

simultaneous deposition and decomposition of ferric bromide vapor. This phase of the equilibrium study is being investigated further.

The straight line drawn in Fig. 1 represents the equation of the form $\log P(\text{mm.}) = -A/T + B$, where the constants were determined from the data by the method of least squares ($A = 3478.6$; $B = 11.327$). From this equation ΔH^0 for the reaction $2\text{FeBr}_3(\text{s}) = 2\text{FeBr}_2(\text{s}) + \text{Br}_2(\text{g})$ is found to be 15.9 kcal. at an average temperature of 102° . The average deviation of $\log P$ (experimental) from $\log P$ calculated from the least squares solution is 0.0102. This corresponds to a mean deviation of P of 2%. The estimated uncertainty in ΔH^0 is ± 0.4 kcal.

The data obtained are not sufficiently precise to determine ΔC_p for the reaction. Since this factor is expected to be small on the basis of comparison with similar reactions, the heat of formation of ferric bromide has been calculated at 25° assuming that $\Delta C_p = 0$, and using a value of -60 kcal./mole for the heat of formation of ferrous bromide.^{8,9} Table II contains a summary of the thermodynamic constants at 25° obtained by extrapolation of these data (liquid bromine taken as standard state; $S^0(\text{Br}_2 \text{ liq.}) = 36.7$

(8) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publ. Co., New York, N. Y., 1936, p. 90.

(9) H. Hieber and A. Woerner, *Z. Elektrochem.*, **40**, 287 (1934).

	ΔH_{298}^0 , kcal.	ΔF_{298}^0 , kcal.	ΔS_{298}^0 cal./ mole/deg.
$\text{FeBr}_3(\text{s}) - \text{FeBr}_2(\text{s})$	-4	-1.8	9.8
$\text{FeBr}_3(\text{s})$	-64		

e. u.).¹⁰ ΔS^0 is somewhat less than one would expect from Latimer's rule; however, this does not appear to be uncommon for compounds of this type.

From the extrapolated value of ΔF^0 , it is observed that ferric bromide is thermodynamically stable at room temperature if the bromine pressure in the system is greater than 0.5 mm. The equilibrium pressure of bromine reaches one atmosphere at 139° . These factors must be considered in the preparation and handling of anhydrous ferric bromide.

Summary

The thermal dissociation of ferric bromide has been studied in the temperature interval 65 – 140° . The data have been interpreted as characterizing the equilibrium $\text{FeBr}_3(\text{s}) = \text{FeBr}_2(\text{s}) + 1/2\text{Br}_2(\text{g})$. The results may be summarized as follows: $\log P^{1/2}(\text{mm. Br}_2) = -(1739.3/T) + 5.663$. At 25° (extrapolated), $\Delta H^0 = 8.0$ kcal.; $\Delta F^0 = 2.2$ kcal.; $\Delta S^0 = 19.5$ cal./mole/deg.

(10) K. K. Kelley, U. S. Bureau of Mines, Bull. 434 (1940).

SEATTLE 5, WASHINGTON RECEIVED DECEMBER 28, 1949

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

The Partial Hydrolysis of Silicon Tetrachloride

BY WALTER C. SCHUMB AND ARTHUR J. STEVENS

In a preliminary communication¹ it was shown that by the partial hydrolysis of silicon tetrachloride, dissolved in anhydrous diethyl ether, by means of moist ether, the first two members of the homologous series of oxychlorides, $\text{Si}_n\text{O}_{n-1}\text{Cl}_{2n+2}$, could be prepared, namely, Si_2OCl_6 and $\text{Si}_3\text{O}_2\text{Cl}_8$. The existence of such homologous series of silicon oxychlorides and of oxybromides, prepared by other methods, had been established definitely in earlier papers from this Laboratory.^{2,3} These results showed sufficient promise to warrant a more extensive study of the hydrolysis reaction carried out under various conditions. In the preliminary notice it had been reported that attempts to effect partial hydrolysis in the vapor phase were unsuccessful. It had also been observed that while partial hydrolysis in ether and in *p*-dioxane was possible, the use of other liquids as solvents, such as benzene, toluene, chloroform, pentene-1, and petroleum ether, led only to the formation of silica. The significance of

these facts led us to undertake a systematic study of the reaction in an attempt to determine the role of the ether and the optimum conditions for carrying out the reaction leading to the oxychlorides.

The effect upon the course of the reaction of three molar ratios was studied—the silicon tetrachloride–water ratio, the ether–water ratio, and the ether–silicon tetrachloride ratio. A knowledge of these three ratios prevailing in the separate experiments, considered together with the proportions of the products obtained, should throw light upon the part played by the ether and other theoretical aspects of the hydrolytic process.

Because of the ease of separation and measurement of the quantities of Si_2OCl_6 formed, the quantitative interpretation of the experimental results was based upon the yields obtained from this first member of the homologous series; the higher members being reported as a mixture of known silicon, oxygen and chlorine content. The average chain lengths of the mixtures of oxychlorides of higher molecular weight than Si_2OCl_6 were also calculated from the elementary analysis of the mixture, as discussed below.

(1) Schumb and Stevens, *THIS JOURNAL*, **69**, 726 (1947).

(2) Schumb and Klein, *ibid.*, **59**, 261 (1937).

(3) Schumb and Holloway, *ibid.*, **63**, 2753 (1941).

TABLE I
 MOLAR RATIOS EMPLOYED

Run no.	Series I— SiCl ₄ /H ₂ O = 4						Series II— (C ₂ H ₅) ₂ O/H ₂ O = 12				Series III— (C ₂ H ₅) ₂ O/SiCl ₄ = 3			
	12	11	5	2	6	3	4	9	2	10	1	7	2	8
SiCl ₄ /H ₂ O	4	4	4	4	4	4	2	3	4	6	2	3	4	6
(C ₂ H ₅) ₂ O/H ₂ O	2	4	8	12	16	24	12	12	12	12	6	9	12	18
(C ₂ H ₅) ₂ O/SiCl ₄	0.5	1	2	3	4	6	6	4	3	2	3	3	3	3

Method of Hydrolysis.—It seems evident that, in order to hydrolyze silicon tetrachloride only partially and to inhibit the formation of silica, the water must be introduced into an excess of silicon tetrachloride. Three different means of introduction of the water were considered. The first method was that employed in the earlier work, consisting of adding a solution of ether saturated with water to an ethereal solution of silicon tetrachloride. This method presents, however, several disadvantages. It offers little opportunity for varying the quantity of solvents used with the reactants, since water is but sparingly soluble in ether—about 1.3% at room temperature⁴—so that in order to add any appreciable quantity of water, a large quantity of ether must be added with it. Furthermore, in low temperature runs it was found that water precipitated out of the ether and appeared as a solid phase in the reaction mixture.

The second method attempted was the entrainment of moisture in previously-dried air or nitrogen, which was then passed through the silicon tetrachloride dissolved in ether. Objections to this method include the fact that at all concentrations silica was formed at the aperture of the tube which led the moist gas into the silicon tetrachloride solution, resulting in an eventual plugging of the tube; and there was also reason to believe that some of the moisture could escape unreacted with the current of air which had carried it.

The third method, which was used in all the work described below, consisted of cooling the ethereal solution of silicon tetrachloride to -78° with a solid carbon dioxide-trichloroethylene-bath, and running in water from a buret while the solution was agitated vigorously with a motor-driven stirrer. The water froze the instant it came into contact with the solution. No statement can be made, on the basis of observation, as to whether reaction of the silicon tetrachloride took place with solid ice, or with water which resulted from ice first dissolving in the solution. However, the amount of silica produced in this way was found to be negligibly small to entirely absent. In the majority of cases the resulting solution was clear, water-white. This method permitted the variation of the molar ratios of the reacting substances and of the solvent within any desired limits.

(4) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 388.

Experimental

The silicon tetrachloride was of C. P. quality (obtained from the Stauffer Chemical Company, Niagara Falls, New York); its chloride content closely checked the theoretical value and its boiling point agreed with that given in the literature.

Three series of runs were made in which the molar ratios of ether:water, ether:silicon tetrachloride and silicon tetrachloride:water were systematically varied in order to observe the effect of changing proportions of the reactants and of the solvent. In the first series the silicon tetrachloride:water molar ratio was held constant at four while the quantity of ether was varied; in the second series the ether:water molar ratio was held constant at twelve while the quantity of silicon tetrachloride was varied; and in the third series the ether:silicon tetrachloride molar ratio was held constant at three while the quantity of water was varied, as shown in Table I.

Since the series of compounds resulting from the reaction have closely similar properties, and the separation of the individual members by fractional distillation is attended with increasing difficulty as the molecular weights of the components rise, the problem arose of measuring the yields obtained. It was noted that after the evaporation of the hydrogen chloride formed in the reaction as well as the ether and the excess unchanged silicon tetrachloride, the first member of the series, Si₂OCl₆, could be distilled at atmospheric pressure from the mixture with a fairly sharp break between this compound and the next higher boiling component. Consequently, it was decided to base all theoretical interpretations and calculations derived from the experimental results upon the yields of Si₂OCl₆ obtained.

However, although the break between Si₂OCl₆ and its higher boiling homologs was adequately sharp, a quantitative separation from silicon tetrachloride was found to be possible only with very careful, hence time-consuming fractionation; otherwise, some loss of Si₂OCl₆ with the tetrachloride was inevitable. This difficulty was obviated in the following way, which, although indirect, was believed to be more reliable than the direct measurement of the Si₂OCl₆ for the reason indicated.

Samples of residues of known weight boiling higher than Si₂OCl₆ were analyzed for chlorine and silicon, and the residual composition was assumed to be oxygen. On the further assumption that all of the water added reacts, and since the amount of silica formed was either negligibly small or none at all, it follows that the quantity of oxygen in the Si₂OCl₆ must equal that present in the water added minus that present in the higher-boiling residue. In this way, the quantity of Si₂OCl₆ formed could be calculated, and as indicated above, this calculated value is believed to be more accurate than that obtained by direct measurement of the Si₂OCl₆ fraction obtained on distillation.

Because attempts to obtain partial hydrolysis of silicon tetrachloride in the vapor phase had been unsuccessful,¹ it appeared reasonable to believe that the nature of the solvent plays an important role in the hydrolysis reaction, and accordingly several solvents other than diethyl ether were tried. Restrictions concerning the properties of a suitable solvent limit the number of common reagents that may be used for the purpose: the solvent must be inert both toward silicon tetrachloride and toward water; and if the reaction is to be carried out at -78° the solvent should not freeze at this temperature. Since Si₂OCl₆, the lowest member of the homologous series, boils at 134° , the

TABLE II
ANALYSES OF RESIDUES BOILING ABOVE Si_2OCl_6

Run	Si, %	Cl, %	O (by difference), %
1R	23.20	65.36	11.44
2R	22.53	66.33	11.14
2RR	22.06	68.20	9.74
3R	22.31	67.72	9.97
4R	23.23	65.20	11.57
4RR	23.13	65.62	11.25
5	22.42	67.44	10.14
6	23.65	66.20	10.15
7	21.81	67.55	10.64
8	22.31	67.30	10.39
8R	22.36	67.42	10.22
9	21.70	67.63	10.67
10	23.20	65.33	11.47
10R	22.65	66.88	10.47
11	23.09	65.85	11.06
12	22.42	66.73	10.85

9 were combined and fractionally distilled at a pressure of 15 mm. After six fractions had been obtained and the quantity of material in each succeeding fraction had become progressively smaller, a point was reached where attempts to obtain further fractions appeared fruitless. Furthermore, the boiling points had begun to approach each other to the point where clean separation became increasingly difficult.

The recorded boiling points were taken at about the mid-way point of the refractionation of each fraction first obtained. Samples for analysis were also taken at this point. The results of these fractionations are given in Table III. The quantities of each oxychloride listed in Table III are the quantities of each fraction obtained in the first fractionation. The quantity of hexachlorodisiloxane, which is included in the table for completeness, was obtained by adding the calculated yields of Si_2OCl_6 from all runs except 7, 8 and 9, together with approximately 25 g. which came over as the first fraction in the first fractionation of the higher members; 450 g. of higher members were subjected to this fractionation. About 175 g. of material which boiled above 190° at 15 mm. remained in the boiler after the fractionation.

No evidence of the cyclic tetramer, $\text{Si}_4\text{O}_4\text{Cl}_8$, was obtained.

TABLE III
RESULTS OF SEPARATING THE OXYCHLORIDES OF SILICON

Compound	Boiling point at 15 mm.		Approx. quantity, g.	Theor.	% Cl		Theor.	% Si	
	Found	Reported			Found	Found		Found	Found
Si_2OCl_6	34.5	137 ^a	325	74.68	74.31	74.28	19.70	19.76	19.72
$\text{Si}_3\text{O}_3\text{Cl}_8$	80.5	76	125	70.95	70.91	70.93	21.05	21.07	21.15
$\text{Si}_4\text{O}_3\text{Cl}_{10}$	114.7	109-110	80	68.87	68.91	68.83	21.80	21.84	
$\text{Si}_5\text{O}_4\text{Cl}_{12}$	140	130-131	50	67.56	67.65	67.49	22.28	22.26	22.36
$\text{Si}_6\text{O}_5\text{Cl}_{14}$	166-167	139-141	35	66.65	66.84	67.01	22.61	22.66	22.57
$\text{Si}_7\text{O}_6\text{Cl}_{16}$	187-188	145-147	25	65.99	66.00	65.64	22.85	22.73	22.80

^a At 760 mm. The value found in this work at 760 mm. was 134° .

solvent should boil as far as possible below this temperature so as to facilitate the separation of the solvent from the products by distillation. Of common solvents possessing these qualifications, the principal examples include ethers, hydrocarbons and alkyl and aryl halides.

Experiments with such solvents as benzene, chloroform, diethyl ether, *p*-dioxane, pentene-1, petroleum ether and toluene indicated that oxychlorides were formed only with diethyl ether and with dioxane; the others led only to complete hydrolysis of part of the silicon tetrachloride with formation of silica. Because of the much lower freezing point of the ether as compared with that of dioxane (-116° as opposed to 11.7°), ether was selected for use throughout the study, especially as the reaction could thus be carried out at -78° .

After removal of the hydrogen chloride formed by the reaction as well as the ether and excess silicon tetrachloride, the first member of the oxychloride series, Si_2OCl_6 , was separated from the higher boiling residue by distillation through a four-foot Podbielniak column. As previously indicated, the break in the distillation between Si_2OCl_6 and the higher members was sharp, but that between Si_2OCl_6 and the tetrachloride was not sharp. All runs were made under as closely similar conditions as possible. The materials employed were brought to a total of 450 ml., contained in a 500-ml. round-bottom flask, provided with a slip-seal, motor-driven stirrer and a vent to the hood.

Samples for analysis were taken in small, thin-walled tubes, either by means of a secondary, revolving receiver in the case of fractionated products, or by means of a micro-pipet in the case of higher boiling mixtures. Silicon analyses were made gravimetrically after hydrolysis of the sample in a stoppered flask. Chloride analyses were made volumetrically by titration of the hydrogen chloride liberated by the hydrolysis with 1 *N* sodium hydroxide. The analytical results are given in Table II.

The higher boiling residues from all runs except 7, 8 and

Discussion

Of the three molar ratios mentioned earlier, only the silicon tetrachloride-water ratio appears to lend itself readily to theoretical treatment. Regardless of the mechanism of the reaction, an expression for the number of moles of any particular member of the series of oxychlorides produced per mole of water added may be obtained in terms of only the silicon tetrachloride-water molar ratio, by means of purely statistical considerations. This expression is a modification of the equation derived by Stockmayer,⁵ which gives the distribution of species of varying molecular weights resulting from the polymerization of a polyfunctional monomer.

Stockmayer's derivation was based on two fundamental assumptions which also apply in the present instance: (1) Intramolecular reactions, leading to cyclic structures are assumed not to occur. For example, since no cyclic tetramer, $\text{Si}_4\text{O}_4\text{Cl}_8$, was found in the products of hydrolysis, the reaction $\text{Si}_4\text{O}_3\text{Cl}_{10} + \text{H}_2\text{O} = \text{Si}_4\text{O}_4\text{Cl}_8 + 2 \text{HCl}$ probably did not occur to any appreciable extent. (2) At any stage during the reaction all unreacted functional groups are considered to be equally reactive, regardless of the nature of the molecule to which they are attached. For this work the assumption that all hydrolyz-

(5) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).

able chlorides are equivalent with respect to their rates of hydrolysis must be made, although it may not be rigidly true, since there is no simple way to account for any differences theoretically, even if the magnitudes of the differences were known.

Stockmayer's derivation was based upon a statistical treatment, only the results of which are given below. The size distribution law obtained by Stockmayer may be modified for the reaction of silicon tetrachloride with water to predict the yield in moles of hexachlorodisiloxane per mole of water added in terms of the silicon tetrachloride-water molar ratio. The result obtained is given by the following expression, wherein the formulas represent molar quantities

$$\frac{\text{Si}_2\text{OCl}_6}{\text{H}_2\text{O}} = \left(1 - \frac{1}{2\text{SiCl}_4/\text{H}_2\text{O}}\right)$$

As might be expected from qualitative considerations, it is obvious from this equation that the yield of hexachlorodisiloxane per mole of water added increases with increasing silicon tetrachloride-water molar ratio.

The above equation was used to calculate the theoretical yield of hexachlorodisiloxane for each of the runs made. This equation was used to eliminate the effect of the silicon tetrachloride-water molar ratio on the yield of hexachlorodisiloxane. The results obtained are given in Table IV.

TABLE IV

Run	YIELDS OF Si_2OCl_6		Fract. yield Si_2OCl_6
	Si_2OCl_6 (calcd.), g.	Si_2OCl_6 (theor.), g.	
1	17.7 ^a	26.2	0.68
1A	27.4		1.045
2	20.9 ^a	33.2	0.63
	15.5		.46
	21.4		.64
3	5.5 ^a	19.5	.28
3R	9.1		.47
4	8.7 ^a	15.5	.53
4R	7.0		.45
4RR	9.6		.62
5	34.7	44.1	.79
6	12.8	27.0	.48
7	18.5	33.1	.56
8	6.6	29.6	.22
8R	10.5		.36
9	13.7	26.7	.51
10	16.4	39.0	.42
10R	21.9		.56
11	34.8	35.9	.97
12	43.3	46.7	.93

^a These values were not calculated, but measured directly.

While the effect of the ether-water molar ratio on the yield of hexachlorodisiloxane did not readily lend itself to theoretical treatment, it could be observed experimentally. The average fractional yields of hexachlorodisiloxane, cal-

culated as described above, were plotted against the corresponding ether-water molar ratios, as shown in Fig. 1. While the points of the plot only demonstrate a trend, it is clear that as the ether-water molar ratio increases, the yield of hexachlorodisiloxane decreases within the limits studied. The dotted line is drawn to emphasize the trend of values.

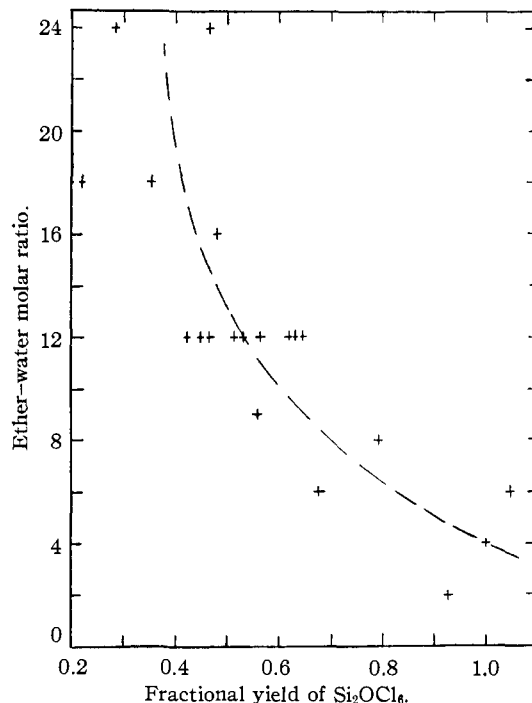


Fig. 1.

When the effect of the ether-silicon tetrachloride ratio upon the yield of hexachlorodisiloxane was similarly observed and plotted, the trend of values was absent over the range studied with the exception of the very lowest ether:silicon tetrachloride ratios. The conclusion which may be drawn from this result, namely, that in the mechanism of the hydrolytic process there is likely to be less interaction between the ether and the silicon tetrachloride than there is between the ether and the water, is borne out by the findings of Sisler, Batey, Pfahler and Mattair⁶ who studied the freezing points of mixtures of ether and silicon tetrachloride and observed no indications of any compound formed between the two substances, as well as Kennard and McCusker⁷ and Lane, McCusker and Columba,⁸ who likewise found no apparent interaction between silicon tetrachloride and dioxane.

The boiling points found for the silicon oxychlorides vary appreciably from those reported by Schumb and Holloway.² The earlier method

(6) Sisler, Batey, Pfahler and Mattair, *THIS JOURNAL*, **70**, 3821 (1948).

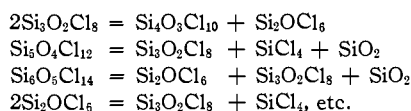
(7) Kennard and McCusker, *ibid.*, **70**, 1039 (1948).

(8) Lane, McCusker and Columba, *ibid.*, **64**, 2076 (1942).

of preparation consisted of the passage of mixed chlorine and oxygen over hot silicon, and the resulting mixture of products might be expected to include both oxychlorides and the normal chlorides, $\text{Si}_n\text{Cl}_{2n+2}$. Since the insertion of an oxygen between two silicon atoms does not in general greatly affect the boiling point, this mixture might be exceedingly difficult to separate into pure components. Further, the analyses of adjacent members of the series of oxychlorides do not differ greatly, especially between higher members. The presence of small amounts of normal chlorides in the earlier preparation of the oxychlorides may be responsible for the difference in the boiling points reported from those observed in the present study.

The fact that in the present work no trace was found of the cyclic tetramer, $\text{Si}_4\text{O}_4\text{Cl}_8$, is of considerable interest, and indicates that the assumption made by Stockmayer that intramolecular reactions do not occur probably is valid in this instance.

A question may be raised concerning the possibility of rearrangement of the oxychlorides, particularly at higher temperatures, by such reactions as those indicated in the equations

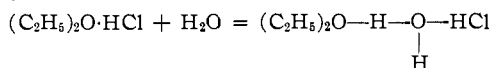


No evidence for such rearrangements was found during the course of this work. Were this type of reaction to occur at any appreciable rate under 250° , it is doubtful if the higher members could be separated by fractional distillation. No evidence for the formation of either silica or silicon tetrachloride was found at any time during the fractionation of the higher members.

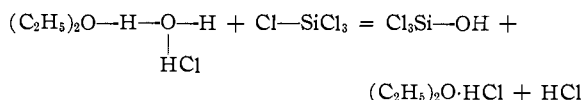
After the completion of this paper and while it was pending publication, an account of a similar investigation by Goubeau and Warnecke appeared in *Z. anorg. Chem.*, 259, 109 (1949), in which the techniques employed in most respects were identical with those indicated by us in the preliminary communication¹ to THIS JOURNAL in 1947, and the results reported essentially confirm our observations reported then and in the present paper. An alternative interpretation of the results is presented by these authors accounting for the formation of the various oxychlorides, in which a condensation of chlorosilanols is assumed to occur, and the latter compounds are considered as intermediate hydrolysis products formed by the stepwise replacement of chlorine atoms by hydroxyl—(February 10, 1950).

Conclusions.—The following hypothesis is suggested for the mechanism of the partial hydrolysis of silicon tetrachloride. Admittedly speculative, the hypothesis, however, does explain the pertinent facts observed in the present study of this reaction.

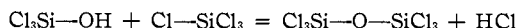
Hydrogen chloride, produced by the reaction, is known to form an oxonium compound with ether which might then react with water, especially at the low temperature employed (-78°)



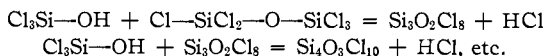
The resulting compound has essentially one active hydrogen which could then react with a chlorine atom on silicon tetrachloride



followed by interaction of the trichlorosilanol with silicon tetrachloride

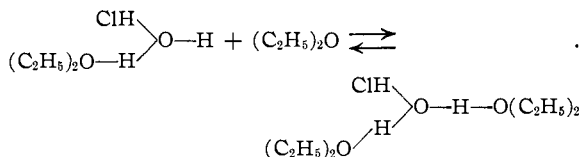


or with oxychlorides already formed



In this way the various oxychlorides could be formed. The other solvents, except *p*-dioxane, could not support such a series of reactions, since they are not Lewis bases.

The decrease in yield of hexachlorodisiloxane with increasing ether-water molar ratio might be explained by the equilibrium



The compound on the right would have two essentially equivalently active hydrogens, as opposed to having one hydrogen more active than the other, as would be true in the case of the compound on the left. As a result, the compound on the right would be difunctional, or a chain-former, and could cause the formation of a larger quantity of the higher members, with a corresponding sacrifice in the yield of hexachlorodisiloxane. In all probability, *p*-dioxane, which is known¹ also to promote partial hydrolysis, behaves similarly to ether.

Summary

The homologous series of oxychlorides of silicon of general formula $\text{Si}_n\text{O}_{n-1}\text{Cl}_{2n+2}$ were prepared up to $\text{Si}_7\text{O}_6\text{Cl}_{16}$ by the partial hydrolysis of silicon tetrachloride in ether solution. The homologs were separated by fractional distillation and analyzed.

The conditions of the reaction were studied. While the ether-silicon tetrachloride molar ratio was found to be without effect upon the yield of hexachlorodisiloxane, Si_2OCl_6 , the ether-water molar ratio was found to affect the yield of this compound inversely within the limits used.

No cyclic tetramer, $\text{Si}_4\text{O}_4\text{Cl}_8$, was found among the products of hydrolysis. No evidence was found for the rearrangement of the oxychlorides.

An hypothesis for the mechanism of the partial hydrolysis has been suggested.