

Redox selective reactions of organo-silicon and -tin compounds

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The C–Si and C–Sn σ orbitals are higher in energy than C–H or C–C σ orbitals, and therefore can interact with neighboring π systems, non-bonding orbitals of heteroatoms, and other σ systems such as those of C–Si and C–Sn. Such interactions cause an increase of the HOMO level which in turn favors electron transfer. On the basis of this effect various types of redox selective reactions of organo-silicon and -tin compounds have been developed.

1 Introduction

In the past decades the chemistry of organo-silicon and -tin compounds has witnessed a steady advance in progress, revealing their unique properties and the development of their synthetic applications.¹ In the last several years redox reactions of organo-silicon and -tin compounds have received significant research interest and the activity in this area has grown rapidly.² This account will provide a brief outline of redox selective reactions of organo-silicon and -tin compounds using electrochemical methods, with special emphasis on their mechanistic principles.

2 Redox Reactions on the Surface of an Electrode: Molecular Orbital Considerations

Before discussing the redox reactions of organo-silicon and -tin compounds, let us start off by analyzing the redox reactions on the surface of the electrode³ from a view point of molecular orbital theory (Fig. 1). There is an energy band of electrons in the electrode, and this band is filled up to the Fermi level. In the solution phase there exist substrate molecules and they have molecular orbitals of discrete energies. The molecular orbitals are filled up to the HOMO (highest occupied molecular orbital). In the case of oxidation, an electron moves from the HOMO of the substrate molecule to the electrode to produce a cation radical species which undergoes subsequent reactions. In

the case of reduction, an electron moves from the electrode to the LUMO (lowest unoccupied molecular orbital) of the substrate molecule to produce an anion radical species which undergoes subsequent reactions to give final products. Hereafter we only discuss oxidation because of the simplicity of the discussion, but we should keep in mind that a similar discussion can be applied to reduction, although the direction of the electron transfer is reversed.

One of the major advantages of electrochemical reactions is that the reactivity of the electrode, *i.e.* the position of the Fermi level, can be easily adjusted by external tuning (*i.e.* tuning of the dial of a potentiostat). When the electrode potential is adjusted properly, the electron transfer from the HOMO of the substrate molecule to the electrode takes place smoothly, although there usually exists some energy barrier for this process. If there are two kinds of substrate having different HOMO levels, selective

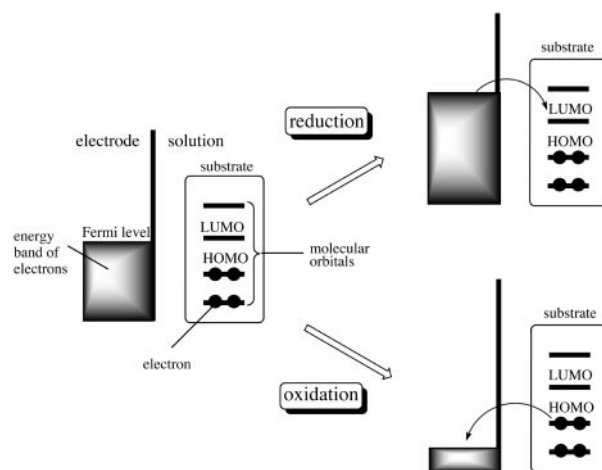


Fig. 1 Schematic diagram of the electron transfer on the surface of the electrode



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After receiving an M.S. from Osaka City University in 1994, Keiji Nishiwaki enrolled in a doctoral course at Kyoto University. In 1997 he joined Kinki University as a research associate. His current research interest is the development of new electron donors based on β -effects of Group 14 elements in electron transfer.

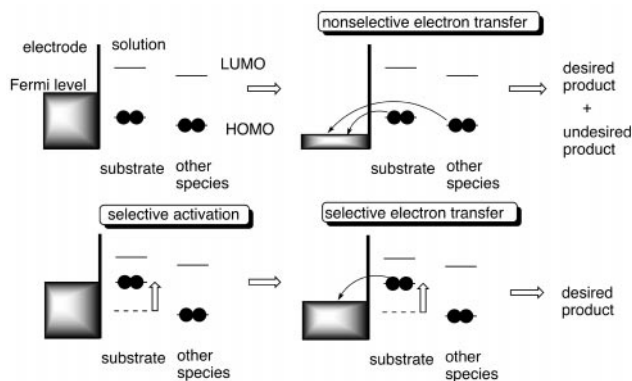


Fig. 2 Schematic diagram of the selective and non-selective electron transfer on the surface of the electrode

oxidation can be accomplished by tuning the electrode potential appropriately as shown in Fig. 2. If the HOMO levels are very close to each other, however, it is difficult to oxidize one substrate without affecting the other. When the substrate that we wish to oxidize has a lower HOMO level than that of the other species, it is, in principle, impossible to accomplish selective oxidation. However, we often use tricks to accomplish the desired reaction in spite of unfavorable orbital situations. For example, if the substrate that we wish to oxidize is adsorbed onto the electrode selectively and the other species are not, then electron transfer takes place selectively to accomplish the desired reaction. Therefore, the use of different electrode material sometimes gives rise to different reaction pathways.

Although such external control of electron transfer, *i.e.* control by electrode materials, solvent, current density, and so on, is important, we have recently proposed the importance of the internal control approach, and demonstrated that silicon and tin are quite effective as controlling groups in redox reactions. We call such a group 'electroauxiliary'. Silicon and tin promote the electron transfer from β -situated π systems, heteroatoms having non-bonding p orbitals, and some σ orbitals. The following sections focus on the principle of the action of silicon and tin as controlling groups and their applications to redox selective reactions.

3 Control of Redox Reaction by Orbital Interaction

3.1 Electron transfer reactions of allylsilanes and benzylsilanes (σ, π -interaction)

The C–Si bonding σ orbital is higher in energy than C–H or C–C bonding σ orbitals, the energy match of the C–Si σ orbital with the π orbital of a carbon–carbon double bond is better than that with C–H or C–C bonds. Therefore, considerable interaction between the C–Si σ orbital with the neighboring π orbital is attained in allylsilanes and benzylsilanes⁴ (Fig. 3). Such interaction produces two new molecular orbitals. The energy level of the orbital produced by a bonding interaction is lower than the original two⁵ and that of the orbital produced by an antibonding interaction is higher than the original two. As the original orbitals are both filled, the two new orbitals should also be filled, and the orbital of higher energy becomes the HOMO. Therefore, the interaction between the C–Si σ orbital and the π orbital of the carbon–carbon double bond causes a significant increase of the HOMO level which in turn favors electron transfer. The magnitude of such an interaction depends upon the torsion angle Si–C–C–C. As shown in Fig. 4 the HOMO level is maximum when the torsion angle is 90°, where the C–Si σ orbital and the π orbital of the carbon–carbon double bond are in the same plane. Fig. 5 shows the computer generated picture of the HOMO of the allylsilane (torsion angle 90°) which exhibits the antibonding interaction

Table 1 Oxidation potential of allylsilane and related compounds

| Compound | E_p/V (vs. Ag–AgCl)* |
|----------------------------|------------------------|
| | 1.30 |
| | 1.85 |
| $(\text{CH}_3)_4\text{Si}$ | >2.5 |

* Determined with cyclic voltammetry using a Pt working electrode in $\text{LiClO}_4\text{-CH}_3\text{CN}$.

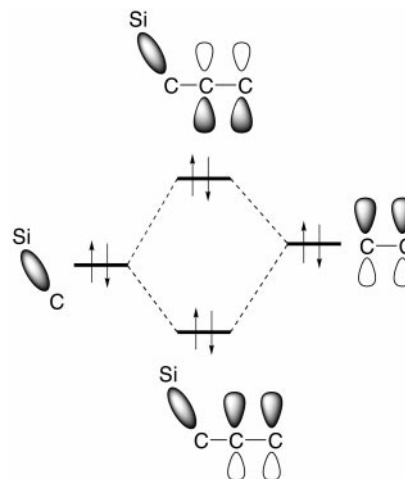


Fig. 3 Energy diagram of the interaction of the C–Si σ orbital and the π orbital of the C=C bond of the allylsilane

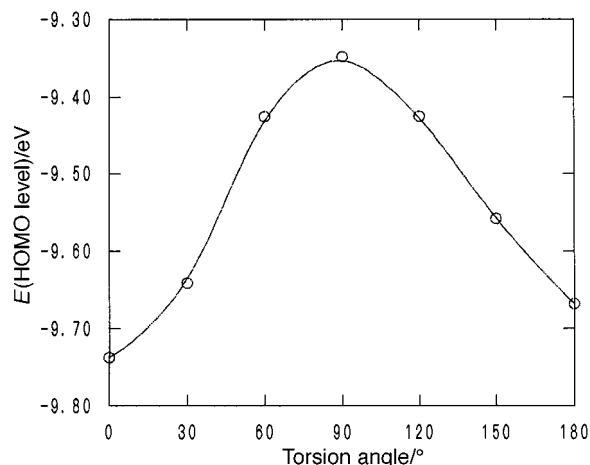


Fig. 4 Plots of HOMO level of $\text{H}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ vs. torsion angle of Si–C–C–C (MP2/LANL2DZ) ($\text{eV} \approx 1.602 \times 10^{-9} \text{ J}$)

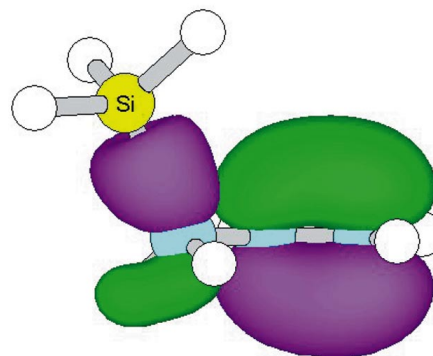
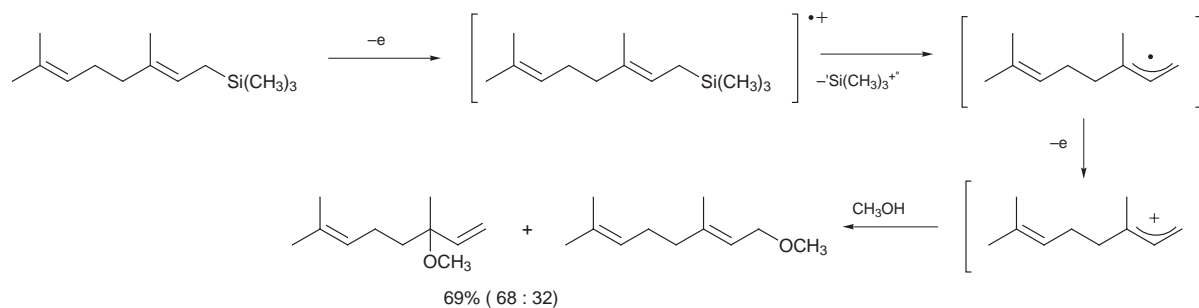


Fig. 5 The HOMO of $\text{H}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (HYPERCHEM 5,⁶ HF/3-21G*)



Scheme 1

Table 2 Oxidation potential of α -heteroatom-substituted heteroatom compounds and related compounds

| Compound | E_p/V (vs. Ag–AgCl)* |
|----------------------------------|------------------------|
| $C_7H_{15}-OMe$ | >2.5 |
| $C_7H_{15}-OMe$ $SiMe_3$ | 1.72 |
| $C_7H_{15}-SPh$ | 1.20 |
| $C_8H_{17}-SPh$ $SiMe_3$ | 1.10 |

* Determined with cyclic voltammetry using a Pt working electrode in $LiClO_4-CH_3CN$.

between the C–Si σ orbital and the π orbital of the carbon–carbon double bond.

The oxidation potentials of allylsilanes are less positive than those of the corresponding alkenes as shown in Table 1, indicating that the silyl group at the allylic position acts as an activating group for alkenes toward oxidation.⁷ The selective electrochemical oxidation of the carbon–carbon double bond neighboring the C–Si bond in geranyltrimethylsilane is remarkable (Scheme 1). The other carbon–carbon double bond is not affected at all. It is also noteworthy that the C–Si bond is cleaved selectively in the cation radical intermediate⁸ to give the allyl radical which is further oxidized to the allyl cation. The oxygen nucleophiles such as methanol are introduced to the allyl cation intermediate to produce a mixture of two regioisomeric products.

Chemical oxidation and photoelectron transfer oxidation of allylsilanes have also been studied extensively. Such reactions proceed by closely related mechanisms to cleave the C–Si bond selectively.⁹

3.2 Electron transfer from heteroatoms (σ, n -interactions)

The introduction of a silyl group at the carbon adjacent to a heteroatom (e.g. oxygen,¹⁰ sulfur¹¹ or nitrogen¹²) causes a significant decrease of the oxidation potential (Table 2). In the case of the ether, the effect of silicon is especially remarkable. The oxidation potential decreases at least 0.8 V by the introduction of a silyl group on the carbon adjacent to the oxygen atom. The decrease of the oxidation potential by silyl-substitution is attributed to the interaction between the C–Si σ orbital and the non-bonding p orbital of the heteroatom (i.e. oxygen) increasing the HOMO level¹³ as shown in Fig. 6. The important role played by the orbital interaction is demonstrated by the geometric dependence of the HOMO level. The plots of the HOMO level of H_3SiCH_2OH (a model compound of silyl-substituted ethers) obtained by *ab initio* molecular orbital calculations vs. the torsion angle Si–C–O–H is shown in Fig. 7. When the C–Si σ orbital and the non-bonding p orbital of the oxygen atom are in the same plane (torsion angle 90°) the HOMO level is at maximum. The HOMO shown in Fig. 8

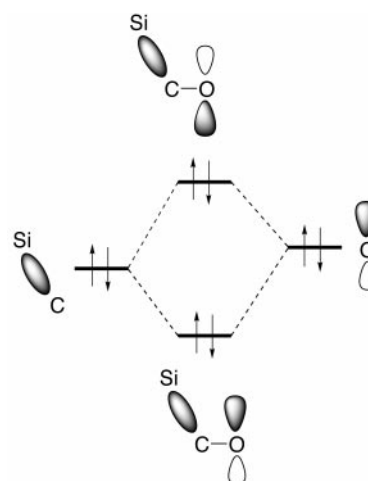


Fig. 6 Energy diagram of the interaction of the C–Si σ orbital and the non-bonding p orbital of oxygen

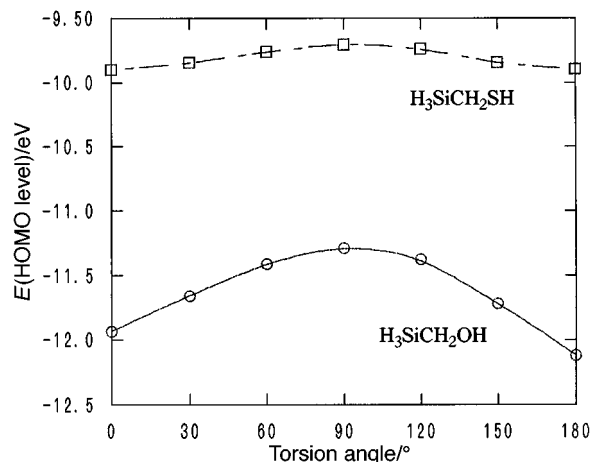


Fig. 7 Plots of HOMO levels of H_3SiCH_2OH and H_3SiCH_2SH vs. torsion angle of Si–C–O–H and Si–C–S–H, respectively (MP2/LANL2DZ)

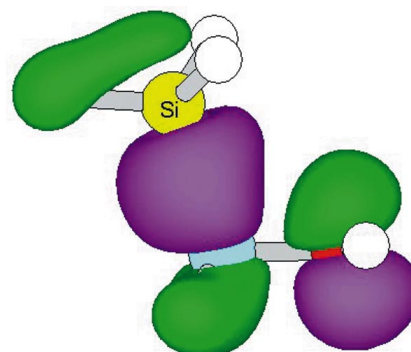
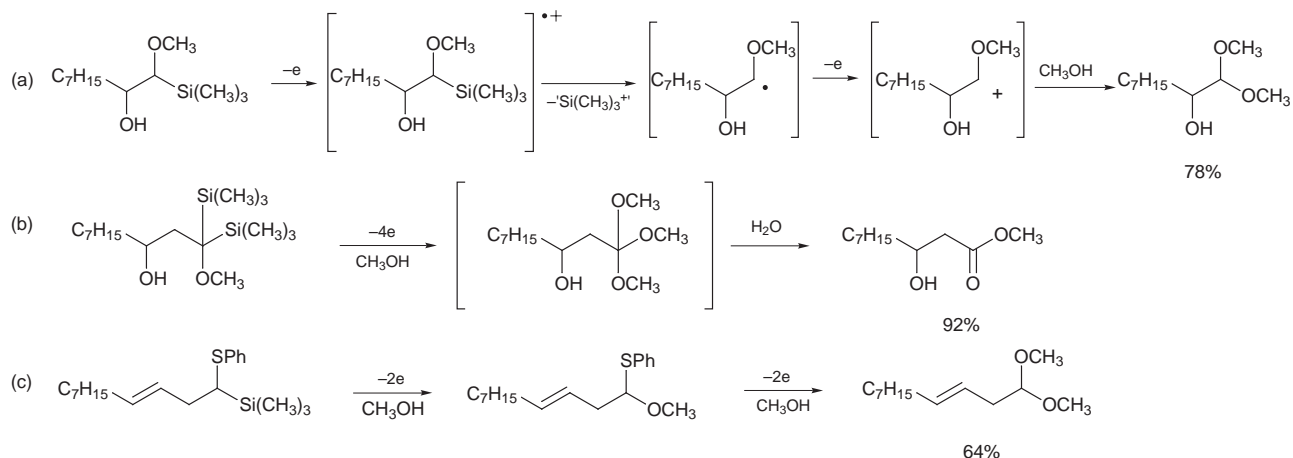
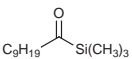

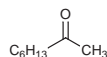


Fig. 8 The HOMO of H_3SiCH_2OH (HYPERCHEM 5, HF/3-21G*)



Scheme 2

Table 3 Oxidation potential of acylsilane and related compounds

| Compound | E_d/V (vs. Ag–AgCl)* |
|---|------------------------|
|  | 1.23 |
|  | >2.00 |
|  | >2.00 |

* Decomposition potential determined with rotating-disc voltammetry using a Pt working electrode in $LiClO_4-CH_3CN$.

exhibits the antibonding interaction between the C–Si σ orbital and the non-bonding p orbital. When they are in a perpendicular orientation (torsion angle 0 and 180°) the HOMO level is at a minimum. It is noteworthy that we can design molecules having specific oxidation potentials by controlling their geometry.¹⁴

The magnitude of the orbital interaction strongly depends on the nature of the heteroatom. In the case of sulfide the effect of silyl-substitution is not so large. The molecular orbital calculations of a model compound, H_3SiCH_2SH (Fig. 7) are consistent with the experimental oxidation potentials (Table 2). This is probably because the energy match between the C–Si σ orbital and the non-bonding p orbital of the sulfur is not good, thus the effective interaction between the two orbitals cannot be attained (see below).

The silyl group also controls the reaction pathway in preparative electrochemical oxidation. The oxidation of silyl-substituted heteroatom compounds leads to the selective cleavage of the C–Si bond and the introduction of nucleophiles on the carbon. Weakening of the C–Si bond by the interaction of the C–Si σ orbital with the half-vacant p orbital of the cation radical of the oxygen¹⁵ seems to be responsible for the facile C–Si bond cleavage. Several examples of the use of silicon in electrochemical oxidation of heteroatom compounds are shown in Scheme 2.¹⁶ In the case of β -hydroxy- α -trimethylsilyl ether [Scheme 2(a)], the C–Si bond in the initially formed cation radical is cleaved selectively without affecting other parts of the molecule to give the carbon radical which is further oxidized to the cationic intermediate. The attack of methanol gives β -hydroxyacetal as the final product. The free hydroxy group is not affected at all during the course of the reaction.

The anodic oxidation of compounds having two C–Si bonds is interesting. Two C–Si bonds are cleaved successively to give an ester probably *via* the hydrolysis of the initially formed orthoester [Scheme 2(b)]. The electrochemical oxidation of silyl-substituted sulfides also takes place smoothly. The cleavage

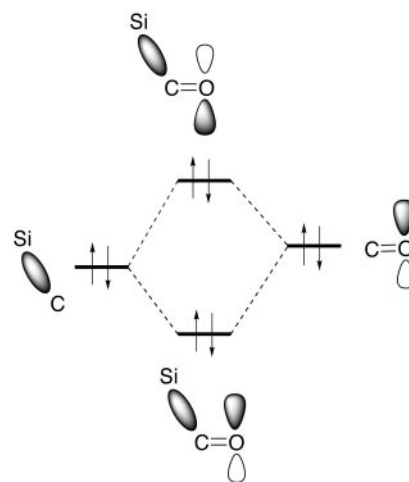


Fig. 9 Energy diagram of the interaction of the C–Si σ orbital and the non-bonding p orbital of carbonyl oxygen

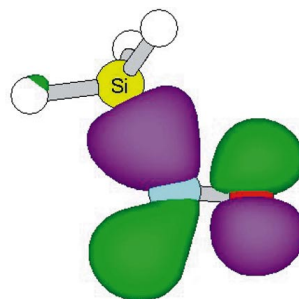


Fig. 10 The HOMO of $H_3SiC(=O)H$ (HYPERCHEM 5, HF/3-21G*)

of the C–Si bond followed by the introduction of methanol gives the O,S-acetal which is further oxidized under the same conditions to give the acetal. In the example shown in Scheme 2(c), the carbon–carbon double bond is not affected at all during the course of the transformation.

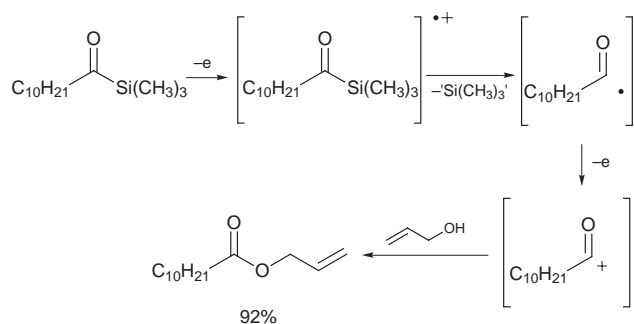
Oxidation reactions of silicon-substituted heteroatom compounds by chemical oxidizing agents and photoelectron transfer oxidation reactions have also been studied extensively.¹⁷

Silicon also activates carbonyl compounds toward electron transfer (Table 3). The introduction of a silyl group on the carbonyl carbon (acylsilanes) causes a significant decrease in the oxidation potential.¹⁸ The interaction of the C–Si σ orbital with the non-bonding orbital of the oxygen is responsible and this interaction is facilitated by the fixed geometry; the rotation around the carbon–oxygen double bond is prohibited (Fig. 9). This interaction is also responsible for other unique properties of acylsilanes.¹⁹ The HOMO of $H_3SiC(=O)H$ is shown in Fig.

Table 4 Oxidation potential of α -heteroatom-substituted organo-silicon compounds

| Compound | E_1/V (vs. Ag–AgCl)* |
|----------------|------------------------|
| | 0.97 |
| | 1.47 |
| | 1.44 |
| | 0.74 |
| $(C_4H_9)_4Sn$ | 1.52 |

* Determined with rotating-disc voltammetry using a Pt working electrode in $LiClO_4-CH_3CN$.



Scheme 3

10 to demonstrate the antibonding interaction between the C–Si σ orbital and the non-bonding p orbital of the carbonyl oxygen. The electrochemical oxidation of silyl-substituted carbonyl compounds (acylsilanes) proceeds smoothly to cleave the C–Si bond, and various nucleophiles such as alcohols, water and amides can be introduced to the carbonyl carbon. In the example shown in Scheme 3, allyl alcohol is effectively introduced as a nucleophile to give the corresponding allyl ester. The oxidation of acylsilanes by chemical oxidizing agents such as H_2O_2 also cleaves the C–Si bond.²⁰

Tin is also effective for the oxidation of heteroatom compounds. The introduction of a stannyl group on the carbon adjacent to the heteroatom decreases the oxidation potential significantly (Table 4).²¹ The effect of tin is attributed to the interaction between the C–Sn σ orbital and the non-bonding p orbital of the heteroatom, increasing the HOMO level which in turn favors electron transfer. The variation of the HOMO levels of the model compounds H_3SnCH_2OH and H_3SnCH_2SH with torsion angle is shown in Fig. 11. Whereas silyl substitution causes little decrease in the oxidation potentials of sulfides, stannyl substitution causes a significant decrease. Although the energy level of the p orbital of sulfur is much higher than the C–Si σ orbital and they do not interact with each other effectively, the energy level of the C–Sn σ orbital is similar to that of the sulfur p orbital and they interact effectively to increase the HOMO level (Fig. 12). Therefore, tin exhibits significant effects for electron transfer from organosulfur compounds, whereas silicon has little effect.

The reaction pattern of the oxidation of stannyl-substituted heteroatom compounds is quite similar to that of silyl-substituted heteroatom compounds.²¹ Electrochemical oxidation leads to selective cleavage of the C–Sn bond and the introduction of nucleophiles on the carbon.

The effect of tin is especially important for oxidative carbon–

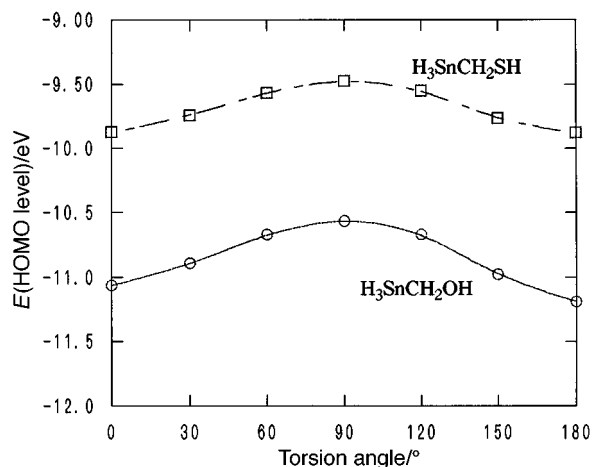


Fig. 11 Plots of HOMO levels of H_3SnCH_2OH and H_3SnCH_2SH vs. torsion angle of Sn–C–O–H and Sn–C–S–H, respectively (MP2/LANL2DZ)

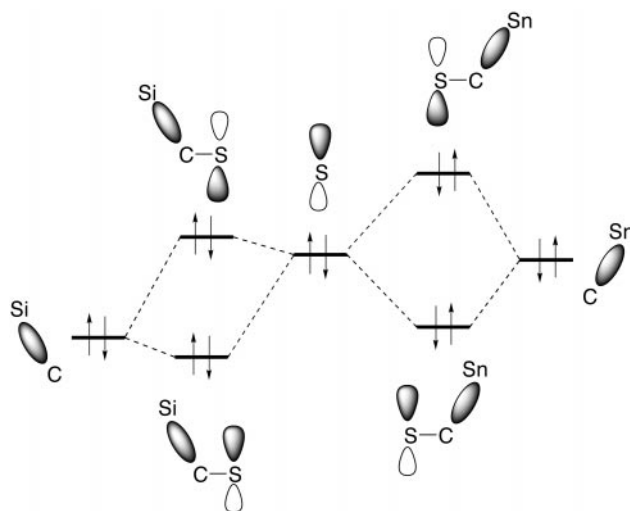
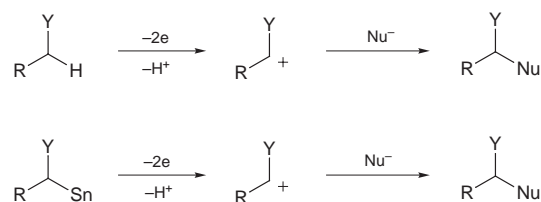


Fig. 12 Energy diagram of the interaction of the C–Si σ orbital and the C–Sn σ orbital with the non-bonding p orbital of sulfur

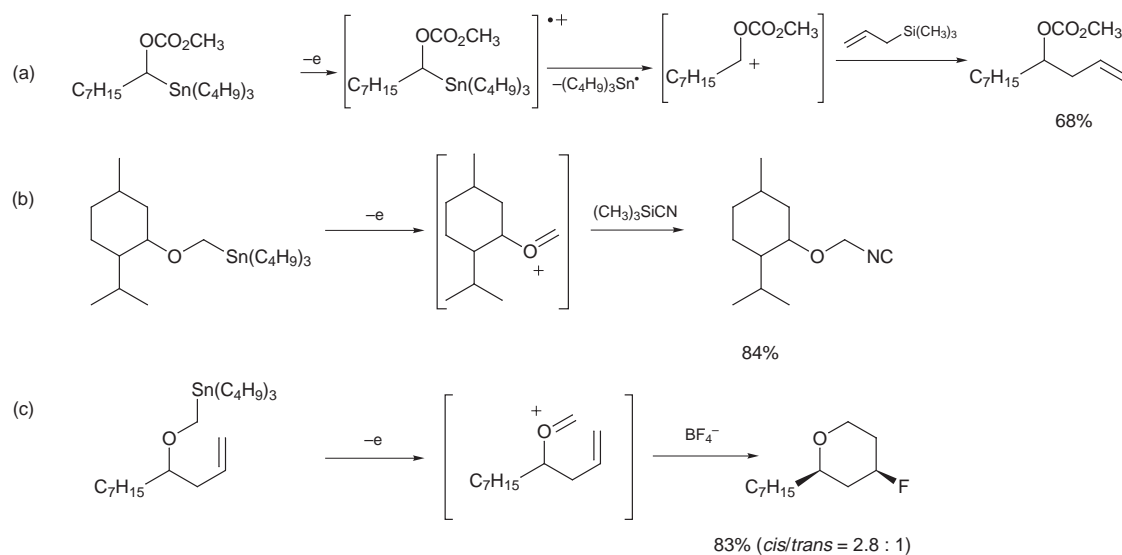


Y = heteroatom

Nu = carbon nucleophile

Scheme 4

carbon bond formation.²² During oxidation of heteroatom compounds the carbocation, stabilized by the adjacent heteroatom, is generated *via* proton elimination under suitable conditions. The reaction of this carbocation with carbon nucleophiles should lead to effective carbon–carbon bond formation (Scheme 4). There are, however, two major problems. The first is the oxidation of carbon nucleophiles. The oxidation potential of carbon nucleophiles is often lower than that of the starting heteroatom compounds, and therefore it is often difficult to oxidize the heteroatom compounds without affecting the carbon nucleophiles. The second problem is overoxidation. Since the carbon–carbon bond formation products are also heteroatom compounds and carbon is slightly more electron donating than hydrogen, the oxidation potentials of the products are



Scheme 5

Table 5 Oxidation potentials of 1,2-disilyl- and 1,2-distannyl-substituted ethanes and related compounds

| Compound | E_d/V (vs. Ag–AgCl) * | Compound | E_d/V (vs. Ag–AgCl) * |
|----------|-------------------------|----------|-------------------------|
| | 2.19 | | >2.5 |
| | 2.20 | | 1.65 |
| | 1.74 | | 1.41 |
| | 2.02 | | 1.41 |
| | 1.45 | | 0.66 |
| | 1.22 | | |

* Decomposition potential determined with rotating-disc electrode voltammetry in $\text{LiClO}_4\text{-CH}_3\text{CN}$ using a glassy carbon working electrode and a Ag–AgCl reference electrode.

slightly less positive than those of the starting material. Therefore, oxidation of the product is difficult to avoid.

The use of tin as an activating group (electroauxiliary) solves these two problems. The introduction of tin causes a dramatic decrease in the oxidation potentials of heteroatom compounds. The oxidation potential of tin-substituted heteroatom compounds is less positive than that of various carbon nucleophiles such as enol silyl ethers and allylsilanes. Therefore, tin-substituted heteroatom compounds can be oxidized selectively in the presence of these carbon nucleophiles. The carbocation intermediate generated by the cleavage of the C–Sn bond reacts with carbon nucleophiles to give the product. Since the product does not contain tin, its oxidation potential is higher than the starting tin-containing compounds.²³ Therefore, there is no longer a problem with overoxidation. Several examples of electrooxidative carbon–carbon bond formation using tin-substituted heteroatom compounds are shown in Scheme 5. Chemical oxidation reactions of α -heteroatom-substituted organotin compounds aimed at achieving carbon–carbon bond formation have also been developed.²⁴

3.3 Electron transfer from σ systems (σ,σ -interaction)

The interaction of a carbon–metal (metal = Si or Sn) σ orbital with a neighboring carbon–metal σ orbital is also effective in raising the HOMO level.²⁵ As a matter of fact, the oxidation potential of 1,2-bis(trimethylsilyl)ethane is much less positive

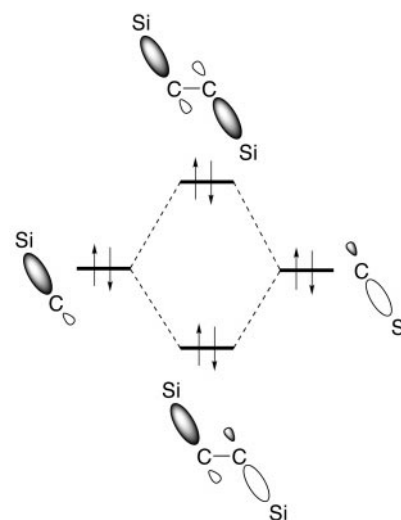


Fig. 13 Energy diagram of the interaction of two neighboring C–Si σ orbitals

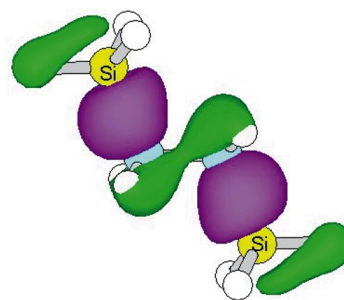


Fig. 14 The HOMO of $\text{H}_3\text{SiCH}_2\text{CH}_2\text{SiH}_3$ (HYPERCHEM 5, HF/3-21G*)

than that of (trimethylsilyl)ethane which has only one C–Si bond (Table 5).²⁶ The lower oxidation potential of 1,2-bis(trimethylsilyl)ethane is attributed to the interaction between the C–Si σ orbitals raising the HOMO level (Fig. 13). The HOMO of $\text{H}_3\text{SiCH}_2\text{CH}_2\text{SiH}_3$ is shown in Fig. 14, which indicates the antibonding interaction between two neighboring C–Si σ orbitals. It is also noteworthy that the oxidation potential of 1,2-bis(trimethylsilyl)ethane is much lower than those of bis(trimethylsilyl)methane and 1,3-bis(trimethylsilyl)propane, indicating the importance of the interaction of the two neighboring orbitals. The geometric requirements of the present

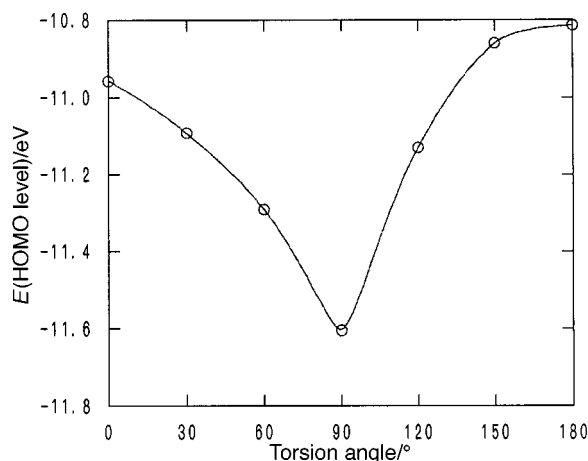
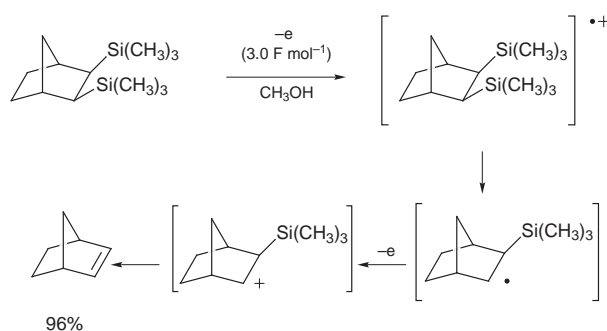


Fig. 15 Plots of HOMO level of $\text{H}_3\text{SiCH}_2\text{CH}_2\text{SiH}_3$ vs. torsion angle of Si-C-C-Si (MP2/LANL2DZ)



Scheme 6

effect are also interesting. The oxidation potential of *cis*-(*exo,exo*)-1,2-bis(trimethylsilyl)norbornane (Si-C-C-Si torsion angle *ca.* 1°) is less positive than that of *trans*-1,2-bis(trimethylsilyl)norbornane (torsion angle *ca.* 107°). This is consistent with the molecular orbital calculations which indicate that the HOMO is at a minimum when the torsion angle is 90° (Fig. 15).

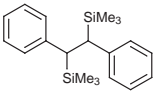
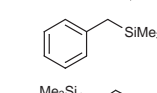
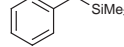

The concept of σ - σ interaction is also applicable to organotin compounds.²⁶ The oxidation potential of 1,2-bis(tributylstannyl)ethane is much lower than that of (tributylstannyl)ethane, indicating significant interaction between the two C-Sn σ orbitals raising the HOMO level. It is also interesting that the C-Si σ orbital and the C-Sn σ orbital interact with each other less effectively, as demonstrated by the oxidation potential of 1-tributylstannyl-2-(trimethylsilyl)ethane. Probably the energy match between the two σ orbitals is not good for effective interaction because the energy level of the C-Sn σ orbital is much higher than that of the C-Si σ orbital.

The preparative electrochemical oxidation of 1,2-bis(trimethylsilyl)norbornane results in the cleavage of two C-Si bonds to yield norbornene (Scheme 6).²⁶ Presumably one of the C-Si bonds is cleaved in the cation radical intermediate to generate the carbon radical which is further oxidized to give the carbocation. The subsequent facile β -elimination of the silyl group produces a carbon-carbon double bond.

4 Combination of the σ, π -Interaction System and the σ, σ -Interaction System

In the previous part of this account it was demonstrated that the C-Si and C-Sn σ orbitals interact with neighboring π -systems, n-systems and σ -systems to raise the HOMO level which in turn favors electron transfer. It is interesting to examine whether such interaction systems interact with each other. 1,2-Diphenyl-1,2-bis(trimethylsilyl)ethane is an example of a system which involves σ, π -interaction systems and a σ, σ -inter-

Table 6 Oxidation potential of 1,2-diphenyl-1,2-bis(trimethylsilyl)ethane and related compounds

| Compound | E_d/V (vs. Ag-AgCl) * |
|--|-------------------------|
|  <i>meso</i> | 1.23 |
|  DL | 1.32 |
|  | 1.39 |
|  | 1.74 |

* Decomposition potential determined with rotating-disc electrode voltammetry using a glassy carbon working electrode in $\text{LiClO}_4\text{-CH}_3\text{CN}$.

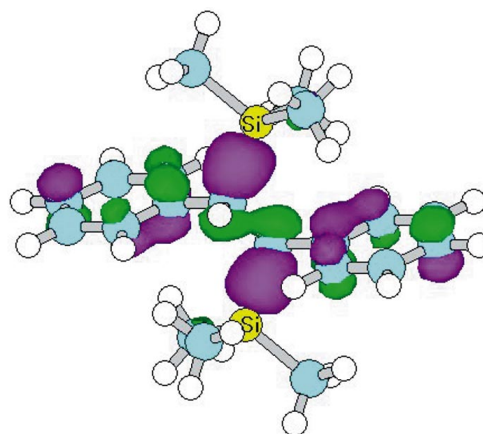


Fig. 16 The HOMO of $\text{PhCH}(\text{SiMe}_3)\text{CH}(\text{SiMe}_3)\text{Ph}$ (HYPERCHEM 5, PM3)

action system. The oxidation potential of this compound is less positive than that of benzyltrimethylsilane (σ, π -interaction system) and that of 1,2-bis(trimethylsilyl)ethane (σ, σ -interaction system), indicating that the two systems interact with each other effectively to raise the HOMO level (Table 6).²⁷ The molecular orbital calculations also indicate that the HOMO is localized through two C-Si bonds and two benzene rings as shown in Fig. 16. This fact demonstrates the potential of the conjugation between the σ, σ -interaction systems and the σ, π -interaction systems to construct various new electronic systems. Such effective conjugation provides a new concept in material science.

5 Conclusion

It is hoped that with the aid of molecular orbital calculations and computer graphics this Perspective helps to demonstrate to the reader that silicon and tin promote electron transfer from β -situated π systems, heteroatoms and σ systems, and that this effect is attributed to the interaction of C-Si or C-Sn σ orbitals with neighboring p-type orbitals. Such σ - π interaction, σ -n interaction and σ - σ interaction enjoy versatile applications in the field of electron transfer. Several examples of the redox selective reactions of organo-silicon and -tin compounds based on these orbital interactions are demonstrated in this Perspective, although many other examples are omitted because of space limitations. Further work is in progress to explore the full scope of this concept and its application to synthetic transformations.

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