397. *The Thermal and Photochemical Oxidation of the Chlorinated Silanes.*

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Analytical methods have been developed for the examination of mixtures of hydrogen chloride, chlorine, and silicon oxychlorides formed in the oxidation of the chlorinated silanes. The relationship between the ignition temperature and pressure of mixtures of tri-, di-, and mono-chlorosilane with oxygen has been studied, and shows a gradual transition from a degenerate chain reaction for trichlorosilane to what is probably a branched chain reaction for monochlorosilane. The photo-oxidation of these three substances has been examined analytically; in that of trichlorosilane a definite intermediate of the formula $Si(OH)Cl_3$ has been isolated, which decomposes slowly at room temperature with evolution of hydrogen chloride. Similar hydroxylation takes place in the photo-oxidation of di- and mono-chlorosilane.

THE first record of the inflammability of trichlorosilane is due to its discoverers, Buff and Wöhler (*Annalen*, 1857, **104**, 96), the products formed on burning the liquid in air being hydrogen chloride and silica. These observations were confirmed by Friedel and Ladenburg (*ibid.*, 1867, **143**, 121), and by Pape (*ibid.*, 1884, **222**, 359). No attempt has hitherto been made to study the oxidation of this substance from the kinetic standpoint, or to trace the change in the character of the oxidation reactions as one passes from trichlorosilane and the di- and mono-chloro-derivatives to monosilane itself. This paper reports observations on the thermal and photochemical oxidation of the three chlorinated silanes, and also describes analytical methods suitable for dealing with the gaseous mixtures encountered in this work.

EXPERIMENTAL.

Trichlorosilane was prepared by the method of Booth and Stillwell (*J. Amer. Chem. Soc.*, 1934, **56**, 1529), fractionally distilled through a 40-cm. glass column filled with small glass rings, transferred to a Stock vacuum apparatus, and submitted to a process of fractional condensation at − 100°. 6·4 C.c. of homogeneous liquid material having a vapour pressure of 217—219 mm. at 0° were obtained, which was unchanged by further fractionation. Tensimetrically pure mono- and di-chlorosilane were prepared by Stock's method (*Ber.*, 1919, **52**, 695).

The oxidation of the three chlorinated silanes and the analysis of the products were studied in the apparatus shown in Fig. 1. Certain incidental apparatus, such as vacuum lines for evacuating the reservoirs, has been omitted for the sake of clearness.

Mixtures of the chlorosilane and oxygen were made up manometrically in *A* (4·5 cm. diameter, 20 cm. long). These mixtures, particularly those containing trichlorosilane, always contained traces of hydrogen chloride owing to attack of tap grease and to traces of adsorbed water in the apparatus. The reaction system is included by taps 5, 6, 7, and 8. Different reaction vessels, depending on the nature of the work in progress, could be fitted to the apparatus by means of the standard ground joint *C*. The mixtures were admitted to the reaction vessel through the auxiliary bulb *B*. Pressure measurements during slow reactions, and in the analysis, were made on the glass spoon gauge, *F*, which was a modification of the Foord gauge (*J. Sci. Instr.*, 1934, **11**, 126) in which a silk bifilar suspension for the mirror, and a butyl phthalate " dash-pot " for damping, were employed. The sensitivity, with a comparatively robust membrane, was 300 mm. deflection of the light spot per cm. pressure, with a galvanometer lamp and scale at 1 m. distance. The gauge was practically dead-beat. Where necessary, corrections were made for the dead space formed by the gauge and its connecting tubing.

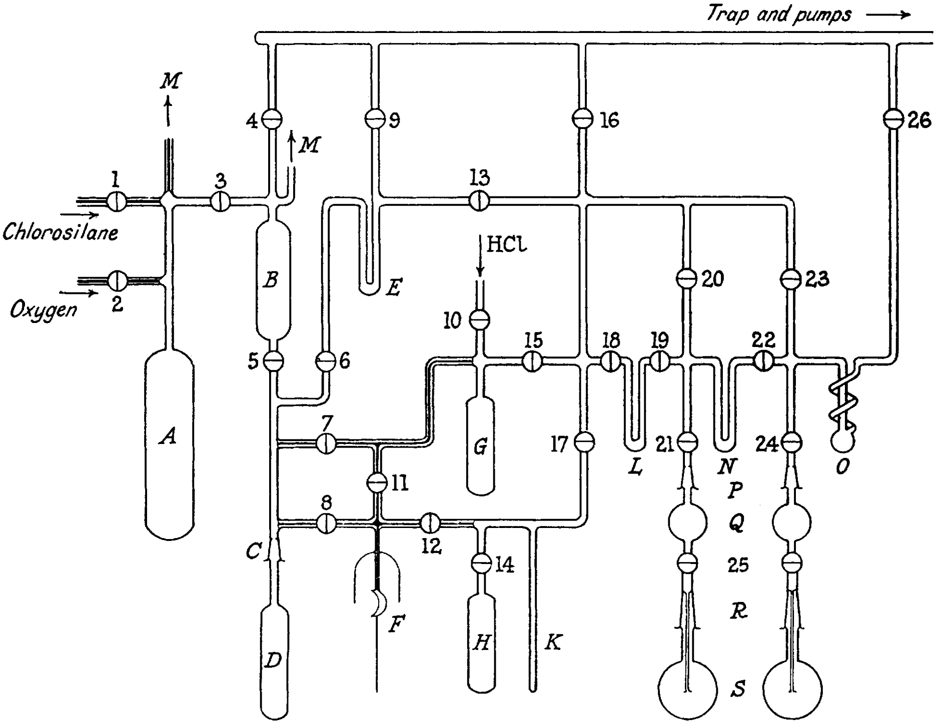
After the completion of an experiment on either the thermal or the photochemical oxidation, the mixture of reaction products was condensed out by pumping the contents of the reaction vessel *via* taps 6, 13, 18, 19, 22, and 26, through the U-bulbs *L* and *N* and the spiral condensing tube *O*, all of which were surrounded by Dewar vessels containing liquid nitrogen. After 5 mins.' pumping to remove excess oxygen, the condensed products were distilled back into *E*, and then fractionated, *L*, *N*, and *O* being used as a fractionation system.

In all cases encountered in the present work the condensable reaction products were readily separated by a single fractionation into three groups : (*A*) least volatile fraction, condensed at − 70°, containing Si_2OCl_6 (v.p. 0·004 mm. at − 70°), $Si(OH)Cl_3$, and less volatile oxychlorides

($Si_4O_4Cl_8$, etc.); (*B*) intermediate fraction, condensed at − 120°, containing unreacted $SiHCl_3$ (v.p. 0·006 mm. at − 120°, 2·5 mm. at − 70°), unreacted SiH_2Cl_2, and $SiCl_4$ (v.p. 0·002 mm. at − 120°, 0·8 mm. at − 70°); (*C*) most volatile fraction, hydrogen chloride and chlorine, which distilled through the − 120° bath, but were trapped in the liquid nitrogen-cooled tube. The fractionation was carried out by allowing the mixture, initially condensed with liquid nitrogen in *E*, to distil slowly through *L*, *N*, and *O*, which were cooled to − 70°, − 120°, and in liquid nitrogen, respectively. The distillation was continued for 10 mins., during which time *E* warmed to room temperature. The substances in groups (*A*), (*B*), and (*C*) condensed in *L*, *N*, and *O*, respectively, and were isolated by closing the appropriate taps. The fractions were then removed separately for further examination.

The volumes of fractions (*B*) and (*C*) (as gas) were determined by distilling them in turn into the calibrated constant-volume system enclosed by taps 8, 11, and 17, and measuring the gas pressure on the spoon gauge; $SiHCl_3$ and $SiCl_4$ are sufficiently volatile to be measured by this method. The bulb *H*, representing the greater part of the volume of the system, was water-jacketed. The volumes of different portions of the apparatus were determined by pressure comparisons with a fixed amount of gas, and expressed in terms of the volume of the bulb *G* and its connecting tubes, which was taken as an arbitrary standard. Both *G* and *A* were immersed in a large bath of water. Vapour-pressure determinations on samples were carried out in the usual manner, the tube *K* and the spoon gauge being used.

FIG. 1.



(M *denotes a mercury manometer.*)

In the volumetric determination of free and combined chlorine, the fraction under examination was distilled into one of the titration bulbs, *S*, taps 21 (or 24) and 25 closed, and the bulb detached at the ground joint *P*. Chlorine combined in silicon compounds in fractions (*A*) and (*B*) was determined by hydrolysing the silicon compounds with water at 50—60°, and estimating the hydrochloric acid produced by the iodide–iodate method; this method had the advantage that a single solution of sodium thiosulphate sufficed for all the volumetric determinations, including those of free chlorine and hydrogen chloride. If no free chlorine had been formed in the reaction, hydrogen chloride occurred alone in fraction (*C*), and a volume measurement sufficed for its determination. When chlorine was also present, the whole fraction was first absorbed in potassium iodide solution and the liberated iodine titrated, the determination of free acid (HCl) being carried out afterwards by adding potassium iodate and titrating the additional amount of iodine. The sodium thiosulphate (0·02N) was standardised by admitting a measured pressure of hydrogen chloride into the bulb *G* through tap 10, and titrating in the usual way after distilling the gas into one of the titration bulbs. The concentration was expressed as the pressure of hydrogen chloride at 0° in bulb *G* equivalent to 1 c.c. of the solution.

The method of fractionation used in the analysis was tested by the following typical separation : 172 c.c. of trichlorosilane (measured as gas) were distilled through successive bulbs cooled to − 120° and in liquid nitrogen, the conditions being similar to those used in analysing the oxidation products. After 15 mins.' distillation with the pumps connected to the free side of the condensing vessel cooled in liquid nitrogen, only 0·15 c.c. (gas) was found in the cooler condensing vessel. The remainder of the trichlorosilane had condensed at − 120°. Thus, although a physical separation of this character is necessarily not quantitative, it gave in this case a substantially correct analysis of the oxidation products.

The Thermal Oxidation of Trichlorosilane.—The products formed in the explosive oxidation of trichlorosilane were first studied. The explosion was accompanied by a very small pressure decrease. Ignition was effected either by sparking or by heating the reaction vessel rapidly to *ca.* 300°, and after an explosion the reaction vessel was immersed in liquid nitrogen and excess oxygen pumped off through *E*, which was also held in liquid nitrogen. The condensate in *E* was distilled back into the reaction bulb, and the amount of oxygen pumped off deduced from the diminution in pressure. The residue was analysed as already described. Table I contains analytical results obtained in a series of experiments with spark and thermal ignition, excess of oxygen being used throughout; all pressures are recorded in mm.

TABLE I.

Products of Explosion of $SiHCl_3$–O_2 *Mixtures.*

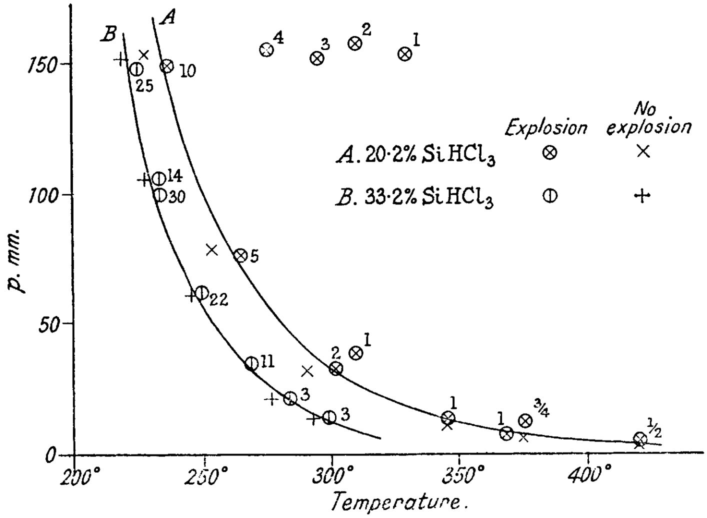
Initial press.							
O_2.	$SiHCl_3$.	Δp in reaction.	O_2 used.	Cl_2 formed.	HCl formed.	Total Cl (mols.).	Type of ignition.
88·2	72·9	−6·2	73·5	64·1	79·8	2·86	Spark
93·1	77·0	−4·8	77·9	67·9	84·2	2·85	,,
97·2	80·3	−4·2	81·9	71·7	89·0	2·89	,,
102·2	84·5	−4·7	87·8	78·5	91·3	2·94	,,
98·4	81·0	−3·8	—	77·2	83·9	2·94	,,
103·0	84·7	−3·8	—	82·4	87·4	2·97	,,
157	78	—	—	67	93	2·87	Thermal
133	67	—	—	56	75	2·82	,,
115	57	—	—	47	63	2·72	,,

There was no excess of trichlorosilane in the reaction products. If the amount of trichlorosilane used be taken as unity, the molecular proportions of oxygen used, and of chlorine and hydrogen chloride formed are 1·01—1·04, 0·82—0·92, and 1·03—1·19, respectively. The molecular proportion of the total chlorine accounted for in the analysis (max., 3·0) is given in the penultimate column. These results accord with the equation $SiHCl_3 + O_2 = SiO_2 + HCl + Cl_2$. The excess of hydrogen chloride is attributed to attack of tap grease and to slight hydrolysis of trichlorosilane by adsorbed water in the apparatus. In these experiments the reaction vessel was cleaned with dilute hydrofluoric acid after each explosion, except between the fourth, fifth, and six runs recorded in Table I, in which the silica deposit was allowed to accumulate. The deficit in chlorine is partly due to the above hydrolysis, but is also due to the fact that the solid deposit formed in the reaction contained some chlorine, as was shown by qualitative analysis. Previous observers probably failed to detect formation of free chlorine in this reaction because they used excess of trichlorosilane, which would react with chlorine to form silicon tetrachloride.

Lower Explosion Limit Curve for Trichlorosilane–Oxygen Mixtures.—The relationship between the ignition temperature of trichlorosilane–oxygen mixtures and the pressure was determined for a series of pressures by trial (cf. Sagulin, *Z. physikal. Chem.*, 1928, *B*, **1**, 275). Preliminary experiments showed that mixtures ignited in the temperature range 200—300° at pressures of the order of 100—200 mm., and that a curve of the usual type could be drawn marking the boundary of the explosion region. Ignition took place after an induction period. Erratic results were obtained if the silica formed in the reaction was allowed to remain in the reaction vessel, and accordingly the latter was washed with 5% hydrofluoric acid and rinsed with distilled water after each trial, whether an explosion had occurred or not. Results were then reproducible, and it was possible to use reaction vessels in turn, each being fitted with a standard cone for the ground joint. The bulbs used were of 2·7 cm. internal diameter and 15 cm. long. The results of experiments made with mixtures containing 33·2 and 20·2% of trichlorosilane are shown in Fig. 2. The small figures in the diagram indicate the induction period (secs.) for ignition in the particular observation. The crosses show observations at which there was no explosion. Ignition at the very low pressures was observed in a darkened room.

The data in these curves may be used to test the relationship $\log p/T = A/T + B$ (cf. Semenoff, " Chemical Kinetics and Chain Reactions," Oxford University Press, 1934), and it is found that, with natural logarithms and pressures expressed in mm., the constants A and B have the values 7500 and 16, respectively, in the case of the 20·2% mixture. For the 33·2% mixture these values are 9400 and 20, *i.e.*, a marked variation occurs in the values of A and B as the mixture composition is changed. In this respect the reaction is exceptional (cf. Sagulin, *loc. cit.*). In the course of these observations it was repeatedly shown that the induction period of the explosive reaction decreases as one moves from pressures corresponding with points on the curves in Fig. 2 to higher pressures. The curves correspond to ignition after a very long induction period. The pressure change in the reaction is too small to allow the progress of the reaction before ignition to be studied, but the induction period characterises it as a chain reaction with degenerate branching. Explosions of the above mixtures at higher pressures were too violent for the upper branch of the limit curve to be traced.

FIG. 2.



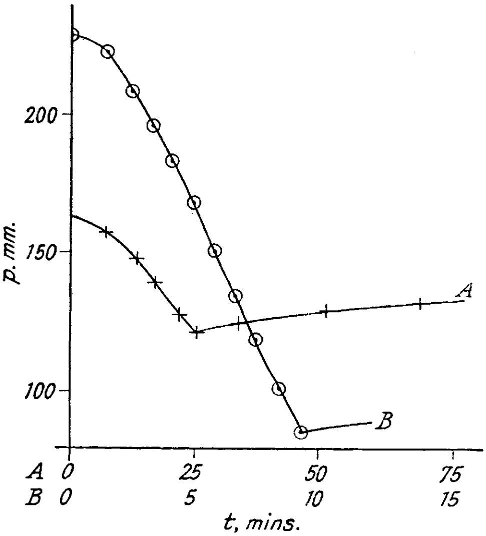
Explosion limit curves for $SiHCl_3$–O_2 *mixtures.*

A slow reaction took place below the explosion limit, but was not fully studied. A typical analysis obtained in this region is the following : a mixture at an initial pressure of 169·5 mm. ($SiHCl_3$ 56·5 mm.) was used. After reacting for 90 minutes at 190° the mixture contained 32 mm. of hydrogen chloride, 8 mm. of chlorine, 7 mm. of silicon tetrachloride, 12 mm. of unreacted trichlorosilane, and a small quantity of a less volatile substance (Si_2OCl_6 ?) which gave 22 mm. of hydrogen chloride on hydrolysis. Combined chlorine equivalent to 32 mm. of hydrogen chloride remained in the reaction vessel, very probably as silicon oxychlorides of high molecular weight. According to Stock (*Ber.*, 1923, **56**, 986), pyrolysis of trichlorosilane does not occur below 400°, and is therefore excluded in these experiments.

Photochemical Oxidation of Trichlorosilane.—The object of our experiments on the photochemical oxidation of trichlorosilane was primarily to obtain analytical evidence of the reaction mechanism. No attempt was made to study the kinetics of the reaction. It was first verified that at a pressure of 100 mm. in a quartz cell 50 mm. thick there was no detectable absorption of light down to about 1900 A. At 350 mm. pressure there was slight absorption, but the oxygen absorption bands were still observed on the plates.

Irradiation was carried out either with a hot mercury arc, or with a cold mercury arc of the resonance type. The reaction was the same for each, but the latter was preferred, as it eliminated appreciable heating of the reaction vessel. Typical pressure–time curves obtained on irradiating with the cold arc are shown in Fig. 3. A pressure decrease approximately equal to the original trichlorosilane pressure occurred in the first 20—25 mins., and was followed by a much slower increase in pressure which was not followed to completion owing to its low rate. During the first part of the irradiation a viscous liquid deposit collected; it was not removed by long pumping, and was evidently of very low volatility. No other products were formed apart from hydrogen chloride and a small amount of a colourless liquid which condensed in the fractionation (cf. p. 1928) at – 70°. Preliminary experiments showed the ratio of the volumes of trichlorosilane and oxygen used in the reaction to be approximately 2 : 1. More exact analytical data are given in Table II (pressures in mm.). In runs A—E, irradiation was continued to the end of the initial pressure decrease. In F, irradiation was continued for a further 90 mins., with the result that the pressure increased by 11·3 mm. from the minimum value.

FIG. 3.



Pressure–time curves for photochemical oxidation of $SiHCl_3$.

(*Initial pressures : A,* $SiHCl_3$ 54, O_2 109 *mm.*; *B,* $SiHCl_3$ 142, O_2 80 *mm.*)

TABLE II.

Photochemical Oxidation of Trichlorosilane : Analysis of Products.

	Initial press.				
Run.	O_2.	$SiHCl_3$.	Δp in reaction.	O_2 used.	HCl formed.
A	80·9	143·6	–160·7	69·1	50·9
B	89·2	158·3	–179·9	79·1	50·1
C	75·0	133·1	–136·9	65·4	58·6
D	72·2	128·7	–142·4	61·9	37·9
E	87·9	156·5	–168·0	81·9	64·8
F	79·0	141·0	–135·3	69·8	65·7

Run F shows that the slow pressure rise subsequent to the rapid decrease is not due to an oxidation reaction, the oxygen used in this case not being in excess of the values for runs A—E. This pressure rise is therefore due to the decomposition of one or more of the reaction products, the pressure minimum marking the end of the oxidation reaction. In runs A—E a negligible quantity of unused trichlorosilane was recovered in the fractionation of the reaction products, confirming that oxidation is complete at the end of the initial pressure decrease. The analytical figures for hydrogen chloride (Table II) show that at the pressure minimum 60% or more of the hydrogen in the original trichlorosilane had not been eliminated as hydrogen chloride, but was retained in the liquid products. The nature of these products and of their decomposition was therefore investigated.

Examination of Liquid Products of the Photo-oxidation.—The liquid products of the reaction were examined by the methods already described. They consisted of (*a*) a colourless mobile liquid condensing in the fractionation in the tube at − 70°, and (*b*) a colourless viscous liquid of low volatility which remained in the reaction bulb. When an attempt was made to measure the vapour pressure of (*a*), the pressure rose steadily, and the liquid evolved a gas which was found to be hydrogen chloride (v.p. 62·5 mm./− 119°, 154 mm./− 109°). The evolution of hydrogen chloride had practically ceased after 16—18 hours, and measurement of the gas formed showed that it made up the total quantity of hydrogen chloride recovered from the reaction products to approximately 1 mol. per mol. of trichlorosilane. Thus the liquid (*a*) must consist of an unstable compound, or a mixture of such compounds, which readily eliminates all its hydrogen as hydrogen chloride. Data illustrating this point are given in the following table. The inevitable slight attack of tap grease and hydrolysis account for the slightly high values for the total hydrogen chloride recovered. The residue after decomposition of the volatile liquid (*a*) was a viscous colourless liquid which was found by the Emich micro-method to have b. p. 200° ± 5°, in good agreement with the known b. p. (200°) of the oxychloride $(SiOCl_2)_4$.

Determination of Hydrogen Chloride evolved on Decomposition of Unstable Liquid Product.

Run.	$SiHCl_3$ used.	Initial HCl recovered.	HCl from liquid product.	Total HCl (mm.).	Total HCl (mols.).
P	104·7	86·5	28·2	114·7	1·095
Q	150·7	59·7	98·6	158·3	1·050
R	124·4	38·0	93·5	131·5	1·058
S	135·0	41·5	95·3	136·8	1·013

The total chlorine occurring in the combined state in the volatile liquid product (*a*) was determined volumetrically in the usual way after several runs in which this liquid was examined before it had decomposed appreciably. A comparison of the combined chlorine value with the amount of hydrogen recoverable as hydrogen chloride showed that the liquid contained approximately 3 chlorine atoms per atom of hydrogen (see Table III last column). The quantity of combined hydrogen (Table III, col. 5) was evaluated by assuming, as is justified by the previous experiments, that the liquid product contained all the hydrogen not directly recoverable as hydrogen chloride in the reaction.

TABLE III.

Determination of Combined Hydrogen and Chlorine in Liquid Product (a).

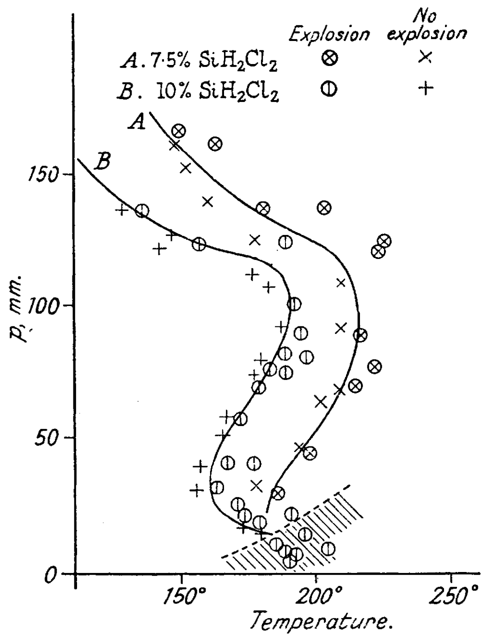
$SiHCl_3$ used (mm.).	Initial HCl recovered, (mm.).	Initial HCl recovered, (mols., M).	Combined Cl in −70° fraction (mols., N).	$1 - M$.	$N/(1 - M)$.
122·0	35·8	0·294	1·910	0·705	2·71
131·3	38·3	0·292	2·190	0·708	3·09
136·0	36·0	0·265	2·370	0·735	3·22
85·0	19·5	0·229	2·350	0·771	3·05

These analytical results point to the conclusion that the volatile liquid condensed at − 70° is a new compound with the empirical formula $Si(OH)Cl_3$. That it is not a solution of hydrogen chloride in the oxychloride $(SiOCl_2)_4$ is shown by the fact that the fraction in which it occurs is isolated by fractional condensation and not by fractional distillation. Moreover, hydrogen chloride is evolved quantitatively *without change of temperature*. The reactions taking place in the photo-oxidation under the conditions which we have employed may accordingly be written as: $2SiHCl_3 + O_2 = 2Si(OH)Cl_3$, $Si(OH)Cl_3 = SiOCl_2 + HCl$, $4SiOCl_2 = (SiOCl_2)_4$.

The viscous liquid product remaining in the reaction bulb after each experiment on the photo-oxidation [(*b*), see above] was not examined in detail, but its formula follows by difference from the analytical results given, and must approximate to $(SiOCl_2)_n$. There is little doubt that it is $(SiOCl_2)_4$, *i.e.*, it is identical with the decomposition product isolated from the hydroxy-derivative, $Si(OH)Cl_3$. If this be so, it is reasonable to assume, as has been done in the above equations, that the only primary product of this photo-reaction is the hydroxy-derivative, and that any oxychloride present at the completion of the phase of the reaction accompanied by a pressure decrease is due to decomposition of the hydroxy-compound during irradiation. We have no evidence bearing on the mechanism of the initial stages of the reaction, but suggest a primary collision between molecules of oxygen and trichlorosilane, giving addition and the formation of $SiHCl_3,O_2$. This molecule might, on collision with a second molecule of trichlorosilane, give two molecules of the hydroxy-derivative. The use of a mercury arc of the cool type makes it possible that mercury resonance radiation played a part in initiating the photo-oxidation, although the mercury vapour concentration in the reaction bulb was probably low. It is notable, however, that both the hot and the cold arc gave the same products of reaction. A further possibility is that free chlorine may have sensitised the oxidation reaction. Such chlorine, if present, could be formed only during the irradiation with ultra-violet light, and did not appear in the reaction products. Chlorine is known to react very readily with trichlorosilane to form silicon tetrachloride, which was likewise not among the products isolated.

The Thermal Oxidation of Di- and Mono-chlorosilane.—Preliminary experiments on the thermal oxidation of these two substances showed that the ignition temperature decreased with decreasing proportion of halogen in the molecule. Mixtures of dichlorosilane and oxygen rich in the former ignited spontaneously at room temperature. The course of the explosive oxidation of this substance was examined for more dilute mixtures. The explosion was initiated by rapid heating to 300—350°, and analysis of the products was carried out as already described. Data are summarised below :

FIG. 4.



Explosion limit curves for SiH_2Cl_2–O_2 *mixtures.*

Explosive Oxidation of Dichlorosilane : Analyses of Products.

Initial press.		Δp in		Cl_2	HCl	Total Cl recovered
O_2.	SiH_2Cl_2.	reaction.	O_2 used.	formed.	formed.	(atoms/mol. of SiH_2Cl_2).
84·3	21·6	−7·7	23·1	3·3	33·1	1·83
109·5	28·1	−9·7	28·1	4·1	40·8	1·75
109·0	28·0	−9·2	27·2	5·1	40·7	1·81

The amount of chlorine formed in this reaction is relatively small (0·15—0·18 mol.), and it is clear that the main reaction is $SiH_2Cl_2 + O_2 = SiO_2 + 2HCl$. The figures in the last column should be 2·0 if all the chlorine were evolved as such or as hydrogen chloride, and the deficit is probably due to the formation of a non-volatile chlorinated substance which is retained with the silica deposit in the reaction bulb. The quantity of chlorine produced in the reaction increases with the initial mixture pressure, as is shown by the following figures obtained with a mixture containing 7·5% of SiH_2Cl_2 :

Initial pressure, mm.	180	85	35
Ratio HCl/Cl_2	14	34	400

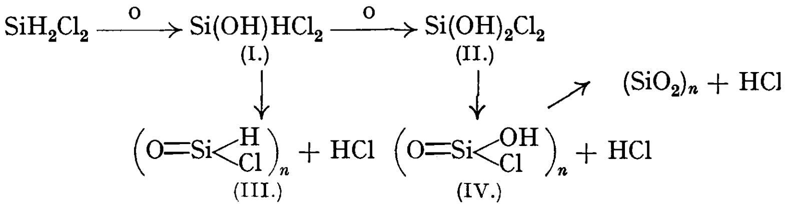
The explosion limit curve was plotted in the same way as for trichlorosilane, and results obtained for mixtures containing 7·5 and 10% of dichlorosilane are shown in Fig. 4. The curves differ completely from those for trichlorosilane in that they show two lower explosion limits. In this the behaviour is parallel to the cases of hydrogen, methane, and hydrogen sulphide. In the low-pressure region, which is shaded in the diagram, readings were erratic, and the explosion was similar in appearance to the " cold flames " observed with certain carbon compounds. Over the remainder of the pressure range studied, ignition was accompanied by a bright flash and an audible click, and took place after an induction period varying from a fraction of a second up to 15 secs. The high pressure range could not be investigated further because of the violence of the explosions. The curves demonstrate the lowering of ignition temperature with increase in the proportion of dichlorosilane in the mixture, as was the case with the trichloro-compound.

The Photochemical Oxidation of Dichlorosilane.—Slight general absorption of light by dichlorosilane was observed below 2100 A. It was found that on irradiation with light from the cold mercury arc under the conditions already described, reaction took place with a decrease in pressure and the deposition of a white solid on the walls of the quartz reaction bulb. The pressure–time curves for the photo-oxidation were similar to those for trichlorosilane, except that after the initial fall in pressure there was no rise corresponding with gas evolution (cf. A. J. E. Welch, Ph.D. Thesis, London University, 1939). At the completion of the reaction, the products were fractionated. Excess of oxygen was present, but apart from this the only volatile substance formed was hydrogen chloride. The amount of this recovered represented 50—60% of the chlorine and hydrogen present in the dichlorosilane, indicating that the non-volatile, white, solid deposit formed in the reaction bulb contained considerable amounts of these elements. Analytical data illustrating this point are given in Table IV. If the photochemical oxidation of di- and tri-chlorosilane occurs by analogous processes, dichlorosilane would be expected to give the primary hydroxylated products $SiH(OH)Cl_2$ and $Si(OH)_2Cl_2$, which would eliminate hydrogen chloride to form polymeric residues according to the reaction scheme :

TABLE IV.

Products of the Photochemical Oxidation of Dichlorosilane.

Initial press.							
O_2.	$SiHCl_3$.	Δp in reaction.	O_2 used.	HCl formed.	p.	q.	r.
120·6	43·1	−18·1	32·2	58·1	0·506	0·144	0·350
125·7	50·8	−30·2	38·2	58·8	0·498	0·342	0·160
136·2	55·0	−30·7	37·7	61·9	0·630	0·244	0·126
114·9	46·3	−26·5	33·6	53·3	0·550	0·300	0·150
92·4	37·3	−21·2	26·5	42·6	0·580	0·277	0·143
127·2	50·8	−24·6	33·3	59·4	0·690	0·140	0·170
129·2	52·0	−23·8	33·5	61·7	0·712	0·100	0·180



$$\begin{tikzcd} SiH_2Cl_2 \arrow[r, "O"] & \underset{(I.)}{Si(OH)HCl_2} \arrow[r, "O"] \arrow[d] & \underset{(II.)}{Si(OH)_2Cl_2} \arrow[d] \arrow[r] & (SiO_2)_n + HCl \\ & \underset{(III.)}{\left(O{=}Si{<}^{H}_{Cl}\right)_n} + HCl & \underset{(IV.)}{\left(O{=}Si{<}^{OH}_{Cl}\right)_n} + HCl & \end{tikzcd}$$

If the reasonable assumption is made that the substances (I) and (II) (which have no doubly linked oxygen atom and therefore cannot polymerise) rapidly give the stable degradation products (III) and (IV) and silica, it is possible to estimate the proportions of (III), (IV), and silica formed. If p, q, and r, respectively, represent the proportions of these three products formed from 1 mol. of dichlorosilane,

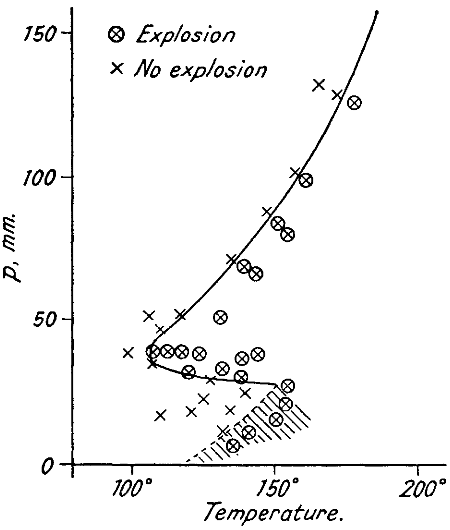
$$\begin{aligned} \text{Oxygen used} &= 1 - \tfrac{1}{2}p \\ \text{HCl formed} &= 2 - (p + q) \\ \text{and } p + q + r &= 1 \end{aligned}$$

By applying the analytical results, values of p, q, and r may be derived, and are inserted in Table IV. It is found that the product (III) predominates in each case. In the fifth run recorded in Table IV the reaction vessel was heated gently with a free flame after the hydrogen chloride and unused oxygen had been pumped off, and a further 11·8 mm. of hydrogen chloride

(0·316 mol.) was evolved. This is in agreement with the process suggested, for the product (IV) should be capable of eliminating q mols. of hydrogen chloride, leaving silica as the final product. In the run specified, q is calculated to be 0·277, compared with the observed value of 0·316. The product (III) contains no hydroxyl group, and is unlikely to evolve hydrogen chloride at moderate temperatures.

The Thermal Oxidation of Monochlorosilane.—The study of this oxidation was complicated by a slow reaction of this substance with oxygen at room temperature during the process of mixing. This reaction was more pronounced in a wide mixing bulb (4·5 cm. diameter), but was negligible in a bulb of 2·5 cm. diameter. Explosions were also liable to occur in the initial stages of the mixing process. The explosion limit curve for a 10% mixture was obtained in the usual manner, and is shown in Fig. 5. There is no third explosion limit of the type observed for dichlorosilane. The solid deposit produced on explosion gave rise to a considerable " inductive " effect upon subsequent reactions. With a coated bulb, for example, explosions could be obtained at temperatures as low as 66° at 8—10 mm. pressure. The hydrofluoric acid washing treatment was therefore used throughout. The induction periods observed were less than for dichlorosilane, and became less at higher pressures. " Cold flames " occurred in the shaded region of Fig. 5 without appreciable lag. Explosions were obtained with the above mixture by admitting it quickly to a pressure above the upper limit and then slowly reducing the pressure. " Cold flame " ignitions were also observed on admitting the mixture to the evacuated reaction bulb to a suitable pressure below the lower limit, and then reducing the pressure to a point corresponding to the shaded region of Fig. 5.

FIG. 5.



Explosion limit curve for SiH_3Cl–O_2 *mixture* (10% SiH_3Cl).

The Photochemical Oxidation of Monochlorosilane.—The photochemical oxidation phenomena of tri- and di-chlorosilane have been shown to be consistent with the occurrence of a primary hydroxylation process, the hydroxylated products undergoing partial or complete decomposition to hydrogen chloride and a polymerised silicon compound. The experiments on monochlorosilane described below are less conclusive, but the analytical data recorded give some indication of the course of the reaction.

It was found that at a pressure of 102 mm. of monochlorosilane in a quartz cell 5 cm. thick there was slight general absorption of ultra-violet light below about 2000 A. Mixtures of mono- chlorosilane and oxygen with 25—30% of the former reacted rapidly on irradiation with a cold mercury arc. There was a decrease of pressure, and a white solid was deposited. Retardation of the reaction rate due to the deposition of solid was more pronounced than in the cases already studied, and the reaction could not be followed to completion. The only gaseous substance isolated from the products, other than unchanged monochlorosilane, was hydrogen chloride. These two substances cannot be separated quantitatively without prolonged vacuum fractionation, and in the table below the measured condensable residues represent the sum of the monochlorosilane and hydrogen chloride recovered from the reaction products. The difference between the pressures of condensable residues and the original monochlorosilane represents in each case the amount of chlorine retained by the solid deposit in the reaction vessel. These

Photochemical Oxidation of Monochlorosilane.

Initial press.		Δp in reaction.	O_2 used.	Condensable residues.	Combined Cl in deposit.
O_2.	SiH_3Cl.				
79·6	40·3	−52·3	47·8	35·8	4·5
110·1	40·1	−61·1	49·4	28·4	11·7
97·7	58·3	−80·5	70·9	48·7	9·6
84·2	60·3	−79·0	69·0	50·3	10·0
73·2	52·3	−12·6	10·1	49·8	2·5

data show that relatively little chlorine remained in the solid deposit. The ratio of oxygen to silicon taking part in the reaction is greater than unity, and probably lies between 1 and 1·5.

DISCUSSION.

The results of this investigation illustrate the gradual decrease in inflammability as monosilane is progressively chlorinated. The oxidation of monosilane shows the characteristics of a branching chain reaction (Emeléus and Stewart, J., 1935, 1182; 1936, 677). The phenomena for monochlorosilane are similar, but the lower explosion limit is observed at higher pressures, and ignition is characterised by short induction periods. Dichlorosilane gives two lower explosion limits (Fig. 4) which are very similar to those observed with hydrogen sulphide and methane. The occurrence of a second lower limit in these instances is ascribed to two distinct reaction processes, one of which causes the usual low-pressure " peninsula ", while the other produces the lower limit at higher pressures (Neumann and Serbinoff, *Physikal. Z. Sowjetunion*, 1932, **1**, 271; Kowalsky and Sadownikow, *ibid.*, p. 567). There is no evidence to show what these two reactions are in the case of dichlorosilane. Trichlorosilane shows clearly the characteristics of a chain reaction with degenerate branching, and its oxidation is analogous to hydrocarbon combustion.

A comparison with the combustion of hydrocarbons reveals an interesting contrast. The explosive oxidation of chloroform in mixtures with oxygen has not been observed, although the slow reaction is well established. The chlorine-sensitised photochemical oxidation of chloroform yields carbonyl chloride and hydrogen chloride, but there is no evidence that the intermediate $C(OH)Cl_3$ is formed (Schumacher and Wolff, *Z. physikal. Chem.*, 1934, *B*, **26**, 453). The formation of peroxides has, however, been detected (Chapman, *J. Amer. Chem. Soc.*, 1935, **51**, 416). The photo-oxidation of methylene and methyl halides has also been fairly fully investigated, but in no case is there evidence that hydroxy-derivatives are formed directly. It is also noteworthy that the oxidation of unsaturated hydrocarbons is very much facilitated by partial or complete halogenation. This is illustrated by the compounds C_2BrF_3 and C_2ClF_3, which undergo explosive oxidation at room temperature (Swarts, *Inst. Int. Chim. Solvay*, V Congress Report, 1935, p. 79), and chloro- and bromo-acetylene afford a further very striking illustration of this point (Bashford, Briscoe, and Emeléus, J., 1938, 1358).

The isolation of the hydroxy-compound $Si(OH)Cl_3$ in the photo-oxidation of trichlorosilane is a unique example of hydroxylation in an oxidation process. It may well be an intermediate in the thermal oxidation, and similar hydroxylation probably takes place with the other halogenated silanes. The relatively great stability of such hydroxy-derivatives is probably specific for the oxidation of silicon compounds, but our observations afford some grounds for supposing the phenomenon to be general.

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