Effects of hydrogen chloride addition to the direct reaction of methylene chloride with elemental silicon

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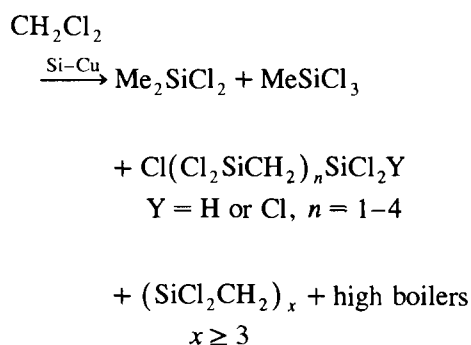
Abstract

Direct synthesis of bis(chlorosilyl)methanes has been reinvestigated by reacting elemental silicon simultaneously with methylene chloride and hydrogen chloride in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator at a carefully controlled temperature between 260 and 340°C. Bis(dichlorosilyl)methane and (dichlorosilyl)(trichlorosilyl)methane were obtained as the major products and bis(trichlorosilyl)methane as a minor product along with trichlorosilane and tetrachlorosilane derived from the reaction between elemental silicon and hydrogen chloride. The decomposition of methylene chloride was suppressed and the production of polymeric carbosilanes reduced by adding hydrogen chloride to the methylene chloride reactant. The optimum mixing ratio of methylene chloride and hydrogen chloride for the direct synthesis of bis(silyl)methanes was 1 : 4. The deactivation problem of elemental silicon owing to decompositions of methylene chloride and polycarbosilanes was eliminated. Cadmium was a good promoter for the reaction, while zinc was found to be an inhibitor for this particular reaction.

Keywords: Silicon; Silane; Direct synthesis

1. Introduction

Although the direct reaction of elemental silicon with alkyl chlorides has been extensively studied and a vast number of reports are available in the literature [1–3], the reports on the direct reaction of elemental silicon with polychlorinated alkanes such as methylene chloride and chloroform are scarce. In 1945, Petnode and Schiessler first reported the direct reaction of methylene chloride with elemental silicon in the presence of copper catalyst [4]. The products obtained from the reaction with methylene chloride were linear compounds of formula $Cl(Cl_2SiCH_2)_nSiCl_2Y$ (Y = H or Cl, n = 1–4) as well as cyclic carbosilanes of formula $(SiCl_2CH_2)_x$ (x ≥ 3). Any further identification of the compounds was not given. Later, Fritz and Matern reported [5] the same reaction using a fluidized-bed reactor at about 320°C and isolated from a similar reaction mixture over 40 compounds containing from one silicon atom up to 12 silicon atoms. The yield of high molecular weight products was around 20%, partly due to the decomposition of the starting methylene chloride and partly due to the

difficulty of efficient removal of the products out of the reactor. This is why this direct reaction has never been used on a large scale in industry.

$$CH_2Cl_2$$
$$\xrightarrow{\text{Si-Cu}} Me_2SiCl_2 + MeSiCl_3$$

$$+ Cl(Cl_2SiCH_2)_nSiCl_2Y$$
$$Y = H \text{ or } Cl, \ n = 1\text{–}4$$

$$+ (SiCl_2CH_2)_x + \text{high boilers}$$
$$x \geq 3$$

We have previously reported the direct synthesis of Si–H-containing bis(silyl)methanes [6] and allylchlorosilanes [7] by reacting elemental silicon with a mixture of hydrogen chloride and (α-chloromethyl)-silanes or allyl chloride respectively. From the allyl chloride reaction, allyldichlorosilane was obtained as the major product and allyltricholorosilane was a minor product. The decomposition of allyl chloride was suppressed and the production of diallyldichlorosilane was reduced by adding hydrogen chloride to the allyl chlo-

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ride reactant. The polymerization problem in the distillation process of the products due to diallyldichlorosilane was eliminated.

This success of the direct synthesis of allyldichlorosilane prompted us to apply this hydrogen-chloride-incorporating method to the direct reaction of methylene chloride with elemental silicon. We studied the effect of hydrogen chloride addition to the direct reaction of elemental silicon with methylene chloride in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator at a carefully controlled temperature between 260 and 340°C. The decomposition of methylene chloride to hydrogen chloride was expected to be suppressed and the production of oligomeric and polymeric carbosilanes to be reduced by adding hydrogen chloride to methylene chloride. We wish to report herein the results obtained from the direct reactions.
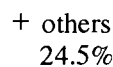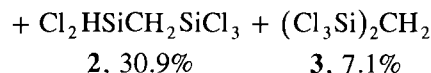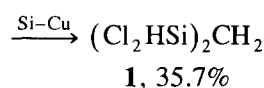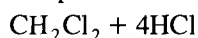
2. Results and discussion

2.1. Effect of hydrogen chloride addition to methylene chloride

A 1 : 4 mixture of methylene chloride and hydrogen chloride was reacted with a contact mixture of elemental silicon and copper catalyst using a stirred reactor equipped with a spiral band agitator at various reaction temperatures for 2 h. The total amount of products and the distributions collected in the receiver are summarized in Table 1. Trichlorosilane and tetrachlorosilane distilled from the product mixture and collected in a dry-ice–acetone trap were excluded for simplicity. Trichlorosilane and tetrachlorosilane are known to be the products of the reaction of silicon and hydrogen chloride [6].

The compounds of 1,1,3,3-tetrachloro-1,3-disilapropane, 1, and 1,1,1,3,3-pentachloro-1,3-disilapropane, 2, were obtained as the major products and 1,1,1,3,3,3-hexachloro-1,3-disilapropane, 3, as a minor product. The formation of 1 can be explained by the reaction of a silicon atom with 1 mol of methylene chloride and 2

mol of hydrogen chloride. Similarly 2 can be formed by the reaction of a silicon atom with 1 mol of methylene chloride, 1 mol of hydrogen chloride, and 1 mol of chlorine, and 3 by the reaction of a silicon atom with 1 mol of methylene chloride and 2 mol of chlorine. The formation of 1, 2, and 3 was also reported in the reaction of elemental silicon with methylene chloride without hydrogen chloride addition, indicating the decomposition of methylene chloride to hydrogen chloride and chlorine at the reaction temperature [5]. In contrast to the direct reaction of methylene chloride without hydrogen chloride addition, the production of polymeric carbosilanes was negligible [5]. The yield of methyldichlorosilane did not increase very much with hydrogen chloride addition in the direct synthesis of methylchlorosilanes owing to the reactivity difference of the two starting chlorides [2]. The major products of Si–H-containing bis(silyl)methanes suggest that the reactivities of methylene chloride and hydrogen chloride are comparable.

$$CH_2Cl_2 + 4HCl$$

$$\xrightarrow{\text{Si–Cu}} (Cl_2HSi)_2CH_2$$
$$\text{1, 35.7\%}$$

$$+ Cl_2HSiCH_2SiCl_3 + (Cl_3Si)_2CH_2$$
$$\text{2, 30.9\%} \qquad \text{3, 7.1\%}$$

$$+ \text{ others}$$
$$\text{24.5\%}$$

As shown in Table 1, the amount of the products drastically increased as the reaction temperature increased from 240°C up to 280°C while the recovery of methylene chloride decreased drastically. Over 20% of the starting methylene chloride was recovered at temperatures below 260°C, indicating that the reaction temperature below 260°C was too low for the reaction. The recovery of methylene chloride dropped to about 5% at 280°C and the selectivity for 1 remained at a high level. However, beyond 280°C the amounts of the starting material recovered and the product yields did not differ

Table 1
Reaction temperature effect on the direct reaction of dichloromethane [a]

Entry No.	Temperature (°C)	Products (g) [b]	Product distributions (%)				Recovered CH_2Cl_2 (%)
			1	2	3	Others	
1	240	18.7	35.2	23.0	5.7	13.6	22.5
2	260	23.8	33.7	25.9	4.3	9.1	27.0
3	280	33.6	34.6	37.1	6.8	16.1	5.4
4	300	31.8	32.4	40.8	4.5	17.3	5.0
5	320	38.5	30.6	45.5	4.7	17.7	1.5
6	340	38.8	25.2	49.8	8.8	15.0	1.2

[a] Methylene chloride, 27.2 g was used for 2 h. Catalyst–co-catalyst, Cu(10%)–Cd(0.5%); mole ratio of CH_2Cl_2–HCl = 1/4. [b] By-products, $HSiCl_3$ and $SiCl_4$, are excluded for simplicity.

Table 2
Effect of the catalyst and co-catalyst on the direct reaction [a]

Entry no.	Catalyst–co-catalyst	Products (g) [b]	Product distributions (%)				Recovered CH_2Cl_2 (%)
			1	2	3	Others	
10	Cu	32.9	30.8	46.5	3.9	16.7	2.1
3	Cu–Cd	33.6	34.6	37.1	6.8	16.1	5.4
11	Cu–Zn	23.5	17.0	46.7	9.7	13.4	13.2

[a] Methylene chloride, 27.2 g was used for 2 h; reaction temperature, 280°C; mole ratio of CH_2Cl_2–HCl = 1/4. [b] By-products, $HSiCl_3$ and $SiCl_4$, are excluded for simplicity.

very much as the temperature increased. However, the selectivity for 1 decreased while the percentage of 2 increased as the temperature increased up to 340°C. This result suggests that the chlorine arising from the decomposition of methylene chloride was more available for forming 2 at the higher reaction temperature. The optimum temperature for the direct synthesis of 1 was 280°C, which was considerably lower than that for other systems such as methyl chloride [2,8] and (α-chloromethyl)silanes [6,9], indicating higher reactivity of methylene chloride.

Fritz and Matern reported the formation of dimethyldichlorosilane and methyltrichlorosilane from the reaction of methylene chloride and silicon using a fluidized-bed reactor at about 320°C [5]. Considering that methylchlorosilanes are the products of the reaction of methyl chloride and silicon, the formation of the methylchlorosilanes can be explained by the decomposition of methylene chloride to methyl chloride and followed by the reaction with silicon. However, methylchlorosilanes were not detected in the products mixture obtained from the reaction of silicon with a mixture of methylene chloride and hydrogen chloride, indicating that methyl chloride was not produced. The results indicate that the decomposition of methylene chloride was suppressed and the production of polymeric carbosilanes reduced by adding hydrogen chloride to the methylene chloride reactant. The deactivation problem of elemental silicon due to decomposition of methylene chloride and polycarbosilanes was eliminated.

2.2. Promoters

Useful copper catalysts for the reaction of alkyl chloride with silicon include copper metal, copper salts,

and partially oxidized copper [2]. In addition to copper catalyst, a number of metals such as zinc, aluminum, magnesium, etc., are known as promoters. The promoters are normally incorporated in a smaller quantity than 1%. Zinc is known as one of the most effective promoters for the direct synthesis of methylchlorosilanes [10]. Cadmium is known as one of the most effective promoters for the direct synthesis of bis(silyl)methanes [5] and trisilaalkanes [9]. The product distributions from the direct reaction of methylene chloride in the presence of different promoters are shown in Table 2. As shown in the table, the yield of 1 varied, 30.8%, 33.6%, and 17.0%, with no promoter, cadmium, and zinc respectively. The higher amount of methylene chloride was recovered from the reaction with zinc promoter. This indicates that zinc is not a promoter but an inhibitor, and cadmium is a good promoter for this reaction. These are consistent with the results observed for the direct reactions of silicon with (α-chloromethyl)silanes and allyl chloride [5,9].

2.3. Mixing ratio of the reactants

The product distributions obtained from the direct reaction using various mixing ratios of methylene chloride and hydrogen chloride in the presence of 0.5% cadmium as a co-catalyst at 280°C are given in Table 3. In order to produce the compound 1, 2 mol of hydrogen chloride should be available for each mole of methylene chloride. Considering that trichlorosilane is produced from the reaction of hydrogen chloride with silicon, the required mixing ratio of methylene chloride to hydrogen chloride for this reaction was 1:2 at minimum to prevent the polycarbosilanes production. As shown in Table 3, the total amount of products increases from

Table 3
Effect of mixing ratio of the reactions [a]

Entry no.	Mole ratio	Product (g) [b]	Product distributions (%)				Recovered CH_2Cl_2 (%)
			1	2	3	Others	
7	1:2	24.1	32.0	32.8	8.0	24.8	4.2
8	1:4	28.3	35.7	30.9	7.1	24.5	1.8
3	1:6	33.6	34.6	37.1	6.8	16.1	5.4
9	1:8	29.3	35.6	38.0	6.7	13.2	6.5

[a] Methylene chloride, 27.2 g was used for 2 h; catalyst–co-catalyst, Cu(10%)–Cd(0.5%); reaction temperature, 280°C. [b] By-products, $HSiCl_3$ and $SiCl_4$, are excluded for simplicity.

1:2 to 1:6 but decreases again when a 1:8 mixing ratio was used. The highest selectivity for **1** and the lowest recovery of methylene chloride were obtained with 1:4 mixing ratio, suggesting that the optimum mixing ratio of methylene chloride to hydrogen chloride for the direct synthesis of bis(silyl)methanes was 1:4.

3. Experimental section

3.1. Reagents and physical measurements

Methylene chloride was purchased from J.T. Baker Inc. and dried over calcium chloride with reflux for 2 h under dry nitrogen and distilled before use. Anhydrous hydrogen chloride was purchased from Matheson Co. and used without further purification. Copper powder was purchased from Alcan Metal Powders (NJ, USA) and cadmium, zinc from Aldrich Chemical Co. Elemental silicon (Si, 98%; Fe, 0.50%; Ca, 0.25%; Al, 0.24%; C, 0.08%; S, 0.05%; P, 0.05%) was from Samchuck Mining Co. (Kangwondo, Korea). Reaction products were analyzed by analytical GLC over a 1.5 m by 1/8″ O.D. stainless steel column packed with packing material (10% OV-101 on Chromosorb W) using a Varian 3300 gas chromatograph, equipped with a thermal conductivity detector. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Gemini 300 spectrometer using a CDCl$_3$ (taken as 7.26 ppm) as the internal lock. Mass spectra were obtained from Hewlett Packard 5890 Series II gas chromatograph equipped with 5972 mass selective detector.

3.2. Reactor

The reactor for the direct synthesis of bis(chlorosilyl)methanes was the same as described elsewhere [6].

3.3. General procedure for the direct reaction of dichloromethane

A mixture of metallic silicon 360 g (100-325 mesh) and 40 g of copper catalyst was placed in the reactor made of Pyrex glass tube, 50 mm inner diameter and 400 mm length, with the electrical heating wire coiled outside and equipped with a spiral band agitator. The mixture was dried at the 300°C for 5 h with stirring with dry nitrogen flush. Then the temperature was raised to 350°C and methyl chloride was introduced at the rate of 240 ml min^{-1} to activate the contact mixture for 4 h. After removing products formed such as dichlorodimethylsilane and methyltrichlorosilane during the activation process, 2.0 g of cadmium as a promoter was added to the reactor at room temperature. After the temperature was raised to 280°C, methylene chloride was introduced using a syringe pump into the evapora-

tor attached at the bottom of the reactor at the rate of 13.6 g h^{-1}. At the same time, gaseous hydrogen chloride was introduced at the rate of 240 ml min^{-1} (mole ratio of dichloromethane:hydrogen chloride is 1:4). About 2 min after starting the reaction, it was observed that the reaction temperature was raised slightly due to the exothermic nature of the reaction and then the liquid product was collected in the receiver.

After 2 h reaction, 45.6 g of the products were collected in the receiver cooled at -20°C and 46.4 g of low boilers were collected in dry-ice–acetone trap. Gas chromatographic analysis showed the low boilers trapped contained a 20:1 mixture of trichlorosilane and tetrachlorosilane. The product of 45.6 g was distilled at atmospheric pressure to give 15.5 g of trichlorosilane, 1.3 g of tetrachlorosilane, and 0.5 g of methylene chloride. The distillation was continued under the vacuum to give 10.1 g of **1**, 8.7 g of **2**, and 2.0 g of **3**. The residue was bulb to bulk distilled to give 6.9 g of a mixture of high boiling products, but nondistillable polymeric materials were negligible. GC–Mass analysis of the high boiling products showed that it contained linear and cyclic carbosilanes with silicon–hydrogen bonds, as reported previously [5].

Compound **1** [5]: b.p. 146-147°C; ^{1}H NMR (CDCl$_3$) δ 1.40 (t, $J = 2.2$ Hz, 2H, CH_2); 5.71 (t, $J = 2.2$ Hz, 2H, Si–H); ^{13}C NMR (CDCl$_3$) δ 14.42 (CH_2).

Compound **2** [5]: b.p. 165-166°C; ^{1}H NMR (CDCl$_3$) δ 1.64 (d, $J = 2.2$ Hz, 2H, CH_2); 5.72 (t, $J = 2.2$ Hz, 1H, Si–H); ^{13}C NMR (CDCl$_3$) δ 18.6 (CH_2).

Compound **3** [5]: b.p. 179-180°C; ^{1}H NMR (CDCl$_3$) δ 1.88 (s, CH_2); ^{13}C NMR (CDCl$_3$) δ 22.5 (CH_2).

Using the same procedure as above, the reactions were carried out by using different promoters such as cadmium or zinc and different mixtures of methylene chloride and hydrogen chloride with various mixing ratios at various reaction temperatures to optimize the reaction conditions.

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