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THE PREPARATION AND REACTIONS OF THE LOWER CHLORIDES AND OXYCHLORIDES OF SILICON

by

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A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major subject - Inorganic Chemistry

Approved

Signature was redacted for privacy.
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Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

Iowa State College

1926

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TABLE OF CONTENTS

Page

Part I.

Part II.

Page

- - -

Part I

A STUDY OF THE OPTIMUM CONDITIONS FOR THE PRESERVATION OF THE LOWER CHLORIDES OF SILICON IN THE CHLORINATION PROCESS

A STUDY OF THE OPTIMUM CONDITIONS FOR THE PRESERVATION OF THE LOWER CHLORIDES OF SILICON IN THE CHLORINATION PROCESS

INTRODUCTION

Stock and Somieski (1916) showed that silicon possesses the power of atomic linkage to a limited degree by their preparation of the hydrosilicons Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{12}, and Si_6H_{14}. The existence of these linked silicon compounds reveals a field in the chemistry of silicon which has scarcely been explored. The reason for our meager knowledge of these compounds and their derivatives bears a definite relationship to the character of these compounds and to the difficulties which have attended their preparation. The hydrosilicons themselves are not suitable compounds for the investigation of the chemistry of compounds containing linked silicon atoms because they are spontaneously inflammable in air.

Some of the halogen derivatives of the hydrosilicons have been prepared. Among these, the chlorine derivatives are the best known. While the preparation of the halogen derivatives is accomplished with much greater ease than the corresponding hydrosilicons, a preliminary study showed that they are obtained in extremely small quantities by the known methods of preparation. The chlorine derivative of silicoethane is the only one of these compounds which has been prepared in sufficient quantities to render it available for research on compounds containing linked silicon atoms. That this chlorine derivative is superior to the hydrosilicon itself for the study of compounds containing the silicon linkage, is shown by a comparison of their physical properties in the following table.

	Vapor Pressure mm.	M.P., °C 760 mm.	B.P., °C 760 mm.
Si_2H_6	725(-15.7°)	-132.5	-15
Si_2Cl_6	2.5(10°)	2.5	147

A Comparison of the Chloro-derivative with Other Halogen Derivatives of Silicoethane:

The chloro-derivative is the only halogen derivative of silicoethane which is a liquid. The bromine and iodine derivatives are solids. Disilicon hexaiodide cannot be distilled at ordinary atmospheric pressure or in vacuo and its preparation from silicon tetraiodide is not adapted to the preparation of relatively large amounts of the compound. Silicon tetraiodide is also difficult to prepare and hence the preparation of disilicon hexaiodide is rendered even more difficult. The fact that disilicon hexabromide depends on disilicon hexaiodide for its preparation, likewise removes it from the field at present as a starting point for the development of the chemistry of linked silicon compounds. Although disilicon hexachloride may not show as much activity as the iodine derivative, because of the stronger bonding of the chlorine, workers in the field of silicon chemistry have selected it as the most accessible compound at the present time for the starting point of their research on the chemistry of linked silicon compounds.

Methods of Preparation of Disilicon Hexachloride:

Disilicon hexachloride was prepared by Friedel (1871) by the action of chlorine upon the corresponding iodide, Si_2I_6, or by gently heating this compound with mercuric chloride. The difficulties involved in this method have already been discussed. Troost and Hautefeuille (1876) obtained the compound in very small amounts by the union of silicon and its tetrachloride, by passing the vapor of the latter over white hot silicon. This method is not a practical one because of the decomposition of the product as it passes through the decomposition range (350°-800°) during the cooling of the vapor. Gattermann and Weinlig (1894) reported a yield of 20 per cent disilicon hexachloride calculated on the basis of the total chlorides formed when crude silicon was chlorinated. These workers began the chlorination at 350° and then lowered the temperature to 300°. This yield of 20 per cent could not be duplicated in this laboratory. Martin (1914) chlorinated 50 per cent ferrosilicon at 180°-200° and obtained a yield of 5.25 per cent when calculated on the basis of the total chlorides condensed. If the percentage is calculated on the basis of the ferrosilicon used, the yield is 2.5 per cent.

Preliminary experiments in this laboratory showed that the method used by Martin was unquestionably the best. The yields by this method, however, are too small for it to lend itself to the preparation of this much desired compound in sufficient amounts for extensive research on the chemistry of linked silicon compounds. With this incentive the author decided to study the chlorination of ferrosilicon with the special purpose of determining the cause of the low yields of disilicon hexachloride and of devising a method by which this compound could be produced in sufficient quantities for research on the chemistry of linked silicon compounds.

A STUDY OF THE EFFECT OF THE VAPOR OF SILICON TETRACHLORIDE ON THE CHLORINATION OF FIFTY PER CENT FERROSILICON

Gattermann and Weinlig (1894) assumed that the chlorination of silicon first gave the tetrachloride and that this was then reduced by more silicon to the lower chloride by the reaction $3\ SiCl_4 + Si = 2\ Si_2Cl_6$. Martin (1914) has shown that this reaction does not take place to any appreciable extent when the vapors of silicon tetrachloride are passed over either silicon or ferrosilicon at temperatures between 200° and 350°. He cites this as refuting Gattermann and Weinlig's idea of the process of the formation of the lower chlorides from the tetrachloride.

Martin (1914) has also shown that the reaction, $Si_2Cl_6 + Cl_2 = 2\ SiCl_4$, does not take place unless the tube through which the vapors are passing is heated above the boiling point of disilicon hexachloride (145°). However, at 300° or above, the reaction takes place very rapidly. This would seem to account for the fact that better yields of disilicon hexachloride are obtained by chlorinating at 180°-200° than at 300°. It also accounts for the fact that better yields are obtained by chlorinating ferrosilicon than silicon since the latter requires a higher temperature than the former in order to effect the chlorination, and, at this higher temperature, the disilicon hexachloride chlorinates readily to the tetrachloride. There is another factor which operates to destroy the lower chlorides of silicon during the chlorination of ferrosilicon. Disilicon hexachloride decomposes somewhat at 350° according to the reaction, $2\ Si_2Cl_6 = 3\ SiCl_4 + Si$. My experiments have shown that this reaction takes place to some extent during the chlorination process. The temperature of the zone in which the chlorination takes place is much higher than the temperature of the tube through which the vapors are passing because of the heat evolved by the chlorination of the iron and the silicon. J. N. Friend (1921) has calculated the heat of formation of anhydrous ferric chloride and gives for the thermo chemical equation $2\ Fe + 3\ Cl_2 = 2\ FeCl_3 + 192{,}080$ calories thus showing that the chlorination of the iron is highly exothermic. The chlorination of silicon to form silicon tetrachloride is also mildly exothermic as shown by Berthelot (1876), $\underset{(crys.)}{Si} + 4\ Cl = \underset{(gas)}{SiCl_4} + 121.8$ calories. It is probable then that the net effect of these two reactions results in a temperature at the immediate zone of the chlorination which is within the decomposition range of disilicon hexachloride.

The Preservation of Disilicon hexachloride in the Chlorination Process:

A device of frequent application to overcome the excessive localization of temperature in gas reactions is the addition of an inert constituent to the gas mixture or the addition in a circulatory process of excess of one of the reacting constituents, or, in a process where the reaction is practically exclusively in one direction, the addition of one of the reaction products to the incoming gases. Taylor (1922) states that these devices operate by diminishing the heat evoluation per unit volume of total gas, thus lessening the temperature increase of the gas mixture per unit of reaction. The problem of the chlorination of hydrocarbons may be cited in which the intensity of the reaction may be minimized by admixing with the incoming gases, carbon tetrachloride or other saturated chlorocompound.

That the passage of silicon tetrachloride with chlorine, during the chlorination of ferrosilicon would operate in a manner favorable to the preservation of the lower chlorides of silicon appeared probable. There were five reasons for this view. (a) If disilicon hexachloride is formed first and this is then chlorinated to silicon tetrachloride the presence of the latter, one of the products of the reaction, would tend to retard the rate of final chlorination. (b) If disilicon hexachloride is heated to its decomposition temperature because of the excessive localization of temperature in the chlorination of the iron or silicon, the presence of silicon tetrachloride, one of the products of the decomposition of disilicon hexachloride, would tend to retard the rate of this decomposition. (c) The silicon tetrachloride would dilute the chlorine and thus operate to retard the final rate of chlorination because of the diminished partial pressure of the chlorinating gas. (d) If silicon tetrachloride is an inert constituent in the process, the admixing of it with the chlorine would raise the specific heat of the gas mixture per molecule of disilicon hexachloride, the specific effect of which, would tend to lower the temperature. Since the final chlorination or the decomposition of disilicon hexachloride does not take place below 300°, this lowering of the temperature of the gas mixture would aid in the preservation of the lower chlorides. (e) The silicon tetrachloride would act as an inert gas to sweep the lower chlorides away from the zone of high temperature where the first action took place to a zone where the temperature is not high enough to allow the final chlorination or decomposition to take place.

The above theories were tested by passing mixtures of silicon tetrachloride and chlorine of different concentrations and at different rates over ferrosilicon heated to 200°.

Experimental

The mixture of chlorine and silicon tetrachloride vapor was made by passing the gas through the liquid tetrachloride. The vapor pressure of the tetrachloride is 78.02 mm. at 0° and 294.39 mm. at 30°. By varying the temperature of the tetrachloride it was thus possible to vary the concentration of the tetrachloride in the reacting vapor between wide limits.

The Chlorination Process:

The apparatus which was used is shown in Figure 1. It is similar to that used by Martin (1914) but with some improve-

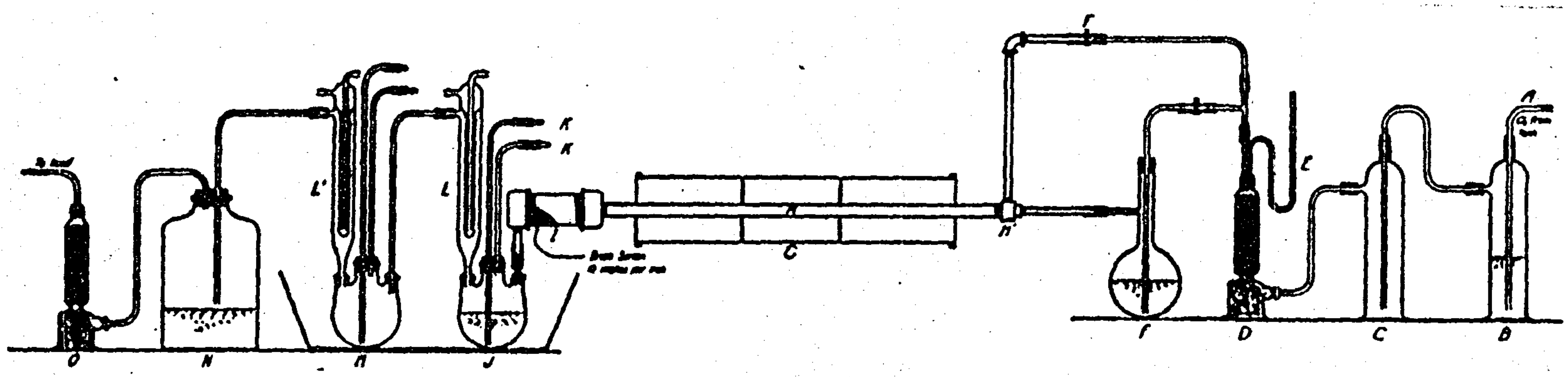


Fig. 1.—Chlorination apparatus.

ments. The chlorine from a cylinder is dried by passing it through a sulfuric acid drying bottle (B) and a gas wash bottle (C) and finally through a phosphorus pentoxide tube (D) to which a manometer (E) is attached to show when the ferric chloride is stopping up the iron pipe (H). The chlorine then passes through the tube (F) into the iron gas pipe (H) set in a three multiple unit electric furnace which is heated to 180°-200° and is charged with 200-250 grams of 50% ferrosilicon. After a period of gestation, usually about thirty minutes, and after the chlorination has begun, the chlorine is allowed to pass through the two liter flask (F) containing the silicon tetrachloride which had previously been saturated with chlorine. The units were heated so that at first the end next to the point where the chlorine entered was the hottest. As the reaction progressed the others were raised.

The 0.75 inch iron pipe (H) is fitted with a detachable iron cap (H') and a ferric chloride trap (I) having a length of 4 inches and a diameter of 2 inches, which are made gas tight by luting with ordinary soap. The trap (I) is fitted with a removable, closed bronze screen containing 24 meshes to the inch. This screen prevents the ferric chloride from entering the three necked flask (J) in which the chlorides are condensed and collected. (M) is also a three necked flask connected to (J) by a Hopkins condenser (L) and a safety flask to catch any silicon chloride that escapes from (J). Both of these flasks are immersed in an ice bath to insure condensa-

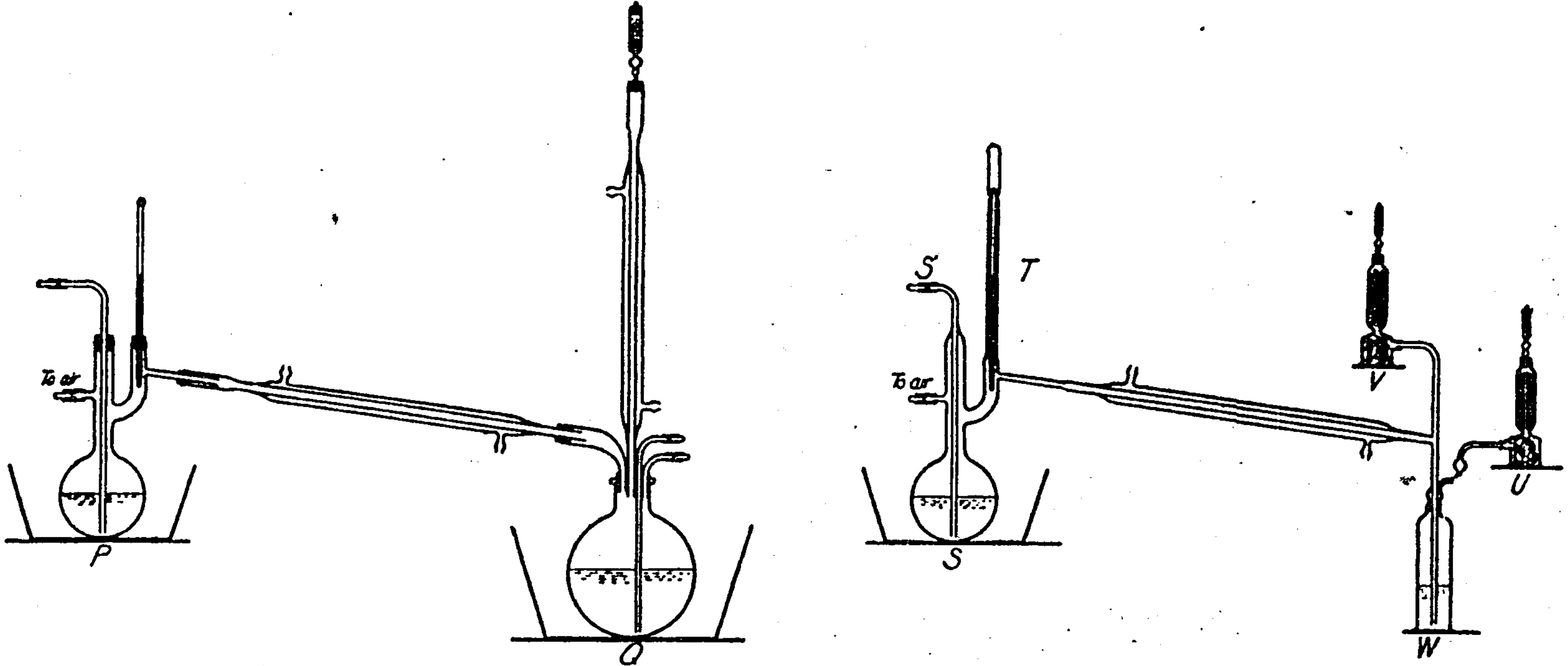


Fig. 2.—Distillation apparatus.

tion and are fitted similarly with tubes (K) and (K') in order that the chlorides may be removed by applying air pressure. (L') is a Hopkins condenser which leads to a large bottle (N) containing sulfuric acid. This aids in preventing hydrolysis and serves as an indicator to show the excess of chlorine passing through the apparatus. (N) is connected to a calcium chloride tower (O) which leads to the hood.

When a sufficient amount of the chlorides has collected in (J) they are forced by the pressure of dry air into a Claissen distilling flask (P) and the silicon tetrachloride is distilled off by means of the heat from a water bath. When a considerable amount of the lower chlorides has collected in the flask (P) the water bath is replaced by an oil bath and the portion distilling between 140° and 155° is collected in the flask (Q). This portion is then forced by the pressure of dry air into the special Claissen distilling flask (S) which is made entirely of glass and sealed to the condenser. The flask (S) is heated with an oil bath and the portion distilling at 144°-148° gives pure disilicon hexachloride. The residue remaining in (P) consists of a considerable quantity of trisilicon octachloride and still lower chlorides. This residue is heated with a sulfuric acid bath and the trisilicon octachloride boiling 210°-215° distills over. A small residue of lower chlorides and black tarry matter remains behind. The trisilicon octachloride upon redistillation in the all glass distilling apparatus distilled at 213°.

The Effect of the Silicon Tetrachloride Vapor:

The first experiment in which silicon tetrachloride was aspirated at the rate of 0.1158 grams per minute gave a yield of 20.3 per cent of disilicon hexachloride as compared with 2.5 per cent obtained by Martin (1914). This indicated that the vapor of silicon tetrachloride had a beneficial effect on the preservation of the lower chlorides of silicon during the chlorination process.

The Optimum Amount of Silicon Tetrachloride Vapor:

In order to determine the optimum amount of silicon tetrachloride vapor to be passed with the chlorine, several chlorinations were made in which the amount of silicon tetrachloride vapor was varied by regulating the temperature of the flask containing the liquid silicon tetrachloride and by changing the pressure of the chlorine. The results of these experiments are shown in Table I, page 22.

Analysis of Disilicon Hexachloride:

The reaction $Si_2Cl_6 + 4\ H_2O = (SiOOH)_2 + 6\ HCl$ proceeds rapidly even in the presence of very minute amounts of moisture and for this reason great care is necessary in obtaining a sample for analysis. For this purpose small glass bulbs with capillary tubes were blown and thoroughly dried by heating in a flame. The disilicon hexachloride was kept in small sealed bottles until ready for analysis. A bottle was then opened and the end of the capillary of the small weighed glass bulb was introduced below the level of the liquid and the bulb heated by a flame and then cooled. This caused a sample from 0.1500 to 0.2000 grams to be drawn up into the bulb which was then sealed and weighed.

It was then placed in a heavy gas bottle with 100 cc. of 0.1 N NaOH and the bottle tightly closed with a rubber stopper. The bottle was then vigorously shaken, thus breaking the bulb and allowing the reaction $Si_2Cl_6 + 10\ NaOH = 6\ NaCl + 2\ Na_2SiO_3 + 4\ H_2O + H_2$ to take place. After considerable shaking the bottle was opened, the remainder of the glass bulb finely crushed with a strong glass rod to be certain that the reaction was complete. The solution was then filtered and diluted to 500 cc. and an aliquot portion of 100 cc. analyzed for chlorine by the Volhard method. This method is superior to the gravimetric method because silver silicate is decomposed by strong acids. The theoretical percentage of chlorine in Si_2Cl_6 is 78.99%. Three results gave 78.92, 78.93, and 78.88%.

Calculation of Results:

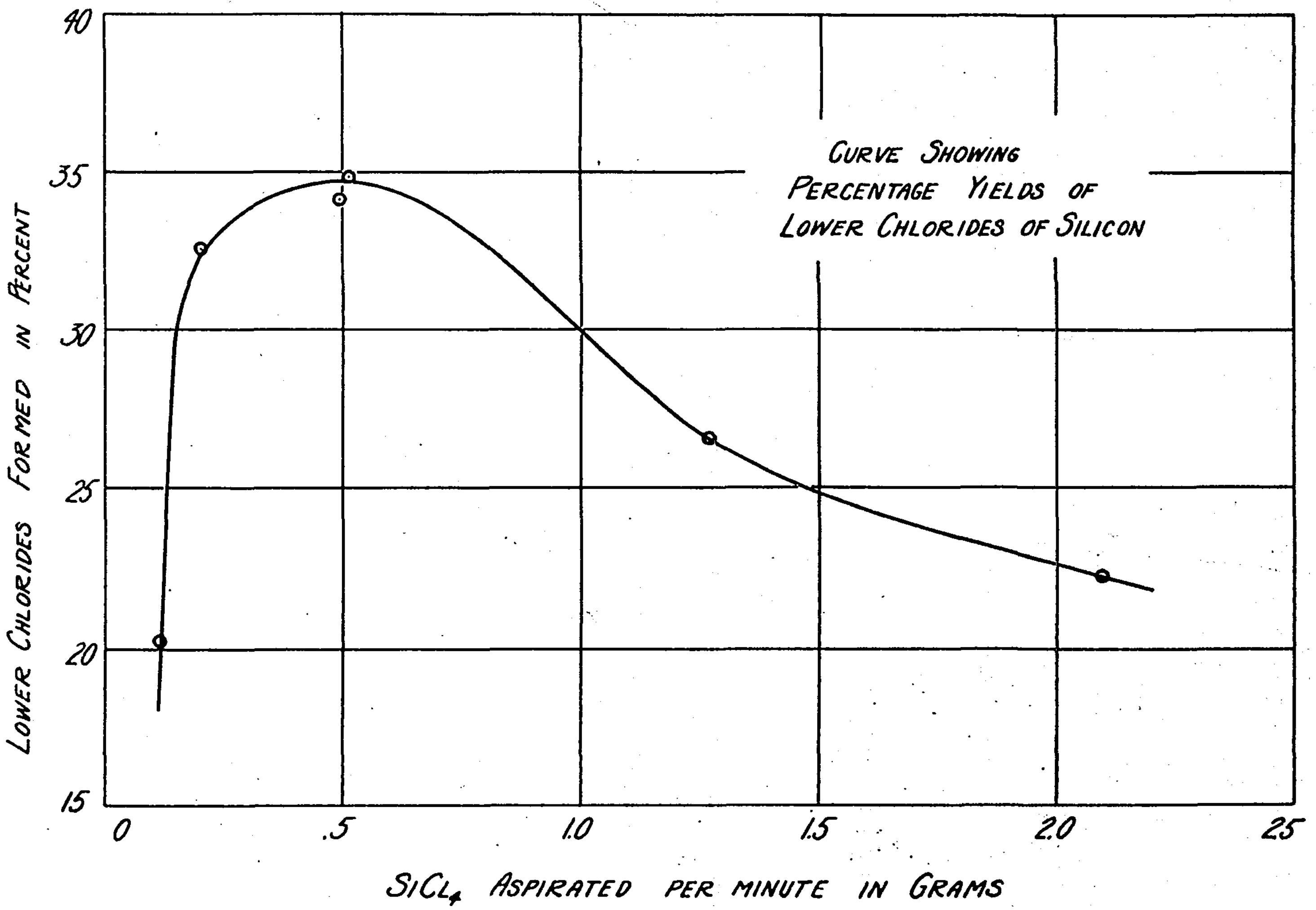
Martin (1914) and others calculated the yield of disilicon hexachloride on the basis of the total chlorides formed. This method assumes that the silicon tetrachloride was entirely condensed and does not consider the large amount of chlorine dissolved in the chlorides of silicon. My experiments have shown that some silicon tetrachloride escapes because of its relatively high vapor pressure and also because of the entrainment by the chlorine gas. That chlorine is appreciably soluble in the tetrachloride was shown by the determination of the solubility of chlorine in the latter at 0° and 25°. One gram of the tetrachloride will dissolve 0.1320 grams of chlorine at 0° and 0.0980 grams at 25°. This shows that the weight of the total condensed product does not represent the true weight of chlorides formed unless the chlorine is entirely removed before they are weighed. Since these experiments required the passage of large amounts of silicon tetrachloride through the furnace, it seemed more desirable to calculate the yield on the basis of the weight of silicon used. The method of obtaining this weight required the removal of the unused ferrosilicon and ferric chloride from the iron tube at the end of the experiment and the subsequent washing out of the ferric chloride. The residue was dried and weighed. The difference between this weight and the weight of the original amount of ferrosilicon was taken to represent the weight of the 50% ferrosilicon used. An objection to this method is found in the assumption that the residue contained the same percentage of silicon as the original ferrosilicon. This may not be the case. If it is not, then the percentages as calculated in these experiments are too low because an experiment in this laboratory showed that iron chlorinates more readily than silicon at the temperature of the experiments.

Table I.

Yields of Disilicon Hexachloride from 50% Ferrosilicon with Chlorine and Silicon Tetrachloride

	1	2	3	4	5	6
Time Min.	720.0	540.0	750.0	720.0	270.0	270.0
Temp., °C	0.0	0.0	25.0	25.0	25.0	25.0
Wg. Ferrosilicon Add	450.0*	250.0	450.0	450.0	450.0	450.0
Wg. Ferrosilicon Used	102.0	76.0	140.0	130.0	105.0	127.0
Wg. $SiCl_4$ Asp.	83.37	108.9	372.6	370.9	343.68	564.86
Wg. $SiCl_4$ Asp. per Min.	0.1158	0.2016	0.4968	0.5152	1.2713	2.092
Wg. Lower Chlorides Formed	49.38	58.91	114.0	108.0	66.41	67.09
Wg. Lower Chlorides Eq. to Si	242.7	180.8	331.1	309.3	249.8	302.2
% Si_2Cl_6 Formed	20.3	32.6	34.2	34.9	26.6	22.3

*When 450 g. were used two furnaces were run in parallel.



Curve Showing
Percentage Yields of
Lower Chlorides of Silicon
Lower Chlorides Formed in Percent
40
35
30
25
20
15
0
.5
1.0
1.5
2.0
2.5
SiCl4 Aspirated per minute in Grams

Fig. 3.

Discussion of Results

The largest yield (34.9%) of disilicon hexachloride is obtained when the chlorine pressure is regulated to deliver 0.5152 grams of silicon tetrachloride per minute to the furnace containing the ferrosilicon. The fact that a further addition of silicon tetrachloride to the chlorine (Fig.3, p.23) reduces the yield of disilicon hexachloride, indicates that the first increase is due to a retarding of the final chlorination and not to the reduction of silicon tetrachloride by silicon.

Summary

1. The yield of disilicon hexachloride may be increased by passing the vapor of silicon tetrachloride with chlorine over 50% ferrosilicon.
2. The largest yield of disilicon hexachloride is obtained when chlorine is passed through liquid silicon tetrachloride at 25° at such a rate that it causes 0.5152 gram of silicon tetrachloride vapor per minute to enter the furnace.
3. The results indicate that the increase in the yields of the lower chlorides of silicon is due to the retarding of the final chlorination of the lower chlorides to silicon tetrachloride and not to the reduction of the latter by silicon.
4. An improved method for the preparation of disilicon hexachloride and the other lower chlorides of silicon has been described.

THE EFFECT OF SILICON AND 50% FERRO-SILICON ON THE VAPOR OF SILICON TETRACHLORIDE AT THEIR CHLORINATION TEMPERATURES

Troost and Hautefeuille (1871) showed that silicon tetrachloride reacts with silicon when the vapor of the tetrachloride is passed over silicon heated to a white heat. Gattermann and Weinlig (1894) explained the formation of disilicon hexachloride when chlorine passes over silicon at 300° by assuming that the chlorine first directly unites with the silicon to form silicon tetrachloride according to the equation, $Si + 2\ Cl_2 = SiCl_4$. Next they supposed that the silicon tetrachloride thus formed, reacts at once with more silicon to produce the hexachloride according to the equation, $3\ SiCl_4 + Si = 2\ Si_2Cl_6$. This explanation of the formation of disilicon hexachloride was accepted for twenty years. Martin (1914) found that when silicon tetrachloride is distilled over either silicon or 50% ferrosilicon heated to any temperature between 200° and 340° that no noticeable amounts of disilicon hexachloride could be detected in the resulting silicon tetrachloride and therefore concluded that Gattermann and Weinlig's theory for the formation of disilicon hexachloride was incorrect. The results obtained by Martin (1914) and by us (Fig.3, p. 23) indicate that the action of silicon and ferrosilicon on silicon tetrachloride are not appreciable at 200° but these results do not justify the definite conclusion that there is absolutely no reaction between the silicon and silicon tetrachloride at the temperature of the chlorination of silicon and ferrosilicon.

In order that the function of the silicon tetrachloride vapor in the preservation of disilicon hexachloride might be studied with some degree of explicitness, it was necessary to determine whether the beneficial effect produced by the silicon tetrachloride in the chlorination process was the result of a physical or chemical phenomenon or perhaps, a combination of both. Since the effect of silicon and 50% ferrosilicon on the vapor of silicon tetrachloride was not known quantitatively, it was necessary to repeat a portion of Martin's work.

Experimental

Preparation of Pure Silicon Tetrachloride:

The necessity of using pure silicon tetrachloride in this experiment is obvious. The solubilities of chlorine and hydrogen chloride in silicon tetrachloride are so pronounced that especial precaution must be observed in its purification. The silicon tetrachloride was purified as described on page 100.

Experimental Procedure:

The procedure used in these experiments was identical with that used by Martin (1914) except in regard to the temperatures employed. In the experiment with Kahlbaum silicon the temperature of the furnace was maintained in the range 300°-

350° because a preliminary experiment showed that crystalline silicon begins chlorinating at 350° and then the temperature of the furnace may be lowered to 300° without stopping the chlorination. In the experiment with 50% ferrosilicon, the temperature was maintained in the range 170°-200° because this is the minimum range of chlorination for this substance.

One kilogram of the purified silicon tetrachloride which was known to be free from chlorine and hydrogen chloride was vaporized and passed very slowly over each one of these substances at the temperatures previously indicated. The process in each case was repeated several times.

Distillation of Product:

When the products from the individual experiments were distilled, the entire amount of liquid in each case distilled at the temperature of the boiling point of silicon tetrachloride (57°-59°). There was no residue whatsoever that would indicate the formation of disilicon hexachloride or other lower chlorides of silicon.

Discussion of Results

The results of these experiments establish the fact that the reaction $3\ SiCl_4 + Si = 2\ Si_2Cl_6$ does not take place when the vapor of silicon tetrachloride is passed over crystalline dilicon or 50% ferrosilicon at the respective temperatures of their chlorination. The result obtained in the case of ferrosilicon also indicates that the iron in this substance does not catalyze the reaction, $3\ SiCl_4 + Si = 2\ Si_2Cl_6$ at a temperature of 170°-200°.

Summary

The vapor of silicon tetrachloride acts as an inert constituent when it is passed over silicon or 50% ferrosilicon in the process for the preparation of disilicon hexachloride or the other lower chlorides of silicon.

THE SUBSTITUTION OF SILICON FOR 50% FERROSILICON IN THE PROCESS FOR THE PREPARATION OF DISILICON HEXACHLORIDE

Some experiments in this laboratory showed that the yield of disilicon hexachloride was negligible when crystalline or amorphous silicon were chlorinated at 300°. Since the yield of disilicon hexachloride had been materially increased by admixing silicon tetrachloride vapor with chlorine in the chlorination of 50% ferrosilicon at 170°-200°, it seemed desirable to ascertain if this same phenomenon would occur when this admixture was passed over silicon which chlorinates one hundred degrees above the chlorination temperature of 50% ferrosilicon. The reactions which destroy the disilicon hexachloride in the chlorination process are operative at the temperature at which crystalline silicon chlorinates (300°-350°) and therefore if the yield of disilicon hexachloride can be increased by admixing the vapor of silicon tetrachloride with chlorine in the chlorination of crystalline silicon, we may conclude that the silicon tetrachloride functions to preserve the disilicon hexachloride when the temperature of the chlorination tube is high enough for the reactions,

$$Si_2Cl_6 + Cl_2 = 2\ SiCl_4$$

$$2\ Si_2Cl_6 = 3\ SiCl_4 + Si$$

to proceed. The experiment will also determine whether ferrosilicon is superior to silicon for the preparation of disilicon hexachloride by the method previously described.

Experimental

The apparatus and experimental procedure were identical with that described on page 14 for the preparation of disilicon hexachloride except that Kahlbaum crystalline silicon was used instead of 50% ferrosilicon and the temperature of the furnace was maintained at 300°-350°. The silicon was pulverized rather finely and placed in an oven at 130° for twelve hours to expel traces of moisture.

The distillation of the resulting product gave an appreciable residue boiling above that of silicon tetrachloride. Further examination of this residue showed that it was disilicon hexachloride. The results of this experiment together with those of an experiment in which approximately the same amount of silicon tetrachloride vapor was passed over 50% ferrosilicon are shown in Table II.

Table II

Yields of Si_2Cl_6 Obtained by Passing Approximately Same Amount of $SiCl_4$ with Cl_2 Over 50% Ferrosilicon and Crystalline Silicon

	Crystalline Silicon	50% Ferrosilicon
Temp. of Chlor., °C	300-350	170-200
Time, Min.	540	540
Material Added, g.	230.0	250.0
Material used, g.	51.4	76.0
$SiCl_4$ Aspirated, g.	118.3	108.9
Si_2Cl_6 Formed, g.	15.9	58.9
Si_2Cl_6 Equiv. Si Used, g	244.6	180.8
$SiCl_4$ Asp. Per Min., g.	0.219	0.201
Si_2Cl_6 Formed, %	6.50	32.60

Table III

Summary Showing the Effectiveness of Passing $SiCl_4$ Vapor at the Same Rate at Different Temperatures

Substance Chlorinated	Temp. of Chlorination: °C	No $SiCl_4$ Vapor: Yield Si_2Cl_6, %	With $SiCl_4$ Vapor: Yield Si_2Cl_6, %
Crystalline Silicon	300	none	6.5
50% Ferrosilicon	200	2.5	32.6

Discussion of Results

An inspection of the results in Table II shows that the vapor of silicon tetrachloride functions to increase the yield of disilicon hexachloride when silicon is chlorinated at 300°-350°. Since the temperature of the furnace was kept within this temperature range, it is significant that there was a fractional preservation of disilicon hexachloride because the final chlorination and, indeed, a partial decomposition of the disilicon hexachloride may take place at these temperatures.

Interesting as this result appears to be, it does not aid greatly in the isolation of the specific function of the silicon tetrachloride vapor. It is plausible that the effect produced in this experiment may be attributed to any of the theories previously proposed (page 13). The results in Table III show the desirability of the employment of a substance which chlorinates at a relatively low temperature. There is a decrease in the yield of disilicon hexachloride corresponding to 0.261 per cent per degree rise in the temperature of the chlorination.

Summary

1. Disilicon hexachloride may be produced in small amounts by passing $SiCl_4$ vapor and chlorine over crystalline silicon at 300°-350°.

2. Fifty per cent ferrosilicon is superior to crystalline silicon for the preparation of disilicon hexachloride.

A DISCUSSION OF THE PROBABLE FUNCTION OF THE VAPOR OF SILICON TETRACHLORIDE IN THE PRESERVATION OF DISILICON HEXACHLORIDE DURING THE CHLORINATION OF SILICON

The previous work has shown that the degree of preservation of the disilicon hexachloride by the influence of the addition of an inert saturated chloro-compound is of greater magnitude when the temperature of the whole system is kept as low as possible. No results up to the present time have contributed anything toward an explanation of the mechanism of the action of the inert constituent.

Probable Functions of the Inert Saturated Chloro-Compound

The Sweeping Effect:

It seems reasonable to believe that the sweeping action of the inert constituent aids in the preservation of the disilicon hexachloride. It is very difficult, however, to determine to what extent this sweeping action aids in the preservation because of the opposing factors involved. An inspection of the curve showing the yields of disilicon hexachloride in relation to the amount of the inert constituent passed with the chlorine, (Fig.3, p.23) shows that a yield of 25 per cent of disilicon hexachloride is obtained by the passage of either 0.15 gram or 1.40 grams of silicon tetrachloride vapor per minute. In the first case the partial pressure of the silicon tetrachloride vapor is small while that of the chlorine is large, the effect of which would be to cause a considerable amount of disilicon hexachloride to be produced. In the latter case the partial pressure of the silicon tetrachloride vapor is large while that of the chlorine is small, the effect of which would be to cause a small amount of disilicon hexachloride to be formed. Since in the first case more disilicon hexachloride is formed by the initial chlorination, and because the concentration of the chlorine is higher, the opportunity for the final chlorination to take place is much greater than in the second case. It is also probable that the temperature of the reaction chamber is somewhat higher in the first case and this would also hasten the final chlorination. The sweeping action of the inert constituent is not appreciable in the experiment in which 0.15 gram of silicon tetrachloride was passed and consequently there must have been additional factors which effected the increased yield of disilicon hexachloride. On the other hand, when 1.40 grams or nearly ten times as much silicon tetrachloride vapor was passed it appears reasonable to attribute a part of the preservation to the sweeping action of the inert constituent. These results cause the author to conclude, however, that the sweeping effect is not the predominant factor in the process of preservation.

Addition of End Product:

The final chlorination and decomposition of disilicon hexachloride may be represented respectively by the equations:

$$Si_2Cl_6 + Cl_2 \xrightarrow{(heat)} 2\ SiCl_4 \qquad (1)$$

$$2\ Si_2Cl_6 \xrightarrow{(heat)} 3\ SiCl_4 + Si \qquad (2)$$

We know that these reactions are principally in the direction indicated at the temperature of the experiment, but if we assume that they are infinitesimally reversible, then when equilibrium is reached at any definite temperature, the conditions are satisfied which are expressed by the following equations:

$$\frac{C^2_{SiCl_4}}{C_{Si_2Cl_6} \cdot C_{Cl_2}} = K_1 \qquad (1)$$

$$\frac{C^3_{SiCl_4}}{C^2_{Si_2Cl_6}} = K_2 \qquad (2)$$

In studying the effect of increasing the concentration of the silicon tetrachloride it must be remembered that a simultaneous dimunition of the concentration of chlorine occurs. A consideration of (1) thus shows that in order to satisfy the conditions expressed by the equation, the concentration of the disilicon hexachloride must increase. Since the reaction is principally in the direction indicated it is apparent that a relatively large concentration of silicon tetrachloride may operate to retard the reaction because of the increasing of ($C^2_{SiCl_4}$) in the numerator and the simultaneous diminution of (C_{Cl_2}) in the denominator. A consideration of equation (2) in which the concentration of the chlorine is not a factor shows clearly how the presence of silicon tetrachloride vapor may function to retard the decomposition of the disilicon hexachloride.

Addition of Inert Saturated Chloro-Compound:

In the case of reactions which take place simultaneously, e.g.,

$$2\ Si + 3\ Cl_2 = Si_2Cl_6 \qquad (1)$$

$$Si_2Cl_6 + Cl_2 = 2\ SiCl_4 \qquad (2)$$

The rate of each reaction is determined by its own specific reaction rate and by the concentrations of the substances involved in it. The specific reaction rate of (1) is appreciable at much lower temperatures than (2) and it is therefore apparent that any agency which serves to lower the temperature of the gases in the reaction chamber will aid in the establishment of a condition in which the reaction velocity of (1) will be appreciable while the reaction velocity of (2) will be decreased.

The addition of the vapor of an inert saturated chloro-compound because of its high heat capacity would operate not only to overcome the excessive localization of temperature in the region of the chlorination of the iron and silicon, but also to diminish the heat evolution per unit volume of the total gases in the reaction chamber. If this lowering of temperature is of such a magnitude that reaction (1) will take place appreciably while reaction (2) will be negligible, then conditions will be present which favor the preservation of the disilicon hexachloride.

The addition of the inert constituent also diminishes the concentration of the chlorine. This has a tendency to decrease both (1) and (2) but since (1) has an appreciable reaction velocity at the lower temperature obtained by adding the inert constituent, the conditions will be more favorable for the formation of the disilicon hexachloride than for the formation of the product of the final chlorination of disilicon hexachloride.

THE SUBSTITUTION OF THE VAPOR OF ANHYDROUS CARBON TETRACHLORIDE FOR THE VAPOR OF SILICON TETRACHLORIDE IN THE CHLORINATION PROCESS

It has been shown that silicon tetrachloride is an inert constituent in the chlorination process. If a different inert saturated chloro-compound were substituted for silicon tetrachloride, it is evident that the results obtained from such an experiment would aid in determining the predominating action of the inert constituent. For if a saturated chloro-compound, which is not an end product of the reactions of the final chlorination or decomposition of the disilicon hexachloride, operates to increase the yield of this lower chloride of silicon to the same extent as silicon tetrachloride, then the conclusion may be drawn that the predominant function of the inert constituent is not a retardation of those reactions which destroy the disilicon hexachloride, because of the addition of an end product of those reactions, but rather a retardation because of a temperature lowering produced by the inert constituent.

Carbon tetrachloride was selected as the inert saturated chloro-compound for testing this theory because the molecule of this analogue of silicon tetrachloride has the same structure and the same number of atoms as the molecule of silicon tetrachloride. The specific heat of $SiCl_{4\,(gas)}$ between 90° and 234° is 0.1322 (Regnault 1862) while that for $CCl_{4\,(gas)}$ at 70° is 0.115 (Mills and MacRae, 1911). The specific heat of $CCl_{4\,(gas)}$ at the temperature of the experiment has not been determined but it is probably less than 0.115.

Since this close similarity exists between silicon tetrachloride and carbon tetrachloride, one might predict that the employing of carbon tetrachloride as the inert constituent in the chlorination process will also increase the yield of disilicon hexachloride. If the retardation of the reactions is not influenced by the addition of an end product, then the increase in the yield of the disilicon hexachloride should be in the order of their relative specific heats at the temperature of the chlorination process.

Experimental

Preparation of Anhydrous Carbon Tetrachloride:

Bakers Analyzed carbon tetrachloride was allowed to stand over calcium carbide for several days. It was then distilled from the calcium carbide and the liquid distilling 76°-78° was collected for the portion used in the experiment.

Effect of 50% Ferrosilicon on CCl_4 at 200°:

Carbon tetrachloride vapor when passed through a red hot tube splits off chlorine and the compounds C_2Cl_4 and C_2Cl_6 result. Camboulives (1910) has also shown that carbon tetrachloride vapor readily chlorinates various oxides. It was therefore necessary to determine whether carbon tetrachloride would undergo any change when passed over 50% ferrosilicon at 200°C.

One kilogram of the purified carbon tetrachloride was passed over 250 grams of 50% ferrosilicon at 200°. The same apparatus employed in the preparation of disilicon hexachloride was used (Fig. 1, p. 15) except that the gas train was omitted. The carbon tetrachloride was placed in the flask (b) which was heated by an electric hot plate covered with a thick asbestos board. The rate of passing the carbon tetrachloride was 2.58 grams per minute.

Upon distillation the resulting product gave no fraction boiling 50°-60° thus indicating that no silicon tetrachloride was formed by chlorination of the silicon. The remainder distilled at 76.7° showing that no C_2Cl_4, C_2Cl_6, or Si_2Cl_6 were formed during the process. These results show that 50% ferrosilicon has no action on carbon tetrachloride vapor at a temperature of 200°.

The Effect of Passing Carbon Tetrachloride Vapor with Chlorine over 50% Ferrosilicon at 200°C:

The apparatus and experimental procedure (Figs. 1 and 2, p. 15) was the same as that used in the preparation of disilicon hexachloride in previous experiments except that carbon tetrachloride was substituted for silicon tetrachloride in the flask (f). It was necessary to heat the carbon tetrachloride near its boiling point in order to raise its vapor pressure sufficiently to allow the chlorine to sweep the vapor into the fornace.

Distillation of Product:

Upon distillation of the resulting product some silicon tetrachloride distilled (64°-70°) and then the temperature rose to 80° with the subsequent distilling of the carbon tetrachloride. A residue remained in the flask and was transferred to a smaller distilling flask and further distilled. The entire portion boiled at 145°. Upon hydrolysis with water it formed silico-oxalic acid. When potassium hydroxide solution was added, hydrogen was evolved. No C_2Cl_6 or C_2Cl_4 were formed. The results of this experiment and a comparison of the yield of disilicon hexachloride obtained by substituting carbon tetrachloride for silicon tetrachloride are shown in Table IV.

Table IV

The Effect of the Substitution of the Vapor of Carbon Tetrachloride for the Vapor of Silicon Tetrachloride

	CCl_4	$SiCl_4$
Time expt., Min.	240.0	270.0
Temp. Liquid Chloro-Compd., °C	50.0	25.0
Ferrosilicon Added, g.	200.0	450.0
Ferrosilicon Used, g.	30.0	127.0
Inert Compd., Aspirated, g.	631.55	564.9
Inert Compd., Asp. Per Min.	2.63	2.09
Si_2Cl_6 Formed, g.	13.52	67.10
Si_2Cl_6 Equiv. to Si Used, g.	71.40	302.20
Si_2Cl_6 Formed, %	18.90	22.3

Discussion of Results

The yield of 18.9% of disilicon hexachloride compared with a yield of 2.5% when no carbon tetrachloride is passed with the chlorine shows that the vapor of carbon tetrachloride is very effective in preserving the disilicon hexachloride in the chlorination of 50% ferrosilicon at 200°C. The comparison with silicon tetrachloride shown in Table IV indicates that carbon tetrachloride vapor is nearly as effective as silicon tetrachloride vapor. It will be noted that the carbon tetrachloride vapor was passed at the rate of 2.63 grams per minute while the silicon tetrachloride vapor was passed at the rate of 2.09 grams per minute. An inspection of the curve (Fig.3, p. 23) shows that the yield of disilicon hexachloride by passing this amount of silicon tetrachloride would be approximately 20%. Hence, the yields of disilicon hexachloride shown in Table are in their proper order in reference to their relative specific heats. It would be desirable to know the effect on the yield of disilicon hexachloride caused by adding different amounts of the carbon tetrachloride vapor, but lack of time prevented further experiments being made.

The results obtained indicate that the predominant function of the inert vapor of the saturated chloro-compound in the preservation of disilicon hexachloride is not a retardation of the reactions which destroy the lower chloride because of the addition of the end product of these reactions, but rather the attainment of a set of conditions, in regard to temperature, in which the reaction velocities for the formation of disilicon hexachloride by the reaction $2\ Si + 3\ Cl_2 = Si_2Cl_6$ are appreciable, while the reaction velocities for the formation of silicon tetrachloride by the reaction, $Si_2Cl_6 + Cl_2 = 2\ SiCl_4$, are decreased.

Comparison of Inert Constituents:

Silicon tetrachloride is the more desirable of the inert constituents because of the ease with which it may be aspirated into the reaction chamber by the chlorine. Because of its wide variation in vapor pressure at different temperatures, the control of the rate of its passage may be carefully regulated by changing the temperature of the liquid. The low boiling point of silicon tetrachloride (59°) permits a ready fractionation of the disilicon hexachloride. Its chief disadvantage is the ease with which it hydrolyzes in the air or when traces of moisture are present in the apparatus. Carbon tetrachloride possesses the advantage of being cheaper and is also more easily obtained than silicon tetrachloride.

Summary

The vapor of the inert saturated chloro-compound carbon tetrachloride acts similar to the vapor of silicon tetrachloride in the preservation of disilicon hexachloride in the chlorination process. This preservation is not due to a retardation of those reactions which destroy the disilicon hexachloride because of the addition of an end product, but rather to a temperature lowering of such a magnitude that the initial chlorination reaction $2\ Si + 3\ Cl_2 = Si_2Cl_6$ will take place while the reaction, $Si_2Cl_6 + Cl_2 = 2\ SiCl_4$ is suppressed.

THE STRUCTURE OF 50% FERROSILICON

Warren (1889) was the first worker to use ferrosilicon for the preparation of silicon tetrachloride but Martin (1914) was the first to realize its importance in the preparation of the lower chlorides of silicon. Fifty per cent ferrosilicon is the only satisfactory compound known at the present time for the successful preparation of the lower chlorides of silicon. No reason has been suggested for the fact that this substance chlorinates one hundred degrees lower than crystalline elemental silicon. This subject is discussed briefly below.

The Iron-Silicon Phase Diagram:

Guertler (1917) in a phase diagram for the silicon-iron alloys shows the 50 per cent alloy to be a mixture of crystals of the compound FeSi and a solid solution of iron in silicon, the latter predominating. It has been previously stated that the chlorination of iron represents a highly exothermic reaction (page 12). If the iron were mixed very intimately with the silicon as it would be in the solid solution of which ferrosilicon consists, it seems probable that some of the silicon would be heated locally by the glowing iron to a high enough temperature to cause it to chlorinate. Since an experiment showed that iron chlorinates at 200°, this explanation would serve to show why the furnace does not have to be heated above this temperature to cause the chlorination of the silicon in 50% ferrosilicon.

The Silicon Molecule in 50% Ferrosilicon:

Jüptner (1898) studied the lowering of the melting point of pure iron by silicon and made some interesting observations in regard to the silicon molecule dissolved in pure iron. He concluded that the size of the silicon molecule grows with the rising silicon content in the iron alloy. He also found by calculation that the molecular weight of silicon in pure iron corresponds to a seven atom molecule. The effect of silicon on the freezing point of copper indicates, however, that the molecule of silicon in molten copper is possibly monatomic. If this data is correct it would seem to offer a plausible explanation for the production of the lower chlorides of silicon in greater abundance when ferrosilicon is chlorinated. It would be of interest to establish a comparison between the yield of lower chlorides obtained from the chlorination of ferrosilicon and the yield obtained from the chlorination of monatomic silicon dissolved in copper. The possible formation of a silicide may spoil the inferences in regard to the monatomic molecule of silicon in molten copper.

THE EFFECT OF CATALYSTS ON THE CHLORINATION TEMPERATURE OF 50% FERROSILICON

The desirability of employing a chlorination temperature as low as possible has been discussed. Very little consideration was given to the subject of increasing the yields of the lower chlorides of silicon by a further lowering of the temperature of the chlorination by means of catalysts.

Ferric Chloride as a Catalyst

It was thought that the effect of the iron in the ferrosilicon might be due to the ferric chloride acting in its familiar role of a halogen carrier and thus causing the silicon to oxidize to the lower chlorides at a temperature which would be too low to cause the disilicon hexachloride thus formed to oxidize to the stable end product silicon tetrachloride.

As it is difficult to mix ferric chloride with silicon and keep the material dry, an intimate mixture of metallic iron and silicon was placed in a combustion tube and chlorine passed over it while it was heated to 200°. The iron near the end of the tube where the chlorine entered began to glow and to chlorinate at this temperature but no silicon chlorides were formed unless the temperature was raised to 300°. This shows that the mere presence of ferric chloride did not act as a catalyst to form the disilicon hexachloride or to lower the temperature at which the silicon was chlorinated.

Wood Charcoal as a Catalyst

The problem of the chlorination of hydrocarbons may be cited as an example of reaction in presence of charcoal as a catalyst, in which the intensity of the reaction may be minimized by admixing, with the incoming gas, carbon tetrachloride or other saturated chloro-compound. In this way the ready tendency to explosive violence, which this reaction shows, may be restrained. Since we had already found that the addition of a saturated chloro-compound to the chlorine minimized the intensity of the chlorination of ferrosilicon, it was thought that the presence of charcoal might act in a similar manner to its role in the chlorination of hydrocarbons.

Experimental

Twenty-five grams of perfectly dry, finely powdered, willow wood charcoal was thoroughly mixed with 200 grams of rather finely ground 50% ferrosilicon and the resulting mixture chlorinated as shown in Fig.1 (p. 15). Silicon tetrachloride was used as the inert saturated chloro-compound in this chlorination. This mixture chlorinated at 170°-200°.

Discussion of Results

The results of this experiment and a comparison with an experiment in which no wood charcoal was used are shown in Table V.

Table V

Effect of Wood Charcoal on the Chlorination of 50% Ferrosilicon

Time, Min.	270.0	750.0
Temp. Liquid $SiCl_4$, °C	25.0	25.0
Wood Charcoal Added, g.	25.0	none
Ferrosilicon Added, g.	200.0	450.0
Ferrosilicon Used, g.	32.0	140.0
$SiCl_4$ Aspirated, g.	130.0	372.6
$SiCl_4$ Asp. Per Min., g.	0.481	0.496
Lower Chlorides Formed, g.	17.4	114.0
Lower Chlorides Equiv. to Si Used, g.	76.2	331.1
Lower Chlorides Formed, %	22.8	34.2

These results indicate that the addition of wood charcoal to silicon lowers the percentage yield of lower chlorides. In this experiment it was found that the yield was lowered 11.4 per cent. This decrease in the yield shows that wood charcoal acts as an inert constituent in the chlorination process. Since approximately 11 per cent of the mixture chlorinated consisted of the inert charcoal, the efficiency of the chlorination was decreased.

Summary

1. The ferric chloride formed by the chlorination of a mixture of iron and silicon does not act as a halogen carrier to increase the yield of lower chlorides nor to lower the temperature at which silicon is chlorinated.

2. Wood charcoal does not act as a catalyst in the chlorination of 50% ferrosilicon.

GENERAL SUMMARY

The known methods of preparation of disilicon hexachloride were unsatisfactory because of the negligible yields. Since this compound was needed as an intermediate in the development of the chemistry of silicon compounds containing the silicon linkage, an investigation was begun. This investigation had for its object the idea of the development of a laboratory process by which disilicon hexachloride and the other lower chlorides of silicon could be produced in sufficient quantities for the much desired research on linked silicon compounds.

Preliminary experiments showed that the production of disilicon hexachloride in appreciable amounts depended upon the suppression of two reactions which destroy the lower chlorides in the chlorination process:

$$Si_2Cl_6 + Cl_2 \text{ (heat)} = 2\ SiCl_4$$
$$2\ Si_2Cl_6 \text{ (heat)} = 3\ SiCl_4 + Si$$

It was found that the admixing of the vapor of silicon tetrachloride with chlorine in the chlorination of 50% ferrosilicon materially increased the yield of disilicon hexachloride and the other lower chlorides of silicon. Further experiments showed that when chlorine was passed through silicon tetrachloride at such a rate that it delivered 0.5152 gram of silicon tetrachloride per minute to the reaction chamber, a maximum yield of 34.9 per cent of disilicon hexachloride was obtained. The yield is 2.5 per cent when no silicon tetrachloride is passed into the reaction chamber.

A study of the function of the silicon tetrachloride vapor revealed that this compound acted as an inert constituent in the process. The substitution of the inert saturated chloro-compound carbon tetrachloride for silicon tetrachloride, produced the same beneficial results in the preservation of the disilicon hexachloride. Since carbon tetrachloride is not an end product of those reactions which destroy the disilicon hexachloride, it was concluded that these inert compounds aid in the preservation of the disilicon hexachloride by causing a temperature lowering of the chlorine and the initial products of the oxidation of silicon by chlorine. When the inert constituent is added to the chlorine in sufficient quantity to produce a temperature lowering of such a magnitude that the initial chlorination reaction $2\ Si + 3\ Cl_2 = Si_2Cl_6$ will take place while the reaction, $Si_2Cl_6 + Cl_2 = 2\ SiCl_4$ is suppressed, then an appreciable preservation of the disilicon hexachloride results. If this condition prevails in the reaction chamber, then the reaction velocity of the reaction, $2\ Si_2Cl_6 = 3\ SiCl_4 + Si$ is negligible.

CONCLUSION

The optimum conditions for the preservation of disilicon hexachloride in the chlorination of silicon demand a set of conditions in regard to temperature which will cause the reaction velocities for the formation of disilicon hexachloride to be appreciable and those for the formation of silicon tetrachloride to be negligible.

The factors which aid in the procurement of these conditions are:

1. The selection of a silicon compound or mixture which chlorinates at a lower temperature than elemental silicon.
2. The minimization of the temperature of chlorination by the addition of an inert saturated chloro-compound.
3. A careful regulation of the temperature of the furnace used in the chlorination process.

Part II

A STUDY OF THE FORMATION OF THE OXYCHLORIDES OF SILICON

A STUDY OF THE FORMATION OF THE OXYCHLORIDES OF SILICON

INTRODUCTION

The importance of research on silicon oxychlorides in addition to contributing to the undeveloped chemistry of silicon is seen in the relationship which the complex silicon oxychlorides are thought to bear to the similarly complex silicic acids of which the natural silicates are probably salts. It is a well known fact that the classification of the natural silicates is a matter of great complexity and that to refer them to a few types of hypothetical silicic acids constructed apriori on theoretical grounds, is not to account for them completely. It is probable that very little knowledge can be obtained concerning the silicates by a study of the mineral compounds of silicon because of their great molecular complexity and their insolubility in neutral solvents. Whether our knowledge is to be extended through a study of inorganic or of the seemingly more advantageous organic derivatives because of their solubility in neutral solvents, is a problem involving a very large amount of research. No matter which line of attack is followed it is evident that elementary compounds of silicon such as the halides and oxychlorides must be available. At the present time, silicon tetrachloride and silico-chloroform are the only known compounds of this nature which may be obtained in the market or prepared in the laboratory with any degree of ease. This has been the case with the lower chlorides of silicon which only recently we have been able to prepare with appreciable yields in this laboratory. Just as the lower chlorides of silicon lend themselves as the starting point for all derivatives containing linked silicon atoms, so the oxychlorides present a series of compounds which may be utilized for the preparation of compounds containing silicon atoms linked by oxygen atoms. Since this manner of linking is thought to exist in the complex silicic acids and silicates it becomes very apparent why our knowledge of the silicon oxychlorides should be augmented by further research on them.

Historical Survey

The following oxychlorides have been prepared, the molecular formula of several of them having been established by vapor density determinations.

	B.P. $0^{o}C$	Vapor Density (air = 1)	Theoretical
Si_2OCl_6	137-138	10.05	9.86
$Si_4O_3Cl_{10}$	152-154	—	—
$Si_4O_4Cl_8$	198-202	15.5	15.9
$Si_6O_{10}Cl_{12}$	300	31.2	28.0
$(Si_2O_3Cl_2)_n$	above 400	—	—
$(Si_4O_7Cl_2)_n$	above 440	—	—

Structural Formulas

The structural formulas which have been assigned to the oxychlorides are as follows:

$Cl_3Si.O.SiCl_3$

$Cl_3Si{\cdot}O{\cdot}SiCl_2{\cdot}SiCl_3$

$Cl_3Si{\cdot}O{\cdot}SiCl_2{\cdot}O{\cdot}SiCl_2{\cdot}O{\cdot}SiCl_3$ etc.

The principal feature of these compounds is the recurrence of the group $—O{\cdot}SiCl_2{\cdot}O—$. Analogous compounds have also been prepared by Kipping (1912) in which the group $—O{\cdot}Si(C_6H_5)_2{\cdot}O—$ is present, while the several silicic acids and silicates contain the group $—O{\cdot}SiO{\cdot}O—$.

Methods of Preparation

The only one of the series concerning which much is known is the first member, Si_2Cl_6O. A review of its methods of preparation show that it was obtained by Friedel and Ladenburg (1868) when the vapor of silicon tetrachloride was passed over feldspar heated to a white heat in a porcelain tube. Later it was prepared by Troost and Hautefeuille (1881) in a more satisfactory manner by passing a mixture of chlorine and oxygen over crystalline silicon heated to 800°. Besson and Fournier obtained it in an entirely different manner by the action of oxidizing agents on silico-chloroform. They found that silico-chloroform interacts with dry oxygen in the sunlight at -80°C, and with ozone, sulfur trioxide, and chromium trioxide at ordinary room temperature. Sanger and Riegel (1912) thought that sulfur trioxide reacted with silicon tetrachloride to form Si_2Cl_6O but they were unable to isolate the oxychloride. The latest work on this compound was done by A. Stock and co-workers (1925) who experimented with the zinc electric arc as a means of reduction. They reduced silicon tetrachloride to di-silicon hexachloride and found that when oxygen was present in their apparatus that the compound Si_2Cl_6O was always formed. If the apparatus was previously filled with nitrogen, no silicon oxychloride was formed.

Theories for the Formation of Silicon Oxychlorides

When the compound Si_2Cl_6O is formed by the action of oxidizing agents on silico-chloroform, it is apparent that the hydrogen in two molecules of silico-chloroform is replaced by oxygen.thus forming a compound in which two silicon atoms are linked by an oxygen atom. This reaction is in accordance with the fact that the hydrogen is loosely joined to the silicon atom as shown by the instability of the hydrides of silicon. The chemistry of the other methods of preparation is not understood. It is not known whether the oxychloride Si_2Cl_6O is formed from silicon tetrachloride by the replacement of the chlorine in two molecules of silicon tetrachloride or from the lower chlorides which may be produced under the favorable conditions of the experiment. The simultaneous formation of silicon oxychlorides in very small amounts when silicon is chlorinated in the presence of oxygen at rather low temperatures and when silicon tetrachloride is reduced to di-silicon hexachloride at a very high temperature, appears to bear some relation with the range of temperature at which di-silicon hexachloride is stable. Duhem (1900) showed that di-silicon hexachloride is stable from ordinary temperatures up to 350°, decomposes into silicon and silicon tetrachloride between 350° and 800°, and then becomes stable above 800°. These facts suggest two possible theories for the formation of the oxychloride Si_2Cl_6O from the silicon halides; (a) silicon tetrachloride is first formed and the chlorine in two molecules subsequently replaced by oxygen, $2\ SiCl_4 + [O] = Si_2Cl_6O + Cl_2$; (b) di-silicon hexachloride is formed which then dissociates forming a nascent molecule of silicon chloride in which the silicon is trivalent, $Si_2Cl_6 = SiCl_3 + SiCl_3$. Two molecules of the nascent chloride then combine with one atom of oxygen to form the compound Si_2Cl_6O. The latter theory is less probable when considered from a knowledge of Schlenk's (1911) work with hexaphenylsilicoethane in which he has shown that trivalent silicon does not exist under the conditions enunciated for trivalent carbon by Gomberg (1914). Hexaphenylsilicoethane shows no dissociation into the tri-phenyl silicyl free radicle even in hot xylene solution. It is very probable, however, that silicon tetrachloride and di-silicon hexachloride act differently than their carbon analogues in the presence of oxidizing agents. The carbon halides react with oxidizing agents to form oxychlorides by the replacement of the chlorine in one molecule of the compound. Chlorine is held so firmly by silicon, however, that the simplest oxychloride, $SiOCl_2$, has never been made. That silicon binds the halogens much more firmly than carbon is shown by a comparison of the behavior of the two elements with the halogens. Silicon and carbon both combine directly with fluorine. Silicon combines with chlorine at 350°C, with bromine at 500°C, but not directly with iodine. Carbon on the other hand, unites directly neither with chlorine, bromine, or iodine. Recent research on di-silicon hexachloride has shown that its chlorine is not held as firmly as the chlorine in di-silicon tetrachloride and for this reason the behavior of di-silicon hexachloride might also be expected to differ from silicon tetrachloride. Martin (1914) prepared the compound $Si_2(OC_2H_5)_6$ by the interaction of di-silicon hexachloride with ethyl alcohol and demonstrated that all of the chlorine atoms of di-silicon hexachloride may be replaced without severing the silicon linkage. Later Schwarz (1926) replaced all of the chlorine of di-silicon hexachloride with amido and imido groups. Thus in addition to securing knowledge concerning the formation of the oxychlorides, the author has in mind an investigation of the stability of the silicon linkage and the bonding of the chlorine in di-silicon hexachloride.

THE ACTION OF OXIDIZING AGENTS OTHER THAN OXYGEN ON DI-SILICON HEXACHLORIDE

The action of oxidizing agents other than oxygen on silicon tetrachloride was studied by Rauter (1892) and on silico-chloroform by Besson and Fournier (1909) but no research concerning their action on a compound containing linked silicon atoms has been made. Di-silicon hexachloride is unstable between 350° and 800°. Previous experiments showed that oxygen had no effect on di-silicon hexachloride unless higher temperatures were employed and that during the experiment some decomposition of the di-silicon hexachloride always occurred. Difficulty is experienced in avoiding the decomposition range entirely because the vapor must necessarily pass through this range as it emerges from the furnace. The temperature control of the furnace is likewise very troublesome because of the cooling effect produced by the passage of the vapor of di-silicon hexachloride and oxygen. Oxidizing agents therefore which give up their oxygen below the decomposition temperature of di-silicon hexachloride appear to present a distinct advantage.

Sulfur trioxide because of its solubility in di-silicon hexachloride presents an interesting possibility from the standpoint of securing contact in the liquid state. Furthermore, its reaction with silicon tetrachloride in which the oxychloride, Si_2Cl_6O is reported to be formed, furnishes an interesting comparison with its action on a silicon chloride containing linked silicon atoms. Chromium trioxide has the property of giving up its oxygen probably in the nascent state, one hundred degrees below the decomposition range of di-silicon hexachloride and thus enables one to study the effect of nascent oxygen at a temperature of 250°C. Ozone, by virtue of the fact that it decomposes at low temperatures especially when catalyzed by silver oxide, presents a powerful oxidizing agent whose action may be studied at ordinary atmospheric temperature.

THE ACTION OF SULFUR TRIOXIDE ON DI-SILICON HEXACHLORIDE

P. Schützenberger (1869), J. Prud'homme (1870), H. E. Armstrong (1870), V. Grignard and E. Urbain (1919), and E. Paterno and A. Mazzucchelli (1920) have shown that sulfur trioxide reacts with carbon tetrachloride forming phosgene and pyrosulfuryl chloride. J. Prud'homme (1870) also demonstrated that hexachlorethane reacts similarly, $C_2Cl_6 + 2\ SO_3 = C_2Cl_4O + S_2O_5Cl_2$. Sanger and Riegel (1912) studied the action of sulfur trioxide on silicon tetrachloride and concluded from their observations that silicon tetrachloride does not act like carbon tetrachloride. They were unable to isolate the silicon oxychloride but represent the reaction, $2\ SO_3 + 2\ SiCl_4 = S_2O_5Cl_2 + Si_2OCl_6$.

The direct object of this experiment is to study the action of sulfur trioxide on di-silicon hexachloride, a homologue of silicon tetrachloride which contains linked silicon atoms, in order to obtain knowledge of two facts; (a) di-silicon hexachloride may react similar to its carbon analogue having a similar structure i.e., form an oxychloride by replacement of chlorine thus leaving the silicon linkage intact; (b) di-silicon hexachloride may form an oxychloride by disruption of the silicon linkage to form a compound containing the siloxan linkage which is the characteristic linkage given to silicon oxychlorides by various workers, (Kipping 1912).

The results obtained show that sulfur trioxide does not react with di-silicon hexachloride in either of the above mentioned ways. Sulfur trioxide does not act as an oxidizing agent with di-silicon hexachloride and therefore its action with this compound is distinctly different from its action on the carbon analogue. The behavior of sulfur trioxide in this reaction is in accordance with the characteristic addition reactions shown by sulfur trioxide. The results of the analysis of the addition compound formed in this case shows that it has the formula $2\ Si_2Cl_6SO_3$. We are able to draw this conclusion because of the isolation and subsequent analysis of the addition compound and the confirmation received from a determination of the amount of silicon linkage present in the compound.

Experimental

The di-silicon hexachloride was prepared by passing chlorine and silicon tetrachloride over 50% ferro-silicon as described elsewhere. It had a boiling point of 145°C and freezing point of 2.5°C. Sulfur trioxide having a boiling point of 47° was used. It was perfectly white and free of impurities. The sulfur trioxide was distilled directly into a small distilling flask containing a weighed amount of di-silicon hexachloride. No rubber was allowed to come in contact with the sulfur trioxide. The two liquids mixed at once and upon gentle shaking formed a homogenous colorless liquid, which upon standing, deposited fine asbestos-like needles of β sulfur trioxide. The flask was then connected to a reflux condenser and refluxed for three hours at 100°C. After cooling, the liquid was siphoned off from the crystals of β sulfur trioxide and then subjected to distillation. A few drops distilled at 45° and the thermometer then rose rapidly to 172°. The entire product distilled between 172°-183°. A test for chlorosulphonic acid (Sanger and Riegel, 1912) was negative. The excess sulfur trioxide was removed from the liquid by the method of Traube (1913) by the addition of extremely fine sodium chloride and subsequent heating. One molecule of sodium chloride absorbs two molecules of sulfur trioxide with the formation of the sodium salt of chloro-pyrosulfuric acid. The liquid was distilled from the sodium chloride and again distilled. The entire product came over 179°-182°.

Properties of the Liquid Boiling 179°-182°

The liquid is mobile and has a slight yellow color. It fumes in air very much like sulfur trioxide. It has a freezing point of -10°C while di-silicon hexachloride and sulfur trioxide freeze at 2.5°C and 14.8°C respectively. When poured into cold water it hydrolyzes vigorously with the formation of silico-oxalic acid, sulfuric acid, hydrochloric acid and a small amount of silicic acid.

Analysis of the Product

The liquid did not hydrolyze as rapidly as di-silicon hexachloride and consequently could be withdrawn in a dry pippette for all of the determinations except the one for the amount of silicon in the silicon linkage. The liquid was weighed in a small weighing bottle with a ground glass stopper. The weighing bottle and its contents were then placed in a precipitation flask containing freshly prepared 20% sodium hydroxide solution prepared from metallic sodium known to be free from chlorine, silicon dioxide, and sulfur. The ground glass stopper was removed under the solution and the flask immediately closed to avoid loss of hydrogen chloride or sulphur trioxide. When all fumes had disappeared, the flask was opened and heated for fifteen minutes to decompose the silico-oxalic acid according to the reaction $(SiOOH)_2 + 4\ NaOH = 2\ Na_2SiO_3 + 2\ H_2O + H_2$. There was no appreciable loss in weight of the glass weighing bottle when the time of its immersion in the sodium hydroxide was not more than fifteen minutes and consequently this procedure was strictly adhered to in all analyses.

Chlorine:

A sample of approximately 0.5000 gram was obtained as described in the analysis of di-silicon hexachloride and the chlorine was determined in the same manner (page 19). The Volhard method was used in preference to the gravimetric method because Hawkins (1890) found that silver silicate is decomposed in the presence of strong acids.

Total silicon:

The sample was placed in a platinum dish, acidified with sulfate free hydrochloric acid and the usual determination made for SiO_2.

Sulfur:

The sample was obtained as previously described, great care being taken to avoid loss of sulfur trioxide fumes. The SiO_2 was removed and the filtrate used for the sulfur determination. The sulfur was precipitated as barium sulfate.

Determination of the Silicon Linkage

G. Martin (1914) has shown that in the presence of attached oxygen atoms eg., H-OH or Na-OH, that two directly linked silicon atoms are severed with the liberation of one mole of hydrogen. Thus by determining the amount of hydrogen liberated from a given weight of the compound, the percentage of silicon as linked silicon may be found. The sample was weighed in a small glass bulb with a long capillary tube. The glass bulb containing the sample was then placed in a bath consisting of nitric acid and ice until the liquid sample was frozen. The capillary of the bulb was then removed with the flame of a micro-burner. The bulb was then placed in a 200 cc pyrex flask having a short neck and wide mouth. Fifty cubic centimeters of 30% sodium carbonate solution were added and the flask closed with a rubber stopper containing two glass tubes bent at right angles and provided with glass stop cocks. One of these tubes led to a Schiffs nitrometer containing 50% potassium hydroxide and the other to a safety gas washing bottle containing sulfuric acid. The gas washing bottle was in turn connected to a carbon dioxide generator which was arranged so that a constant pressure of carbon dioxide could be maintained in the apparatus. Pure carbon dioxide was generated by dropping 1-1 hydrochloric acid on pure sodium bi-carbonate. The air was thoroughly swept out of the apparatus by allowing a slow stream of carbon dioxide to pass through the apparatus for several hours. When the apparatus was free of air, the stop cocks on each side of the flask containing the bulb and the sodium carbonate solution were closed. The bulb was then broken by an abrupt movement of the flask. Hydrogen was evolved at once but it was necessary to heat the flask rather vigorously to bring the reaction to completion. It was found advisable to maintain a slow stream of carbon dioxide through the apparatus during the evolution of the hydrogen and for at least an hour after the evolution had ceased. The hydrogen was allowed to stand for at least twenty-four hours over the 50% potassium hydroxide solution to insure complete absorption of the carbon dioxide. At the end of this time a potassium pyrogallate absorption was made for oxygen. If any oxygen was found it was subsequently calculated to air and the necessary correction made. The vapor pressure of the 50% potassium hydroxide solution according to Kingscott and Knight (1914) may be taken as one-third that of water at the same temperature. The barometer readings were corrected to 0°C.

Analytical Results

Total Chlorine

Wt. Subs., g.	Chlorine, g.	Chlorine, %
0.8852	0.6151	69.49
0.4927	0.3425	69.52
0.5240	0.3642	69.50
		Theory 68.76

Total Silicon

Wt. Subs., g.	SiO_2, g.	Si, %
0.3316	0.1422	20.12
0.7387	0.3170	20.14
0.4156	0.1788	20.19
		Theory 18.30

Total Sulfur

Wt. Subs., g.	$BaSO_4$, g.	S, %
0.1146	0.0408	4.89
0.3316	0.1197	4.96
		Theory 5.18

Silicon Linkage (Si_L)

Wt. Subs., g.	Vol. H_2, cc	Temp., °C	Pressure, mm	Silicon, g	Si_L%
0.4685	38.2	25.0	739.9	0.0848	18.11
0.4164	34.25	23.0	739.1	0.0766	18.40
0.7467	58.82	20.8	744.5	0.1355	18.15

Theory 18.30

Discussion of Results

A review of the results shows that 18.22 per cent of the 20.15 per cent of total silicon of the substance is present as linked silicon. In endeavoring to account for this apparent discrepancy between the percentage of linked silicon and the total silicon it was observed that an addition compound having the formula $2\ Si_2Cl_6SO_3$ contains 18.30 per cent of silicon and 68.76 per cent of chlorine. Since there was no SiO_2 in the compound, it seemed probable that the difference between the percentages of total silicon and linked silicon might be due to a small amount of silicon tetrachloride. In order to test the validity of this assumption it was necessary to calculate the amount of chlorine combined with the linked and unlinked silicon, assuming that the linked silicon existed in the addition compound $2\ Si_2Cl_6SO_3$. The total chlorine calculated by the formula,

$$(Si - Si_L)\,\frac{4Cl}{Si} + Si_L\,\frac{6Cl}{2Si} = \text{total chlorine}$$

gave 69.55 per cent while the percentage of total chlorine found was 69.50%. The calculation also gave 0.95 per cent of chlorine present as chlorine in silicon tetrachloride, and

68.60 per cent as chlorine in the addition compound $2Si_2Cl_6SO_3$. The percentage of chlorine in the hypothetical compound is 68.76 per cent. The purity of the mixture in regard to the addition compound was found to be 97.72 per cent. Subsequent correction of the percentage of sulfur (4.93) for the impurity of silicon tetrachloride in the mixture, then gave 5.05 per cent of sulfur as compared with 5.18 per cent for the theoretical percentage in $2\ Si_2Cl_6SO_3$.

Summary of Results

	Si_L, %	Cl, %	S, %	O_2, % By difference
Determined	18.25	68.60	5.05	8.10
Theoretical	18.30	68.76	5.18	7.76

The analytical results leave much to be desired in regard to the hypothetical compound but they indicate very clearly that the action of sulfur trioxide on di-silicon hexachloride does not form an oxychloride of silicon by the interposition of an oxygen atom between two silicon atoms or by the replacement of chlorine. The results show conclusively that the action of sulfur trioxide on di-silicon hexachloride is entirely different than its action on the homologue silicon tetrachloride (Sanger and Riegel, 1912) and the analogue hexachloroethane, (J. Prud'homme, 1870).

Summary

1. Di-silicon hexachloride in the presence of sulfur trioxide at 180°C does not form an oxychloride by the fission of the silicon linkage or by the replacement of chlorine.

2. Di-silicon hexachloride does not react similar to its carbon analogue hexachlorethane or to its homologue silicon tetrachloride in the presence of sulfur trioxide.

3. A new compound 2 $Si_2Cl_6 \cdot SO_3$ has been prepared and analyzed.

THE ACTION OF CHROMIUM TRIOXIDE ON DI-SILICON HEXACHLORIDE

Besson and Fournier (1909) found that chromium trioxide reacts at ordinary temperatures with silico-chloroform forming oxychlorides of silicon and a compound Cr_3OCl_7 and Rauter (1892) in his comprehensive survey of the action of different oxides on silicon tetrachloride said that when chromium trioxide is added to silicon tetrachloride in the cold a red color is produced. When the mixture was placed in a sealed tube and gradually raised to a temperature of 300°C, the chlorine of the silicon tetrachloride was entirely replaced by oxygen with the formation of silica and chromic chloride.

The results obtained show that chromium trioxide does not react with di-silicon hexachloride at ordinary temperatures. No red color indicating the formation of chromyl chloride was observed as in the case with silicon tetrachloride. At 200° the oxidation proceeds explosively with the complete destruction of the silicon linkage and the complete replacement of the chlorine with oxygen. Our results and those of Rauter (1892) indicate that the chlorine attached to the silicon atom is very stable at ordinary temperatures. At higher temperatures, the predominating bonding of oxygen by silicon is shown in such a vigorous manner that it is impossible for oxychlorides to be formed.

Experimental

The chromium trioxide was prepared by the action of concentrated sulfuric on a solution of potassium dichromate, the crystals were washed with pure nitric acid and heated to 60°-80° in a glass tube through which a current of dry air was passed. The melting point of the chromium trioxide was 193°.

Chromium trioxide gives up its oxygen at 250° according to the equation $2\ CrO_3 = Cr_2 + 3\ [O]$. It was thought that the liberated oxygen might act on the di-silicon hexachloride according to the equation $3\ Si_2Cl_6 + 3\ [O] = 3\ Si_2OCl_6$ and the theoretical amounts of each substance required by this equation were taken in the experiment. Thirty-eight and five-tenths grams of di-silicon hexachloride were placed in a distilling flask containing 5 grams of chromium trioxide and the mixture refluxed for three hours at the boiling point of di-silicon hexachloride (145°-148°). At the end of this time the entire liquid was distilled, the entire amount distilling at 145°, thus indicating that no Si_2Cl_6O (B.P.136°) was formed at the temperature of the experiment. The di-silicon hexachloride was again placed in the distilling flask containing the chromium trioxide and the temperature gradually raised to 200°C. When this point was reached an explosion occurred which blew the cork from the distilling flask. Chromic oxide, silica and a small amount of chromium trioxide remained in the flask. The reaction at 200° may be represented by the equation,

$$8\ CrO_3 + 3\ Si_2Cl_6 = 4\ Cr_2O_3 + 6\ SiO_2 + 9\ Cl_2$$

Another experiment was carried out in which the compounds were taken in the same amounts and placed in a Carius tube. The tube was sealed and then heated at a temperature of 250°-300° for five hours in a Carius furnace. The products remaining in the tube as a result of the reaction were the same as in the previous experiment, with the addition of some red chromyl chloride which decomposed in the moisture of the atmosphere when the tube was opened. The reaction at 250°-300° in a closed tube may be represented by the equation,

$$11\ CrO_3 + 3\ Si_2Cl_6 = Cr_2O_3 + 6\ SiO_2 + 9\ CrO_2Cl_2$$

Summary

1. No oxychlorides of silicon are formed by the action of chromium trioxide on di-silicon hexachloride.

2. The silicon linkage is stable at a temperature of 150° in the presence of chromium trioxide. At 200°C the silicon linkage is disrupted and the chlorine is entirely replaced by oxygen with the formation of silicon dioxide.

THE ACTION OF OZONE ON DI-SILICON HEXACHLORIDE

The action of chromium trioxide on silicon tetrachloride and di-silicon hexachloride indicates that these chlorine derivatives of the hydrosilicons are not easily oxidized at ordinary temperatures but that at higher temperatures the oxidation is complete with the formation of silicon dioxide. In consequence of the behavior of these silicon chlorides with chromium trioxide, it was thought that the employment of an oxidizing agent which has the property of yielding its oxygen at ordinary temperatures would be better adapted for effecting a partial oxidation of di-silicon hexachloride. Clark and Chapman (1908) in their investigations found that ozone possesses remarkable chemical activity at ordinary temperatures. Later Rothmund and Burgstaller (1913) pointed out that ozone is especially active as an oxidizing agent when its decomposition is catalyzed by certain substances such as platinum black and metallic oxides. Friend and Twiss (1924) state that ozone may manifest its oxidizing property in two different ways, namely:

1. Oxidation, during the process of which there is no change in volume insofar as the ozone itself is concerned, each molecule of ozone yielding a molecule of oxygen, the third oxygen atom entering the oxidized product.
2. Oxidation in which all three atoms of oxygen are absorbed.

This behavior of ozone then furnishes a method of bringing di-silicon hexachloride in contact with nascent oxygen at ordinary temperature. Besson and Fournier (1895) state that ozone acts on phosphorus trichloride forming the oxychloride of phosphorus. The same authors (1909) found that ozone acts more vigorously than chromium trioxide on silico-chloroform at ordinary temperatures. In this reaction they obtained some viscous oxychlorides of silicon which indicate that the oxidation proceeded farther than the similar oxidation with chromium trioxide.

The results of our experiments show that ozone has no oxidizing effect on di-silicon hexachloride, either alone or when the decomposition is catalyzed by silver oxide.

Experimental

The ozone was produced by means of a Brodie ozoniser which gave very successful results. The di-silicon hexachloride was placed in a distilling flask which contained a glass tube extending to the bottom of the flask. This tube was sealed into the neck of the flask and thus allowed the ozone to be aspirated through the di-silicon hexachloride without coming in contact with any rubber connections. For the same reason, the distilling flask was sealed to the ozoniser and its outlet tube to a small phosphorus pentoxide tower which protected the di-silicon hexachloride from atmospheric moisture. Dry oxygen was obtained by passing the gas successively through sulfuric acid and phosphorus pentoxide. Twenty-one and two-tenths grams of di-silicon hexachloride (B.P.145°)were placed in the distilling flask and oxygen allowed to enter the ozoniser at the rate of one bubble per second when counted in the sulfuric acid washing bottle. This gave sufficient ozone to cause a very strong odor in the vicinity of the apparatus. The loss of di-silicon hexachloride by entrainment was 0.13 grams for 21.2 grams during a period of six hours. After the ozone had bubbled through the di-silicon hexachloride for six hours, the special distilling flask was removed and the liquid distilled into another dry distilling flask. Distillation from this flask gave 0.2 gram distilling 134°-136° and the entire remainder at 145°-148°. The small portion distilling at 134°-136° gave silico-oxalic acid when hydrolyzed with water. The presence of the silico-oxalic acid was confirmed by a positive test for hydrogen when potassium hydroxide solution was added. Since Si_2Cl_6O hydrolyzes to form silicic acid, it was concluded that no silicon oxychloride was formed. The remainder of the distillate was pure di-silicon hexachloride.

Ozone in the Presence of Silver Oxide

A second experiment was made in which silver oxide was added to the di-silicon hexachloride for the purpose of catalyzing the decomposition of the ozone. Thirty and sixty-seven hundredths grams of di-silicon hexachloride and 5 grams of dry silver oxide were placed in the distilling flask and the operation carried out as before for a period of sixteen hours. There was no apparent rise of temperature or any other indication that any oxidation had taken place. Upon distillation, the entire product came over at the boiling point of di-silicon hexachloride.

Discussion of Results

This behavior of ozone with di-silicon hexachloride is of considerable interest because it shows that the silicon linkage is stable in the presence of nascent oxygen at ordinary temperatures. Martin (1912) found that di-silicon hexachloride is stable in the presence of chlorine at temperatures below the boiling point of di-silicon hexachloride. These facts show that a relatively high temperature is a necessary attribute to the formation of the stable end products of oxidation and chlorination. That di-silicon hexachloride does not form silicon tetrachloride or silicon dioxide when brought in contact with chlorine or ozone at ordinary temperatures serves to demonstrate that this compound possesses greater stability than hitherto supposed. It is very probable that the lack of knowledge, concerning the chemistry of the lower chlorides of silicon, is not a result of their instability but of the difficulty heretofore involved in their preparation.

Summary

1. No oxychlorides of silicon are formed by the action of ozone on di-silicon hexachloride.

2. The silicon linkage is stable at ordinary temperature in the presence of ozone when the decomposition of the ozone is catalyzed by silver oxide.

THE ACTION OF OZONE ON THE VAPOR OF DI-SILICON HEXACHLORIDE

In this experiment the apparatus was designed in a manner which allowed the vapor of di-silicon hexachloride and oxygen to pass simultaneously through the silent electric discharge. By this arrangement we were able to bring the vapor of di-silicon hexachloride and ozone together at a temperature of 145°C. The decomposition of ozone is more rapid at higher temperatures and consequently its oxidizing power is more marked. It is a well known fact that many reactions which will not proceed under ordinary conditions take place when one or both reacting substances are in the vapor or gaseous condition at a higher temperature.

Our results show that ozone even at a temperature of 145°C has no effect on the vapor of di-silicon hexachloride, when these substances are brought in contact in the presence of the silent electric discharge.

Experimental

A Siemans ozoniser was sealed to a small distilling flask which was provided with a side arm through which oxygen entered the apparatus. The apparatus was placed upright in order that the ozoniser might also serve as a reflux condenser for the liquid. The apparatus was thoroughly dried and 5 grams of di-silicon hexachloride placed in the flask. A previous experiment showed that when an oil bath surrounding the flask was raised to a temperature of 180° the vapor rose sufficiently high in the condenser to come in contact with the ozone and the silent discharge. Dry oxygen was allowed to enter the ozoniser at the rate of one bubble per second when counted as the gas passed through sulfuric acid. This gave sufficient ozone to cause a perceptible odor above the apparatus. The vapor was exposed to the action of the ozone and the silent electric discharge for a period of one hour. Dark rings of a brown substance settled out in the flask during the experiment. After cooling, the flask was disconnected from the ozoniser and the liquid distilled. Several cubic centimeters distilled at 55°-60° and were identified as silicon tetrachloride. The remainder distilled at 145° and the percentage of chlorine (78•82) determined . This showed it to be unchanged di-silicon hexachloride. The small amount of residue in the flask was found to be elemental silicon.

Discussion of Results

Ozone has no apparent action on the vapor of di-silicon hexachloride at 145° in the presence of the silent electric discharge, thus showing the stability of the silicon linkage when in the presence of a vigorous oxidizing agent at a temperature somewhat higher than ordinary atmospheric temperature. It will be remembered that chlorine reacts with di-silicon hexachloride at this temperature to form the stable end product silicon tetrachloride. This result shows that di-silicon hexachloride has a greater activity for ordinary chlorine than for activated oxygen at the boiling point of di-silicon hexachloride. The decomposition of di-silicon hexachloride into elemental silicon and silicon tetrachloride in the silent electric discharge proceeds according to the equation, 2 Si_2Cl_6 = Si + $SiCl_4$. This same behavior was found by Troost and Hautefeuille (1871) in the temperature range 350°-800°. The silent electric discharge appears to lower the temperature of initial decomposition two hundred degrees.

Summary

1. No oxychlorides of silicon are formed when the vapor of di-silicon hexachloride and ozone are brought in contact at 145° in the presence of the silent electric discharge.
2. The vapor of di-silicon hexachloride is decomposed into elemental silicon and silicon tetrachloride at 145° in the presence of the silent electric discharge.

GENERAL SUMMARY OF THE ACTION OF OXIDIZING AGENTS OTHER THAN OXYGEN ON DI-SILICON HEXACHLORIDE

1. Vigorous oxidizing agents do not act upon di-silicon hexachloride at ordinary temperatures to form oxychlorides of silicon by the interposition of an oxygen atom between the two silicon atoms to form the siloxan chain, or by the replacement of chlorine.

2. At higher temperatures, strong oxidizing agents convert di-silicon hexachloride completely to silica.

THE ACTION OF OXYGEN ON THE VAPOR OF DI-SILICON HEXACHLORIDE AT HIGHER TEMPERATURES

The previous experiments have shown that di-silicon hexachloride does not form an oxychloride of silicon when brought in contact with vigorous oxidizing agents. The conclusion that di-silicon hexachloride is incapable of forming an oxychloride could not be made from the results of the previous experiments because of the behavior peculiar to some of the oxidizing agents at higher temperatures. Chromium trioxide, for example, loses its oxygen at 250°C and it is thought that the oxygen is in the nascent state at the instant of decomposition. It is probable that the action of nascent oxygen at this temperature is entirely too vigorous to effect a partial oxidation of the di-silicon hexachloride.

In reviewing the methods which have been proposed for the preparation of the oxychloride, Si_2Cl_6O, it was observed that oxygen was used in the method of Troost and Hautefeuille (1881). In this method the chlorination and oxidation processes were carried out simultaneously. The mechanism of the formation of the oxychlorides was unknown to the authors. The conditions under which these workers produced the oxychloride, Si_2Cl_6O do not prohibit the assumption that its formation may involve the lower chloride, Si_2Cl_6 as an intermediate step in the process. Furthermore, there appears to be some relationship between the negligible yields of Si_2Cl_6O obtained by Zanetti (1912), Sanger and Riegel (1912), and by us, and the correspondingly low yields of di-silicon hexachloride produced by the chlorination of silicon.

The theories for the formation of the oxychloride, Si_2Cl_6O from the lower chloride Si_2Cl_6 have been previously discussed (p.58). The object of the present research is to study the action of oxygen on the vapor of di-silicon hexachloride at higher temperatures. This includes (a) a study of the effect of oxygen on pure di-silicon hexachloride vapor at different temperatures under conditions favorable for the preservation of the lower chlorides and (b) a study of the reaction in which the oxygen will come in contact with appreciable quantities of di-silicon hexachloride simultaneously with its formation and under conditions most favorable for the prevention of its decomposition.

The Action of Oxygen on the Vapor of Di-silicon Hexachloride at 300°C and 1000°C

Troost and Hautefeuille (1871) found that the decomposition range of di-silicon hexachloride is between 350° and 800°. Therefore, in studying the action of oxygen on di-silicon hexachloride at higher temperatures, it was necessary to choose temperatures outside of this range. A temperature of 300° was selected for the temperature below the range of decomposition because of a comparison desired with the action of nascent oxygen at this temperature. One thousand degrees was selected for the investigation above the range of decomposition.

Experimental

It was necessary to have an electric furnace capable of reaching a temperature of 1000° and holding this temperature for some time. The ordinary electric combustion furnace was unsuitable because of its inability to remain at this temperature without the destruction of the element.

Description of Furnace:

The 220 V. furnace which was especially constructed for these experiments had a heating length of eighteen inches. It contained a silica tube having an inside diameter of 0.5 inch. The heating element was constructed of No.2 Nichrome wire and was covered with magnesia cement and then packed in sil-o-cel powder. The furnace, which was enclosed in a seamless steel tube, was calibrated for the desired temperature by means of sliding resistance coils. The temperature was measured with a calibrated Alumel-Chromel thermo-couple having a cold junction which was maintained at 0° by means of an ice bath.*

Temperature 300°:

Ten and five-tenths grams of di-silicon hexachloride was placed in a small distilling flask containing a piece of glass tubing extending to the bottom of the flask so that the oxygen could be bubbled through the liquid. The flask was attached to the silica tube of the furnace and the temperature of the

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*The author is indebted to Dr. J.J.Canfield for the construction and calibration of the thermocouple.

furnace raised to 300°. The di-silicon hexachloride was then brought to its boiling point by means of an oil bath and the oxygen bubbled through the liquid. The operation was continued for one hour. No explosive action occurred as in the case of chlorine at this temperature (Martin, 1914). The resulting product was condensed in a small distilling flask immersed in an ice bath and containing a spiral condenser to insure complete condensation of the product. The distillation of the product gave a very small amount of liquid distilling at 59° which proved to be silicon tetrachloride. The thermometer then rose rapidly to 145° and the remainder of the liquid distilled at this temperature. The whole operation was repeated by bubbling oxygen through the last portion of the distillate. The distillation of this product produced a small amount of silicon tetrachloride as in the previous operation thus showing that there was some decomposition of di-silicon hexachloride in the presence of oxygen at a temperature fifty degrees below the reported decomposition range. The remainder of the product distilled at 145°. A determination of chlorine on this portion gave 79.10% chlorine while the theoretical percentage for di-silicon hexachloride is 78.99%.

Temperature 1000°:

At 300° there was a partial decomposition of the di-silicon hexachloride corresponding to the equation $2\ Si_2Cl_6 = Si + 3\ SiCl_4$. It is apparent that the decomposition will be even greater at this higher temperature because the vapor must pass through the decomposition range (350°-800°) when entering and leaving the furnace. In order that the vapor might be raised quickly to the stable range, the flask containing the di-silicon hexachloride was attached to a small silica tube which extended into the hottest zone of the furnace. Another effort was made to prevent this decomposition by aspirating silicon tetrachloride vapor through the furnace as in the preparation of the lower chlorides (p.14). Silicon tetrachloride is one of the products resulting from the decomposition of di-silicon hexachloride and it seemed probable that its presence would aid in the preservation of the di-silivon hexachloride. Further precaution was taken to prevent decomposition by cooling the vapors as rapidly as possible as they emerged from the furnace. A brass condenser was inserted into the end of the furnace for this purpose. The condenser was supported by clamps and held in place in the furnace by wrapping the end of the condenser in asbestos paper coated with sodium silicate. The end of the condenser projected into the furnace several inches and the junction was gas tight. A vigorous stream of water was run through the condenser to keep the temperature as low as possible. The resulting products were received in a three necked flask as described in the preparation of the lower chlorides (p. 15). The entire apparatus was sloped towards the receiving flask to insure removal of the products from the brass condenser. The regulation of the temperature proved to be very difficult on account of the cooling effect produced by the vapor of silicon tetrachloride. When it was observed that the temperature of the furnace was falling, the passage of the vapors was stopped until the furnace regained the original temperature.

Twenty grams of di-silicon hexachloride and 118.4 grams of silicon tetrachloride were passed through the furnace in the presence of oxygen. The oxygen was bubbled through the silicon tetrachloride at the same rate as in the previous experiment. No explosive reaction occurred during the process. In spite of the precautions observed for the prevention of the decomposition of di-silicon hexachloride, it was decomposed to a large extent. The distillate had a dark brown color as it emerged from the brass condenser because of the presence of finely divided elemental silicon.

The contents of the receiving flask were removed by the pressure of dry air and then subjected to distillation. A considerable amount of silicon tetrachloride distilled at 55°-60°. The water bath which had been used was then replaced by an oil bath. The temperature rose to 145° without any distillate coming over at 136°, the boiling point of the compound Si_2Cl_6O. As there was only a small residue remaining in the flask, the distillation was interrupted while the residue was transferred to a smaller distilling flask. Three grams of a liquid boiling 145°-148° were obtained. A chlorine determination on this portion by the Volhard method gave 79.2 per cent while the theoretical percentage for di-silicon hexachloride is 78.99. Hydrolysis of this portion gave the white solid silico-oxalic acid which evolved hydrogen when treated with potassium hydroxide. There was no evidence of the formation of the compound Si_2Cl_6O or any other oxychloride of silicon.

Tabulation of Results

Temperature of furnace, °C . . .	300.0	1000.0
Time, passage vapors, min. . . .	60.0	120.0
Si_2Cl_6 used, g.	5.54	20.0
$SiCl_4$ used, g.	—	118.4
Si_2Cl_6 recovered, g.	5.10	3.0
Decomposition Si_2Cl_6, %	8.0	85.0
Si_2OCl_6 produced, g.	none	none

Discussion of Results

These results indicate that pure di-silicon hexachloride does not react with oxygen to form an oxychloride. The tendency for di-silicon hexachloride to decompose between the temperatures 300° and 1000° is very marked. The experiments show that the decomposition temperature is lower in the presence of oxygen. The rapid decomposition of di-silicon hexachloride even in the presence of silicon tetrachloride vapor serves to show why it is not possible to produce the lower chlorides of silicon by the chlorination of compounds of silicon whose temperatures of chlorination are above 300°. Heretofore, we have regarded the brown residue obtained in the receiving flask during the production of the lower chlorides of silicon as ferric chloride. Further examination shows that much of it is finely divided silicon. It is very probable that the dark residue left in the fractionation of the lower chlorides consists of finely divided silicon mixed with the residue of the known lower chlorides of silicon.

Summary

1. No oxychloride of silicon is formed when the vapor of di-silicon hexachloride and oxygen are brought in contact at 300° and 1000°.

2. In the presence of oxygen the vapor of di-silicon hexachloride is partially decomposed at 300° while at 1000° its decomposition is nearly complete.

A STUDY OF THE EFFECT OF OXYGEN ON THE LOWER CHLORIDES OF SILICON DURING THE CHLORINATION PROCESS

To subxtantiate the results already obtained concerning the action of oxygen on the lower chlorides of silicon, a study was made to determine the effect of oxygen on the lower chlorides during the chlorination process. Since oxychlorides of silicon had been produced by passing chlorine and one-fifth its volume of oxygen over silicon, there existed the probability that the material chlorinated or some of the products of the reaction of the chlorine and oxygen, acted as catalytic agents of oxidation. C. R. Downs (1926) in a discussion of the catalytic gas phase oxidation of organic compounds states that there are several catalysts known which will produce partial oxidation products at intermediate temperatures. While the oxidation of silicon chlorides may have little analogy to the oxidation of organic compounds it does not justify the conclusion that the same phenomenon may not exist in the oxidation of inorganic compounds. The purpose of these experiments is to determine whether the lower chlorides of silicon and oxygen behave in the same manner in the chlorination process as they do when the two substances are brought in contact at the same temperature in pure state.

1. The Effect of Passing Chlorine and Oxygen over 50% Ferrosilicon in the Presence of Silicon Tetrachloride Vapor at 200°C.

Experimental

Dry chlorine and one-fifth its volume of dry oxygen (compare Troost and Hautefeuille, 1881) were bubbled through pure silicon tetrachloride as in the preparation of the lower chlorides of silicon (Fig.1, p. 15). The furnace was charged with ferrosilicon and heated to 200° before the mixed gases were allowed to enter the furnace. The chlorination began at 200°. The course of the gases was then changed so that they bubbled through the silicon tetrachloride. An inspection of Table I (p. 22) shows that the optimum rate of passing the silicon tetrachloride to obtain the maximum yield of lower chlorides is at the rate of 0.5152 gram per minute. In this experiment the rate of passing the mixed gases through the silicon tetrachloride was so controlled that 0.4766 gram of silicon tetrachloride per minute was obtained. Two hundred four and four-tenths grams of the resulting product gave but 5.8 grams of liquid boiling above the temperature of silicon tetrachloride. This portion boiled at 145° and proved to be di-silicon hexachloride.

2. The Effect of Passing Chlorine and Oxygen over 50% Ferrosilicon at 200°C.

The previous experiment showed that the yield of lower chlorides was very low because of the dilution of the chlorine with oxygen and silicon tetrachloride. This result is in accordance with the results obtained in the preparation of the lower chlorides (Table I, p.22). When silicon tetrachloride is used as a dilutent for the chlorine, the yield of lower chlorides is increased up to a certain point but beyond that a further addition reduces the yield (Fig.3, p.23). Although the optimum amount of silicon tetrachloride was aspirated with the chlorine for the production of a maximum yield of the lower chlorides, the yields were very low. This shows that oxygen also acts as a dilutent in the presence of silicon tetrachloride at a temperature of 200°. The effect, therefore, on the yield of lower chlorides was the same as that produced by the aspiration of more than 0.4968 gram of silicon tetrachloride per minute. Our experiments on the preparation of the lower chlorides of silicon have shown that silicon tetrachloride in addition to its dilutent effect, also operates in the chlorination process by diminishing the heat evolution per unit volume of total gas, thus lessening the temperature increase of the gas mixture per unit of reaction. Since the passage of the silicon tetrachloride caused too great a dilution of the chlorine and a lowering of the temperature of the reaction in the previous experiment, it appeared probable that the action of the oxygen might be intensified by omitting the passage of the silicon tetrachloride with the chlorine and oxygen.

Experimental

The chlorination was carried out as in the previous experiment. Twenty-three and eighty-three hundredths grams of the resulting product was distilled and gave 6.43 grams of liquid boiling above the temperature of silicon tetrachloride. Upon distillation this portion distilled at 145° and proved to be di-silicon hexachloride.

Tabulation of Results

	1	2
Time, min.	360.0	180.0
Ferrosilicon added, g.	150.0	100.0
Ferrosilicon used, g. . . .	56.0	54.0
$SiCl_4$ asp., g.	171.6	none
$SiCl_4$ asp. per min., g. . .	0.4766	none
Lower chlorides formed, g. .	5.8	6.43
Lower chlorides equiv. to Si used, g.	133.3	128.52
Lower chlorides formed, % .	4.35	5.00
Oxychlorides formed, g. . .	none	none

Discussion of Results

No oxychlorides of silicon are formed when chlorine and oxygen are passed over 50% ferrosilicon at 200°. Since pure di-silicon hexachloride does not react with oxygen at this temperature, the results of these experiments show that the material chlorinated and the products of the reaction do not act as catalytic oxidation agents. The low yields of the lower chlorides of silicon are a result of the dilution of the chlorine by the oxygen.

Summary

1. Oxygen has no action on the lower chlorides of silicon in the chlorination process at a temperature of 200°C.
2. The ferrosilicon or other products of the reaction have no catalytic oxidation effect on the lower chlorides of silicon.

THE ACTION OF OXYGEN ON SILICON TETRACHLORIDE AT 1250°C

It has been shown that di-silicon hexachloride does not form the oxychloride Si_2Cl_6O by the interposition of an oxygen atom between two silicon atoms. In consequence of this behavior of the silicon linkage with oxygen, we have concluded that the siloxan linkage which characterizes many stable silicon compounds is not formed in this manner. In view of the fact that the oxychloride Si_2Cl_6O was produced by Troost and Hautefeuille (1881) by the introduction of oxygen into the chlorination zone during the chlorination of silicon, it seemed logical to conclude that the oxygen may have reacted with the silicon tetrachloride to form the oxychloride.

Isolation of the Silicon Oxychloride from Commercial Silicon Tetrachloride

Further confirmation of the action of oxygen on silicon tetrachloride at high temperatures to form compounds containing the siloxan linkage was obtained by the successful isolation of 150 grams of the oxychloride Si_2Cl_6O from 9000 grams of silicon tetrachloride furnished by the Chemical Warfare Service. According to Hutchins (1919) much of the silicon tetrachloride for military purposes during the war was made by the chlorination of silicon carbide at a temperature of 1250°C. Our experiments and those of Martin (1914) have shown that the lower chloride Si_2Cl_6, is extremely unstable in the presence of chlorine at higher temperatures. It is significant that no lower chlorides of silicon were found in the higher boiling residue from this large amount of silicon tetrachloride because it not only confirms the results in regard to the instability of the lower chlorides of silicon in the presence of chlorine at high temperatures, but also substantiates our observations that the lower chloride Si_2Cl_6, is not an intermediate compound concerned in the formation of the oxychloride Si_2Cl_6O. Moreover, it appears to indicate that some oxygen must have been present in the commercial process and that the formation of the oxychloride of silicon was a result of the action of the oxygen on silicon tetrachloride.

The purpose of this experiment is to determine whether oxygen acts on silicon tetrachloride at 1250°C to form the oxychloride Si_2Cl_6O.

Experimental

Description of Furnace:

A special furnace was constructed which was capable of attaining a temperature of 1250°C and holding this temperature for some time. The furnace was of the carbon resistor type. It had 4-inch heavy carbon electrodes at each end. The resistor was placed between the electrodes and had the form of a cylinder. It was 8 inches long, 1.5 inches outside diameter and 0.25 inch thick. A one inch hole was left in the center and sealed to prevent loss of carbon. The resistor was covered with magnesia cement to avoid contact with air. The magnesia combustion tube through the center of the furnace was 18 inches long and had an inside diameter of 0.5 inch. The current consumption of the furnace varied from 70 to 100 amperes and from 50 to 60 volts. The current adjustment was made by means of a series of switches which were connected to various windings of the secondary of a 5-kilowatt step down transformer. The temperature of the furnace was determined by a Leeds and Northrup optical pyrometer of the disappearing film type.

Preparation of Pure Silicon Tetrachloride:

Commercial silicon tetrachloride furnished by the Chemical Warefare Service was distilled and the first and last portions of the distillate were rejected. The portion obtained in this manner was allowed to stand over mercury for several weeks to remove the majority of the chlorine, the bottle being shaken at intervals to bring new portions of the silicon tetrachloride in contact with the mercury. It was then distilled from the mercury into a balloon flask having a volume of 2000 cc. Metallic sodium was added to remove the last traces of hydrogen chloride and chlorine. That these substances were not removed entirely by the mercury was evidenced by a perceptable reaction with the sodium. Distillation was made from the balloon flask directly into the distilling flask used in the process. The silicon tetrachloride was colorless and had a boiling point of 59°C. A chlorine determination by the Volhard method gave 83.33%, (theory 83.37%).

Experimental Procedure:

The procedure of the experiment was the same as in the preparation of the lower chlorides of silicon except that dry oxygen, instead of chlorine, was bubbled through the silicon tetrachloride and the admixed vapor and gas were passed through the magnesia tube of the special furnace. The furnace was first raised to 1250° and then the dry oxygen was allowed to pass through the silicon tetrachloride vigorously enough to cause a slow dropping of the distillate into the receiving flask which was arranged as shown in Fig.1, p.15. The process was continued for six hours.

Distillation of Product:

The resulting product was removed by the pressure of dry air and distilled. Three hundred and ninety grams gave but 10.1 grams boiling above the temperature of silicon tetrachloride. This fraction was transferred to a small distilling flask and distilled. Seven and eight-tenths grams of liquid were obtained at 136°-138°. A small residue remained in the flask. This was not investigated.

Identification of the Fraction B.P. 136°- 138°:

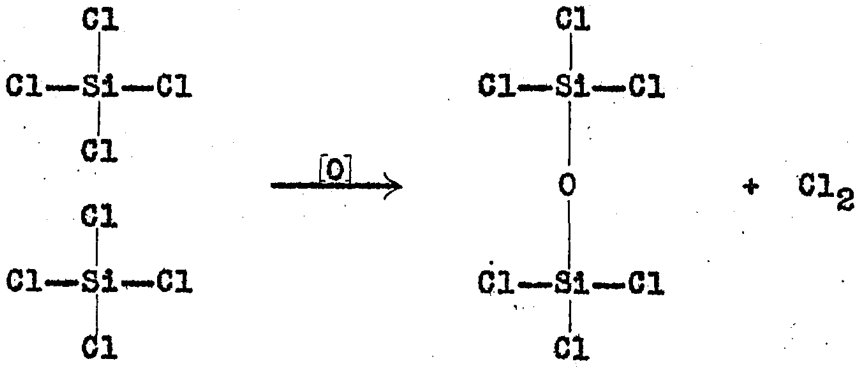
Stock (1925) gave 137°-138° as the boiling point of di-silicon hexachloride while this fraction boiled at 136°-138°. A melting point determination was made by placing a small amount of the liquid into a small test tube which was closed by a rubber stopper containing a calibrated thermometer. This test tube was then fitted into a larger test tube containing anhydrous ether. The whole apparatus was then immersed in a carbon dioxide-ether bath and the liquid frozen. The apparatus was then removed and the melting point determined. The melting point was found to be -32°C while Stock (1925) reported -33°C. A determination of chlorine (p.19) gave 74.45% of chlorine while the theoretical percentage in the compound Si_2Cl_6O is 74.56%.

Comparison of Yields of Si_2Cl_6O Obtained by the Action of Oxygen on Silicon Tetrachloride at 1250°C

	Laboratory Preparation	From Commercial Silicon Tetrachloride
Temp. Furnace, °C	1250.0	1250.0
Wt. Crude product, g.	390.0	9000.0
Wt. Fraction 136°-138°, g.	7.8	150.0
Yield Si_2Cl_6O calc. on wt. crude prod., %	2.0	1.67
Cl_2, det. (theory Si_2Cl_6O 74.56), %	74.45	74.40
B.P. Si_2Cl_6O det., °C (Lit. 137-138°)	136-138	134-136
M.P. Si_2Cl_6O det., °C (Lit. -33°)	-32	-30

Discussion of Results

Berzelius (1824) states that the dissociation point of silicon tetrachloride is above 1600°C. It is reasonably certain then, that the silicon tetrachloride undergoes no dissociation at a temperature of 1250°. The results obtained show that silicon tetrachloride forms the oxychloride, Si_2Cl_6O by the replacement of chlorine in two molecules of silicon tetrachloride with one atom of oxygen at 1250°C. The difficulty in replacing the chlorine in this compound presents a marked contrast to the easy replacement of hydrogen in silico-chloroform and therefore suggests that the latter compound is a much more desirable intermediate compound for the preparation of the oxychloride, Si_2Cl_6O. This method does not lend itself to laboratory practice because of the difficulty of obtaining a high temperature and because of the low yield of the oxychloride. The results indicate that the mechanism of the formation of compounds containing the siloxan (—Si—O—Si—) linkage, involves a condensation type of reaction. The specific reaction in this case is,



Summary

1. Oxygen reacts with silicon tetrachloride at 1250°C to form the oxychloride Si_2Cl_6O.

2. The chlorine of silicon tetrachloride is replaced by oxygen with great difficulty.

GENERAL SUMMARY

1. The silicon linkage in the compound Si_2Cl_6 is stable in the presence of strong oxidizing agents at ordinary temperatures. The linkage is disrupted at 300° in the presence of molecular oxygen and the di-silicon hexachloride decomposes into silicon and silicon tetrachloride. Nascent oxygen breaks the linkage at 200° with the complete conversion of the silicon to silica.

2. The silicon linkage of di-silicon hexachloride is more stable in the presence of oxygen than in the presence of chlorine at the same temperature.

3. Oxidizing agents do not react with di-silicon hexachloride to form oxychlorides of silicon by the interposition of an oxygen atom between two silicon atoms to form the siloxan chain, or by the replacement of chlorine.

4. The oxychloride Si_2Cl_6O is formed by the replacement of one atom of chlorine in each of two molecules of silicon tetrachloride with an atom of oxygen at a temperature of 1250°C.

CONCLUSION

1. Oxychlorides of silicon are formed by the action of oxidizing agents on the chloro-derivatives of silico-methane.

2. The chloro-derivatives of silico-ethane do not form oxychlorides of silicon when acted upon by oxidizing agents. The silicon linkage of di-silicon hexachloride is stable at relatively low temperatures in the presence of vigorous oxidizing agents; at higher temperatures the linkage is broken down and the compound is completely oxidized to silica.

3. That chloro-derivative of silico-methane in which the hydrogen is not completely replaced by chlorine forms an oxychloride of silicon with more ease than that chloro-derivative in which all of the hydrogen is replaced by chlorine.

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