982. *Chlorosiloxanes from the Reaction between Oxygen and Silicon Tetrachloride.*

By D. W. S. Chambers and C. J. Wilkins.

Cyclic chlorosiloxanes $(SiOCl_2)_n$, with $n = 3$, 4, or 5, and lower open-chain compounds $Si_nO_{n-1}Cl_{2n+2}$ are obtained from the reaction between oxygen and silicon tetrachloride at 1000°. At this temperature hexachlorodisiloxane and octachlorotrisiloxane rearrange to a mixture of cyclic and higher open-chain chlorosiloxanes and silicon tetrachloride. Infrared spectra indicate that the $Si_3O_3Cl_6$ and $Si_4O_4Cl_8$ molecules have six- and eight-membered rings respectively.

Investigations [1,2] of silicon oxychlorides over a long period have established the existence of a series of open-chain compounds $Si_nO_{n-1}Cl_{2n+2}$. A crystalline compound $Si_4O_4Cl_8$, now confirmed as octachlorocyclotetrasiloxane, has been assumed to be a member of a possible cyclic series, $(SiOCl_2)_n$.[3] Analogy with hexamethylcyclotrisiloxane (which is obtained in highest yield at high temperature [4]) suggests that hexachlorocyclotrisiloxane, $Si_3O_3Cl_6$, should also be capable of existence. There is no evidence that chlorine substituents on silicon increase the oxygen valency angle [5] and thereby prevent closure of a six-membered ring. A planar hexagonal molecule with tetrahedral silicon would require an angle SiOSi of 130·5°, which lies just within the usual range of values (130—143°) for the oxygen angle.

Since the high-temperature reaction between silicon tetrachloride and oxygen is known to produce the tetrameric octachlorocyclotetrasiloxane,[2] we sought the trimeric hexachlorocyclotrisiloxane from the same source. The latter compound (m. p. 43·5°) was obtained in as great yield as the tetramer, and a small, slightly impure sample of a crystalline pentamer, $Si_5O_5Cl_{10}$, was also isolated. Of the open-chain liquid products, hexachlorodisiloxane and octachlorotrisiloxane were readily separated, but the higher members could not be freed from residual dissolved cyclic material by repeated fractional distillation.

The similar yields of trimer and tetramer suggest that their ring systems (see below) are of comparable stability at high temperature. However, at 300° and in the absence of a catalyst the trimer alone decomposes (to unidentified chlorosiloxanes) so that its smaller six-membered ring is the less stable at lower temperatures. The absence from all preparations of a dimeric cyclic member analogous to tetrachlorocyclodisilthiane, $Si_2S_2Cl_4$,[6] suggests that the oxygen bond angle in this, as in other classes of silicon–oxygen compound, cannot fall so low as to enable the formation of a stable four-membered ring.[7]

Infrared spectra confirm the ring sizes in the trimer and tetramer. The strong absorptions of the chlorosiloxanes due to the Si–O stretching vibration (see Fig.) are so closely similar in form, intensity, and relative positions to those of the corresponding open-chain and cyclic dimethylsilicones [8] (but at wavelengths shorter by 0·4—0·45 μ) as to indicate structural identity of the two classes of compound. The displacement of the absorption peak on passing from $Si_3O_3Cl_6$ (9·48 μ) to $Si_4O_4Cl_8$ (8·85 μ) parallels that

---

[1] Friedel and Ladenburg, *Annalen*, 1868, **147**, 355; *Compt. rend.*, 1868, **66**, 539; Schumb and Holloway, *J. Amer. Chem. Soc.*, 1941, **63**, 2753; Schumb and Stevens, *J. Amer. Chem. Soc.*, 1947, **69**, 726; 1950, **72**, 3178; Goubeau and Warncke, *Z. anorg. Chem.*, 1949, **259**, 109, 233.

[2] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, **7**, 452; *Bull. Soc. chim.*, 1881, **35**, 360; Rheinboldt and Wisfeld, *Annalen*, 1935, **517**, 197.

[3] Emeléus (*Proc. Chem. Soc.*, 1959, 205) commented on previous uncertainty as to the structure.

[4] Patnode and Wilcock, *J. Amer. Chem. Soc.*, 1946, **68**, 358; Hunter, Hyde, Warrick, and Fletcher, *ibid.*, p. 667.

[5] Yamasaki, Kotera, Yokoi, and Ueda, *J. Chem. Phys.*, 1950, **18**, 1414.

[6] (*a*) Etienne, *Bull. Soc. chim. France*, 1953, 791; (*b*) Panckhurst, Wilkins, and Craighead, *J.*, 1955, 3395.

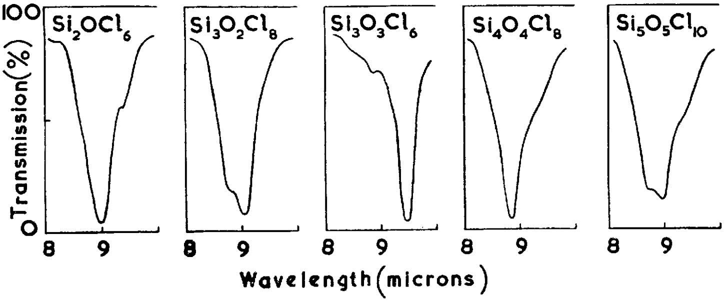
[7] Weiss and Weiss (*Z. anorg. Chem.*, 1953, **276**, 195) have reported an unstable crystalline form of silicon dioxide having a four-membered ring.

[8] Wright and Hunter, *J. Amer. Chem. Soc.*, 1947, **69**, 803; Richards and Thompson, *J.*, 1948, 124.

found for the corresponding dimethylsilicones whose six- and eight-membered cyclic structures are beyond doubt. Moreover, the single absorption peak of the tetramer, rather than a composite absorption such as would be expected from a six-membered ring with an $-O{\cdot}SiCl_3$ substituent, excludes this alternative to the eight-membered ring. The broadened unsymmetrical peak given by the pentamer is characteristic of the higher methylcyclopolysiloxanes.[8] It is thus likely that this chlorosiloxane contains a ten-membered ring, but in this instance the possibility of a smaller ring with a substituent cannot be ruled out.

The composition of a chlorosiloxane preparation varies with the reaction temperature. Below 950° the hexachlorodisiloxane formed as the primary reaction product comprises at least 90% of the mixture. With rising temperature thermal rearrangement and continuing oxidation of the disiloxane increase the proportion of the higher chlorosilanes.

Infrared spectra of chlorosiloxanes in carbon tetrachloride.



At 1000° (the usual preparative temperature) thermal decomposition of pure hexachlorodisiloxane is relatively fast and yields, in the first place, chiefly silicon tetrachloride and octachlorotrisiloxane (Table 1). The pure trisiloxane in turn gives an increased proportion of cyclic members and higher-boiling material under the same conditions. A black mirror of silicon was formed in the hottest part of the apparatus and free chlorine was carried from the reaction zone. The deposition of silicon suggests the production from this siloxane of the $SiCl_2$ radical, which is known to participate in the equilibrium $2SiCl_2 \rightleftharpoons Si + SiCl_4$ above 800°.[9] At lower temperatures the chlorosiloxanes become metastable with respect to decomposition to silicon tetrachloride and an involatile silica-like solid which still contained chlorine. A trace of trimethylamine hydrochloride [6b] catalyses the decomposition at 200°.

TABLE 1. *Decomposition of chlorosiloxanes at* 1000°.

Compound	Weight taken (g.)	Reaction time (hr.)	Products recovered (g.)			
			$SiCl_4$	Si_2OCl_6	$Si_3O_2Cl_8$	Higher fractions
Si_2OCl_6	175	3	22	88	26	16
Si_2OCl_6	195	9 [b]	43	49	50	22
$Si_3O_2Cl_8$	185	2·5	42	6	21 [c]	46 [d]
Si_2OCl_6, with oxygen [a]	190	6	6	118	8	12

[a] The oxygen flow rate was 22 l./hr. [b] The boiler temperature became steady after 6 hr., indicating no further reaction thereafter. [c] A trace of $Si_3O_3Cl_6$ was also found. [d] This includes $Si_4O_4Cl_8$ (5 g.) and a fraction (5 g.) distilling at 114—115°, but excludes silica deposits.

In the presence of oxygen but under otherwise similar conditions in an unpacked reaction tube the purely thermal rearrangement of hexachlorodisiloxane is retarded (Table 1). This must assist the escape of the disiloxane from the reaction zone during preparative experiments.

For preparative purposes the present method has the advantages and disadvantages of a process leading to diversified products. Apart from yielding cyclic members the

---

[9] Schäfer and Nickl, *Z. anorg. Chem.*, 1953, **274**, 250; Schäfer, *ibid.*, p. 265.

reaction is suited to the preparation of hexachlorodisiloxane[10] and octachlorotrisiloxane. The yield of the latter can be doubled by conducting a subsequent decomposition of the former (see Tables 1 and 2). With higher members, formation of isomers seems probable and this could contribute to the difficulty in their separation.

TABLE 2. *Fractions from distillation of* 1076 g. *of chlorosiloxanes.*[a]

	Fraction	Boiling range	Weight (g.)	Probable main constituent
(i)	Liquid	135°/760 mm., 33—34°/15 mm.	621	Si_2OCl_6
(ii)	Solid (+ liquid)	49—50°/15 mm.	46	$Si_3O_3Cl_6$
(iii)	Liquid	77·5—78·5°/15 mm.	176	$Si_3O_2Cl_8$
(iv)	Liquid[b]	78—111°/15 mm.	20	
(v)	Solid (+ liquid)[c]	89°/13 mm.	39	$Si_4O_4Cl_8$
(vi)	Liquid	111—116°/15 mm.	27	$Si_4O_3Cl_{10}$
(vii)	Liquid	129—130°/15 mm.	19	
(viii)	Solid (+ much liquid)	118—121°/5 mm.	16	$Si_5O_5Cl_{10}$ (solid)
(ix)	Liquid	110—180°/3 mm.	24	
(x)	Tarry residue[d]		40	

[a] Prepared at 1000—1020°. [b] This liquid distilling on each side of solid (v) was difficult to resolve completely. [c] The quantity of liquid distilling during collection of the crystalline material was, however, small. [d] Pyrolysis gave silicon tetrachloride

EXPERIMENTAL

Preparation of Chlorosiloxanes.—Silicon tetrachloride vapour and oxygen were passed through a heated silica tube packed with unglazed porcelain to accelerate the reaction. Unchanged tetrachloride was automatically recirculated. At 960° the hourly yield of siloxanes was 8 g., of which 10% was less volatile than hexachlorodisiloxane. At 1000—1010° it was 30 g., with 25—30% less volatile, and at 1000—1020° 35 g. and 40%. (Temperatures were recorded outside the reaction tube.)

Separation and Characterisation of Chlorosiloxanes.—Unchanged silicon tetrachloride and most of the hexachlorosiloxane were removed under atmospheric pressure. Distillation was continued under reduced pressure with use of an 80 cm. tapered column packed with glass helices, to give the factions in Table 2. Fraction (i) yielded pure hexachlorodisiloxane (b. p. 135·3°/760 mm.) on redistillation. Fraction (iii) was held at $-60°$ and filtered at this temperature to remove impurities which crystallised. The liquid was redistilled to give analytically pure octachlorotrisiloxane. A sample (40 g.) passed over completely at 190·7°/759 mm. (cf. Goubeau *et al.*[1]). The crystalline *hexachlorocyclotrisiloxane* from fraction (ii) was drained on a filter, washed with carbon disulphide at $-60°$, and sublimed at room temperature under a high vacuum. Likewise octachlorocyclotetrasiloxane was recovered from fraction (v) and sublimed at 60°. The slurry of crystals from fraction (viii) was blotted on (pre-dried) filter-paper in a dry box, and the residue sublimed at 95°. The identity of the product (0·8 g.) as a pentamer of the cyclic series is inferred from its volatility relative to that of the other members. It melted quite sharply, but the liquid contained a trace of silica. Characterisation data on the compounds are given in Table 3.

TABLE 3. *Identification of purified compounds.*

	Found			Calculated			
	Si (%)[a]	Cl (%)[b]	*M*[c]	Si (%)	Cl (%)	*M*	M. p.
Si_2OCl_6	19·6	74·7, 74·8	*	19·7	74·7	285	$-28·1° \pm 0·2°$[d]
$Si_3O_2Cl_8$	21·3	70·9, 70·9	382	21·1	70·9	400	$-47°$
$Si_3O_3Cl_6$	24·5, 24·2	61·6, 61·5	320, 348	24·4	61·7	345	43·5°
$Si_4O_4Cl_8$	24·3, 24·5	61·5, 61·3	450, 454	24·4	61·7	460	77°
$Si_5O_5Cl_{10}$	24·2	59·3, 59·1	*	24·4	61·7	575	96—97°

[a] Determined as SiO_2 after hydrolysis. [b] Determined by Mohr titration. [c] Cryoscopically in benzene. [d] Schumb and Holloway, ref. 1. * Not measured.

Redistillation of the liquid (vi) [with additional similar material (7 g.)] gave fraction (via), 5 g., passing over at 100—114° (Cl, 63·7, 63·6%); (vi*b*), 19 g., 114—115° (Cl, 65·6, 65·6%); (vi*c*), 5 g., 115—118° (Cl, 65·0, 65·3%). Fraction (vi*b*), whose narrow distillation range covers

---

[10] Grigor and Wilkins, " Inorganic Syntheses," McGraw-Hill, New York, Vol. VII.

the b. p. of decachlorotetrasiloxane, 114·7°,[5] had a chlorine content lower than that required for this compound. Cyclic impurity must still have been present. Another fraction, 5 g., also distilling at 114—115° from the thermal decomposition of octachlorotrisiloxane gave Cl, 65·9%.

Fractions (vii) and (ix) had Cl, 60·3 and 61·5%, respectively. The former value is below that required even for the cyclic series $(SiOCl_2)_n$. More highly oxygenated material must therefore have been present.

Thermal Decomposition of Chlorosiloxanes.—For high-temperature rearrangements (Table 1) a compact silica circulating vessel using the liquid-seal principle and having the (unpacked) hot tube, 2 cm. × 20 cm., directly above the boiler was used.[11] Changes in boiler-temperature indicated the progress of the reaction and showed the threshold reaction temperature to be 760—800°. Silicon tetrachloride from the trisiloxane decomposition was tapped off at intervals to prevent the temperature of the boiler from falling too much.

For stability tests at lower temperatures with and without catalyst sealed tubes were used. In an experiment where octachlorotrisiloxane (1·846 g.) and trimethylamine hydrochloride (0·013 g.) were held at 220° for 24 hr., the products were silicon tetrachloride (1·201 g.) and involatile residue (0·610 g.).

Infrared Spectra.—These were taken with a Perkin–Elmer double-beam spectrophotometer model 221, with use of carbon tetrachloride solutions of concentration ~0·5% for hexachlorodisiloxane and octachlorotrisiloxane, and ~0·25% for the remainder. The cell length was 0·5 mm.

The authors are indebted to Mr. B. A. Grigor, who made the initial chlorosiloxane preparations, and to Mr. J. Vaughan who recorded the infrared spectra. The work has been assisted by a research grant from the University of New Zealand.

University of Canterbury,
Christchurch, New Zealand.

[*Received, June 7th,* 1960.]

---

[11] Cf. Chambers, M.Sc. Thesis, University of Canterbury, 1960.