*Preparation of Chloropolysilane from the Copper-catalyzed Reaction of Silicon Metal and Hydrogen Chloride**

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The copper-catalyzed reaction of silicon metal powder with hydrogen chloride by the flow method was studied in order to find a convenient preparative method for chloropolysilanes, and to elucidate the mechanism of this reaction which seems to have a close relationship with the so-called direct method of preparing alkylchlorosilanes. Hitherto, the conventional way to prepare chloropolysilanes has been to use a binary alloy such as magnesium-silicon[1,2] or ferrosilicon[1] so as to smooth the reaction of silicon and chlorine, and to work at a temperature as low as possible. However, the yields were not satisfactory.

The present investigation was carried out with several kinds of silicon-copper powder mixtures, varying the species of silicon metal, the reaction temperature, the flow velocity of reactant gas, and the ratio of copper powder to silicon. Under the optimum conditions, the yield of chloropolysilane was found to reach 30 wt. % based on the amount of hydrogen chloride. The preferable species of metallic silicon were those which contained aluminum as a main impurity.

Experimental

Materials. — *Metallic silicon of commercial grade.*—Three species of metallic silicon which contained aluminum (Samples A and C) and iron (Sample B), respectively, as main impurities were used in these experiments after being crushed and pulverized into minus 80 mesh. The analytical values of each sample were as follows:

Sample	Exptl. run No.	Fe%	Al%	Ca and Mg%	Particle size (mesh)
A	1, 4, 5, 7	2.70	1.60	0.2	80∼150
B	2, 3	7.94	0.42	—	80∼120
C[3]	6, 8	trace	0.52	—	120∼170

Silicon-aluminum and silicon-calcium alloys. — An alloy having the composition Si:Al=8:2 was prepared by melting 98% silicon and aluminum block in a sealed graphite crucible. Another was a commercial silicon-calcium alloy. Both were crushed and pulverized into minus 80 mesh. The analytical values of the two alloys were as follows:

Sample	Si%	Al%	Fe%	Cu%	Ca%	Particle size (mesh)
Si-Al alloy	80.6	17.2	1.02	0.01	—	80∼120
Si-Ca alloy	27.3	—	—	—	68.6	80∼120

Copper powder.—Finely pulverized copper for catalyst, prepared by the Fukuda Metal Plate and Powder Mfg. Co., and known as "3L3" (Purity: >98%; size minus 200 mesh[4]), was used.

Hydrogen chloride. — It was prepared in the usual way by the reaction of ammonium chloride and sulfuric acid, washed and dried by concentrated sulfuric acid, and reserved in a 20 l. glass bottle tank which was sealed by concentrated sulfuric acid. The gas was made to flow by the pressure of the sealed liquid head and was measured by its volume (Fig. 1).

Apparatus and Experimental Procedure.—The whole apparatus is shown in Fig. 1. About 20∼200 g. of contact mass was charged into a reaction tube of 3 cm. diameter and 1 m. length in an electric furnace. After replacing the air in the apparatus with nitrogen, it was heated to about 150°C in order to dry off the absorbed water and cooled. Then the temperature was raised again from room temperature at the rate of 4∼5°C/min. while passing hydrogen chloride at the rate of 8 l./hr. The initiation of the reaction was observed by sudden rise of temperature, change in volume of evolved hydrogen gas, and fuming in the adapter part which was due to the generation of aluminum chloride or chlorosilanes. As explained in our former report[5], the temperature at which this initiation occurred was designated as initiation temperature, or I.T. as abbreviated. Once the reaction occurred, the contact mass was activated and thus the succeeding reaction could proceed at a somewhat lower temperature. Accordingly the reaction tube was cooled to room temperature and then re-heated gradually in order to determine the actual

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* Presented before the Symposium on the organosilicon and organometallic compounds held at Osaka under auspices of Kinki Chemical Industries Association, Oct. 15, 1957.

[1] W. C. Schumb and E. L. Gamble, "Inorganic Synthesis", (H. S. Booth, Editor in Chief), McGraw-Hill Book Co., Inc., New York (1939), p. 42.

[2] W. L. Walton, U. S. Pat. 2,602,728 (1952).

[3] A powder of silicon-aluminum alloy was treated with dilute hydrochloric acid and washed with water and dried.

[4] −200∼+250 mesh 9%; −250∼+325 mesh 15%, −325 mesh 76%; covering power 1900 cm^2/g.

[5] I. Shiihara and J. Iyoda, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 1388 (1957).

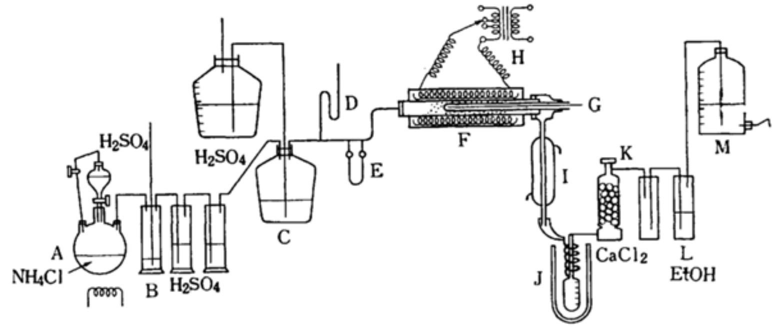

Fig. 1. Reaction apparatus for Si(Cu)+HCl gas.
A: HCl generator B: Drying bottle and prevention of backflow
C: Storage and measuring bottle of HCl gas D: Manometer
E: Flowmeter F: Reaction tube and electric furnace
G: Thermocouple H: Transformer I: Water condenser
J: Dry Ice condenser K: Prevention of moisture and backflow
L: Absorption bottle of HCl M: Mariotte bottle.

starting point of reaction, or R.T. as abbreviated. After the confirmation of R.T., the reaction was carried out by making hydrogen chloride flow under the appropriate conditions. The condensates, both in the water-cooled receiver and in the Dry Ice trap, were combined and distilled through a Widmer column and separated into trichlorosilane, silicon tetrachloride and residue with a high boiling point. The residual contact masses were analyzed by the usual methods as to metallic silicon, volatile silicon component on treating with hydrofluoric acid, copper and chlorine. In each experiment, the unreacted hydrogen chloride and volatile chlorosilane in the effluent gas were absorbed in ethanol and the amount of acidic chlorine was measured by titration and silica by weight. Thus insoluble gas was accumulated as hydrogen in a Mariotte bottle and measured.

Results

Effect of the Other Metallic Ingredients in Silicon Metal.—In our previous experiments it was found that the species of silicon metal have a direct influence upon the so-called direct method of preparing methylchlorosilanes. Accordingly, in order to investigate the effect of ingredients in silicon metal, three representative species of silicon metal powder (Samples A, B and C) and silicon-calcium were chosen as contact masses in the present experiments. Because of the prominent catalytic action of copper in the reactions, experiments were conducted with special addition of 3 wt. % copper powder with three kinds of silicon metals. In the case of chips of silicon-calcium alloy no catalyst was used because of the great reactivity of the alloy at lower temperatures, i.e., about 150°C.

A summary of experimental results is shown in Table I. It was found that Sample A—fairly rich in aluminum ingredient—was the best contact mass among the four species tested, and showed its optimum temperature of 215°C for forming the best yield of chloropolysilanes. In silicon-calcium, the product was found to be almost exclusively chloromonosilane, although the R.T. was as low as 150°C.

Influence of Elapse of Reaction Time.—It was found that with long reaction runs the yield of chloropolysilane gradually increased as the reaction time increased. An example with the silicon Sample A is shown in Table III.

The flow rate of hydrogen chloride in the run was almost equal from beginning to end, i.e., 8 l./hr. It seems that the higher molecular weight polysilane derivatives which were produced on the contact mass as intermediates would increase as the elapse of reaction time, just as it will be shown in the case of the contact mass of high copper ratio. From these intermediates some lower series of chloropolysilanes, such as di- or trisilane, might be split out.

Effect of the Copper Catalyst.—As was known in many previous experiments, the reaction of silicon metal or silicon alloy with hydrogen chloride was promoted when a small per cent of copper was added as catalyst.

Copper enables this reaction to proceed even at 215°C; without the copper catalyst

TABLE I. EFFECT OF THE OTHER METALLIC INGREDIENTS IN SILICON METAL

Contact masses	Run No.	Reacn. temp.	Reacn. time	HCl used	Liquid product	Yield	Absorption in EtOH		Distillation analysis				
							HCl	SiO$_2$	H$_2$SiCl$_2$	HSiCl$_3$	SiCl$_4$	High b.p. materials	Loss
		(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(g.)	(%)	(%)	(%)	(%)	(%)
Si (A) (Al rich)	H-1-(10)	215	6	85.2	102	119	7.55	0.1	0	35.5	24.0	37.5	3
200 g.	H-4-(4)	170	6	79.6	42	52.7	35.6	2.0	0	58.5	13.6	23.4	4.5
Cu 6 g.	H-4-(6)	275	6	90.0	107.5	111	4.25	1.7	0	65.7	21.9	8.6	3.8
	H-4-(9)	180	6.5	86.1	56	65.0	35.0	2.8	0	86.5	13.4	26.8	3.4
Si (B) (Fe rich)	H-2-(4)	215	6	97.3	93	95.7	20.4	1.1	0	57.3	18.3	23.1	1.3
200 g.	H-2-(8)	355	6	92.0	78.5	85.2	29.8	0.7	0	63.2	25.7	8.7	2.4
Cu 6 g.	H-3-(6)	275	7	107	131	112	1.2	0.3	0	60.8	23.2	12.7	3.3
Si (C)	H-8	275	5	111.8	97	86.8	27.0	0.5	5.8	65.6	13.2	12.2	3.2
(HCl aq. treated)													
107 g.													
Cu 3.3 g.													
Si—Ca* 1.1 kg.	previously performed	150	6.5	144.2	87	61.2	—	—	0	41.7	52.5	2.8	3.0

* 2∼3 mm. chip was used.

TABLE II. THE EFFECT OF ADDITION RATIO OF COPPER CATALYST TO SILICON METAL

Contact mass	Run No.	Cu added ratio	Reacn. temp.	Reacn. time	HCl used	Liquid product	Yield	Absorption in EtOH		Distillation analysis			
								HCl	SiO$_2$	HSiCl$_3$	SiCl$_4$	High b.p. materials	Loss
		(%)	(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(g.)	(%)	(%)	(%)	(%)
Si (A)	H-1-1	3	300	3	40.2	43.5	10.8	1.34	0.11	40.4	28.7	25.6	5.3
	H-4-7	3	270	6	86.5	100.5	115.5	4.1	2.3	66.3	20.1	6.5	7.1
	H-4-4	3	215	5	71.4	59	82.6	15.6	3.5	33.9	21.9	36.5	5.9
	H-7-5	10	300	2.5	53.6	8	15	40.0	9.8	(10.9 g.)*			
	H-7-4	10	215	2	33.4	3.5	11	39.0	4.4	(4.9)*			
	H-5-2	20	300	2	65.5	61	93.1	20.4	2.7	37.7	26.4	6.6	34.3
	H-5-6	20	215	2.3	40.3	1	2.5	34.9	11.8	(13.2)*			

* As H$_3$SiCl calculated from absorbed SiO$_2$ in ethanol (g.).

TABLE III. THE INFLUENCE OF ELAPSE OF REACTION TIME

Contact mass	Cu added ratio	Time elaspe	Reacn. temp.	Reacn. time	HCl	Liquid product	Yield	Absorption in EtOH		Distillation analysis			
								HCl	SiO$_2$	HSiCl$_3$	SiCl$_4$	High b.p. materials	Loss
	(%)	(hr.)	(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(g.)	(%)	(%)	(%)	(%)
Si (A)	3	12	215	3	55.4	57	103	10.2	0.05	47.7	16.5	29.4	6.4
		22	215	6	45.6	58	127	7.5	0.07	35.5	24	37.5	3
		34	215	6	92.5	94	102	19.1	2.4	34.6	22.7	40.0	2.7

TABLE IV. i. YIELDS OF CHLOROPOLYSILANE AND DISTILLATION ANALYSIS OF THEM

Contact masses	Run No.	Mean reacn. temp.	Reacn. time	HCl used	Liquid product	Yield (HCl based)	Chloropoly-silane		Distillate to b.p. 180°C (disilane fracn.)		Residual liq. (trisilane fracn.)		Loss
		(°C)	(hr.)	(g.)	(g.)	(%)	(g.)	(%)	(g.)	(%)	(g.)	(%)	(%)
Si (A)	H-1	210	69.3	1053	860	82	248	28.8	202	81.5	42.7	17.2	1.3
Si (A)	H-4	210	68.2	937.4	783	83.4	181.5	23.2	154	85.0	25.5	14.1	0.9
Si (B)	H-2	210	60.0	933.8	813.5	87	150	18.5	123	82.2	25.0	16.1	1.7
Si (B)	H-3	210	47.1	697.5	767	110	62	8.1	52	83.9	8.9	14.3	1.8

ii. REDISTILLATION OF DISILANE FRACTION

Charge: H-1 168.5 g.

B.p. (°C)	~75	120~143	143~148	148~149	Residue	Loss
Fracn. %	8.6	12.7	5.3	65.1	5.9	1.5
Cl %		80.5		80.0		

Charge: H-4 101 g.

Fracn. %	7.0	19	12	46	16	0

iii. REDISTILLATION OF TRISILANE FRACTION[a)]

Charge: 86 g.

B.p. (°C)	~145	145~190	213~215	215~115[b)]	gel residue
Fracn. %	10.5	2.6	35.5	32.5	19.7
Cl %	78.3				

a) The fact that the total sum of this distillation fraction and residue was over 100% and other distillation losses of chloropolysilane were very small, was reasonably explained by the ease of oxidation of chloropolysilane.

b) Violent thermocracking was occurred.

TABLE V. PHYSICAL CONSTANT OF SOME CHLOROMONOSILANES AND CHLOROPOLYSILANES

	Compound	Formula	Mol. wt.	B.p. (°C)	M.p. (°C)	D_{20}^{10}	Cl%
Monosilanes	Silicon tetrachloride	$SiCl_4$	170.0	57.5	−70	1.48	83.5
	Silicochloroform	$HSiCl_3$	135.5	31.5	−128.2	1.34	78.5
	Dichloromonosilane	H_2SiCl_2	102.1	8.0		—	69.6
Disilanes	Hexachlorodisilane	Si_2Cl_6	269.2	149	2.5	1.47	79.3
	Pentachlorodisilane	HSi_2Cl_5	234.5	125			75.6
Trisilanes	Octachlorotrisilane	Si_3Cl_8	367.9	215	−67	1.56	77.1
	Heptachlorotrisilane	HSi_3Cl_7	333.5	unknown		—	74.4

TABLE VI. REACTION OF THE CHLOROPOLYSILANES $H_nSi_mCl_{2m+2-n}$ AND COPPER POWDER

Expt. No.	Samples of chloro-polysilanes	(g.)	Catalyst	(g.)	H_2 generated (cc.)	Reacn. time (min.)
1	Disilane fracn. B.p. 120~143°C in Table IV	3.729	Cu powd.	0.5	2.8	20
2		2.440	Cu+$AlCl_3$	0.5+0.5	16.9	10
3		2.570	CuCl	0.5	0	10
4		2.570	CuCl+$AlCl_3$	0.5+0.5	0.4	10
5		6.859	HCl+$AlCl_3$	0.5	ca. 60	15
6	Si_2Cl_6 b.p. 143~148°C	15.0	Cu+$AlCl_3$	0.5+0.5	4.0	10
7	H-3 residual contact mass	5.0	Cu+$AlCl_3$	0.5+0.5	7.4	10

TABLE VII. ANALYTICAL RESULTS OF THE RESIDUAL MASSES IN EACH RUN

Run No.	H-1	H-2	H-3	H-4	H-5-2	H-5-6
Residual wt. (g.)	33	60	43	35.08	116	55[a]
Si species	A	B	B	A	A	A
Ignition loss (%)	46.97	48.43	2.19	35.40	−3.50[b]	−6.74[b]
SiO_2[c] (%)	16.10	12.43	29.83	57.11	7.43	6.61
Si (%)	6.91	4.10	23.88	0	62.82	56.48
Fe (%)	11.76	18.33	26.67	11.42	2.35	4.24
(Recovery)[d] (%)	(71.7)	(69.7)	(72.8)	(74.2)	(100)	(86.4)
Cu (%)	15.21	7.18	11.14	18.05	19.75	24.20
(Recovery)[d] (%)	(83.7)	(71.8)	(80.2)	(106.0)	(95.4)	(93.8)
Cl (%)	34.62	37.10	2.19	3.69	1.74	0.55
Total (%)	84.60	79.14	93.71	90.27	94.09	92.08

a) 37 g. was sampling out at intervals.

b) When the content of chlorine and volatile silicon hydrides in contact masses was small, this value often became a negative value because of the increase of weight caused perhaps by oxydation of the contact mass in air.

c) This value was calculated so as to take the weight difference after and before the treatment of HF solution as silica, but presumable some Si—Cl and Si—H might be remained even if they were ignited in air.

d) % of recovery to the starting contact masses.

it was necessary to raise the temperature to 300°C[6] in order to get a sufficient yield of liquid product. This effect makes it possible to get chloropolysilane and siliconhydrides in more satisfactory yield, which are both unstable at temperatures higher than 250°C, the temperature used in the hitherto-performed procedures.

As to the amount of the copper added to the silicon metal, it was remarkable that it showed optimum at 1~3 wt. % copper content, and the increased ratios of copper, for instance 10% or 20%, yielded less liquid chlorosilane (Table II). This was due to the formation of monochloromonosilane which could not be condensed in a Dry Ice-acetone trap but was absorbed in alcohol. The reason for the formation of a small amount of chloropolysilanes may be the smaller reactivity of some higher molecular weight cupropolysilanes which might be formed by the reaction of Eq. E proposed in the discussion part of this report. These compounds

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[6] F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 2108 (1947).

might be produced proportionally to the amount of copper, and would not be able to accept further cleavage reaction of hydrogen chloride and remained as solid materials on contact mass. Moreover, the life of contact mass was defined as the interval of the time in which the contact mass is active and forms the liquid product; then the life of the contact mass having a large amount of copper was very short. For instance, 10% and 20% copper masses, have lives of 6.9 and 7.8 hr. respectively as compared to the longer time of 3% copper (Table IV).

Composition of the Chloropolysilanes Condensates.—The contact masses have their own lives and lose their reactivity toward hydrogen chloride at the step where a considerably large amount of silicon component still remains in the residual contact masses (see Table VII). The total figures of a few runs are shown in Table IV. The mean yield of the liquid product was 800 g. from 200 g. silicon metals, and the yields of chloropolysilanes were found to be 8.1～28.8 wt. % as the high boiling residue in the crude product. Distillation analysis was carried out for several intervals of the run in order to investigate the change of the compositions of the crude chlorosilanes with elapse of reaction time (see Table III); however, the distillation of a high boiling point fraction was performed with the gathered sample of several runs. The physical constants of some chlorosilanes and chloropolysilanes of this experiment are shown in Table V. Upon distillation of these chloropolysilanes, the chlorodisilane fraction was found to be 80～85 wt. % and the higher fraction, chlorotrisilane, was found to be 14～17 wt. % based on the charged crude chloropolysilanes. The fraction of trisilane was found to be accompanied by some iron compound, and darkened after some elapse of time. This impurity finally deposited as a brown coagulate of ferric oxychloride, and the upper trisilane distillate became a colorless, transparent liquid. The residual gel substance which was obtained after distilling trisilane was brownish black, generated some hydrogen by hydrolysis in water, violently evolved hydrogen by cleavage in alkaline solution, burned in air with a red flame, and left white ashes. This must have been impure higher chloropolysilanes and did not contain any copper component although it had silicon, iron, aluminum and chlorine in it.

Naturally, it was expected that these chloropolysilanes would possibly have silicon hydride bonds in their molecules arising from the hydrogen atom of hydrogen chloride, contrary to the hitherto-used preparative methods in which chlorine and silicon alloys were used as starting materials. Among the series of $H_nSi_m \cdot Cl_{2m+2-n}$[7], both pentachlorodisilane HSi_2Cl_5 and heptachlorotrisilane HSi_3Cl_7, which were expected to be formed but unknown in literature, were found only in traces in the produced chloropolysilanes and moreover, judging from its boiling point and its hydrogen analysis (Table VI), it was found that the chlorodisilane fraction was rather pure hexachlorodisilane and the chlorotrisilane fraction was also octachlorotrisilane.

As to the hydrogen analysis of the chloropolysilane, there has been no adequate method hitherto[8], but the authors have found that silicon hydride bonds are reactive with metallic copper, especially in the presence of small amounts of anhydrous aluminum chloride when their reactions are carried out in liquid phase.

Therefore, this analysis was performed by the apparatus shown in Fig. 2 in which the polysilanes containing hydrogen were treated with copper powder and $AlCl_3$ in

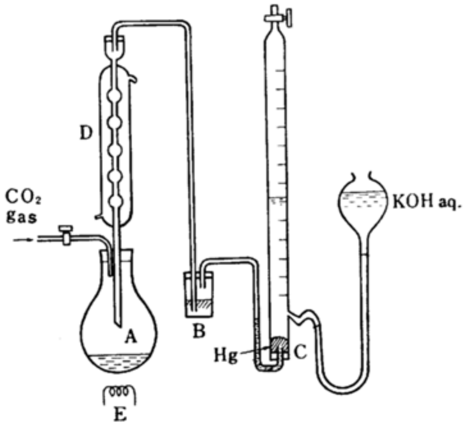

Fig. 2. Apparatus for analysis of Si-H containing chloropolysilane.

A: Reaction bottle
B: Washing bottle with C_2H_5OH
C: Gas burette with KOH aq. and Hg
D: Reflux condenser
E: Heater

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[7] R. Schwarz, *Z. anorg. u. allgem. Chem.*, **235**, 247 (1938).

[8] V. G. Fritz, ibid., **280**, 135 (1955).

a bottle A. The method devised was almost analogous to that of Dumas' nitrogen analysis, i.e., the evolved hydrogen was carried by carbon dioxide and the hydrogen produced gathered in a gas burette on potassium hydroxide solution and measured. The results of this hydrogen analysis are shown in Table VI. This method was confirmed previously with the known silicon-hydride containing substance, for instance, with Ph_3SiH, and showed a fairly good agreement. The occurrence of silicon-copper bond which was made by the reaction of silicon hydride and copper may be recognized by the change of metallic copper to gray metallic silicon color. It was also known that the liberated gas was hydrogen. The contents of silicon hydride in these chloropolysilanes were proved to be very small according to this analysis.

One must be careful in treating chloropolysilanes, because they are apt to form certain dangerous materials. When hydrolyzed in air, they form compounds which exqlode with slight friction or shock. These chloropolysilanes have a flammable nature although they consist only of silicon and chlorine.

Composition of the Residual Reaction Mass.—The final residual masses which were left after reaction had an appearance of very voluminous light powder possessing no metallic lustre like starting silicon, and were caqable of burning in air when ignited, revealing a very brilliant blue flame by burner test.

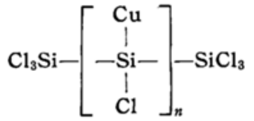
The results of chemical analysis are shown in Table VII. The amounts of hydrogen evolved on treating the residues with alkali solution are given in Table VIII.

TABLE VIII. HYDROGEN GENERATION ON TREATING THE RESIDUAL MASSES WITH 10% SODIUM HYDROXIDE SOLUTION

Sample	(g.)	H_2 evolved (m mol./g.)	SiO_2 (g.)	Si%	H/Si atom ratio
H-2	0.1240	2.00	0.0114	4.30	2.61
H-2	0.1280	1.85	0.0160	5.65	1.78
H-3	0.1330	5.75	0.0412	14.50	2.23
H-3	0.0950	5.34	0.0351	17.20	1.74
H-4	0.1570	3.20	0.0461	13.70	1.31

These facts led to the conclusion that the remainder may be the higher molecular weight chloropolysilanes and that some chloropolysilanes, especially those which have much silicon-copper bond in them, could not be cleaved by hydrogen chloride even if the copper catalyst were present, and so the reaction ceased.

If it was supposed that all iron was converted into ferrous chloride and copper remained as metal[9], the residual number of chlorine atoms of the final contact masses in H-1 and H-2 would be almost equal to the number of the silicon atoms, and the hydrogen atoms generated by alkali solution would be also twice as much as the silicon atoms (Table VIII). As the final reaction temperature, rather high temperatures, say 475°C for H-1, 460°C for H-2, were applied, and so it may be reasonably considered that all the iron changed to ferrous chloride, and in the final stage of this reaction almost every silicon atom has one chlorine atom linked to it, and the silicon atoms are linked to each other with silicon-silicon bonds. Thus, the proposed structure of these chloropolysilanes is as follows:



$$Cl_3Si-\left[-\overset{\overset{\large Cu}{|}}{\underset{\underset{\large Cl}{|}}{Si}}-\right]_n-SiCl_3$$

However, the contact mass in the reaction course was thought to contain much more silicon hydride bond than the final structure proposed above, because samples H-3 and H-5 in the reaction were of a more flammable nature than that of H-1, H-2 and H-4 of the final stages. The amount of silicon hydride bond in the former contact masses was measured by the generation of hydrogen with copper and aluminum chloride and found to be high (Table VI).

I. T. and R. T. Measurements.—Many I. T. and R. T. measurements were performed at the beginning of each run and with the special contact mass species. The results of observations are listed in Table IX, and also some examples of the graph with I. T. and R. T. measurements are shown in Fig. 3. The sudden rise in the temperature curve in comparison with the blank curve[10] showed the occurrence

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[9] The forms of iron and copper componet were found by extracting H-1, H-2 residual contact masses with dimethylformamide. Their salts are both soluble in this solvent, but the extracted ones were almost ferrous chloride and not cuprous chloride.

[10] The blank curves were figured separately by measuring temperature versus time at several voltages in an electric furnace. Nitrogen gas was passed at the rate of 8 l./hr. (the same as that of hydrogen chloride) into the reaction tube containing the same amount of contact mass as in the actual measurements. This was repeated several times and each time the same curve was obtained. Thus, this curve could be considered as a blank.

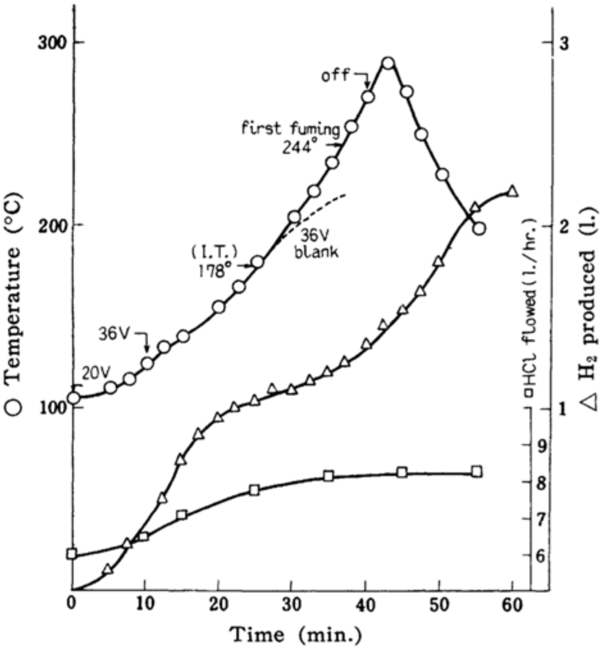


Fig. 3a. An example of the graph with I.T. measurement (H-3-1).

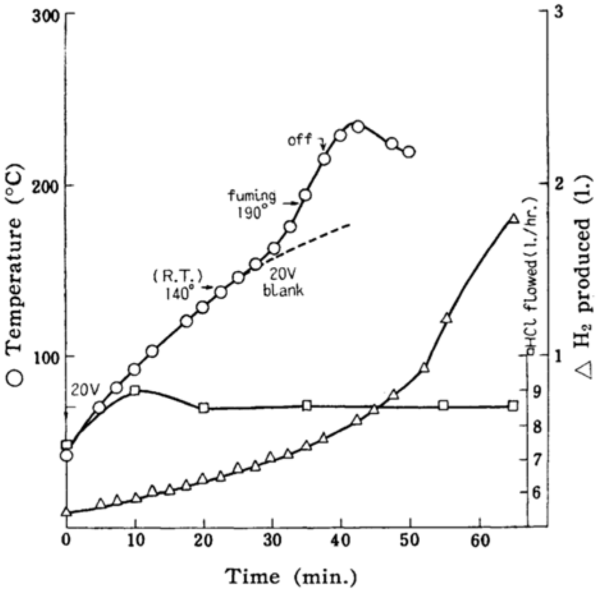


Fig. 3b. An example of the graph with R.T. measurement (H-3-2).

TABLE IX. I.T. AND R.T. OF THE REACTION OF SOME SILICON CONTACT MASSES WITH HCl UNDER ATMOSPHERIC PRESSURE

Silicon materials	Catalyst (%)	I.T. (°C)	R.T. (°C)
Si (A)		205	103, 172, 223, 298
Si (A)	Cu(3)	180	105, 146
Si (A)	Cu(10)	230	186
Si (A)	Cu(20)	236	119, 197
Si (B)		190	105
Si (B)	Cu(3)	178	106, 140, 218
Si (C)	Cu(3)	265	52, 172
Si—Al(8:2)		205	56
Si—Al(8:2)	Cu(5)	180	50
Si—Ca(3:7)		145, 180	100, 176
Si—Ca(3:7)	Cu(3)	165, (65)*	122, (85)*

* It appears as shoulder.

of the reaction about the contact mass. At this critical point, usually some gas evolution, or rate change of gas generation, or fuming caused by the product in the adaptor part were also present, and these could be also considered the evidence of the reaction occurrence, but these phenomena often had time lags and the precise points could not be determined by them. Therefore, only the temperature curve was chosen for determining the precise value. It was found from many observations that the I. T. value is not always the same in a contact mass, sometimes as much as 10°C difference, although it is always higher than R. T. The I. T. values obtained in the present experiment seemed to originate mainly from the composition of the materials or alloys of the contact masses tested, even though these values fluctuated somewhat with the changes of the particle surfaces. As to the R. T. value, there are more than two values for some samples of silicon metal or alloy. Moreover, as was seen in many observations, the 50, 105, 145 and 170°C points are prominent and sometimes common to the same kind of contact mass species. They seemed to correspond to the R. T. as shown in the following reaction Eqs. A, B, C and D.

$$\text{Al (in solid phase Si—Al)} + HCl \xrightarrow{50°C} AlCl_3 + H_2 \quad (A)$$

$$\text{Fe (in solid phase Si—Fe)} + HCl \xrightarrow{105°C} FeCl_2 + H_2 \quad (B)$$

$$\equiv Si-Al= \text{(in solid phase Si—Al)} + HCl \xrightarrow{145°C} \equiv Si-H + =AlCl \quad (C)$$

$$\equiv Si-\underset{|}{\overset{|}{Si}}-H + HCl \xrightarrow[AlCl_3 \text{ present as catalyst}]{170°C} \equiv Si-H + Cl\underset{|}{\overset{|}{Si}}H \quad (D)$$

The following is a brief explanation to substantiate this relation. As is seen in

Table IX, Si (C)[11] and Si—Al alloy have almost the same R. T. at 50°C, as in the case of the metallic aluminum and hydrogen chloride reaction[12]. Therefore, Eq. A, which mainly concerns the presence of metallic aluminum in the contact mass, was given for the 50°C value. By the same speculation, 105°C value corresponding to the iron component which exists as the other main impurity in most silicon metal or silicon alloys, is indicated by Eq. B[13], the 145°C value has been assigned to Eq. C[5] by the authors. In almost all the reactions the forming of chlorosilane actually began at 170°C. Thus it was plausible that Eq. D was adequate for this R. T. value.

It was very interesting and important that when a small amount of anhydrous aluminum chloride was added to the contact masses as mixture or as vapor, the I. T.'s of these reactions were depressed close to the R.T.'s of their own. The fact that the commercial silicon Si(A)—fairly rich in aluminum ingredient—had a good yield of liquid product (Table I), might be proved by the above effect of aluminum chloride. Because in this reaction system the aluminum chloride could be easily derived from the reactions shown as Eqs. A and C. However, the remarkable effect of copper to each contact mass could not be understood from the results of I. T. and R. T. Unexpectedly the copper was reasonably considered only to promote the rate of this reaction.

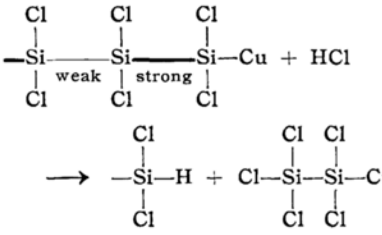
Discussion

The results of this experiment mentioned above and an assumption which will be proposed afterward afford the following reaction mechanism of the formation of chloropolysilane, i.e., the activation and main course stages for the reaction between commercial silicon and hydrogen chloride which gave monosilanes were explained as the formulae A, B, C and D mentioned above, but by those mechanisms alone no important part of the mechanism of forming chloropolysilane using copper catalyst could be explained. It might be reasonable to assume that copper combines with Si—H bond on the silicon mass which is formed as an intermediate of the C or D reactions (see Table VI):

$$\equiv\mathrm{SiH}+\mathrm{Cu} \xrightarrow[\mathrm{AlCl_3\ catalyst}]{150^{\circ}\mathrm{C}} \equiv\mathrm{Si{-}Cu} + 1/2\ \mathrm{H_2} \qquad (\mathrm{E})$$

Hence, the co-catalytic action of aluminum chloride, produced by A and C reactions in the above reaction, is seen in the comparison of the experiments No. 1 and 2 in Table VI. Therefore, apart from the before mentioned I. T. depressing effect of aluminum chloride, it is preferable to use commercial silicon metal which has a small amount of aluminum as impurity or the vapor of aluminum chloride purposely conducted to the reaction zone of the pure silicon metal.

The authors have proposed the following assumption for the catalytic action of copper, i.e., the silicon-silicon bond which is adjacent to the silicon-copper bond formed by E reaction is difficult to be cleaved by hydrogen chloride as was shown in the above-mentioned results and the supposed cleavage is as follows:



$$-\mathrm{SiCl_2}\underset{\text{weak}}{-}\mathrm{SiCl_2}\underset{\text{strong}}{-}\mathrm{SiCl_2}{-}\mathrm{Cu} + \mathrm{HCl} \longrightarrow -\mathrm{SiCl_2}{-}\mathrm{H} + \mathrm{Cl}{-}\mathrm{SiCl_2}{-}\mathrm{SiCl_2}{-}\mathrm{Cu}$$

This assumption may also facilitate the understanding of the mechanism of the chlorodisilane formation, and the catalytic action of copper for the present reaction. This unequalness of silicon-silicon bond strength may well be explained by the unequal electron density on the silicon atoms like the alternative strength-change theory of carbon bonds proposed by Ingold. If this assumption is correct at all, the reasons for the large yield of chlorodisilane in the main course of reaction by addition of a few per cent of copper and its sharply diminished formation at the final stage of the reaction may also be plausible. Hence, the copper content at the surface of the contact mass at the final stage may become so high that the copper atoms can be distributed enough through the adjacent silicon atoms.

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[11] As was mentioned Si (C) was originated from the Si-Al alloy. It was somewhat curious that Si (A), Si (B) which had more aluminum content than Si (C) did not show this 50°C R. T. value. However, this may be explained by the fact that iron masked the free aluminum character, perhaps by forming some kind of alloy.

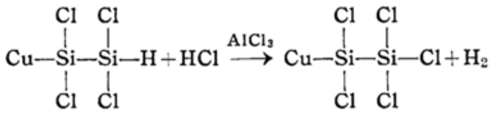
[12] J. Iyoda and I. Shiihara, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), in press.

[13] Generally speaking, the iron component in a silicon alloy must form some intermetallic compounds with silicon, but here in these contact masses, part of it combined with aluminum, forming some kind of easily reactive alloy.

The reaction between a typical silicon-copper bond and hydrogen chloride is shown as follows:

$$\equiv\mathrm{Si{-}Cu+HCl \longrightarrow \equiv Si{-}H+CuCl} \tag{F}$$

This reaction can also explain the formation of much H_3SiCl when a large amount of copper is added as catalyst. However, the reason for the meager existence of Si–H bond in chloropolysilane product seems to be plausible when the hydrogen chloride exchange reaction with some species of compounds on contact mass is assumed. A typical reaction can be considered:



$$\mathrm{Cu{-}\underset{Cl}{\overset{Cl}{Si}}{-}\underset{Cl}{\overset{Cl}{Si}}{-}H+HCl \xrightarrow{AlCl_3} Cu{-}\underset{Cl}{\overset{Cl}{Si}}{-}\underset{Cl}{\overset{Cl}{Si}}{-}Cl+H_2} \tag{G}$$

The reverse reaction of F about the Si–H in the above compound is excluded from the results of experiments No. 3 and 4 in Table VI, and the possibility of E reaction of the Si–H is also taken to be small, since the chance of Si–H in this compound fixed on contact mass coming in contact with copper metal is supposed to be slight.

Also, the reaction of silicon and cuprous chloride is excluded under the reaction temperature of this experiment as 215°C, which is far from the R.T. value[14] (295°C) of this reaction.

$$\equiv\mathrm{Si{-}Si}\equiv+\mathrm{CuCl} \xrightarrow{\mathrm{R.T.\ 295^{\circ}C}} \equiv\mathrm{Si{-}Cu}+\equiv\mathrm{Si{-}Cl} \tag{H}$$

Therefore, cuprous chloride produced by F reaction may be reduced[15] mainly by hydrogen formed by E and G reactions.

$$\mathrm{2CuCl + H_2 \longrightarrow 2Cu + 2HCl} \tag{I}$$

And so regenerated metallic copper can be recycled to E reaction.

Summary

The copper catalyzed reaction of silicon metal powder with hydrogen chloride by flow method was studied in order to find a convenient preparative method of chloropolysilane, and also to elucidate the mechanism of this reaction.

This reaction was found to start at about 170~230°C, and once the reaction occurred, the contact mass is activated and the reaction takes place even at 170°C. When the most adequate conditions were adopted, chloropolysilanes were obtained in the condensate as efficiently as 30 wt.% yield based on hydrogen chloride.

As to the mechanism of the reaction, it seems to be plausible that the first step of the reaction is an attack of hydrogen chloride on aluminum which is usually present in the commercial silicon metal. The second step is the reaction between silicon hydride, which is derived from the first step reaction upon the silicon contact mass and metallic copper forming the silicon-copper bonding. The third step is the cleavage reaction of copper-activated silicon by hydrogen chloride to produce chlorosilanes under the presence of aluminum chloride. The aluminum chloride is also derived from the first step reaction, and copper is regenerated in metal form which can circulate among the latter two reaction steps as long as the effective silicon component is present.

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[14] Details will be published before long. About the formation of Si·Cu bond presented before the 7th Annual Meeting of Chem. Soc. of Japan, April 3, 1954, Paper No. 7075 by Shiihara.

[15] M. Rubalkin, *J. Russ. Phys. Chem.*, **21**, 155 (1889).