buffers, and tetramethyl- and tetraethylammonium bromides. The following points are of special interest:

1. A reversible oxidation of chromous ion and a nearly reversible reduction of chromic ion occurs in saturated calcium chloride solutions at −0.51 v. *vs.* the S.C.E.
2. The thiocyanate complex is irreversibly oxidized with a half-wave potential of −0.85 v. *vs.* the S.C.E.; this potential is a function of the thiocyanate concentration.
3. In weak acids, no complex is formed and the wave is similar to that in potassium chloride. At higher *p*H, the oxidation wave is displaced negatively, but it becomes irregular or is suppressed completely.
4. The salicylate complex is an exception to (3), and in alkaline solution is reversible oxidized with a half-wave potential of −1.23 v. *vs.* the S.C.E. This complex is the most powerful reductant known in aqueous solution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Pseudo Halides of Silicon; Reactions of Pseudo Halides and Halides

BY HERBERT H. ANDERSON*

This article—a continuation of our earlier studies on pseudo halides of silicon—describes the preparation of three new substituted silicon isothiocyanates and one new substituted silicon isocyanate. In addition, eleven reactions involving halides and pseudo halides have been studied, five of which went to completion.

New Pseudo Halides

Preparation.—Two of the starting materials were made using the Grignard reagent, benzyltrichlorosilane and *n*-butyltrichlorosilane; triethoxychlorosilane, boiling range 154–157°, was prepared from tetrachlorosilane and absolute ethanol. The individual substituted chlorosilane was added gradually to a 25% excess of silver isothiocyanate, or silver isocyanate, suspended in benzene—with a final reflux for thirty minutes.[1] After the usual filtration and washing of the silver salts,[1] the benzene was distilled off, and center fractions of the pure pseudo halides collected under the conditions listed in Table I. In all cases the yields were approximately 80%. *n*-Butylsilicon triisothiocyanate foamed so severely during the removal of the last of the benzene that the addition of an antifoam, Dow Corning "Antifoam A," was necessary.

Analyses.—Each individual isothiocyanate was decomposed in absolute ethanol, with addition of water after two minutes; thereupon thiocyanate—in this place the word has no structural implication—was determined through titration with standard silver nitrate solution in the presence of ferric nitrate as indicator. Triethoxysilicon isothiocyanate *only* was analyzed (in June, 1947) *without weighing* as follows: the contents (at 24°) of a 0.401-ml. micropipet was delivered into absolute ethanol, rinsed with ethanol and then titrated as above, requiring 18.80 ml. of 0.1 *N* silver nitrate solution.[2] Calcd. for the *n*-butyl compound: H, 3.47. Found: H, 3.45.

Properties.—The chief numerical data of the new compounds are collected in Table I. Other properties are as follows: All of these substances are colorless when pure and hydrolyze rapidly without the evolution of much heat. Benzylsilicon triisothiocyanate is easily soluble in acetone, benzene and carbon disulfide, and is moderately soluble in hexane; thus it is definitely more soluble in these solvents than is methylsilicon triisothiocyanate.[3] *n*-Butylsilicon triisothiocyanate was readily soluble in the same solvents. For the triethoxysilicon compound: vapor pressure equation, $\log p = 8.1510 - 2524/T$; λ (calcd.) 11.3 kcal./mole; λ/T_B 24.1. Supercooling below the freezing point of the liquid took place in the following amounts: benzylsilicon triisothiocyanate, 36°; benzylsilicon triisocyanate, 44°; *n*-butylsilicon triisothiocyanate, 50°.

TABLE I

NEW COMPOUNDS

Compound	Distillation range °C.	Mm.	B. p., °C.	M. p., °C., ±1.0	n^{20} ±0.0010	d^{20}_4	Mol. refr. Calcd.	Mol. refr. Found	Mol. wt. Calcd.	Mol. wt. Found	Isothiocyanate Calcd.	Isothiocyanate Found
$(C_6H_5CH_2)Si(NCS)_2$	171–172	3	348.9 ± 1.0	36.0	....	1.275[a]	...	...	293	260[b]	59.4	59.32, 59.2
$(C_6H_5CH_2)Si(NCO)_3$	111–112	3	265 ± 2	−11.0	1.5230	1.225	60.2	61.1	245	235[b]	(17.14	16.81, 16.80)[d]
$(nC_4H_4)Si(NCS)_3$	135–136	3	300.6 ± 1.0	− 0.5	1.5928	1.189	73.9	73.7	259	239[b]	67.0	67.2, 66.6
$(C_2H_5O)_3Si(NCS)$	122.2–122.8	53	205.8 ± 0.5	....	1.4431	1.036	56.6	56.67	221	235[c]	26.24	26.3

[a] Supercooled liquid. [b] Through freezing point depression of camphor. [c] Dumas method. [d] Values of nitrogen determined as Kjeldahl ammonia, at New York University in 1948.

Silver isothiocyanate and either diethoxydichlorosilane or ethoxytrichlorosilane reacted, yielding a mixture of a liquid and a solid, undoubtedly $(C_2H_5O)_3Si(NCS)$ and $Si(NCS)_4$, respectively.

Reactions of Pseudo Halides and Halides

$SiCl_4$ + HNCO.—Gaseous isocyanic acid was bubbled through tetrachlorosilane at 30° for an hour, without any elevation of the boiling point such as would occur in the presence of $SiCl_3(NCO)$.[4]

$SiCl_3(SH)$ + AgNCO.—When 14 g. of the former was added gradually to a suspension of 60 g. of the latter in 80 ml. of benzene, there was a reaction with much heat and the silver salts turned black. After thirty minutes at 90°, the solution was filtered, with washing of the black silver salts; after distillation of the benzene, the liquid product boiled at 106° under 34-mm. pressure and contained no sulfur. $SiCl_3(SH) + AgNCO \rightarrow Si(NCO)_4{}^1 + Ag_2S + AgCl$.

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(1) Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

(2) For a later, smaller-scale modification see: Anderson, *ibid.*, **71**, 1801 (1949).

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

(4) Anderson, *ibid.*, **66**, 934 (1944).

$SiCl_2Br_2$.—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

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

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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).