# GERMANIUM VS. SILICON: A BRIEF DESCRIPTION

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The chemistry of germanium is not as well-studied as silicon. In general the chemistry of the two elements is similar, but a number of differences emerge.

## Inorganic Chemistry

Like silicon, germanium is a semi-conductor. In fact, germanium was fabricated into diodes, the first practical semiconductor devices. As a consequence, a significant body of literature relating to the electrical properties of germanium has developed. The mobility of holes in germanium is greater than that of silicon and of any other common semiconductor. The hole and electron mobilities are closer in germanium than other semiconductors, particularly at low temperatures. This has made germanium an attractive candidate for high performance CMOS technology. In high speed digital communications, germanium is expected to have a role in the production of heterojunction bipolar transistors (HBT's). It is currently of interest in the fabrication of monolithic fiber-optic receivers, since germanium photodiodes perform well at 1.3-1.5 micron wavelengths. Germanium metal is also of utility in infrared detectors, which comprise the metal's largest current use.

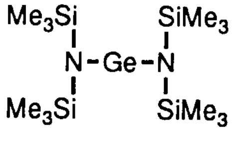
Bond energies of Ge-X bonds are generally considered to be about 10% less than corresponding Si-X bonds. This is reflected in somewhat lower thermal stability of germanium compounds. The electronegativities of germanium and silicon are 2.01 and 1.90, respectively on the Pauling scale; their configuration energies are 11.80 eV and 11.33 eV, respectively. While silicon is apparently more electropositive than germanium, reactivity indicates that polarization parameters may be more equivalent. Valence states of +2 are readily accessible for germanium and $GeCl_2$, $GeBr_2$ and $GeI_2$ are isolable compounds. In contrast, silicon dihalides are known as reactive intermediates by studies of emission bands or trapping experiments. The chemistry of both elements proceeds primarily in the +4 state, although hyper-coordinate states, particularly for fluorocompounds, are known.

Both silicon and germanium metal react with halogens and hydrogen halides to give analogous products. Halides of both elements react rapidly with water to give oxides and hydroxides. Germanium oxides can be converted back to the halides by reaction with the appropriate acid. In the case of silicon, only hydrofluoric acid reacts with the oxides to form fluorosilanes.

Germanium compounds have higher optical densities than silicon compounds. This leads to the second major application of germanium compounds: the controlled combustion of germanium tetrachloride in a hydrogen-oxygen flame in chemical vapor axial deposition for the formation of ingots from which step-index fiber optics are drawn.

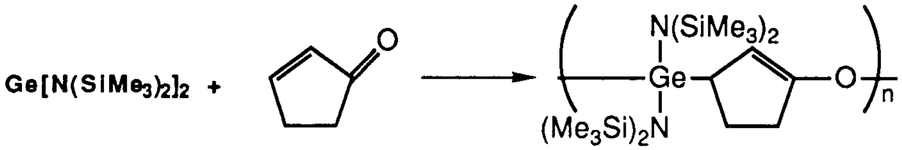
## Organic Chemistry - Differences

Sterically hindered organogermanium compounds in the +2 state are known, including dicyclopentadienylgermanium, di[bis(trimethylsilyl)methyl]germanium and di[bis(trimethylsilyl)amino]germanium. No analogous compounds are known for silicon.



$(Me_3Si)_2N{-}Ge{-}N(SiMe_3)_2$

Germanium +2 compounds have recently been used in a novel polymer synthesis.



Di[bis(trimethylsilyl)amino]germanium also reversible binds $H_2$ and $CO_2$ in 3-coordinate complexes.

Alkyl and aryl halides react with germanium dihalides to yield alkyl and aryl germanium trihalides. No comparable reactions are observed with silicon.

$$CH_3CH_2CH_2CH_2CH_2Cl + GeCl_2 \longrightarrow CH_3CH_2CH_2CH_2CH_2GeCl_3$$

Perfluorinated methyl and ethyl germanes are isolable and stable. Only recently, simple trifluoromethyl(methyl)silanes have been prepared. Other perfluorinated methyl and ethyl silanes are unstable.

Germanium forms Ge-Ge bonds readily through Grignard chemistry in addition to alkali metal coupling, which is the most accessible route for Si-Si bond formation. While Si-Si bonds can be readily cleaved by Na-K in ether, Ge-Ge are cleaved only under more rigorous conditions such as the use of higher boiling solvents like tetrahydrofuran. In both cases multiple metal-metal bonds give photoreactive compounds.

Silicon undergoes migration from carbon to oxygen in the Brook rearrangement of $\alpha$-silyl ketones. Germanium does not appear to undergo a similar migration.

Repeating silicon-oxygen bonds tend to form extended linear polymers in preference to cyclic structures. Repeating germanium-oxygen bonds tend to form cyclic structures in preference to extended linear polymers.

In contrast to silicon hydrides, germanium hydrides readily undergo metallation. For example, the reaction of triphenylgermane with butyl lithium followed by carbonation yields triphenylgermanecarboxylic acid.

Trichlorogermane reacts with activated aromatic rings yielding trichlorogermyl substituted cyclic alkanes and olefins.

Applications of organogermanes in organic synthesis are only incipient, while applications of organosilanes in organic synthesis are well-developed for a variety of reasons. Until recently organogermanes have had relatively poor availability compared to organosilanes. Also, the germanium oxygen bond is somewhat more susceptible to hydrolysis compared to the silicon oxygen bond. Beyond these facts, the largest determinant for differences in applications is the higher cost of germanium compounds. Consequently, only unique applications of organogermanium compounds are likely to be of importance. Potential applications include trimethylgermylacetonitrile as a carbanion source, trimethylbromogermane and trimethylchlorogermane employed in the preparation of masked dienolates in a variety of regioselective syntheses, trichlorogermane for ether cleavage, and germanium diiodide and cesium trichlorogermanate for conversion of alkyl halides to alkylgermyltrihalides.

## Organic Chemistry - Similarities

In general there are many more similarities between organogermanium and organosilicon compounds than differences. The following enumeration is extremely incomplete. The cited references should be consulted for more detail.

Organogermanium and organosilicon compounds can both be prepared by the copper catalyzed direct reaction of alkyl and aryl halides with the metal.

Grignards and alkali metal organics will displace halides bound to germanium and silicon to give the organo-substituted compound.

Germanium hydrides and silicon hydrides react with olefins in hydrogermylation and hydrosilylation reactions. Both are catalyzed by platinum compounds, but catalysis is not a requirement for hydrogermylation.

Doubly bonded silicon-silicon and germanium-germanium compounds have been demonstrated, but are not representative of large classes of chemistry for the elements.

Like organosilanes, organogermanes can be fluorodemetallated. Additionally, organogermanes can be demetallated with bromine.

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