Silicon-Carbon-Chlorine molecules

Silicon and carbon atoms do not generally bond together at moderate temperatures, but rather only at high temperature to make silicon carbide, in an electric arc furnace. SiC is very non-reactive ceramic material. However, silicon and carbon can be bonded in conjunction with chlorine at more moderate temperatures, where the carbon atom is the part of an organic group (e.g., methyl, ethyl, phenyl).

Silicon-carbon-chlorine bonded molecules do not occur naturally, are completely synthetic and are generically known as organo-chlorosilanes. More specifically when the organic grouping(s) are methyl, they are referred to as methyl chlorosilanes. A variety of aliphatic and aromatic substitutions for methyl groups are common. Organo-chlorosilanes can be thought of as chlorosilanes (see Silicon-Chlorine bonded molecules), but with an organo-functional group replacing either a hydrogen or chlorine atom. For example the methyl chlorosilane family includes methyl, dimethyl, trimethyl, and tetramethyl silane; methyl, dimethyl and trimethyl monochlorosilane; methyl and dimethyl dichlorosilane; and methyl trichlorosilane.

Unusual/Noteworthy Properties

1. Many of the properties of organo-chlorosilanes are similar to their chlorosilane counterpart (see Silicon-Chlorine bonded molecules). Organo-chlorosilanes are likewise incompatible with water or any hydroxyl compound – whether organic or inorganic in nature. These compounds are also similarly incompatible with oxygen. The products of such a hydroxyl compound (e.g., water, alcohol, glycol) and/or oxygen reaction include various silicon-carbon-oxygen bonded molecules, and a combination of hydrogen and hydrogen chloride.

Depending on the degree of substitution of organo-functional groups (e.g., methyl, ethyl, propyl, phenyl) for hydrogen and chlorine, the personal hazard level is reduced somewhat from that of chlorosilanes. Likewise the reactivity of organo-chlorosilanes with hydroxyl compounds is lessened somewhat from that of chlorosilanes. This lessened hazard level and reactivity does not mean that organo-chlorosilanes should not be treated with the same respect as chlorosilanes.
The degree of lessened reactivity has much to do with the steric hindrance of the organic grouping. Therefore propyl chlorosilanes will react slower than methyl chlorosilanes, given the same number of hydrogen and chlorine atoms that are bonded to the core silicon atom.

1. Organo-chlorosilanes have many of the same odd physical properties (e.g., viscosity, thermal conductivity, surface tension) as chlorosilanes, but to a somewhat lesser amount than might be expected. Again, this reduced level of oddity is a function of the amount of substitution of chlorine atoms for organic groupings in the molecular structure.

It would be inappropriate for these compounds to be viewed as organic compounds that have a chlorosilyl substitution. Instead, their nature is that of chlorosilanes with organic substitutions. In many references, the physical properties of organo-chlorosilanes are found in the “organics” section — as opposed to being in the “inorganics” section. This is merely an issue of the author’s organization of topics and properties.

Organo-chlorosilanes form covalent bonds and occupy a middle ground as being both somewhat organic and somewhat inorganic. It is from this intermediate position that they have so many applications (see below section in this module on applications and uses).

1. Organo-chlorosilanes are similar to chlorosilanes in their tetrahedral molecular structure. A methyl (or other organo-functional group) substitution for a chlorine atom alters the structure, both in its steric nature as well as its polarity. For example, methyl trichlorosilane has its three chlorine atoms at a significantly lesser 3-D angle than those of trichlorosilane. Trichlorosilane has a dipole moment of 0.86 Debye, whereas methyl trichlorosilane has a dipole moment of 1.91 Debye.

As in chlorosilane chemistry, disproportionation occurs in organo-chlorosilanes. There can be either Si-Cl swaps with Si-H bonds (leaving the Si-organic grouping untouched); or Si-Cl swaps with Si-organic groups (leaving the Si-H bonds untouched). The means by which the catalyst is conditioned appears to influence which type of disproportionation is favored.

There is more interest in moving around the Si-organic groupings, in order to maximize the production of organo-chlorosilanes with two organic groupings, and two chlorine atoms attached to the core silicon atom, such as (CH3)2-SiCl2 = dimethyl dichlorosilane. Having two chlorine atoms will maximize the chain length of its later reaction product. (Although there is utility in using three chlorines/molecule to increase cross-linking, or just one chlorine/molecule to control chain length, in secondary reactions)

An example of such a disproportionation reaction would be to dehydrate a tertiary methylamine ion-exchange catalyst and treat with anhydrous HCl to activate the amine’s N-Cl adducts. Two by-products of a methyls reaction (trimethyl monochlorosilane and methyl trichlorosilane) are then disproportion reacted to make a more desirable product, dimethyl dichlorosilane.

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[(\text{CH}_3)_3\text{SiCl} + (\text{CH}_3)\text{SiCl}_3 \rightarrow 2 (\text{CH}_3)_2\text{SiCl}_2]\]

1. The synthesis of organo-chlorosilanes actually begins with the preparation of a consumable catalyst, Cu3Si (aka, eta-phase copper silicide). Elemental copper and metallurgical silicon are combined with a zinc promoter, and then batchwise reacted with HCl at 300°C. The solid Cu3Si is milled to the correct size for fluidization, and then small amounts fed into a fluidized bed reactor along with metallurgical-grade silicon, HCl and the appropriate organic chloride. For example, to add just methyl groups to the silicon, use methyl chloride as the organic reactant; or to add just ethyl groups, use chloroethane. This synthesis is called the Rochow reaction <http://en.wikipedia.org/wiki/Direct_process>.
A wide variety of organo-chlorosilane compounds can be custom-synthesized by altering the relative amounts of organic chlorides, the temperature of the reaction, and with fine-tuning by disproportionation. When finally reacted to make coupling agents or silicones, the mixture will dictate the final product molecular weight and chemical resistance. See the module “Silicon-Carbon-Oxygen bonded molecules” for more details.

**Main Applications/Uses**

1. The main application of organo-chlorosilanes is in the manufacture of silicones. For more detail see “Silicon-Carbon-Oxygen bonded molecules”. Silicones are made by the reaction of organo-chlorosilanes with glycols, alcohols and organic acids like acetic acid. Each chlorine atom reacts with the hydrogen atom of a hydroxyl group, to form HCl and an -Si-O-C- linkage. By varying the amount of cross-linkage and end groupings, the properties of these silicones are adjusted.

By leaving significant amounts of reactants in the end product (most commonly acetic acid), the final polymerization can be delayed for long periods of time. The most common example of that is ambient temperature house-hold caulk (as is used around bath-tubs, sinks, and countertops).

Silicone products can be oils, greases, gels, or solid, depending on the degree of cross-linkage. Once “cured”, there is no solvent for silicones, which makes them rugged enough for a variety of conditions. They are also water, UV, and mold/mildew resistant.

In our modern culture silicones are pervasive, being found in wide variety of products from paints and coatings, to lubricants and finishes, as well as synthetic rubber products. Their long life and minimal biological activity has made them acceptable consumer products for several decades.

1. A secondary use of organo-chlorosilanes is in the manufacture of specialty pharmaceuticals and cosmetics. The customization of molecular structure allows for controlled skin absorption with minimal allergenic reaction. The addition of acetate end groups has been found to limit their biologic rejection and allow use as human implants and prosthetics.

2. Organo-chlorosilanes can serve as coupling agents, to bond together organics and inorganics, making unusual products. An example of that is in the surface treatment that creates thin film chromatographic media, or in the surface treatment of thin film liquid crystal displays.

The flexible ultra-thin circuit boards of modern cell phones utilize such coupling agents. The treatment of fiberglass with such coupling agents allows it to act as a filler in making various moldable reinforced plastic components. A final category of applications is in structural co-polymers, such as used in automotive and construction. By co-polymerizing organo-chlorosilanes with other plastic monomers (e.g, acrylate, polyester, urethane, epoxy, phenolic and vinyl chloride), a wide variety of light and flexible parts can be made. This has been widely employed by auto manufacturers to comply with regulations on reduced fuel usage, and to make various residential products.