Silicon-Chlorine Bonded Molecules

Silicon - chlorine bonded molecules do not occur naturally and are completely synthetic. This family includes silane, monochlorosilane (MCS), dichlorosilane (DCS), trichlorosilane (TCS), and silicon tetrachloride (STC), and is generically known as chlorosilanes.

Unusual/Noteworthy Properties

Chlorosilanes are incompatible with water, and are stable only in a completely zero-water environment. With the exception of silicon tetrachloride, these compounds are also incompatible with oxygen. Water and chlorosilanes can be viewed much the same as matter and anti-matter, since any mixture will cause mutual annihilation and result in a significant exotherm. In such case, the compound in the greater molar amount will remain to absorb the exotherm. The products of water and/or oxygen reaction include various silicon-oxygen bonded molecules, and a combination of hydrogen and hydrogen chloride.

STC is non-reactive with oxygen, there is no combustion or further oxidation possible. Combustibility/explosability increases as the chlorosilane molecule becomes more hydrogenated/less chlorinated. Silane gas is pyrophoric in all but the most pure form, and has a similar TNT-equivalency as methane. Impurities in silane of the order of parts per billion will result in silane being pyrophoric (as reported by others), including disilane and disiloxane.

The reaction of chlorosilanes with moisture is immediate and intense. They will react with moisture-of-hydration of any salts, or with moisture adsorbed onto metal surfaces or in the pores of materials. Spills on skin will involve de-fleshing of exposed areas. Breathing these compounds will result in destruction of mucous membranes and lung tissue. Extreme caution must be exercised in handling these compounds. DCS is probably the greatest exposure hazard of the homologue family, in that it is still quite reactive with any moisture source, plus it has the explosive and ground-hugging nature of ether. Silane is generally treated a non-corrosive pyrophoric gas, but when sufficiently purified can have an
ignition delay that leads to a detonation.

**Properties**

Chlorosilanes have unusual physical properties, combining low viscosity, low thermal conductivity, low surface tension and low heat capacity, but having a moderate liquid density. They also have low latent heats of vaporization and high volatility. Collectively this means that they are poor conductors of heat, and will leak easily, and can form explosive vapors when released to the atmosphere. They will diffuse through all rubber sealant compounds and conventional plastics, swelling and making them brittle. Their low lubricity requires use of special types of canned pumps: magnetic-driven rotary pumping equipment is insufficient.

Teflon and other fluorocarbons are suitable sealants, but only in virgin form and at low temperature. If such fluorocarbons are made more flexible by use of plasticizers, chlorosilanes will dissolve them.

Chlorosilanes are non-corrosive to carbon steel and other metals, but will leach out the phosphorus typically found in metal alloys. Therefore when used to make electronic silicon, acid-pickled or electropolished stainless steel is used as a material of construction. For sealants in electronic service, nickel-plated O-rings are used in lieu of elastomers. Metal-to-metal seals are always preferred.

**Bonding**

Although classified as inorganic compounds, chlorosilanes feature covalent bonding and a nominal tetrahedral molecular structure, much the same as chloromethanes. Silane and STC have no dipole moment. The TCS molecule has a small dipole moment of 0.86 Debye, with the three chlorine atoms spreading out their bond angles almost to the 120° of a planar shape. MCS has the largest dipole moment of the family at 1.31 Debye. DCS has a “Vee” shaped molecular arrangement, with a dipole moment of 1.17 Debye. The differing molecular shapes contribute to significant binary interactions in their mixture properties.

Analogous to chloromethanes, chlorosilanes can form aliphatic structures consisting of 2-4 silicon-silicon bonds (e.g., tetrasilane and octochloro-trisilane). Higher chlorosilane molecules with five or more silicon members tend to form ring compounds, similar to their carbon analogs. However there is no evidence of a stable silicon-silicon double or triple bond.

One of the more unusual properties of chlorosilanes is their ease of disproportionation. In such a reaction for example, two TCS molecules will form one DCS and one STC molecule. Similar reactions occur with DCS and MCS. A wide variety of catalysts serve to drive these disproportionation reactions, including medium chain-length amines, imines, nitriles, and chlorinated Lewis Acids (e.g., FeCl3 and AlCl3). Even the smallest amount of such catalysts in liquid or vapor phase chlorosilanes will suffice to cause disproportionation. Disproportionation will occur at low temperatures, but does not occur in the solid phase.

This disproportionation property causes much angst with analytical chemists, since they cannot readily obtain pure samples for calibration of their analyzers unless they take special precautions in pre-cleaning, use special preparation of their analyzers and use specially constructed sample containers.
However, the ease of disproportionation allows chlorosilanes to be the vehicle of choice for manipulating silicon compounds for purification purposes. The decomposition of purified chlorosilanes results in all modern semi-conductors, integrated circuits and most photo-voltaic solar panels. See Applications/Uses, below.

Chlorosilane synthesis always begins with the formation of TCS by the reaction of impure silicon with HCl. The synthesis can either be done directly ( \( \text{Si} + 3\text{HCl} \rightarrow \text{TCS} + \text{H}_2 \)) or indirectly using a recycle STC and hydrogen process ( \( \text{Si} + 3\text{STC} + 2\text{H}_2 \rightarrow 4\text{TCS} \)).

In the more modern indirect method, the STC and hydrogen cause in-situ HCl to be formed, which reacts to form TCS. The unreacted STC and H2 are recycled back. Because fewer unwanted by-products are formed by the indirect method, it is more commonly used.

After forming TCS, disproportionation and purification steps can be used to make DCS, MCS, or silane. Since the disproportionation of item 5 makes STC as a by-product, the indirect TCS synthesis method allows this STC to be recycled. See also the module “Silicon-Carbon Chlorine molecules”

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**Main Applications/Uses**

The main application of chlorosilanes is in the purification of silicon, from an impure form to a highly purified form for semi-conductor use, and for solar photo-voltaic use.

Quartzite ore is an abundantly occurring mineral, mined at many locations globally. By combining with either coke or charcoal in an electric-arc furnace, the silica content of the quartzite is reduced to make impure silicon plus carbon dioxide.

Then the impure silicon is converted to TCS via one of two routes ( see above Properties, item 6) and the TCS is either purified or converted to DCS or silane by disproportionation (see above Properties, item 5). Such purification is a combination of high-reflux distillation, adsorption and use of molecular sieves. After decomposition and recycle of the by-products, the resulting silicon has several important uses ( see module “Elemental Silicon). Without the chemical route through chlorosilanes, the modern electronic age would not have occurred, and computers would still be driven by vacuum tubes. Photovoltaic panels would still be laboratory curiosities.

High temperature combustion of STC with hydrogen @ 800-900C, followed by rapid air quenching results in the production of stable amorphous silicon monoxide solid, otherwise known as fumed silica. See the module on Silicon-Oxygen bonded molecules.

Chlorosilanes are used to modify the reactions in the manufacture of silicones as a cross-linking agent, especially TCS and DCS.