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

The Thiochlorides of Silicon[1]

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An investigation has been made to determine the existence of a homologous series of chlorosilthianes, as an analog of the homologous series of chlorosiloxanes. It was found that the thermal decomposition of trichlorosilanthiol results in a small yield of hexachlorodisilthiane, the first member of the expected series, and octachlorocyclotetrasilthiane. No evidence was found for higher members of the series. Hexachlorodisilthiane was also synthesized by the reaction between silver sulfide and iodotrichlorosilane at 250°.

Within recent years it has been shown that the partial hydrolysis of silicon tetrachloride[3] leads to a homologous series of oxychlorides of the general formula $Si_{n+1}O_nCl_{2n+4}$ and in a like manner hexachlorodisilane[4] yields a series represented by the general formula $Si_{2n+2}O_nCl_{4n+6}$. Schumb and Towle have also prepared the first member of a series of chlorosilazanes by the ammonolysis of silicon tetrachloride.[5] From these considerations it was believed that a series of chlorosilthianes would also be capable of formation by the reaction between hydrogen sulfide and silicon tetrachloride. The work of previous investigators indicated that the only volatile products of this reaction were the colorless liquid, Cl_3SiSH,[6] and the white crystalline solid, $SiSCl_2$.[7]

In the present work it was found that H_2S and $SiCl_4$ give no evidence of reaction below 500° but above that temperature a slow reaction takes place. The initial product is trichlorosilanthiol, Cl_3SiSH, and further reaction leads to a small yield of $SiSCl_2$. The latter compound, reported by Étienne to be dimeric,[8] in our measurements was found to be tetrameric. Calcd. for $Si_4S_4Cl_8$: mol. wt., 524. Found: mol. wt., 536, 497. The tetrameric formula indicated a further analogy with the chemistry of silicon with oxygen, corresponding to the well known cyclic tetramers, $(SiOCl_2)_4$ and $(SiOBr_2)_4$. The systematic name for this substance is octachlorocyclotetrasilthiane.

The major products of reaction are silicon disulfide and a polymerized solid of uncertain composition. The higher the temperature at which the reaction is carried out, the smaller is the yield of Cl_3SiSH, due to the increased formation of non-volatile products, the optimum temperature for reaction being 650°. Members of the homologous series of chlorosilthianes were not observed by the continuous reaction between H_2S and $SiCl_4$; but the first member of the series, hexachlorodisilthiane, Si_2SCl_6, was identified in the thermal decomposition products of Cl_3SiSH in the absence of H_2S. This previously unreported compound would be expected to result from the condensation of two molecules of Cl_3SiSH with elimination of H_2S. Analysis of the gaseous products of decomposition showed that both H_2S and HCl were formed. The source of HCl was presumed to be the intramolecular decomposition of Cl_3SiSH, giving rise to $(SiSCl_2)_4$ which was also observed as a product of the reaction.

The small yields of both Si_2SCl_6 and $(SiSCl_2)_4$, and the fact that their boiling points lie close together (approximately 75 and 80°, respectively, at 17 mm.) prevented complete separation by fractional distillation. Positive identification of Si_2SCl_6 as a product of the reaction was obtained by comparison of its Raman spectrum with the spectra of pure Si_2SCl_6 and a 40% solution of $(SiSCl_2)_4$ in benzene. The two strongest lines of $(SiSCl_2)_4$ were observed in the spectrum of the mixture and all the rest were attributed to Si_2SCl_6, as shown in Table I.

TABLE I

THE RAMAN SPECTRA OF Si_2SCl_6 AND $(SiSCl_2)_4$

Si_2SCl_6		Cl_3SiSH decomp. product		$(SiSCl_2)_4$ in benzene	
$\Delta\bar{\nu}$ (cm.$^{-1}$)	Intensity	$\Delta\bar{\nu}$ (cm.$^{-1}$)	Intensity	$\Delta\bar{\nu}$ (cm.$^{-1}$)	Intensity
118	5	116	5		
136	5	134	5	135	2
191	5	193	4	175	2
228	4	222	4	215	6
266	2	262	1.5		
		277	0	280	6
397	10	396	10		
		435	1.5	433	10
546	0	543	0		
592	2W	592	2W		
631	1	630	1		

There was no evidence of any higher members of the expected series of silthianes in the products of decomposition of Cl_3SiSH. Si_2SCl_6 and $(SiSCl_2)_4$ were actually minor constituents, the major products being $SiCl_4$ and a non-volatile solid corresponding closely to the composition $Si_2S_3Cl_2$.

The action of Cl_2 on silicon disulfide was also studied as a possible source of chlorosilthianes. The major products at 700° were $SiCl_4$ and $(SiSCl_2)_4$, as well as free sulfur. The yield of $(SiSCl_2)_4$ was about 10%. Fractional distillation of the product showed that a small amount of Si_2SCl_6 was also formed. This is presumably the liquid which Besson reported as a product of the reaction, but did not identify.[9] It was found that below 700° the reaction resulted almost completely in $SiCl_4$, and again above 750°. The failure to obtain increased yields of chlorosilthianes at higher temperatures was found to be due to the instability of such compounds. A run at 800°

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[1] Based on part of a thesis presented by W. J. Bernard to the Department of Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] National Science Foundation Fellow, 1953–1954.

[3] W. C. Schumb and A. J. Stevens, THIS JOURNAL, **72**, 3178 (1950).

[4] W. C. Schumb and R. A. Lefever, *ibid.*, **76**, 2091 (1954).

[5] W. C. Schumb and L. H. Towle, *ibid.*, **75**, 6085 (1953).

[6] C. Friedel and A. Ladenburg, *Ann.*, **145**, 179 (1868); *Ann. chim. phys.*, **27**, 416 (1872).

[7] M. Blix and W. Wirbelauer, *Ber.*, **36**, 4220 (1903).

[8] Y. Étienne, *Bull. soc. chim. France*, 791 (1953).

[9] A. Besson, *Compt. rend.*, **113**, 1040 (1891).

resulted in the deposition of SiS_2 in a zone of the reaction tube beyond the point at which the disulfide had been placed. Since SiS_2 has a negligible vapor pressure at this temperature, the formation of the disulfide must have been due to the decomposition of $(SiSCl_2)_4$ and Si_2SCl_6, the other product being $SiCl_4$. The action of chlorine on silicon monosulfide was studied at lower temperatures. At 170° the products of reaction were identified as SCl_2, S_2Cl_2, $SiCl_4$ and Si_2Cl_6.

Experimental

Procedure.—In the thiohydrolysis experiments $SiCl_4$ was recycled by use of an all-glass apparatus constructed of Pyrex and Vycor tubing. This piece of equipment was similar to that described by Blix[7] except that standard-taper ground joints were used to connect the flask and the water condenser to the system, and the return line was joined by a side-arm ring seal to the entrance line. The section of the apparatus made of Vycor was used as the reaction tube. The flask containing $SiCl_4$ was equipped with a thermometer well and connected to the cyclic apparatus by means of a 24/40 standard-taper joint. The flask contents were electrically heated and kept constantly boiling during the course of a run. Hydrogen sulfide, which was bubbled into the flask, was previously dried by passing through Drierite and P_2O_5. The volatility of $SiCl_4$ (vapor pressure = 76 mm. at 0°) did not permit satisfactory condensation by the water condenser and to prevent undue loss a trap cooled to $-78°$ was used beyond the condenser. H_2S was also condensed to a certain extent by this trap and before returning $SiCl_4$ to the flask it was necessary to allow the trap to warm to room temperature. A P_2O_5 drying tube was connected to the exit of the trap to prevent diffusion of atmospheric moisture into the system. Before each run the entire apparatus was thoroughly flushed with an inert gas.

Cl_3SiSH was prepared in desired quantities by use of this equipment. In a typical run 65 g. of $SiCl_4$ yielded, upon distillation, 26 g. of Cl_3SiSH in 14.5 hours, corresponding to a yield of 40%. H_2S was passed in at the rate of 4 bubbles per second and the temperature of the reaction tube was 650°. As well as being easily affected by moisture, Cl_3SiSH is extremely sensitive to oxygen, which causes sulfur to precipitate. For this reason vessels and other apparatus were thoroughly flushed with carbon dioxide before introducing the liquid. Cl_3SiSH may be distilled at atmospheric pressure; its boiling point is 95.0° at 768 mm. *Anal.* Calcd. for Cl_3SiSH: Si, 16.77; S, 19.14; Cl, 63.49. Found: Si, 16.75, 16.25; S, 18.38, 19.13; Cl, 63.80, 63.78.

The thermal decomposition of Cl_3SiSH was carried out by passing the vapors of the thiol in a stream of helium through a tube heated to 650° and condensing the products at $-78°$. Repeated fractionation of the products resulted in a colorless liquid boiling at 98° at 47 mm. *Anal.* Calcd. for Si_2SCl_6: Si, 18.64; S, 10.66; Cl, 70.70; mol. wt., 301. Calcd. for $(SiSCl_2)_4$: Si, 21.43; S, 24.47; Cl, 54.10; mol. wt., 524. Found: Si, 19.68, 19.97, 20.15; S, 11.48, 11.29; Cl, 68.89, 68.90; mol. wt., 313, 327, 334. On the basis of the analysis for Cl, it was calculated that the liquid contained 90% Si_2SCl_6. $(SiSCl_2)_4$ was not obtained as a pure substance from this distillation but was wet with Si_2SCl_6. It could be separated from the liquid by filtration and pressing dry on the filter paper. Further purification could be achieved by recrystallizing from benzene in a stream of dry nitrogen. *Anal.* Found: Si, 20.60, 21.85; S, 23.54, 23.67, 23.87; Cl, 53.93, 54.10.

The preparation of Si_2SCl_6 was carried out by means of the reaction between iodotrichlorosilane and silver sulfide. Eaborn[10] was able to prepare hexamethyl- and hexaethyldisilthiane in good yield by refluxing trimethyl- and triethyliodosilane with Ag_2S, but in this case simple refluxing of $SiCl_3I$ with Ag_2S failed to bring about reaction and it was necessary to use a higher temperature. The reaction was carried out in a bomb constructed of heavy-walled 25 mm. o.d. Pyrex tubing. The bomb was charged with 42 g. of $SiCl_3I$ and the theoretical amount of Ag_2S needed for complete reaction, sealed, and heated for 17 hours at 230–250°. The liquid product of reaction was decanted and the yellow solid in the bomb was extracted three times with benzene, the washings being added to the liquid product. The benzene was removed by distillation at atmospheric pressure and the remaining liquid was distilled at 50 mm. Si_2SCl_6 boiled at 100–100.5°, 5 ml. being collected. A slight discoloration of the product, due to free I_2, was eliminated by shaking with Hg and redistilling under vacuum at room temperature. The resulting clear, colorless liquid when cooled to $-78°$ formed a white solid melting at $-45°$. The recovered yield was 7 g., or 30%, based on the amount of $SiCl_3I$ used. *Anal.* Calcd. for Si_2SCl_6: Si, 18.64; S, 10.66; Cl, 70.70; mol. wt., 301. Found: Si, 19.22, 18.76; S, 10.82, 10.81; Cl, 69.78, 70.00; mol. wt., 289, 306.

$SiCl_3I$ was prepared by the high temperature reaction between HI and $SiCl_4$.[11] Hydrogen was passed over the surface of boiling $SiCl_4$ and then over iodine heated just below its melting point. The mixture of gases was then passed through a Vycor tube heated to 700° and the products were collected in a flask cooled to $-78°$. Free I_2 was eliminated from the products by distilling over mercury. The fraction boiling between 110–117° was collected in glass receivers which were immediately sealed.

SiS_2 was prepared by the metathetical reaction between aluminum sulfide and silica,[12] and the monosulfide was prepared by the reaction between SiS_2 and Si.[13] Chlorination of these compounds was carried out using helium as a diluent. A diluting gas was found to be particularly necessary in the case of the chlorination of SiS, since that compound reacts with great ease with oxidizing agents.

Analytical.—All samples for analysis and molecular weights were prepared in a dry, inert atmosphere. Liquid samples were pipetted into weighed thin-walled glass bulbs, which were immediately sealed with an oxygen torch after being removed from the dry-box.

Sulfur was determined by decomposing the sample under an excess of standard acidified I_2 solution, the excess I_2 being titrated with standard sodium thiosulfate solution. Samples for chlorine and silicon determinations were decomposed under 200 ml. of distilled water so that the resulting acid solution was about $0.01N$ H_2S, which would interfere with the subsequent titration, was removed by boiling the solution cautiously for a few minutes. This procedure does not result in the loss of any HCl.[14] Silicon was determined in the resulting solution as silica by the usual procedure.

Molecular weights were determined by the Beckmann freezing-point method in benzene.

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[10] C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

[11] P. Hautefeuille, *Bull. soc. chim.*, [2] **7**, 198 (1867).

[12] E. Tiede and M. Thimann, *Ber.*, **59**, 1703 (1926).

[13] W. C. Schumb and W. J. Bernard, THIS JOURNAL, **77**, 904 (1955).

[14] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947, p. 545.