

Reacting with the Substrate

Leaving Groups

The reaction of an organofunctional silane with a surface bearing hydroxyl group results in a substitution reaction at silicon and the formation of the silylated surface where the silicon is covalently attached to the surface via an oxygen linkage. This connection may be formed directly or in the presence of water through a reactive silanol intermediate. In general the reactivity of hydroxylated surfaces with organofunctional silanes decreases in the order: $\text{Si-NR}_2 > \text{Si-Cl} > \text{Si-NH-Si} > \text{Si-O}_2\text{CCH}_3 > \text{Si-OCH}_3 > \text{Si-OCH}_2\text{CH}_3$. An analysis of the relevant bond energies indicates that the formation of the Si-O-surface bond is the driving force for the reaction under dry and aprotic conditions. Secondary factors contributing to the reactivity of organofunctional silanes with a surface are the volatility of the byproducts, the ability of the byproduct to hydrogen bond with the hydroxyls on the surface, the ability of the byproduct to catalyze further reactions, e.g. HCl or acetic acid, and the steric bulk of the groups on the silicon atom.

Although they are not the most reactive organosilanes, the methoxy and ethoxysilanes are the most widely used organofunctional silanes for surface modification. The reasons for this include the fact that they are easily handled and the alcohol byproducts are non-corrosive and volatile. The methoxysilanes are capable of reacting with substrates under dry, aprotic conditions, while the less reactive ethoxysilanes require catalysis for suitable reactivity. The low toxicity of ethanol as a byproduct of the reaction favors the ethoxysilanes in many commercial applications. The vast majority of organofunctional silane surface treatments are performed under conditions in which water is a part of the reaction medium, either directly added or contributed by adsorbed water on the substrate or atmospheric moisture.

Bond Dissociation Energies

Bond	Dissociation Energy (kcal/mole)
$\text{Me}_3\text{Si-NMe}_2$	98
$\text{Me}_3\text{Si-N}(\text{SiMe}_3)_2$	109
$\text{Me}_3\text{Si-Cl}$	117
$\text{Me}_3\text{Si-OMe}$	123
$\text{Me}_3\text{Si-OEt}$	122
$\text{Me}_3\text{Si-OSiMe}_3$	136

Common Leaving Groups

Type	Advantage	Disadvantage
dimethylamine	reactive, volatile byproduct	toxic
hydrogen chloride	reactive, volatile byproduct	corrosive
silazane (NH_3)	volatile	limited availability
methoxy	moderate reactivity, neutral byproduct	moderate toxicity
ethoxy	low toxicity	lower reactivity