroacetic acid, b.p. 73°, then 0.40 g. of excess tri-*n*-butylgermanium trifluoroacetate distilled at 29 mm., next 0.45 g. of crude tri-*n*-butylgermanium methanesulfonate distilled under 1 mm. pressure, and finally 4.35 g. of fair grade tri-*n*-butylgermanium methanesulfonate at approximately 150° (1 mm.), leaving 0.4 g. undistilled. The yield was 89%. Redistillation of the 4.35-g. fraction furnished a 2.6-g. center cut of b.p. 150–152° (1 mm.) for measurements. The analyses and properties of these five new compounds are in Table I.

**Infrared Measurements.**—A Perkin-Elmer Model 421 spectrophotometer served for the measurements, which indicated strong asymmetric sulfonate stretch[14-16]: triethylgermanium methanesulfonate, 1152 cm.$^{-1}$; diisopropylgermanium bis(methanesulfonate), 1157 cm.$^{-1}$; tri-*n*-butylgermanium methanesulfonate, 1151 cm.$^{-1}$; also, tri-*n*-butylgermanium ethanesulfonate, 1150 cm.$^{-1}$. Weak absorptions at 1078 and 1079 cm.$^{-1}$, possibly symmetric sulfonate stretch, appeared only in the butylgermanium derivatives. Flat circular plates of silver chloride (under study by Dr. L. L. Pytlewski at this institute) proved inert to thin films of pure liquid alkylgermanium alkanesulfonates at 25°; sodium chloride or potassium bromide plates were too reactive at 25° to be of any use.

**Hydrolysis.**—A 0.0310 $M$ solution of tri-*n*-butylgermanium ethanesulfonate in 59% aqueous ethanol had a pH of 1.90 and thus 0.0125 mole of hydrogen ion per liter. This is approximately 40% hydrolysis.

**Conductance.**—The molar conductance of 0.060 $F$ tri-*n*-butylgermanium ethanesulfonate in 99.7% acetic acid was only $8.2 \times 10^{-3}$ cm.$^2$ ohm$^{-1}$ mole$^{-1}$.

**Solubility.**—Tri-*n*-butylgermanium methanesulfonate was easily soluble in an equal volume of petroleum ether (100–115°) or carbon tetrachloride at 25°.

**Exchange Reactions (Table II).**—Sixteen reactions, with distillation under reduced pressure, were complete in 10 min. or less and used very small distilling units with ground joints, calibrated receivers, and calibrated thermometers. Typically, after reflux under atmospheric pressure for 8 min., distillation under 1–150 mm. pressure followed; identification of each alkylgermanium product included a later measurement of boiling point and a qualitative test for the halide or halogenoid. However, the slow reaction with silver chloride furnished 0.14 g. of triethylgermanium chloride in the first 30 min. of reflux and then distillation; the second 30 min. of reflux and then distillation supplied another 0.14 g. of triethylgermanium chloride, while unchanged triethylgermanium ethanesulfonate still persisted. The average difference between the observed boiling point of each alkylgermanium chief product in Table II and the published boiling point is 1.5°, with a maximum difference of 3°. Nine of these compounds appearing as alkylgermanium chief products are compounds prepared for the first time at an earlier date by the present author. There was no further study of other reaction products.

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# Volatile *n*-Butyltin and Phenyltin Tricarboxylates. Organotin Oxymonocarboxylates[1]

BY HERBERT H. ANDERSON

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No mention of volatile alkyltin tricarboxylates or aryltin tricarboxylates occurs in a recent organotin review.[2] Recent publications carry the names of compounds such as phenyltin triacetate (without data),[3] *n*-butyltin tris(2-ethylhexoate) as a catalyst (without physical properties),[4] *n*-butyltin S,S′,S″-tris(mercaptoacetate) (with analyses),[5] *n*-butyltin trioctoate catalyst (without physical properties),[6] phenyltin trilaurate stabilizer,[7] and also methyltin triacetate, ethyltin trihexoate, phenyltin tristearate, and other catalysts (without physical properties).[8]

Crystalline $CH_3Sn(OCOR)_2OSn(CH_3)(OCOR)OSn(OCOR)_2$ is the product[9] of the reaction of the corresponding aliphatic carboxylic acid with either methanestannonic acid or $[CH_3Sn(O)OCOR]_6$ and then crystallization. However, the present publication reports successful distillation at 1 mm. pressure of *n*-butyltin tricarboxylates, starting with the corresponding aliphatic carboxylic acids and *n*-butyltin oxacetate, *n*-butyltin oxy-*n*-butyrate, or *n*-butanestannonic acid anhydride. This surprising difference may result from the use of distillation instead of crystallization, or from the longer length of the *n*-butyl group as compared to methyl. Also, the preparation and properties of $[CH_3Sn(O)OCOR]_6$[9] are in agreement with those of the five new related polymeric organotin oxycarboxylates in this publication.

In the present publication an excess of the silver carboxylate converts *n*-butyltin trichloride, phenyltin trichloride, or tin(IV) chloride, in carbon tetrachloride solution, into nine organotin tricarboxylates and one tin tetracarboxylate; distillation is possible at 1 mm. pressure. Analyses in Table I establish the formulas.

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