A.2 Silicon

Position in Periodic Table

Period 3, Group 14 (old group IV)

Electronegativity of Si

1.90 (Pauling scale) - more electropositive than carbon; displays metallic character. C–Si bonds are polarised:

Electron Configuration

$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$.

Four electrons in the valence shell and like carbon can form four covalent bonds (after hybridisation).

The availability of relatively low energy empty 3d AOs allows the possibility for a higher coordination number (hypervalent silicon compounds) and expansion of the valence state of Silicon. This has ramifications on the mechanisms of some reactions proceeding at Si.

Substitution reactions.

You should already know the mechanisms of S_N2 and S_N1 substitution and the situations where they occur.

Substitution at silicon is very fast in the case of Si–Cl and Si–Br (much faster than the C–X analogues) and often also proceeds with inversion of configuration just like in S_N2 reactions (especially with good leaving groups). The mechanism, however, is best described as an addition-elimination process. The pentacoordinate species is believed to be an intermediate (albeit a very short-lived one); compare this with the S_N2 mechanism in which the pentacoordinate species only ever represents the transition state.

The S_N2-Substitution Reaction Mechanism - REVISION!

Substitution at Silicon

Notes:

1. In the example shown the nucleophile is attacking a tertiary silicon centre in an S_N2-like fashion (back-side attack). S_N2 substitution does not proceed (at least in intermolecular reactions) with tertiary alkyl halides. So why can it proceed at Silicon?

- C–Si bond length is *ca*. 1.25 times longer than C–C bond length (1.89 Å *vs*. 1.54 Å)
- Silicon is a much larger atom than carbon (covalent radii 1.18 Å *vs*. 0.77 Å)

Both these factors combine to provide much more space about the silicon centre and allow back-side attack at a tertiary silicon centre.

2. The pentavalent silyl species can be considered as an intermediate whereas in reactions at carbon, this type of species can only ever represent the transition state. Although the presence of a hypervalent silyl species as an intermediate has been hotly debated, the fact that silicon has empty 3d AOs (relatively low lying in energy) into which it can accept electron density from a nucleophile means that its existence as an intermediate is at least possible.

3. Substitution reactions at silicon more closely resemble the S_N2 reaction mechanism than they do the S_N1 reaction mechanism:

- the rate-determining step involves both the nucleophile and the substrate (*i.e.* a bimolecular process)
- the reaction is often stereospecific and generally proceeds with inversion of configuration when there is a good leaving group (*e.g*. Cl, Br, I).

Stereoelectronic Effects: Stabilisation of β-Carbocations and α-Carbon-Metal Bonds

The regio- and stereoselectivity of many reactions (electrophilic addition across vinyl silanes, Lewis acid-mediated allylation reactions of allylsilanes and allylstannanes *etc.*) can be understood by attributing a stabilising effect by the proximal Si atom on the build-up of charge in the T.S. This stabilisation is a stereoelectronic effect.

Revision of Molecular Orbitals

When two orbitals have the appropriate symmetry they can overlap (or mix) to provide two new molecular orbitals. (Conservation of orbitals means that *n* orbitals overlap to provide *n* molecular orbitals).

Consider the formation of the π-bond in ethene.

Now consider the scenario of two filled orbitals overlapping:

Now consider the scenario of a filled orbital overlapping with an unfilled orbital:

The degree of orbital overlap (and associated stabilisation) is dependent on the relative energies of the overlapping orbitals:

Overlap between orbitals of similar "size" is energetically more favourable than overlap between orbitals of different sizes:

We are now in a position to rationalise the stabilising effects of a proximal silicon atom on β-positive charge and α-carbon-metal bonds.

The β-Effect: Stabilisation of β-Carbocations

Carbocations are trigonal planar in structure; the empty orbital is a p AO and is orthogonal to the three σ-bonds. We know that is energetically favourable for a filled orbital to overlap with an unfilled orbital. A suitably aligned C–Si σ-bond can therefore provide a net bonding interaction.

Clearly any filled orbital can stabilise a carbocation in this fashion. This so-called hyperconjugative stabilisation can be used to rationalise the relative stability of carbocations: tertiary > secondary > primary > methyl.

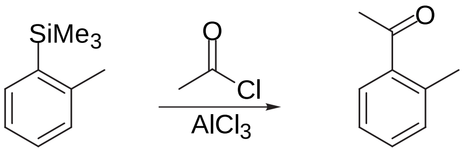
The stabilising effect of a C-Si σ bond is greater than that provided by a C-C σ bond for two reasons both of which stem from the fact that Si is more electropositive than C (1.90 for Si *vs* 2.55 for C (Pauling electronegativity scale)) and is in period 3.

As a consequence:

- the $\sigma_{C\text{-}Si}$ bonding MO is higher in energy than the $\sigma_{C\text{-}C}$ MO and therefore closer in energy to the vacant p AO (Remember that the closer is the energy of overlapping orbitals, the more significant is the interaction).

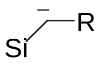
- The coefficient on the C in the $\sigma_{C\text{-}Si}$ bonding MO is larger leading to more efficient overlap with the proximal p AO.

You should now be able to rationalise the regio- and stereoselectivity of the electrophilic addition-elimination to vinyl silanes and *ipso* substitution in the electrophilic aromatic substitution of aryl silanes.

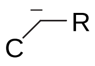


Stabilisation of α-Carbon-Metal Bonds

Observation: carbanions with an α-silicon group are more stable than their carbon analogues.



is more stable than



- Si is more electropositive (metallic) than C and therefore exerts a weak +I inductive effect through the σ-framework - but this should destabilise α-negative charge.

This weak effect is overridden by a number of factors:

- Si is in period 3 in the periodic table and the presence of relatively low energy empty 3d AOs allows dπ-sp$^3\pi$ bonding:

- Overlap between the filled σ orbital of the metal-carbon bond and the unfilled $\sigma^*_{C\text{-}Si}$ orbital is another energetically favourable interaction. The larger coefficient on the silicon atom in the σ* MO further improves the orbital overlap:

- Silicon is a relatively large atom and therefore readily polarised. Induced dipoles will also help stabilise proximal negative charge. This effect is probably the most important factor for stabilising α-negative charge.

Bond Strengths

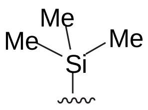
bond	bond strength (kJ mol^{-1})
Si–C	318 (in Me_4Si)
Si–O	452 (in Me_3SiOMe)
Si–F	565 (Me_3SiF)

The important point to note is that bonds to O and F are stronger than those with C, whilst Si–H and Si–C bonds are weaker than C–C and C–H bonds.

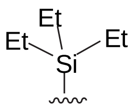
Silyl Ethers

Silyl ethers are important *protecting groups* for alcohol functional groups. It is easy to vary the robustness (stability) of these groups by varying the substituents on the silicon group; thus silyl ethers bearing large bulky alkyl groups tend to be more stable towards hydrolysis.

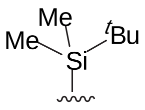
Some common silyl ether protecting groups:



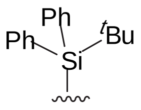
trimethylsilyl
TMS



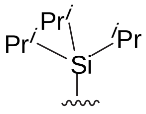
triethylsilyl
TES



tert-butyldimethylsilyl
TBDMS or TBS



tert-butyldiphenylsilyl
TBDPS



triisopropylsilyl
TIPS

increasing stability towards hydrolysis on treatment with fluoride

Although silyl ethers can be hydrolysed using base or acid, a very important alternative is to use fluoride since this provides a method for *chemoselectively* deprotecting silyl ethers in the presence of commonly used protecting groups which might otherwise also react with acid or base. This is an example of an *orthogonal* protection strategy.

Fluoride-induced deprotection proceeds by a nucleophilic addition-elimination sequence (see earlier) and is thermodynamically driven by the high strength of the Si–F bond.

Brook Rearrangement

Silyl carbinols are useful intermediates in synthesis. On treatment with *catalytic* quantities of base, the initially formed alkoxide undergoes a 1,2-rearrangement to provide the more reactive carbanion. The reaction is potentially reversible but favours the silyl ether on account of the much higher Si–O bond strength.

Summary

1. Silicon is more electropositive than both carbon and hydrogen.
    - This polarises the C-Si bond inducing a δ^- charge on the carbon atom and making a hydrogen substituent hydridic in character.
    - It also affects the orbital coefficients in MOs which has important stereoelectronic consequences.

2. Silicon is in period 3 of the Periodic Table.
    - It is a lot larger than carbon; bonds to Si are usually at least 1.25 times longer than the corresponding bonds to C.
    - The presence of relatively low energy vacant 3d AOs allows an expansion of the coordination sphere (hypervalent silicon species) and $p\pi$-$d\pi$ bonding.

- The greater electron density around a large atom means that polarisation-induced dipoles can also be important for stabilising proximal charge (especially for α-negative charge).

3. Partial pπ-dπ bonding strengthens Si–O and Si–F bonds. These bonds are much stronger than Si–H and Si–C bonds and their formation is a frequent thermodynamic driving force in reactions.