tion, and other experimental conditions which change during a single experiment.

Discussion of Results

The heat of hydrolysis of pyrophosphate in dilute aqueous solution, catalyzed by non-crystalline enzymes, was reported by Ohlmeyer and Shatas[7] to be $\Delta H = -8950$ (average deviation = ± 440) cal. per mole. Their solutions contained initially 2×10^{-3} *M* pyrophosphate, 2×10^{-3} *M* orthophosphate and 2.5×10^{-4} *M* $MgCl_2$, and were buffered at *p*H 7.2 by 0.024 *M* veronal. Their measurements were carried out at 29°. The value for ΔH which we obtained in veronal buffer (Table I) is -7310 cal. per mole, 18% lower. The cause of this discrepancy is unknown.

A considerably more negative value for ΔH than -5810 cal. per mole is expected for the hydrolysis of a high energy phosphate bond. It is interesting to note that Berthet, Thibaut and Berthet[13] have obtained preliminary results indicating an unexpectedly small apparent equilibrium constant for this reaction.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A New Series of Silicon Oxychlorides[1]

BY WALTER C. SCHUMB AND ROBERT A. LEFEVER[2]

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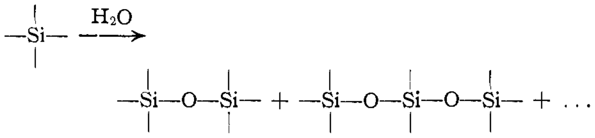
The partial hydrolysis of hexachlorodisilane, Si_2Cl_6, at −78° was found to result in a new series of silicon oxychlorides, represented by the general formula, $Si_{2n+2}O_nCl_{4n+6}$. The distinguishing feature of these compounds is the presence of alternating Si–Si and Si–O–Si linkages as the basic structure of the molecule. The first three members of the series, Si_4OCl_{10} (b.p. 130–131° (15 mm.)), $Si_6O_2Cl_{14}$ (b.p. 159–162° (3 mm.)), and $Si_8O_3Cl_{18}$ (b.p. 170–173° (2 mm.)), have been isolated and identified.

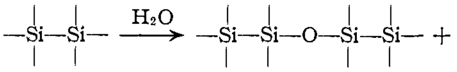
Introduction

Although it had been known for some time that the direct chlorination of silicon and calcium silicide produced higher chlorides of the series Si_nCl_{2n+2}, it was not until 1941[3] that the existence of an analogous series, $Si_nO_{n-1}Cl_{2n+2}$, of silicon oxychlorides was clearly established by Schumb and Holloway. The oxychlorides were prepared in this work by the action of a mixture of oxygen and chlorine on silicon at red heat. The absence of appreciable quantities of higher chlorides of silicon in the products was noted indicating that the silicon–silicon bonds were effectively ruptured in the process.

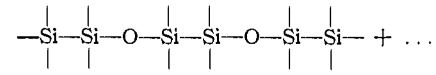
In 1950, Schumb and Stevens[4] reported the preparation of oxychlorides of the series $Si_nO_{n-1}Cl_{2n+2}$, by the partial hydrolysis of silicon tetrachloride at −78°. The success of this method suggested to us a possible means of preparing oxychlorides containing alternating Si–Si and Si–O–Si linkages in the same molecule. Thus, in a reaction analogous to the partial hydrolysis of silicon tetrachloride (bonds without second atoms refer to chlorine bonds), the partial hydrolysis of hexachlorodisilane might be expected to result in a new series of oxychlorides by the reaction



$$-\overset{|}{\underset{|}{Si}}- \xrightarrow{H_2O} -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + \ldots$$



$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}- \xrightarrow{H_2O} -\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}- +$$



$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{Si}}- + \ldots$$

Although rupture of Si–Si bonds could yield oxychlorides of the established series (actually, evidence for the occurrence of such a side reaction during hydrolysis was not found), higher chlorides would not be expected, thus simplifying the problem of separation.

In a preliminary communication,[5] isolation of the first member, Si_4OCl_{10}, of the new series, $Si_{2n+2}O_nCl_{4n+6}$, was reported. In the following work, further evidence for the existence of this compound as well as the second, $Si_6O_2Cl_{14}$, and third, $Si_8O_3Cl_{18}$, members of the new series is presented.

Experimental

Procedure.—Hexachlorodisilane was diluted with anhydrous diethyl ether, cooled to −78° in a solid carbon dioxide–trichloroethylene bath and hydrolyzed by the gradual addition of a measured quantity of water. The hexachlorodisilane used in this work was prepared by the chlorination of calcium silicide as described in reference 6. Analytical reagent ether was redistilled and stored over sodium.

The reactions were carried out in a 1-liter, three-necked round-bottom flask fitted with a mercury-seal stirrer. One neck of the flask was connected directly to a water condenser to allow removal of ether after the reaction, while the other neck was used for the introduction of reagents. The hexachlorodisilane was added to the ether in the flask and the mixture was cooled, with stirring, to −78°. The desired quantity of water was then added dropwise from a 10-ml. buret. After the addition of water, the contents of the flask was held at −78°, with constant stirring, for about two hours and then allowed to warm to room temperature. The amounts of ether, hexachlorodisilane and water were varied in order to obtain information concerning the optimum molar ratios for oxychloride formation.

After removal of the ether by distillation directly from the reaction flask, the remaining material was transferred to a fractionation column. The unreacted hexachlorodisilane (b.p. 45° (15 mm.)) was recovered by fractionation under

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(1) Based on part of a thesis presented by R. A. Lefever to the Department of Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Owens–Illinois Research Fellow, 1952–1953.

(3) W. C. Schumb and D. F. Holloway, THIS JOURNAL, **63**, 2753 (1941).

(4) W. C. Schumb and A. J. Stevens, *ibid.*, **72**, 3178 (1950).

(5) W. C. Schumb and R. A. Lefever, *ibid.*, **75**, 1513 (1953).

(6) H. S. Booth, Ed., "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 42–45.

reduced pressure and reserved for further partial hydrolysis reactions. The material remaining was combined with like products of further partial hydrolysis reactions and then subjected to fractional distillation under reduced pressure.

A 21-inch helix-packed column, electrically heated, was used to separate the oxychlorides. The still-head was fitted with an automatic, magnetically operated take-off device.

Analytical.—Small thin-walled Pyrex tubes were weighed and filled by pipetting the sample directly from the storage ampule. Precautions against hydrolysis were found to be unnecessary if the transfer was effected rapidly. Silicon was determined gravimetrically by the following method. The bulb with sample was broken by agitation in a 250-ml. ground glass stoppered erlenmeyer flask containing 50 ml. of dilute nitric acid. The contents of the flask were heated almost to boiling and 10-ml. portions of fuming nitric acid were added at intervals until the formation of silicic acid was observed. After completion of the reaction, the silicic acid was filtered and ignited in the usual manner and corrected for the weight of the sample bulb to give the amount of silica resulting from the sample.

TABLE I

MOLAR RATIOS EMPLOYED AND QUANTITIES OF HEXACHLORODISILANE HYDROLYZED

Run	Si_2Cl_6, g.	Ether volume, ml.	Ether–Si_2Cl_6 molar ratio	Si_2Cl_6 recovd., g.	% Si_2Cl_6 reacted
1	180	520	7.5	210	41
2	174	520	7.7		
3	210	700	8.6	130	38
4	210	520	6.5	122	42
5	122	520	11	74	39

Chloride determinations were made by breaking the sample bulb in a ground glass stoppered erlenmeyer flask containing water and titrating the liberated hydrogen chloride with a standard solution of sodium hydroxide. After the chloride determination, a volume of 40% sodium hydroxide equal to the volume of the contents of the flask was added thereto. The evolved hydrogen was collected in a gas buret by displacement of mercury. After allowing to cool to room temperature, the volume of hydrogen was measured and corrected to standard conditions.

Molecular weights were determined by the Beckmann freezing point method, using *p*-dioxane (USP quality, fractionally distilled from sodium; b.p. 100.8–101.5°) as the cryoscopic solvent. To prevent access of atmospheric moisture during measurements, the stirrer was fitted with a tube containing a side arm through which a rapid flow of dry nitrogen was maintained. After obtaining the freezing point of the solvent, the sample bulb was added and broken just prior to measuring the freezing point depression.

Results.—In a total of five reactions, 360 g. of hexachlorodisilane was partially hydrolyzed. A hexachlorodisilane–water molar ratio of four was used throughout, while the ether–hexachlorodisilane molar ratio was varied. The data pertaining to these reactions are summarized in Table I. The amount of solid material formed on hydrolysis was considerable in run 4, negligible for run 5 and moderate for the other runs. Since the percentage of hexachlorodisilane reacted was approximately the same in all cases, high dilution can be seen to favor oxychloride formation.

Before the addition of water, the cold ether solution of hexachlorodisilane was colorless to pale yellow. As the water was added, a pronounced color change through yellow to yellow-green, requiring about five minutes for completion, was observed. As the solution was allowed to warm, a lemon-yellow color resulted. During the initial stages of the removal of unreacted hexachlorodisilane under reduced pressure, a yellow solid sublimed onto the walls of the condenser. Attempts were made to isolate this material, but the quantity proved too small for identification.

The results of the fractionation of the combined higher boiling partial hydrolysis products and analyses of the resulting fractions are summarized in Table II. About 3 ml. of material was removed before the first temperature plateau was observed at 130–131° (15 mm.). After removal of this fraction, the pressure was reduced to about 3 mm. to attempt the prevention of thermal decomposition observed in preliminary investigations. A second plateau was observed at about 159–162° (3 mm.), while a third plateau occurred at about 170–173° (2 mm.). The large variations in temperature with changes in pressure (greater than 5°/mm. in the latter case) caused some difficulty in the accurate determination of boiling points.

As the reflux temperature gradually increased above 170° (2 mm.), the column began to operate erratically. Flooding in the still-head became increasingly difficult to avoid, while behavior in general indicated the presence of low boiling material. After increasing the temperature to 220° without the appearance of a plateau, fractional distillation was discontinued and the column allowed to cool. About 5 ml. of material boiling between 46° (15 mm.) and 145° (15 mm.) was found in the pot, indicating that some decomposition had taken place.

TABLE II

FRACTIONATION AND ANALYTICAL DATA

Fraction	B.p. °C.	Mm.	Approx. amount, ml.	Chlorine, %		Silicon, %		Mol. wt.		Si–Si bonds (from hydrogen evolution)		Compound[a]
				Found	Theory	Found	Theory	Found	Theory	Found	Theory	
1	130–131	15	18	73.4	73.4	23.2	23.3	478	483	1.95	2	Si_4OCl_{10}
				73.4		23.1		472		1.90		
				73.2								
2	159–162	3	10	71.1	71.2	24.3	24.2	739	697	2.8	3	$Si_6O_2Cl_{14}$
				71.1		24.3		723		2.73		
				71.0		24.1				2.75		
3	170–173	2	4	70.3	70.1	24.5	24.7	906	911	3.76	4	$Si_8O_3Cl_{18}$
				70.0		24.6		881		3.73		
				70.1		24.8				3.77		

[a] Members of the homologous series $Si_{2n+2}O_nCl_{4n+6}$.

Discussion

The analytical data given in Table II indicate that the first three members of a new series of silicon oxychlorides, of the general formula $Si_{2n+2}O_nCl_{4n+6}$, have been isolated and identified. Although the number of Si–Si bonds calculated from hydrogen evolution data are 5–10% low, the same situation was found to be true for pure hexachlorodisilane. This may result from the rupture of some of the bonds during the initial hydrolysis.

The samples were all colorless liquids, increasing in viscosity with increasing boiling point. Only the first member was found to fume slightly on exposure to the air. Treatment with water caused immediate hydrolysis yielding a white solid, and, when dry, this solid sputtered and burned in a manner similar to the hydrolysis product of hexachlorodisilane when ignited. Although the first member supercooled to about −50° before crystallizing, it appeared to melt between −5° and −10°. When cooled in a solid carbon dioxide–trichloroethylene bath, the second and third members became highly viscous liquids from which fine crystals were deposited after several hours. When rapidly cooled in liquid nitrogen, they gradually solidified to transparent glassy solids.

The boiling point recorded for Si_4OCl_{10} is higher than the value reported in the preliminary communication (120–123° (13 mm.)). While part of this discrepancy is due to the difference in pressure (the temperature variation with pressure was found to be 2–3°(mm.)), the original value is still low, probably as a result of the small amounts of material and relatively large fractionating column used in the preliminary investigations.

The infrared absorption curves reproduced in Fig. 1, were taken on a Baird model B spectrophotometer with an 0.025 mm. sample cell against a salt block reference cell. Undiluted samples of the first (Si_4OCl_{10}) and third ($Si_8O_3Cl_{18}$) members of the series were compared with hexachlorodisilane and hexachlorodisiloxane. The pronounced absorption band at 9 μ occurs at the same position as the C–O absorption band in saturated organic ethers and is presumably associated with the Si–O bond.

The following Raman lines were obtained for Si_4OCl_{10} and compared with hexachlorodisilane and hexachlorodisiloxane as well as published information: 111 (10), 135 (10), 194 (7), 306 (7), 335 (1), 353 (4), 459 (1), 591 (9), 631 (7), and 683 (1) cm.$^{-1}$. These lines cannot be considered to constitute the complete spectrum, since a relatively high degree of scattering made it impossible to identify the weaker lines. By comparison with the published Raman data for hexachlorodisilane[7,8] and oxychlorides of the series, $Si_nO_{n-1}Cl_{2n+2}$,[9] it can be seen that the compound under consideration does not contain any appreciable amounts of any of these. If, for example, the 335 cm.$^{-1}$ line were the result of hexachlorodisiloxane contamination, the stronger 424 cm.$^{-1}$ line of the latter oxychloride would be expected to be present as well. Likewise, if hexachlorodisilane were responsible for any of the lines, its strong line at 211 cm.$^{-1}$ would be expected to appear. Katayama, *et al.*, assigned the hexachlorodisilane line at 622 cm.$^{-1}$ to the Si–Si bond vibration. In view of the fact that a line in this vicinity occurs in all of the oxychlorides, while a line in the vicinity of 590 cm.$^{-1}$ occurs only in the two compounds containing Si–Si bonds, it would appear that the latter frequency is more likely to be associated with this bond.

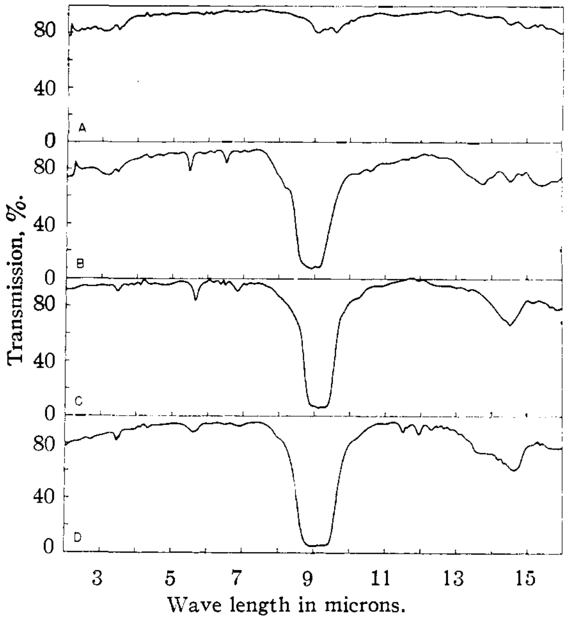

Fig. 1.—Infrared absorption spectra: (A) Si_2Cl_6, (B) Si_2OCl_6, (C) Si_4OCl_{10}, (D) $Si_8O_3Cl_{18}$. Instrument, Baird model B spectrophotometer; state, liquid; solvent, none; temperature, 20–25°; cell length, 0.025 mm.; reference cell, salt block.

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(7) M. Katayama, T. Simanouti, Y. Morino and S. Mizushima, *J. Chem. Phys.*, **18**, 507 (1950).

(8) F. Stitt and D. M. Yost, *ibid.*, **5**, 90 (1937).

(9) J. Goubeau and R. Warncke, *Z. anorg. Chem.*, **259**, 234 (1949).