$SiCl_2Br_2$.—In the original preparation,[1] when 20 g. of this substance was added to 80 g. of silver isocyanate in the presence of 200 ml. of benzene the product was $Si(NCO)_4$—bearing several per cent. of $Si(OCN)_4$.

SiI_4.—A mixture of 10 g. of this substance and 10 g. of antimony trifluoride was heated at approximately 150° in a distilling flask, whereupon a fast reaction occurred, with the escape of a gas containing no iodine, while an orange solid remained in the flask. $SiI_4 + SbF_3 \rightarrow SiF_4 + SbI_3$.

$Si(NCO)_4 + H_2S$.—When hydrogen sulfide was bubbled through this substance at 180° with or without aluminum chloride as a catalyst, there was no elevation of the boiling point at the end of an hour—indicating no formation of $Si(NCO)_3(SH)$ or $SiS(NCO)_2$, both yet unknown.

$Si(NCO)_4 + SbCl_3$.—When equal weights of both were heated for thirty minutes at 200°, without a solvent and under free reflux, silicon tetraisocyanate, b. p. 186°, was still the lowest-boiling constituent. No silicon chloroisocyanates, of lower boiling points, were present.

$Si(NCO)_4 + AgNCS$.—Similarly, when 7 g. of the former and 37 g. of the latter with 40 ml. of benzene were subjected to reflux for ninety minutes at 90°, the resultant solution contained at most ten milligrams of isothiocyanate—some of which could have been due to side reactions involving hydrolysis.

$Si(NCS)_4 + AgNCO$.—Eleven grams of the former and 30 g. of the latter with 60 ml. of benzene—after an hour of reflux at 90°—yielded an essentially unaltered $Si(NCS)_4$, the lowest-boiling tenth of which, b. p. 275–285°, melted at about 100°. Since 90% was higher-melting and higher-boiling it is beyond reasonable doubt that no silicon tetraisocyanate was formed.

$Si(NCS)_4 + SbCl_3$.—When equal weights of the two were heated under free reflux without a solvent at 220° for an hour, there was no detectable amount of $SiCl_3(NCS)$ formed. $Si(NCS)_4$ melts at 143.2° and boils at 314.2°,[5] while $SiCl_3(NCS)$, the only stable silicon chloroisothiocyanate[6] boils at 129.5°.

$Ge(NCO)_4 + SbF_3$.—When 50 g. of the former and 20 g. of the latter were given the same kind of treatment as were $P(NCO)_3$ and SbF_3[7] products were formed boiling between 25 and 120°; however, upon redistillation the only two constant-boiling compounds were GeF_4 and $Ge(NCO)_4$.

$PI_3 + AgNCO$.—A mixture of 10 g. of the former and 30 g. of the latter in 20 ml. of benzene evolved no heat and showed no other sign of reaction. However, when 20 ml. of nitromethane was the solvent, there was an immediate reaction in the cold, with easily detected warming of the flask. After the usual reflux and filtration,[1] the filtrate contained much isocyanate and no iodide, since the precipitate obtained with silver nitrate solution fizzed in nitric acid and dissolved completely. $PI_3 + 3AgNCO \rightarrow P(NCO)_3 + 3AgI$.

Acknowledgments.—The author thanks Professor George S. Forbes of this Laboratory for sustained interest in pseudo halides.

Summary

1. Silver isothiocyanate or silver isocyanate reacted with the appropriate individual alkylchlorosilanes to yield four new pseudo halides: benzylsilicon triisothiocyanate, benzylsilicon triisocyanate, *n*-butylsilicon triisothiocyanate and triethoxysilicon isothiocyanate, the latter being the only stable ethoxysilicon isothiocyanate. Certain of their physical properties are listed in Table I.

2. Under the conditions specified in the text no reaction occurs in any of the six following instances: $AgNCO + Si(NCS)_4$; $AgNCS + Si(NCO)_4$; $SbCl_3 + Si(NCO)_4$; $SbCl_3 + Si(NCS)_4$; $H_2S + Si(NCO)_4$; $HNCO + SiCl_4$.

3. Five new reactions are summarized in the equations

$SiCl_3(SH) + AgNCO \longrightarrow Si(NCO)_4 + AgCl + Ag_2S$
$SiCl_2Br_2 + 4AgNCO \longrightarrow Si(NCO)_4 + 2AgCl + 2AgBr$
$PI_3 + 3AgNCO \longrightarrow P(NCO)_3 + 3AgI$
$3Ge(NCO)_4 + 4SbF_3 \longrightarrow 3GeF_4 + 4Sb(NCO)_3$
$3SiI_4 + 4SbF_3 \longrightarrow 3SiF_4 + 4SbI_3$

CAMBRIDGE, MASSACHUSETTS

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[5] Reynolds, *J. Chem. Soc.*, **89**, 397 (1906).

[6] Anderson, THIS JOURNAL, **67**, 223 (1945).

[7] Runs 3, 4 in Table I: Anderson, *ibid.*, **69**, 2495 (1947).

[CONTRIBUTION FROM WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Bis-(triethylgermanium) Sulfate and Diethylgermanium Sulfate

BY HERBERT H. ANDERSON*

Hexamethyldisiloxane and hexaethyldisiloxane both react with concentrated sulfuric acid to form bis-(trialkylsilicon) sulfates, $(R_3Si)_2SO_4$.[1,2]

In extension of studies on germanium chlorobromides,[3] germanium chloroisocyanates,[4] and ethylgermanium isocyanates[5] of which only the ethylgermanium isocyanates were sufficiently stable for purification, two stable ethylgermanium sulfates are the subject of the present report.

Preparation of Bis-(triethylgermanium) Sulfate.—Two grams of 95% sulfuric acid and 2.70 g. of bis-(triethylgermanium) oxide,[5] without any solvent, reacted with warming; the mixture was brought to 90° for seven minutes, with agitation. Thereupon, petroleum ether (34–66°) failed to extract the organogermanium sulfate from the sulfuric acid; however, 7 ml. of pure benzene extracted the organogermanium sulfate most easily. After shaking with a second 4-ml. portion of benzene, followed by evaporation of the solvent, the resultant 3.8 g. of colorless liquid product boiled at approximately 173° under 3-mm. pressure, and had the following properties: d^{22}_4 1.333; refractive index at 22°, 1.475; the composition, 27.5% SO_4, indicating a mixture of 94% $[(C_2H_5)_3Ge]_2SO_4$ and 6% of (95%, concentrated) sulfuric acid.

In the second, corrected preparation, 2.00 g. of 95% sulfuric acid and 2.90 g. of the organogermanium oxide gave a crude mixture similarly. An altered method of purification consisted of a quadruple extraction with mixed solvent (7 ml. of benzene and 3 ml. of cyclohexane, each time), evaporation of the solvent [combination with the product from the first run] and heating of a mixture containing 5.3 g. of the organogermanium sulfate, 7 g. of benzene–cyclohexane solvent, 2.0 g. of dry, powdered am-

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[1] Sommer, Pietrusza, Kerr and Whitmore, THIS JOURNAL, **68**, 156 (1946).

[2] Sommer, Kerr and Whitmore, *ibid.*, **70**, 445 (1948).

[3] Forbes and Anderson, *ibid.*, **66**, 931 (1944).

[4] Forbes and Anderson, *ibid.*, **67**, 1911 (1945).

[5] Anderson, *ibid.*, **71**, 1799 (1949).

monium sulfate[2] and 0.3 g. of Norite charcoal, in a two-hour reflux. After centrifuging and washing, then distillation of solvent, there resulted 4.2 g. of colorless distillate at 164.0–165.0° under 3-mm. pressure—bis-(triethylgermanium) sulfate, bearing only 0.6% of 95% sulfuric acid.

Properties of Bis-(triethylgermanium) Sulfate.—Observed m. p., −5.0 ± 2.0°, with evidence of a higher-melting impurity, probably sulfuric acid; d^{25}_4 1.314; refractive index at 20°, 1.474_8; boiling point (760 mm.) 342 ± 3°, with slight decomposition. Upon correction for 0.6% of 95% sulfuric acid: m. p. −4°; d^{25}_4, 1.311 for $[(C_2H_5)_3Ge]_2SO_4$.

This liquid organogermanium sulfate was miscible at 15° with the following liquids: cyclohexane, benzene, carbon disulfide, carbon tetrachloride, methyl acetate and 95% sulfuric acid.

In the equilibrium $[(C_2H_5)_3Ge]_2O + H_2SO_4 \rightleftarrows [(C_2H_5)_3Ge]_2SO_4 + H_2O$, 11 *M* sulfuric acid shifts the equilibrium to the right, and one phase only; equal volumes of pure water and 99.4% pure organogermanium sulfate upon shaking for several hours shifts the equilibrium quantitatively to the left, with 2.64 *N* acid in the aqueous layer. Less than 8% of the germanium was unextracted by the benzene–hexane mixture, and therefore the yield of the organogermanium sulfate was over 90%.

Analysis of Organogermanium Sulfates.—Ethanolic sodium hydroxide, with methyl red as indicator, served for titration of the sulfuric acid derived from the individual organogermanium sulfates. With some loss, germanium was obtained as the dioxide, using fuming nitric acid and ammonium persulfate.[6] For $[(C_2H_5)_3Ge]_2SO_4$, found: SO_4, 23.7, 23.6; Ge, 34.3; mol. wt. (camphor), 400. Calcd., SO_4, 23.1; Ge, 35.0; mol. wt., 415.7. For $(C_2H_5)_2Ge(SO_4)$, found: SO_4, 43.7, 43.7; Ge, 31.7; mol. wt. (camphor), 422, 455. Calcd. for the dimer $[(C_2H_5)_2Ge(SO_4)]_2$: SO_4, 43.8; Ge, 32.1; mol. wt. 453.2.

Preparation of Diethylgermanium Sulfate.—In the best run 3.7 g. of 100% sulfuric acid (this is better than 30% oleum) and 2.20 g. of diethylgermanium oxide[7] reacted with vigor accompanied by darkening in color; even seven successive 7-ml. portions of boiling benzene failed to extract[1] diethylgermanium sulfate completely from the sulfuric acid layer. (Undeniably the yield of diethylgermanium sulfate *in situ* in the sulfuric acid layer exceeded 85%, although in the recrystallization the actual recovery as the pure solid was only about 40%.) Thereupon, enough of the benzene was evaporated to permit crystallization upon cooling to room temperature over a period of several hours. (Occasionally supersaturation occurred, involving a delay of several days in crystallization.) After siphoning off the mother liquor carefully, the crystals were recrystallized from fresh boiling benzene which had been dried with calcium chloride.

In this procedure the points for caution are: not to heat either diethylgermanium sulfate or a concentrated solution of it above 100°; to allow a two-hour settling whenever possible, to facilitate separation of droplets of sulfuric acid which were carried mechanically along with the benzene extract; to exclude moist air as completely as possible.

Properties of Diethylgermanium Sulfate.—A crystalline, white, fluffy solid melting at 115.5–116.5°; the bulkiness and porosity almost certainly render this sulfate undesirable in separation of trialkyl- and dialkylgermanium compounds. Solubility in benzene, 21 g./liter at 17.5°, 38 g./liter at 23°, and at least 100 g./liter at 80°.

Conversion of Diethylgermanium Sulfate into the Chloride.—Following the method previously devised,[2] 12 ml. of benzene, containing 0.49 g. of the organogermanium sulfate, together with 4 g. of dry, powdered ammonium sulfate yielded approximately 0.25 ml. of diethylgermanium dichloride, b. p. 172° (after a two-hour passage of dry hydrogen chloride into the mixture, followed by separation of the solid, and distillation).

In contrast, concentrated sulfuric acid did not react with diethylgermanium dichloride at any appreciable rate even at 150°.

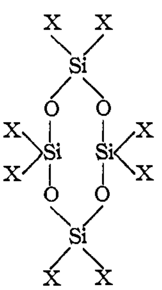
Polymeric Diethylgermanium Oxide.—In a test of Flood's observation[8] that polymeric diethylgermanium oxide, according to him a trimer, could be easily separated from bis-(triethylgermanium) oxide, the properties of the diethylgermanium oxide were reinvestigated. Upon treatment of diethylgermanium dichloride with excess aqueous sodium hydroxide, followed by extraction into redistilled petroleum ether (34–66°), then by drying (with calcium oxide) overnight, thereupon by centrifugal separation of the solid calcium oxide, and then by distillation of the solvent—a diethylgermanium oxide resulted which distilled at 128.5–129.5° under 3-mm. pressure. This preparation boiled at 291° under 762 mm., was absolutely colorless, upon the day of purification melted at 27.1 ± 0.5°, and had a molecular weight of 560 in camphor, indicating a tetramer since the monomer would be 146.6.

Dimethylsilicon Oxide and Sulfuric Acid.—In a procedure resembling that used in the final preparation of bis-(triethylgermanium) sulfate, 20 g. of liquid, polymeric dimethylsilicon oxide and an excess of 95% sulfuric acid failed, even at 140°, to form a compound such as $(CH_3)_2Si(SO_4)$.

Discussion

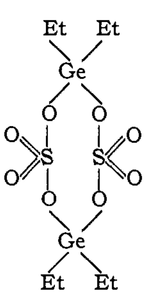
1. The existence of bis-(triethylgermanium) sulfate is completely in keeping with that of the previously known bis-(triethylsilicon) sulfate; however, the existence of (dimeric) diethylgermanium sulfate stands in contrast to the apparent lack of a reaction between polymeric liquid dimethylsilicon oxide and 95% sulfuric acid under comparable conditions. Herein the dialkylgermanium oxide appears to be more basic than the dialkylsilicon oxide, in accord with previously observed trends in the elements carbon, silicon, germanium and tin.

2. Dimeric diethylgermanium sulfate, Formula II, is probably an eight-membered ring; dialkylgermanium oxides such as the methyl, phenyl and possibly ethyl, Formula III, are also eight-membered rings; in addition, the $(SiOCl_2)_4$ and $(SiOBr_2)_4$ analogs, Formula I, are probably eight-membered rings. A melting point of 116° for dimeric diethylgermanium sulfate is consistent with the molecular symmetry which probably exists in eight-membered rings such as the silicon oxybromide, m. p. 123°, or the silicon oxychloride, m. p. 77°.

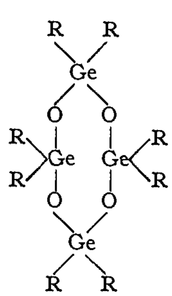


I

(X = Cl or Br)



II



III

($R = CH_3$, C_6H_5 or C_2H_5)

Summary

1. Bis-(triethylgermanium) oxide and 95%

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(6) Rochow, This Journal, 70, 1801 (1948).

(7) From pure diethylgermanium dichloride, kindly furnished by Professor Eugene G. Rochow, of Harvard University.

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

sulfuric acid react rapidly at 25°, yielding (new) bis-(triethylgermanium) sulfate, $[(C_2H_5)_3Ge]_2SO_4$. Bis-(triethylgermanium) sulfate melts at −4° into a colorless liquid which boils at 165° under 3-mm. pressure, or, with slight decomposition, at 342° under 760-mm. pressure. This sulfate is readily miscible with carbon tetrachloride, methyl acetate, carbon disulfide, cyclohexane, benzene and concentrated sulfuric acid. In the system $[(C_2H_5)_3Ge]_2O + H_2SO_4 \rightleftarrows [(C_2H_5)_3Ge]_2SO_4 + H_2O$ a concentration of 11 M in sulfuric acid produces one liquid phase, with a shift of the equilibrium to the right.

2. Tetrameric (or trimeric) diethylgermanium oxide, $[(C_2H_5)_2GeO]_{3\text{ or }4}$, and 100% sulfuric acid react rapidly at room temperature, yielding (new) dimeric diethylgermanium sulfate, $[(C_2H_5)_2Ge(SO_4)]_2$, a fluffy, crystalline white solid melting at 116°, and only moderately soluble in benzene, 21 g./l. at 17.5° and 38 g./l. at 23.5°.

3. Diethylgermanium oxide, previously found by Flood to polymerize easily, has polymerized very slowly in these studies, so slowly as to render separation of $[(C_2H_5)_3Ge]_2O$ and $[(C_2H_5)_2GeO]_4$ difficult in two instances. The polymeric form of diethylgermanium oxide appears to be variable, although Flood found it to be trimeric.

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[CONTRIBUTION FROM WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Ethylsilicon Isocyanates. Monopropylsilicon Isocyanates and Isothiocyanates

BY HERBERT H. ANDERSON*

In continuation of previous studies on alkylsilicon isocyanates and isothiocyanates, the present paper includes: the synthesis of all three ethylsilicon isocyanates, which are the second complete series of alkylsilicon isocyanates; the synthesis of *n*-propylsilicon triisocyanate, isopropylsilicon triisocyanate, *n*-propylsilicon triisothiocyanate and isopropylsilicon triisothiocyanate; an investigation of analytical possibilities including the titration of isocyanic acid, and also the unsuccessful use of semicarbazide hydrochloride to yield hydrazodicarbamide—in the actual procedure the hydrazodicarbamide weight was far short of the expected amount.

New Alkylsilicon Pseudo Halides

Preparation.—The following halides served as starting materials: $EtSiCl_3$, boiling at 98.5-98.6° under 771 mm. pressure, prepared from silicon tetrachloride and ethylmagnesium bromide, the presence of a little bromine being of no consequence in any of these reagents, since isocyanate and isothiocyanate both replace chlorine and bromine; Et_2SiCl_2, obtained similarly; Et_3SiCl, obtained pure, from Anderson Laboratories, Inc., of Adrian, Michigan; *i*-$PrSiCl_3$, boiling at 119.0-120.0° under 760 mm. pressure,[1] distilled from antimony trichloride to remove all bromine[2]; *n*-$PrSiCl_3$, boiling at 124-126°, prepared from silicon tetrachloride and *n*-propylmagnesium bromide.

For the most part, the preparations followed the previous general method used with silicon tetraisocyanate,[3] with methylsilicon triisocyanate,[4] and with methylsilicon isothiocyanates.[5] Twenty grams of the individual alkylchlorosilane and a 30% excess of silver isocyanate (or isothiocyanate) constituted the typical amounts, while the solvent varied somewhat; 50 ml. of benzene was satisfactory for the monoethyl and diethyl derivatives, with a half-hour of reflux.[3,5] However, the triethylsilicon reaction *was incomplete* under similar circumstances. To remedy this, 20 g. of Et_3SiCl and 30 g. of silver isocyanate were mixed with 30 ml. of nitromethane and 20 ml. of benzene, whereupon the temperature of the system rose from 18 to 40° within ten minutes, with good agitation; an hour on the steam-bath ensured completion of the reaction. (Nitromethane, at present under investigation, does not dissolve all organosilicon halides completely; hence dilution with benzene was advantageous.) A mixed solvent consisting of 90 volume % benzene and 10 volume % nitromethane was satisfactory in making *n*-propylsilicon triisocyanate and isopropylsilicon triisocyanate; although both reactions started slowy, they reached completion in an hour of reflux, and the purified liquid isocyanates contained no chlorine. *n*-Propylsilicon triisothiocyanate and isopropylsilicon triisocyanate were prepared in the usual manner,[5] with the addition of 0.05 ml. of water to serve as a catalyst. In all cases the yields were 80-90%.

Chemical Properties.—The hydrolysis of $EtSi(NCO)_3$ when shaken with an equal volume of water was slow at first, then speeded up in rate; this compound hydrolyzes at a slower rate than does $Si(NCO)_4$, and the amount of heat involved is less. When emulsified with water, $Et_2Si(NCO)_2$ hydrolyzes at a moderate rate, without detectable heat. Triethylsilicon isocyanate can be heated to 85° and shaken with water at the same temperature without a reaction of detectable speed or heat; however, if shaken with 50% ethanol the monoisocyanate reacts rapidly with warming. Both *n*-propylsilicon triisocyanate and isopropylsilicon triisocyanate when emulsified with an equal volume of water hydrolyze at an initially slow rate, but suddenly, after about five minutes, build up to a very fast rate of hydrolysis; because of this, such mixtures should never be prepared on a large scale. In comparison, it would be dangerous to shake either $Si(NCO)_4$ or $Si_2O(NCO)_6$[6] with an equal volume of water. All seven new compounds decompose completely within five minutes in 95% ethanol; they should all dissolve easily in a variety of organic solvents.

Physical Properties (See Table I).—All seven new compounds are colorless liquids of approximately the same viscosity as that of carbon tetrachloride. Triethylsilicon isocyanate had a camphoraceous odor, while the other isocyanates had an odor similar to that of isocyanic acid. Although the variation in indices of refraction of the new isocyanates is small, there is a more characteristic spread in densities and the observed molar refractions are in good

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(1) Booth and Spessard, THIS JOURNAL, **68**, 2660 (1946).

(2) See prototype in Schumb and Anderson, *ibid.*, **59**, 651 (1937).

(3) Forbes and Anderson, *ibid.*, **62**, 761 (1940).

(4) Forbes and Anderson, *ibid.*, **70**, 1222 (1948).

(5) Anderson, *ibid.*, **69**, 3049 (1947).

(6) Forbes and Anderson, *ibid.*, **69**, 3048 (1947).