

SILICON COMPOUNDS, SILICON HALIDES

The study of silicon halides began in the early 1800s (1). Since then, essentially all of the monomeric silicon halides have been extensively studied and reported in the literature. These include mixed silicon halides and halohydrides. A large number of halogenated polysilanes have also been reported (1). Despite the extensive research in silicon halides, only two of these chemicals are produced on a large industrial scale (excluding organohalosilanes). These are tetrachlorosilane [10026-04-7], SiCl_4 , and trichlorosilane [1025-78-2], HSiCl_3 .

1. Physical Properties

The physical properties of silicon tetrahalides are listed in Table 1; those of the halohydrides are listed in Table 2. A more complex review of the physical properties of these chemicals is available (2). Detailed lists of properties of the colorless fuming liquids, silicon tetrachloride and trichlorosilane, are given in Table 3. A review of the physical and thermodynamic properties of silicon tetrachloride is given in Reference 3.

Several of the mixed silicon halides are formed simply by heating a mixture of the tetrahalosilanes at moderate temperature (4), eg,

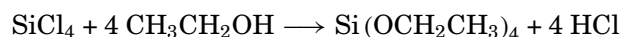


Mixed halosilanes can also be prepared by heating a mixture of the appropriate halides of silicon and aluminum (5, 6). Some physical properties of these mixed tetrahalosilanes are listed in Table 4. In addition, the properties of several halogenated polysilanes are listed in Table 5. A summary of the preparation and properties of the chlorinated polysilanes has been published (7).

2. Chemical Properties

Silicon halides are typically tetrahedral compounds. The silicone–halogen bond is very polar; thus the silicon is susceptible to nucleophilic attack, which in part accounts for the broad range of reactivity with various chemicals. Furthermore, reactivity generally increases with the atomic weight of the halogen atom.

Halosilanes are very reactive toward protic chemicals. They generally react violently with water, forming silicon dioxide and the respective hydrohalogens. Other examples include reaction with alcohols and amines as follows:



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Table 1. Properties of Silicon Tetrahalides

Compound	CAS Registry Number	Mp, °C	Bp, °C	Density ^a , g/cm ³	Bond energy, kJ/mol ^b
SiF ₄	[7783-61-1]	−95.0	−90.3	1.66 _{−95}	146
SiCl ₄	[10026-04-7]	−68.8	56.8	1.48 ₂₀	381
SiBr ₄	[7789-66-4]	5	155.0	2.81 ₂₉	310
SiI ₄	[13465-84-4]	124	290.0		234

^aSubscripted values are temperature in °C.

^bTo convert J to cal, divide by 4.184.

Table 2. Properties of Silicon Halohydrides

Compound	CAS Registry Number	Mp, °C	Bp, °C	Density ^a , g/cm ³
H ₃ SiF	[13537-33-2]		−99.0	
H ₂ SiF ₂	[13824-36-7]	−122.0	−77.8	
HSiF ₃	[13465-71-9]	−131.2	−97.5	
H ₃ SiCl	[13465-78-6]	−118.0	−30.4	1.145 _{−113}
H ₂ SiCl ₂	[4109-96-0]	−122.0	8.3	1.42 _{−122}
HSiCl ₃	[1025-78-2]	−128.2	31.8	1.3313 ₂₅
H ₃ SiBr	[13465-71-1]	−94.0	1.9	1.531 ₂₀
H ₂ SiBr ₂	[13768-94-0]	−70.1	66.0	2.17 ₀
HSiBr ₃	[7789-57-0]	−73.0	111.8	2.7 ₁₇
H ₃ SiI	[13598-42-0]	−57.0	45.4	2.035 _{14.8}
H ₂ SiI ₂	[13760-02-6]	−1.0	149.5	2.724 _{20.5}
HSiI ₃	[13465-72-0]	8.0	111.0 ^b	3.314 ₂₀

^aSubscripted values are temperature in °C.

^bAt 2.9 kPa (21.8 mm Hg).

Table 3. Physical Properties of Silicon Tetrachloride and Trichlorosilane^a

Property	SiCl ₄	SiHCl ₃
refractive index	1.4146	1.3983
d_4^{25} , g/cm ³	1.4736	1.3313
viscosity, at 25°C, mm ² /s(=cSt)	0.35	0.23
vapor pressure, kPa ^b		
at −50°C		1.7
−30°C	1.8	6.3
−10°C	6.1	18.1
10°C	16.4	44.2
30°C	38.5	94.7
50°C	79.9	182.9
heat of vaporization, J/g ^c	167.4	195.4
standard heat of formation, at 25°C, kJ/kg ^c	−4075.6	−3861.5
flash point, Cleveland open cup, °C		−28
autoignition temperature, °C		182
specific heat, J/g ^c	0.20	0.96
coefficient of expansion, °C ^{−1}	0.0011	0.0019

^aBoth SiCl₄ and SiHCl₃ are soluble in organic solvents and react with H₂O and alcohol.

^bTo convert kPa to mm Hg, multiply by 7.5.

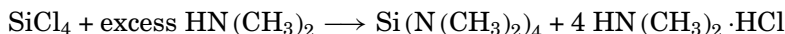
^cTo convert J to cal, divide by 4.184.

Table 4. Properties of Mixed Silicon Halides

Compounds	CAS Registry Number	Mp, °C	Bp, °C
SiBr ₃ Cl	[13465-76-4]	−208	128
SiBr ₂ Cl ₂	[13465-75-3]	−45.5	104.4
SiBrCl ₃	[13465-74-2]	−62.0	80
SiClH ₃	[13932-03-1]	2.0	234–237
SiCl ₂ I ₂	[13977-54-3]	< −60.0	172
SiCl ₃ I	[13465-85-5]	< −60.0	113–114
SiBr ₃ I	[13536-76-0]	14.0	192
SiBr ₂ I ₂	[13550-39-5]	38.0	230–231
SiBrI ₃	[13536-68-0]	53.0	255
SiBr ₃ F	[18356-67-7]	−82.5	83.8
SiCl ₃ F	[14965-52-7]	−120.8	12.2
SiBr ₂ F ₂	[14188-35-3]	−66.9	13.7
SiCl ₂ F ₂	[18356-71-3]	−139.7	−32.2
SiClF ₃	[14049-36-6]	−142.0	−70.0
SiBrF ₃	[14049-39-9]	−70.5	−41.7
SiBrCl ₂ F	[28054-58-2]	−112.3	35.5
SiBr ₂ ClF	[28054-61-7]	−99.2	59.5

Table 5. Properties of Some Halogenated Polysilanes

Compound	CAS Registry Number	Mp, °C	Bp, °C	Density ^a , g/cm ³
Si ₂ F ₆	[13830-68-7]	−18.6	−19.1	0.008 ₀
Si ₂ Cl ₆	[13465-77-5]	−1.0	144.5	1.5624 ₁₅
Si ₃ Cl ₈	[13596-23-1]	−67.0	216.0	1.61 ₁₅
Si ₄ Cl ₁₀	[13763-19-4]	93.6	149 ^b	
Si ₅ Cl ₁₂	[13596-24-2]	−80.0	190 ^b	
Si ₆ Cl ₁₄	[13596-25-3]	319.0 dec		
Si ₂ Br ₆	[13517-13-0]	95.0	265	
Si ₃ Br ₈	[54804-32-9]	133.0		
Si ₄ Br ₁₀	[81626-34-8]	185.0		
Si ₂ I ₆	[13510-43-5]	250.0 dec		

^aSubscripted values are temperature in °C.^bAt 0.2 kPa (1.5 mm Hg).

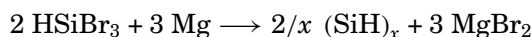
Such substitution reactions typically are reversible and are facilitated by the removal of the hydrohalogen being formed. This is commonly accomplished by adding a tertiary amine or excess amine reactant, which generally precipitates as the amine hydrogen halide. The halosilanes are reduced to silicon with hydrogen at elevated temperatures. Tetrafluorosilane [7783-61-1] reacts with hydrogen only above 2000°C, whereas tetrachlorosilane and tetraiodosilane [13465-84-4] are reduced by hydrogen at 1000–2000°C (1, 8–10). The silicon halohydrides and mixed halides are reduced at lower temperatures.

Silicon halides are stable to oxygen at room temperature but react at high temperature to form mixtures of oxyhalosilanes (11, 12). Silicon halides are also reduced by a number of metals. One of the earliest methods of producing silicon was the reduction of a silicon halide with sodium or potassium (1). A similar reduction process

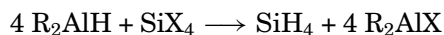
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with zinc was the first commercial process for producing semiconductor-grade silicon from silicon tetrachloride (13, 14).

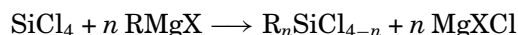
Magnesium does not form stable Grignard reagents with silicon halides, although some silicon halohydrides do react, forming polysilanes (15).



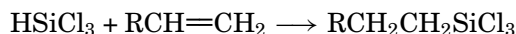
All silicon halides are readily reduced by hydride ions or complex hydrides (qv) to silicon hydrides (16–18).



Historically, among the most important reactions of silicon halides are those occurring with metal alkyls and metal alkyl halides. The Grignard reaction, for example, was the first commercial process for manufacturing organosilicon compounds, which were later converted to silicones (19).



The silicon halohydrides are particularly useful intermediate chemicals because of their ability to add to alkenes, as follows (19, 20):



This reaction, catalyzed by uv radiation, peroxides, and some metal catalysts, eg, platinum, led to the production of a broad range of alkyl and functional alkyl trihalosilanes. These alkylsilanes have important commercial value as monomers and are also used in the production of silicon fluids and resins. Additional information on the chemistry of silicon halides is available (19, 21–24).

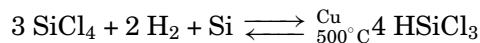
3. Manufacturing Processes

Silicon halides can be easily prepared by the reaction of silicon or silicon alloys and the respective halogens (24). Fluorine and silicon react at room temperature to produce silicon tetrafluoride. Chlorine reacts with silicon exothermally, but the mixture must be heated to several hundred degrees centigrade to initiate the reaction (25). Bromine and iodine react with silicon at red heat.

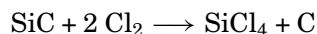
Hydrogen halides also react freely with elemental silicon at moderate temperatures to yield halosilanes (26–31).



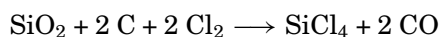
Although a mixture of silicon halides and hydrides is formed, the formation of silicon tetrachloride can be maximized by increasing the temperature (22). The direct reaction of silicon and hydrogen chloride (qv) is also the primary manufacturing procedure for producing trichlorosilane, HSiCl_3 . In this case, the reactor-bed temperature is maintained so as to optimize the yield of trichlorosilane. Trichlorosilane can also be produced according to the following reaction in a fluid-bed reactor (30).



At equilibrium the vapors are predominantly hydrogen and silicon tetrachlorides. However, these can be easily removed from the trichlorosilane and recycled. A once-common commercial manufacturing procedure for silicon tetrachloride was the reaction of chlorine gas with silicon carbide.



This reaction is highly exothermic; thus, it is difficult to control the reaction temperature (31). The oldest method for producing SiCl_4 is the direct reaction of silica and chlorine in the presence of carbon as a reducing agent (24).



In one modification of this procedure, the starting material is pyrolyzed rice hulls in place of more conventional forms of silicon dioxide (31). Another unique process involves chlorination of a combination of SiC and SiO_2 with carbon in a fluid-bed reactor (32). The advantages of this process are that it is less energy-intensive and substantially free of lower silicon chlorides.

3.1. Silicon Tetrachloride

Most commercially available silicon tetrachloride is made as a by-product of the production of alkylchlorosilanes and trichlorosilane and from the production of semiconductor-grade silicon by thermal reduction of trichlorosilane.



The United States is the largest regional producer of silicon tetrachloride. The leading U.S. producers are Dow Corning and General Electric. The next-leading global producing area is Japan, led by Shin-Etsu, Tokuyama Soda, and Mitsubishi Materials. The remaining silicon tetrachloride is produced in Europe by Wachter and Hüls.

3.2. Trichlorosilane

The primary production process for trichlorosilane is the direct reaction of hydrogen chloride gas and silicon metal in a fluid-bed reactor. Although this process produces both trichlorosilane and silicon tetrachloride, production of the latter can be minimized by proper control of the reaction temperature (22). A significant amount of trichlorosilane is also produced by thermal rearrangement of silicon tetrachloride in the presence of hydrogen gas and silicon.

The two largest global producers of trichlorosilane are Wachter in Europe and Dow Corning in the United States. In addition, there are three primary producers in Japan: Tokuyama Soda, Mitsubishi Materials, and Osaka Titanium.

4. Health and Safety Factors

Halosilane vapors, except for fluorosilanes, react with moist air to produce the respective hydrohalogen acid mists. Federal standards have not been set for exposure to halosilanes, but it is generally believed that there is no serious risk if vapor concentrations are maintained below a level that produces an irritating concentration of acid mist. The exposure threshold limit value (TLV) for HCl is 5 ppm, expressed as a ceiling limit, which means

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that no exposure above 5 ppm should be permitted. Because most people experience odor and some irritation at or below 5 ppm, HCl is considered to have good warning properties. Liquid halosilanes react violently with water to produce the respective hydrohalogens. Contact with skin and eyes produces severe burns. Eye contact is particularly serious and may result in loss of sight.

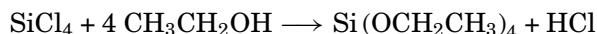
Halosilanes should only be handled in areas that are equipped with adequate ventilation, eye-wash facilities, and safety showers. It is recommended that personnel handling halosilanes wear rubber aprons and gloves and chemical safety goggles. Furthermore, all personnel handling halosilanes should be thoroughly trained in safe handling procedures, the hazardous characteristics of halosilanes, and emergency procedures for all foreseeable emergencies.

5. Uses

5.1. Silicon Tetrachloride

Although the range of industrial applications is broad, the vast majority (ca 95%) of SiCl₄ use is in the manufacture of fumed silica. This production process is carried out by burning silicon tetrachloride in a mixture of hydrogen and oxygen (33). High purity grades of silicon tetrachloride are also used to prepare silica, which is used in the manufacture of optical waveguides, ie, fiber optics (qv). Some silicon tetrachloride is also used to produce polycrystalline silicon for the semiconductor (qv) industry.

Silicon tetrachloride is also used to prepare silicate esters, eg, tetraethylorthosilicate:



Silicate esters are used in the production of coating and refractories and in some semiconductor manufacturing operations. A broad range of purity grades of silicon tetrachloride are available to meet the requirements of these different applications.

5.2. Trichlorosilane

There are essentially only two large industrial applications for trichlorosilane. These are the synthesis of organotrichlorosilanes and the production of semiconductor-grade silicon metal (see Silicon and silicon alloys, pure silicon). In the production of semiconductor-grade silicon metal, the purified trichlorosilane is reduced in the presence of hydrogen at temperatures greater than 1000°C. Although a large number of silicon halides and silicon halohydrides can be reduced to semiconductor-grade silicone, trichlorosilane is most commonly used because of its favorable balance of manufacturing, purification, handling, and chemical reduction properties (1, 12, 30).

5.3. Dichlorosilane

Dichlorosilane [4109-96-0] is produced in relatively modest commercial quantities compared to the above chlorosilanes. This silane is generally recovered as a by-product of the production of other silanes. It is used exclusively in the semiconductor industry to produce a range of inorganic films.

Although consumption of dichlorosilane is modest, it is a very high value material, generally selling in the range of hundreds of dollars per kilogram, depending on purity grade. Dichlorosilane is sold in cylinders by gas distributors such as Solkatronic, Air Products, and Matheson.

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