[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Silicon Oxyisocyanates and Silicon Oxyisothiocyanate

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

The compounds formulated as Si_2OCl_6 and $Si_3O_2Cl_8$, also the corresponding bromides, are well known.[1] Large scale preparations of silicon isocyanate undertaken by us in 1944 had yielded residues the boiling points of which steadily increased, and were considerably higher than that of silicon (ortho) cyanate at the same pressure.[2] The present investigation indicates that these samples, before purification, contained several per cent. of silicon oxyisocyanates analogous to the above-mentioned oxyhalides. We have now isolated and studied these compounds: hexaisocyanatodisiloxane, $Si_2O(NCO)_6$, and octoisocyanatotrisiloxane, $Si_3O_2(NCO)_8$. In addition a single isothiocyanate, hexaisothiocyanatodisiloxane, $Si_2O(NCS)_6$, has been prepared. This series agrees with the general formula $Si_nO_{n-1}X_{2n+2}$ established by Schumb and co-workers[1] for the analogous chlorides and bromides. Evidence of the existence of still higher members of this oxyisocyanate series was encountered.

Experimental

I. Preparation of Silicon Oxyisocyanates

A. From Oxychloride and Silver Isocyanate.—Samples of the two silicon oxychlorides were prepared through partial hydrolysis of silicon tetrachloride in ether, following the recently described method of Schumb and Stevens.[3] The two pure compounds were separated through fractional distillation, and were completely converted to isocyanates by refluxing with silver isocyanate in 30% excess suspended in benzene solution.

Two ml. of Si_2OCl_6 and 12 g. of AgNCO ultimately furnished 1.6 ml. of solid having the m. p. 42° and b. p. 160° at 15 mm., in good agreement with the larger sample described in section C, and proved to have the formula $Si_2O(NCO)_6$ by analysis for silicon and nitrogen.

Sixty grams of silver isocyanate were suspended in 100 ml. of benzene, and approximately 3 g. of $Si_3O_2Cl_8$ was added; after refluxing for ten minutes, the reaction started. Thereupon 11 g. more of the oxychloride was added through the condenser in four portions at intervals with frequent cooling of the flask. After a half-hour of reflux, chloride was absent from the liquid phase. Washing of the silver salts with benzene proved inefficient, but several washings with warm acetone removed nearly all the adsorbed liquid isocyanate. The major portion of the solvent was evaporated at 760 mm. and the last portion at low pressure, with two liquid phases temporarily present. Vacuum distillation of the twelve gram product yielded a very small distillate of b. p. 55° at about 2.5 mm. (evidently silicon isocyanate) and then at 169–171° and about 2 mm. a main fraction, 5–6 g. in amount; subsequent analysis indicated the formula $Si_3O_2(NCO)_8$ for the clear light yellow liquid, the viscosity of which was perceptibly higher than that of silicon tetrachloride. A substantial residue of much higher viscosity and of very high boiling point was not further investigated.

B. Hexaisocyanatodisiloxane from Silicon Isocyanate and Water without a Solvent.—With some mechanical agitation, 4 ml. of water was added very gradually to 15 ml. of silicon isocyanate, while large amounts of isocyanic acid escaped as a gas. The residue contained 1.4 ml. only of hexaisocyanatodisiloxane together with 1 ml. of silicon isocyanate, and 2.7 ml. of higher boiling products.

C. Hexaisocyanatodisiloxane from Silicon Isocyanate and Water in Organic Solvents.—We followed the general method now being developed by Schumb and Stevens.[3]

Diethyl Ether.—Four ml. of water in 2800 ml. of ether was added at room temperature, over a period of five minutes, to 66 ml. of silicon isocyanate in 200 ml. of ether. After filtration of insoluble cyanuric acid and evaporation of ether, vacuum distillation yielded 38 g. of $Si(NCO)_4$, 23 g. of colorless $Si_2O(NCO)_6$ boiling at 160° at 14 mm., and also 11 g. of a yellowish residue containing higher oxyisocyanates of much higher b. p. and viscosity. Efforts to distil this residue at 1 mm. resulted in decomposition with loss of silicon.

Acetone.—Silicon isocyanate, unlike silicon tetrachloride, does not react with this solvent. Seventeen ml. of water in 170 ml. of acetone was added to 450 g. of silicon isocyanate in 150 ml. of acetone. Subsequently, 50 g. of $Si_2O(NCO)_6$ was obtained at 125° and 2 mm., together with 100 g. of higher oxyisocyanates, which could not be separated by distillation, by freezing or by crystallization from solvents.

Benzene.—Forty grams of $Si(NCO)_4$ in wet benzene yielded 6 g. of $Si_2O(NCO)_6$ and 1.5 g. of a higher residue. Thus is explained the presence of oxyisocyanates in the high-boiling final fraction of the large sample of silicon isocyanate mentioned in the first paragraph of this paper, prepared without rigorous exclusion of atmospheric moisture.

II. Preparation of Hexaisothiocyanatodisiloxane

Silicon isothiocyanate when mixed with a solution of water in benzene yielded much red thiocyanuric acid and apparently large amounts of other by-products. Therefore 20 g. of Si_2OCl_6 in 100 ml. of benzene was refluxed for half an hour with 90 g. of silver isothiocyanate. After filtration and washing, evaporation to 50 ml. volume yielded a first crop of crystals. Upon recrystallization from benzene at 20°, 6 g. of clear colorless crystals was obtained, with a solubility of 12 g. per 100 ml. of solvent. This sample of $Si_2O(NCS)_6$ melted at 120–121° using a capillary tube in a liquid bath.

III. Purification and Analysis

Hexaisocyanatodisiloxane, $Si_2O(NCO)_6$, was distilled at 163–164° under 14 mm. through a 30 cm., 4 mm. i. d. column without a spiral. Analyses for silicon by very careful hydrolysis and ignition gave 17.2 and 17.4% Si, calcd. 17.3% for $Si_2O(NCO)_6$; nitrogen (Dumas), found 26.0%, calcd. 25.9%. Octaisocyanatotrisiloxane, $Si_3O_2(NCO)_8$, gave 18.2 and 18.5% Si and 24.6% N compared with 18.6 and 24.8% calcd.

The percentage of silicon in crystallized hexaisothiocyanatodisiloxane, $Si_2O(NCS)_6$, found by hydrolysis and ignition was 13.6, higher than the calculated value of 13.3% because of the presence of some carbon in the ignited silica. Recalling the ease of determining isothiocyanate in liquid $(CH_3O)_3Si(NCS)$,[4] the analysis of $Si_2O(NCS)_6$ was undertaken similarly, by decomposition in absolute methanol, dilution with water and titration with silver nitrate solution in the presence of ferric iron. Two samples of $Si_2O(NCS)_6$ were prepared by separate distillations, in which middle fractions boiling at approximately 200° under 3 mm. were taken. These samples gave 83.5 and

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(1) Schumb and Klein, THIS JOURNAL, **59**, 261 (1937); Schumb and Holloway, *ibid.*, **63**, 2753 (1941), including references.

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

(3) Schumb and Stevens, *ibid.*, **69**, 726 (1947).

(4) Anderson, *ibid.*, **67**, 2176 (1945).

83.0% NCS, compared with 82.9% calculated for $Si_2O(NCS)_6$.

Molecular weights were determined by depression of the freezing point of camphor. Hydrolysis during the measurements was at least partly responsible for the low values observed, but all these substances were shown to be monomeric. For $Si_2O(NCO)_6$ found 317, calcd. 324; for $Si_3O_2(NCO)_8$ found 417, calcd. 452; for $Si_2O(NCS)_6$ found 390, calcd. 421.

IV. Physical Properties

Hexaisocyanatodisiloxane, a white solid, melted at 44.5° to a clear colorless liquid boiling at 163° at 14 mm., at 190° at 63 mm., or at approximately 260° and one atmosphere—in the last case with decomposition. A specimen originally boiling at 260° and one atmosphere boiled at 235° after a half hour, without formation of silica. This indicates a reaction such as $Si_2O(NCO)_6 \rightarrow Si(NCO)_4 + Si_4O_3(NCO)_{10}$, in general agreement with previous observations on the partial instability of Si_2OCl_6[5] and Si_2OBr_6.[1] The vapor pressure data were not accurate enough for calculation of the heat of vaporization. To determine the molar refraction of the oxyisocyanate as a liquid at 20° its melting point was lowered by a sufficient quantity of silicon isocyanate the molar refraction of which is 37.29 ml. From the law of mixtures the molar refraction of the oxyisocyanate is 57.4 ml.

Octoisocyanatotrisiloxane remained a viscous yellowish liquid even at −78°; it boiled at 170° and 2 mm. Direct measurement gave $d^{20}{}_4$ 1.508 and index of refraction 1.4658 in white light, from which a molar refraction of 78.1 ml. results.

Hexaisothiocyanatodisiloxane, a white crystalline solid, melted into a clear and nearly colorless liquid at 120–121°. A specimen previously distilled under low pressure showed an initial boiling point of 347°; in light of the low thermal stability of $Si_2O(NCO)_6$ even this first reading was noted with reservations.

Solubilities.—The oxyisocyanates are apparently completely miscible with acetone and with 1,4-dioxane, but are not completely miscible with carbon disulfide, carbon tetrachloride, benzene and diethyl ether.

Comparison of Molar Refractions.—Stoichiometrically, $Si(NCO)_4 + Si_3O_2(NCO)_8 = 2Si_2O(NCO)_6$ and the numbers of silicon–oxygen bonds are identical but $R_{Si(NCO_4)}$[6] $+ R_{Si_3O_2(NCO)_8} = 37.29 + 78.1$ or 115.4 ml. and $2R_{Si_2O(NCO)_6} = 114.8$. Apparently two linkages to oxygen on a single silicon atom have less effect than two such linkages distributed between two silicon atoms.

Summary

1. The oxyisocyanates and oxyisothiocyanate of silicon exemplify a new type of pseudo halide. As earlier attempts to isolate hexaisocyanatodisilane, $Si_2(NCO)_6$, had been unavailing, the stabilizing effect of the Si–O–Si bonding is apparent. Hexaisocyanatodisiloxane, $Si_2O(NCO)_6$, melts at 44.5° into a colorless liquid boiling at 163° and 14 mm., or at 260° and 760 mm. with decomposition. It may be prepared from Si_2OCl_6 and silver isocyanate, or from silicon isocyanate and water, either with or without a solvent. Octoisocyanatotrisiloxane, $Si_3O_2(NCO)_8$, is a clear light-yellow liquid boiling at 170° and 2 mm.; it is made from $Si_3O_2Cl_8$ and silver isocyanate, rather than by controlled hydrolysis of silicon isocyanate. The existence of higher oxyisocyanates is indicated, but the separation of these would be exceptionally difficult.

2. Hexaisothiocyanatodisiloxane, $Si_2O(NCS)_6$, melting at 120–121°, is prepared from Si_2OCl_6 and silver isothiocyanate, followed by recrystallization from benzene.

3. Acetone and 1,4-dioxane are very good solvents for the oxyisocyanates, while benzene, carbon disulfide, carbon tetrachloride and diethyl ether are unexpectedly poor solvents, in view of the high solubility of silicon isocyanate in the same solvents.

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(5) Troost and Hautefeuille, *Ann. chim. phys.*, [5] **7**, 452 (1876).

(6) Forbes and Anderson, *ibid.*, **66**, 1703 (1944).

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Methyl Silicon Isothiocyanates. Molar Refractions

BY HERBERT H. ANDERSON

Previous efforts in this Laboratory to prepare certain complete series of mixed compounds have yielded monoisothiocyano derivatives[1] exclusively—silicon trimethoxyisothiocyanate and trichloroisothiocyanate; phosphorus difluoroisothiocyanate and dichloroisothiocyanate; phosphoryl dichloroisothiocyanate. Several considerations suggested that methyl groups in such molecules would greatly retard disproportionation and favor isolation of compounds containing two or three isothiocyano groups. The preparation of all three methyl silicon isothiocyanates has now fulfilled this prediction, and measurements of molar refractions have identified them as isothiocyanates.

Preparation of Methyl Silicon Isothiocyanates.—The Dow Corning Corporation of Midland, Michigan, kindly furnished the samples of pure trimethylchlorosilane, dimethyldichlorosilane and methyltrichlorosilane used in this investigation. In accordance with the established method,[2] a 30% excess of silver isothiocyanate converted each individual chloride into the corresponding isothiocyanate in benzene or hexane as a solvent; the yield was always about 85% of the theoretical amount. After thirty minutes at 80–90°, the suspended silver salts were filtered off and washed; the solution was then distilled. Repeated distillations in all-glass systems with a 50 cm., 4 mm. i.d. column without packing produced the follow-

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(1) Anderson, THIS JOURNAL, **67**, 223, 2176 (1945); **69**, 2495 (1947).

(2) Forbes and Anderson, *ibid.*, **62**, 761 (1940); Anderson, *ibid.*, **64**, 1757 (1942).