

*The Products from the High-temperature Reaction between Silicon Tetrachloride and Hydrogen Sulphide.*

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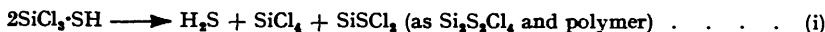
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Silicon tetrachloride and hydrogen sulphide passed through a tube at 700—1100° yield trichlorosilanethiol,  $\text{SiCl}_3\cdot\text{SH}$ , bistrichlorosilyl sulphide,  $(\text{SiCl}_3)_2\text{S}$ , the compound  $\text{Si}_2\text{S}_2\text{Cl}_4$ , and polymeric material  $(\text{SiSCl}_2)_n$ . The inter-relationships of these compounds and their behaviours on thermal decomposition are reported.

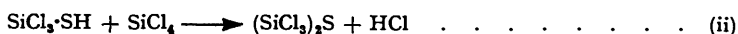
WHEN preparing trichlorosilanethiol (Wilkins and Sutton, *Trans. Faraday Soc.*, 1954, **50**, 783) it was noticed that other products besides the thiol (Pierre, *Ann. Chim. Phys.*, 1848, **24**, 286; Friedel and Ladenburg, *Annalen*, 1867, **145**, 179; *Compt. rend.*, 1867, **64**, 1295) and the crystalline dimeric "silicon sulphochloride  $\text{SiSCl}_2$ " (Blix and Wirbelauer, *Ber.*, 1903, **36**, 4220) arose from the high-temperature reaction between silicon tetrachloride and hydrogen sulphide. More complete examination of the crude product has led to the isolation of bistrichlorosilyl sulphide and polymeric material  $(\text{SiSCl}_2)_n$ . The inter-relationships of these compounds and the effect of reaction conditions upon yields have been studied. For the most part the individual chloro-sulphides constitute a series parallel to the organo-silicon sulphides recently synthesised by Etienne (*Compt. rend.*, 1952, **234**, 1985; 1952, **235**, 967), who further (*Bull. Soc. chim. France*, 1953, 791) showed that the compound  $\text{Si}_2\text{S}_2\text{Cl}_4$  could be obtained by condensation of silicon tetrachloride and hydrogen sulphide in the presence of an organic base. (We agree with Etienne that this compound is tetrachlorocyclodisilthiane). Schumb and Bernard (*J. Amer. Chem. Soc.*, 1955, **77**, 862) recently reported a limited examination of the products of the high-temperature reaction between silicon tetrachloride and hydrogen sulphide but did not identify tetrachlorocyclodisilthiane.

Trichlorosilanethiol, which is obtained from the high-temperature reaction in greatest yield when the vapours are shock-cooled, is considered to be the primary product

(see Chart). Thermal decomposition of the pure thiol yields tetrachlorocyclodisilthiane, polymer, hydrogen sulphide, and silicon tetrachloride in proportions approximating to the scheme



A small quantity of hydrogen chloride which is also produced may arise from reaction (ii).

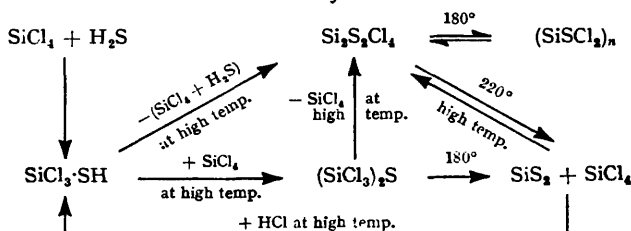


Reaction (i) may proceed by way of intermediate formation of bistrichlorosilyl sulphide, which then decomposes thermally:



and consequently does not accumulate in the product. Evidence was obtained for the formation of bistrichlorosilyl sulphide from trichlorosilanethiol at high temperatures only when it was diluted with silicon tetrachloride. This effect may be due to repression of reaction (iv), or to facilitation of reaction (ii). Trichlorosilanethiol is catalytically decomposed with aluminium chloride at 80–100°. The reaction differs from the thermal decomposition in yielding bistrichlorosilyl sulphide but correspondingly smaller quantities of silicon tetrachloride and “SiSiCl<sub>2</sub>,” and thus provides direct evidence for reaction (iii).

*Thermal interconversion of silicon thio-chlorides.*



Transformation of purified tetrachlorocyclodisilthiane into the liquid thio-dichloride polymer, the least volatile component of the reaction product, is rapid at 180°. At ordinary temperature the dry crystalline cyclodisilthiane is stable, but when moist with solvent it is very slowly transformed into the polymer. Interconversion of the constituents of the liquid polymer occurs with unusual ease even at room temperature and renders impossible isolation of successive members by fractional distillation. Polymer samples freshly obtained by heating tetrachlorocyclodisilthiane, or by distillation of the crude reaction product, rapidly assume a molecular weight close to that of the tetramer. During subsequent slower changes the average molecular weight passes through a maximum. Distillation of a sample whose molecular weight is close to that of, *e.g.*, the tetramer resolves the material into fractions having higher and (initially) lower molecular weights. Etienne mentions no comparable tendency of tetramethylcyclodisilthiane towards polymerisation but found a small quantity of trimer (Me<sub>2</sub>SiS)<sub>3</sub> in the product (personal communication).

At 220° the equilibrium mixture (SiSiCl<sub>2</sub>)<sub>n</sub> undergoes disproportionation:



but some 6–7% of the chlorine is retained in the residual “silicon sulphide.”

The decomposition of trichlorosilanethiol, tetrachlorocyclodisilthiane, and bistrichlorosilyl sulphide at relatively low temperatures suggests that, although the equilibria in the hot tube are favourable to their formation, the compounds are metastable at ordinary temperatures with respect to decomposition to silicon disulphide and silicon tetrachloride. On this view the equilibrium  $\text{Si}_2\text{S}_2\text{Cl}_4 \rightleftharpoons \text{SiS}_2 + \text{SiCl}_4$ , for example, should lie to the left at high temperatures, and it was in fact found that tetrachlorocyclodisilthiane could readily be obtained by passing silicon tetrachloride vapour over silicon sulphide at 900°. Likewise, the thiol could be obtained by passing silicon tetrachloride vapour and hydrogen chloride over silicon sulphide at 1000°.

The reaction between silicon tetrachloride and silicon sulphide also yields a secondary product  $\text{Si}_3\text{S}_4\text{Cl}_4$ , [probably containing some polymer  $(\text{Si}_3\text{S}_4\text{Cl}_4)_n$ ]. This is possibly the monomer (I), the second member of the series  $\text{Si}_n\text{S}_{2n-2}\text{Cl}_4$ , of which tetrachlorocyclodisilthiane is the lowest member. It is probable that the second homologue would, like the first, polymerise through ring enlargement.

Bromination of the *cyclodisilthiane* yields dibromodichlorosilane as the only isolable silicon compound, which again accords with the symmetrical cyclic structure.

## EXPERIMENTAL

*Reaction between Silicon Tetrachloride and Hydrogen Sulphide.*—Four types of run were made: (A) Silicon tetrachloride vapour and hydrogen sulphide (from ferrous sulphide; dried over  $\text{CaCl}_2$ ), generally in the molecular ratio 12 : 1, were passed through a silica tube ( $1\frac{1}{2}'' \times 36''$ ) heated over a 20'' length. Vapours were air-condensed and unchanged silicon tetrachloride was continuously recirculated. (B) As for (A), but the vapours were chilled by passage through an efficient water-cooled silica condenser. (C) Silicon tetrachloride vapour and hydrogen sulphide were passed in approximately equimolecular proportion through a silica tube ( $1'' \times 30''$ ) heated over 14'', with air condensation of the vapours. The product was not recirculated. (D) As for (C), but with shock-cooling of the vapours. In all experiments silicon tetrachloride vapour was condensed from the effluent gas at  $-78^\circ$  and returned to the system after hydrogen sulphide had been boiled off.

The products were separated by vacuum-distillation. For removal of silicon tetrachloride, trichlorosilanethiol, and bistrichlorosilyl ether the pressure was gradually reduced to about 1 mm. and the temperature increased to  $50^\circ$  so that the residual liquid (I, see below) boiled under reflux. The thiol (b. p.  $95.5\text{--}95.6^\circ/759$  mm., m. p.  $-57^\circ$ ) was isolated by redistillation. Table 1 shows the compositions of the products from typical runs.

TABLE 1.

Type and no. of run	A1 <sup>a</sup>	A2 <sup>b</sup>	A3 <sup>c</sup>	B2 <sup>d</sup>	B3 <sup>e</sup>	B4 <sup>f</sup>	C	D
Temperature .....	950°	950°	950°	800° <sup>g</sup>	950°	1100°	950°	950°
H <sub>2</sub> S flow (l./hr.) .....	3.5	3.5	3.5	3.5	3.5	3.5	6	6
Reaction time (hr.) .....	23	22	20	20	20	20	20	20
SiCl <sub>4</sub> used (g.) .....	750	750	750	750	750	750	750	750
SiCl <sub>4</sub> recovered (g.) .....	203	285	111 <sup>e</sup>	141 <sup>e</sup>	364	303	300	400
Yield of SiCl <sub>3</sub> SH (g.) .....	110	64	7	91	79	80	122	163
Higher-boiling product (total) (g.) .....	237	286	299	132	138	139	137	92
Yield of (SiCl <sub>2</sub> ) <sub>2</sub> S (g.) .....	18	18	12	15	21	34	—	—
Yield of Si <sub>3</sub> S <sub>4</sub> Cl <sub>4</sub> (g.) .....	— <sup>f</sup>	— <sup>f</sup>	173 <sup>h</sup>	— <sup>f</sup>	— <sup>f</sup>	— <sup>f</sup>	— <sup>f</sup>	— <sup>f</sup>

<sup>a</sup> Recirculation of trichlorosilanethiol prevented by fractionating column. <sup>b</sup> Unpacked column enabling recirculation of trichlorosilanethiol. <sup>c</sup> Unpacked column; faster recirculation from boiler, and higher (50 : 1) ratio,  $\text{SiCl}_4:\text{H}_2\text{S}$ . <sup>d</sup> The threshold temperature of the reaction is about  $650^\circ$ . A run at  $700^\circ$  gave a small yield of product of similar composition to that at  $800^\circ$ . <sup>e</sup> Considerable mechanical loss of silicon tetrachloride. <sup>f</sup> Not examined. <sup>g</sup> Low yield of tetrachlorocyclodisilthiane. <sup>h</sup> Weight of crude product before recrystallisation.

In experiments of type B yields of thiol based on the total production of silicon-sulphur compounds were almost constant over the temperature range  $700\text{--}1100^\circ$ . The yields of thiol from runs B and D are greater than from A and C, respectively, where shock-cooling was not used. Run D gave the highest yield of thiol, but these conditions are not necessarily maximal.

The small quantities of bistrichlorosilyl ether in the product are assumed to have arisen from attack of silicon tetrachloride on the silica tube. Packing with porcelain increased the yield of this ether but was otherwise without effect.

*Bistrichlorosilyl Sulphide.*—This compound can be distilled from the residue I (above), but its purification is complicated by the similar volatility of tetrachlorocyclodisilthiane. If present in large quantity (as in runs of type A3) much of the latter compound was removed by a preliminary crystallisation at  $-10^\circ$ . Upon continued vacuum distillation (under about 1 mm.) bistrichlorosilyl sulphide was collected at  $40\text{--}50^\circ$  until the *cyclodisilthiane* began to sublime in quantity. Most of this impurity was removed by crystallisation at  $-50^\circ$  and the remainder by discarding the residues from repeated fractional distillation. The pure compound distils at  $70^\circ/10$  mm. [Found: Si, 18.7; S, 10.4; Cl, 69.8%; *M* (cryoscopic in benzene, as in all succeeding determinations), 298, 303. Calc. for  $\text{Si}_2\text{S}_2\text{Cl}_4$ : Si, 18.65; S, 10.65; Cl, 70.7%; *M*, 301]. The compound distilled with decomposition at  $187\text{--}191^\circ$  at atmospheric pressure, and

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when boiled under reflux for 3 hr. it decomposed almost completely into silicon sulphide and silicon tetrachloride. In an experiment to determine the course of its decomposition at higher temperatures the compound (34 g.) was passed through a clear silica tube (flushed with nitrogen) at 950° during 35 min. The products recovered were silicon tetrachloride (14.5 g.), tetrachlorocyclodisilthiane (3 g.), polymer (8 g.), and unchanged bistrichlorosilyl sulphide (<5 g.). A lustrous black film formed within the heated length of the tube.

*Tetrachlorocyclodisilthiane and its Polymerisation.*—Distillation of bistrichlorosilyl sulphide from the crude reaction product is followed by sublimation of tetrachlorocyclodisilthiane (leaving residue II), but this is not readily obtained pure from preparations containing only small quantities. Larger yields were obtained from runs such as A3 in which the thiol re-circulated through the hot tube by increasing the flow of vapour from the boiler and by omitting the packing from the fractionating column. There was no significant trend in yields between 800° and 1100°. The compound was crystallised at -10° and thrice recrystallised from carbon disulphide cooled to -20° (Found: Si, 20.7; S, 24.0; Cl, 52.9%; *M*, 263, 266. Calc. for Si<sub>2</sub>S<sub>2</sub>Cl<sub>4</sub>: Si, 21.4; S, 24.5; Cl, 54.1%; *M*, 262).

The compound melts at 80°, but after being heated for 5 hr. at 160–180° the liquid no longer crystallised on cooling. A limited quantity (7.7 g.) could, however, still be pumped from the liquid (30 g.) at or below 100° (leaving residue III). Further successive quantities of the crystalline dimer could be sublimed at 100° after re-heating to 180° at atmospheric pressure to re-establish the interconversion equilibrium. Decomposition of the liquid with formation of silicon tetrachloride commenced at 220°. In a quantitative experiment 84.9 g. of tetrachlorocyclodisilthiane, heated at 220–250° for 28 hr., gave 6.2 g. unchanged or as polymer, 47 g. of silicon tetrachloride, and 30.5 g. of impure silicon sulphide (containing Cl, 7%). The decomposition is catalysed by trimethylammonium chloride.

*Examination of the Least Volatile Products.*—Continued distillation of residue II caused the proportion of liquid polymer passing over with the crystals to increase gradually. In the vacuum distillation of the high-boiling fraction (132 g.) from preparation B2, for example, three arbitrary fractions were taken: (1) 45–80°, chiefly crystals (7.5 g.); (2) 80–105°, crystals and liquid (60 g.); (3) 105–125°, chiefly liquid (7.5 g.). The chlorine contents of the two phases remained almost constant during the distillation, *viz.*, liquid from (2) 54.4; liquid + crystals from (2), 53.9; liquid (3), 54.3%. Towards the end of the distillation the residue rapidly thickened and solidified and some silicon tetrachloride was formed.

*The Thio-dichloride Polymer.*—The following molecular-weight data are typical of samples obtained by successive distillation of polymer (1) from pure tetrachlorocyclodisilthiane, and (2) from the crude product. (All distillations were made without causing decomposition to silicon tetrachloride or other volatile material). Unless otherwise stated, molecular-weight measurements were made immediately after isolation of the samples. (1) Residue III, obtained as above: 520, 523. (2) High-boiling distillate from runs A1 and A2 combined (Cl, 54.8%), treated as for residue III for equilibration and for removal of "dimer": 523. After distillation from a short still-head at 0.5–1 mm., measurements gave: (1) Distillate, 455 (Cl, 53.1%); residue (about one half of the distilland), 874. (2) Distillate, 468 (Cl, 55.6%). The foregoing distillates were immediately re-distilled from a steam-heated molecular still to give: (1) Distillate, 462, 537 (2 days), 632 (6 days), 563 (83 days); residue (about one third of the distilland), 748, 793 (11 days), 559 (83 days). (2) Distillate (Cl, 56.0%), 515, 589 (7 days), 466 (52 days), 393 (77 days). After 52 days 0.8 g. of 'dimer' had accumulated in 9.9 g. of this last distillate.

Material (1) distilled incompletely in the molecular still, suggesting fractionation, but material (2) distilled completely and more rapidly.

*Thermal Decomposition of Trichlorosilanethiol.*—Decomposition was detectable at 550° and rapid at 700°. Apart from some white solid, the products recovered after passage through a (nitrogen-flushed) silica tube are shown in Table 2. The figures for hydrogen chloride are very approximate (±25%):

TABLE 2.

SiCl <sub>3</sub> (SH) taken (mole)	Temp.	Time of passage through tube (hr.)	Products (moles)				
			SiCl <sub>3</sub> ·SH	SiCl <sub>4</sub>	"SiS <sub>2</sub> Cl <sub>2</sub> " (as dimer)	H <sub>2</sub> S	HCl
0.06	700°	1½	0.07	0.21	0.10	0.24	0.027
1.0	1100	2½	0.084	0.35	0.15	0.32	0.055
0.20	1100	1½	0.021	0.75	0.057	0.10	0.014

{ (+ 0.80 SiCl<sub>4</sub>)

The third run differed from the first two in yielding a little liquid during the initial stages of the distillation of tetrachlorocyclodisilthiane. Purification of the liquid was not practicable, but analysis gave: Cl, 62.7; S, 14.7%, indicating the ratio  $\text{Si}_2\text{SiCl}_4 : \text{Si}_2\text{S}_2\text{Cl}_4$  within the range 1—2.

*Catalytic Decomposition of Trichlorosilanethiol with Aluminium Chloride.*—The thiol (0.35 mole) was heated for 4 hr. with anhydrous aluminium chloride (1.5 g.). The products were hydrogen sulphide (0.13), silicon tetrachloride (0.06), unchanged thiol (0.08), " $\text{SiSiCl}_2$ " (0.035, as dimer), and bistrichlorosilyl sulphide (0.06 mole) (Found: Si, 18.6; S, 10.4; Cl, 69.7%). In certain similar experiments hydrogen chloride was also evolved, the ratio  $\text{HCl} : \text{H}_2\text{S}$  being 1 : 3 in one case.

*Reaction between Silicon Tetrachloride and Silicon Sulphide.*—Silicon tetrachloride (37.5 g.) was passed over silicon sulphide (18 g.; from thermal decomposition of the polymer) at 850—900° during 3 hr. The product was filtered and silicon tetrachloride removed. Vacuum sublimation at 70° gave tetrachlorocyclodisilthiane (8 g.; m. p. 78—80°) and a crystalline residue (about 3 g.) (Found: Si, 23.4; Cl, 39.5%;  $M$  (cryoscopic in benzene), 454. After vacuum sublimation of the product at 140° the values were: Si, 23.0; Cl, 39.9; S, 35.5%;  $M$ , 420. Calc. for  $\text{Si}_2\text{S}_2\text{Cl}_4$ : Si, 23.8; Cl, 40.0; S, 36.2%;  $M$ , 354).

*Reaction between Silicon Tetrachloride, Silicon Sulphide, and Hydrogen Chloride.*—Silicon tetrachloride (37.5 g.) and hydrogen chloride (about 5 l.) were passed over silicon sulphide (16 g.) at 1000° during 1½ hr., and the vapours shock-cooled. The condensate contained 3.5 g. of trichlorosilanethiol, b. p. 95—96°.

*Bromination of Tetrachlorocyclodisilthiane.*—The cyclodisilthiane was warmed carefully during the addition of bromine (29 g.) in small quantities. Fractionation of the product was difficult (owing probably to progressive decomposition of sulphur bromides). 23.5 g. of dibromodichlorosilane (b. p. 102—108°) were obtained, but there was no evidence of higher- or of lower-boiling silicon halides.

*Analyses.*—Liquid samples were weighed from a pycnometer with a ground cap, into an all-glass absorption vessel cooled in liquid air. The head of the vessel was replaced, the unit evacuated and removed from the liquid air, and the sample hydrolysed by water. Chlorine was determined by titration of strong acid (bromophenol-blue as indicator), sulphur as sulphate after hypobromite oxidation, and silicon as silica.