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Theoretical Study of the Reaction of Allylsilanes with Carbonyl Compounds

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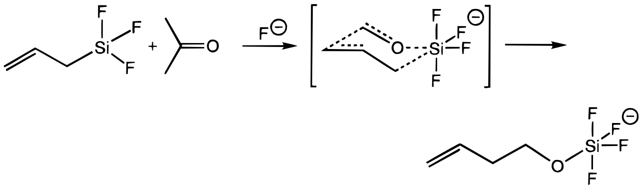
Abstract: We have studied the reaction of allylsilanes with aldehydes by applying the *ab initio* MO theory. It has been shown that the reaction takes place *via* a transition state involving pentacoordinated silicon species. The oxygen of aldehyde attacks an apical site of the silicon center, while the allyl group departs directly from an equatorial site without causing a pseudorotation. The calculation has shown that the reaction of an allylsilacyclobutane model with formaldehyde has a lower activation barrier than the reaction of allylsilane or methyl-substituted allylsilanes. The barrier height is shown to be correlated well with the angle of coordination of substituents on the silicon center. The reactivity of allylsilanes against nucleophiles is discussed by evaluating the local acidic strength of the reaction site.

Introduction

Pentacoordinated silicon species have been studied extensively both from experimental and from theoretical viewpoints.[1−26] In many cases, those species are assumed to intervene as stable intermediates in reactions.[1,3,5] High reactivities of silicon compounds and high stereoselectivities in reactions have been interpreted successfully by invoking pentacoordinated intermediates. One of those examples involving a pentacoordinated silicon species is the reaction between allylsilanes and carbonyl compounds.[27−32] Kira suggested the following mechanism (Scheme 1).[31]

Scheme 1



On the other hand, Oshima and collaborators revealed that there was a marked difference between allylphenylsilacyclobutane and allylphenyldimethylsilane in their reactivities against benzaldehyde.[33] While heating of a mixture of the former and benzaldehyde at 130 °C for 12 h under argon provided 1-phenyl-3-buten-1-ol in 85% yield, the latter resulted in the recovery of starting materials after heating with benzaldehyde at 160 °C for 24 h (Scheme 2). They conjectured that silacyclobutane should be a stronger Lewis acid than the corresponding

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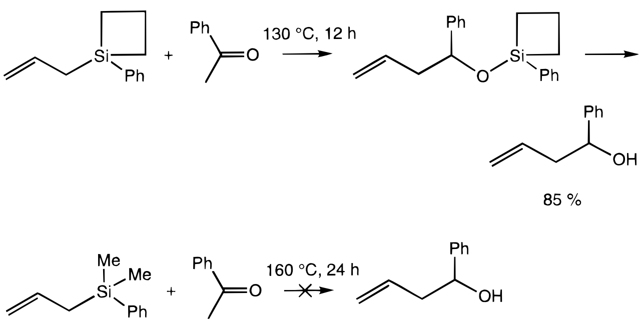
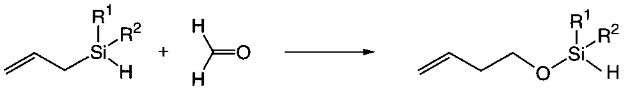
Scheme 2



tetraalkylsilanes. A pentacoordinated species is suggested to be the transition state in this case. In order to clarify whether the pentacoordinated species is a transition state or an intermediate and to understand the reactivities of those compounds, we have attempted an MO study on simplified model systems.

Results and Discussion

Structures and Activation Energy. To make *ab initio* MO calculations feasible, we set up simplified models which consist of allylsilanes, **1a**−**d**, and formaldehyde.[34] All the phenyl groups in allylphenylsilacyclobutane, allylphenyldimethylsilane, and benzaldehyde in the actual systems were replaced by hydrogens. Calculations were made at the RHF level with the 6-31G* and 6-31G** basis sets and at the MP2 level with the 6-31G** basis set by applying the Gaussian 92 program.[35,36] The reacting systems have no electronic charge as a whole.



1a−**d** **2a**−**d**

1a, **2a** : R^1, R^2 = $-CH_2CH_2CH_2-$
1b, **2b** : R^1 = Me, R^2 = Me
1c, **2c** : R^1 = Me, R^2 = H
1d, **2d** : R^1 = H, R^2 = H

The calculated structure of allylsilacyclobutane, **1a**, in an isolated state and that of the transition state for the reaction with formaldehyde are illustrated in Figure 1. It is seen that a six-membered cycle is formed at the transition state, involving the silicon center and the allyl unit of **1a** and the carbonyl group of the formaldehyde molecule. The silicon center provides a pentacoordinated arrangement, where the carbonyl oxygen and one of the carbons C^3 in the trimethylene unit occupy the apical positions. The X(ap.)−Si−Y(eq.) angle in the pentacoordinated silicon species is smaller than the angle between two bonds in the tetravalent species. This may be a reason why the C^1−Si−C^3 angle in the silacyclobutane ring is reduced by a small amount, 2.3°, in going from **1a** to the transition state. The C^3−Si bond is lengthened, however, from 1.898 Å in **1a** to 1.942 Å at the transition state. The strain in the ring may partly be liberated. Notably, the pentacoordinated species is not an intermediate but is the transition state in the present system.

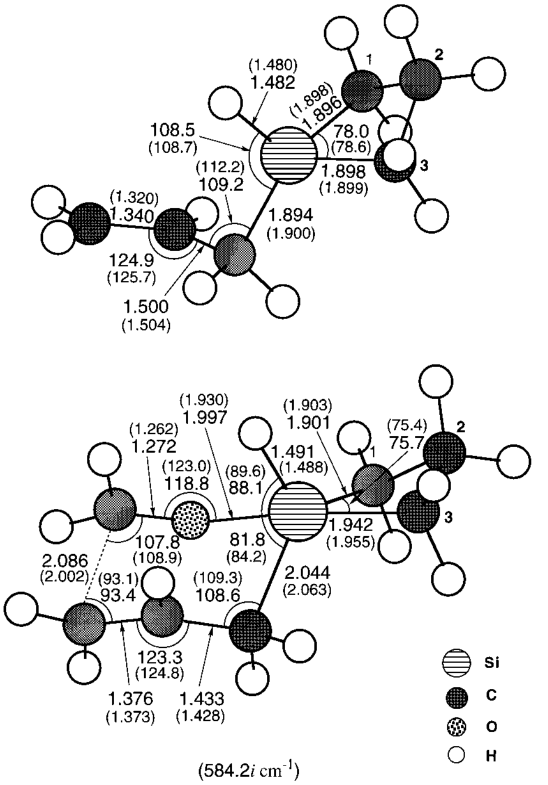


Figure 1. The structures of **1a** (above) and the transition state for the reaction of **1a** with formaldehyde (below) optimized at the MP2/6-31G** level of theory. Values in parentheses indicate the results obtained by RHF/6-31G* calculations.

An analysis of the reaction coordinate has shown that this reaction is initiated by an attack of the oxygen of formaldehyde to occupy an apical site of the silicon center.[37] A ligand leaves usually from an apical site by inducing a pseudorotation of ligands around the pentacoordinated silicon center.[1,7,38] It is interesting, however, to see that the allyl group departs from the silicon in an equatorial plane in this case. In the present system, the formation of the Si−O bond and the breaking of the Si−C bond take place in a concerted manner. The more electronegative oxygen tends to occupy the apical site, while the O−Si−C angle should be retained in the range <110° to form a six-membered ring. Thus, the allylic carbon should depart preferably from the equatorial site.

The calculated structures of **1b** and the transition state for the reaction with formaldehyde are presented in Figure 2. The mechanism is very similar to the reaction of **1a** giving a six-membered ring at the transition state. Similar transition-state structures have also been obtained for **1c** and **1d**. Table 1 compares the activation energy of **1a** with those of **1b**−**d**. It is seen that the barrier height for **1a** having a silacyclobutane unit is considerably lower than that of **1b**−**d**. This result agrees qualitatively with the reactivity trend observed experimentally for the reactions of phenyl-substituted allylsilanes with benzaldehyde.

The major difference between **1a** and **1b** at the transition state is found in the C−Si−C angle. It is 75.7° in the former and 100.8° in the latter. In order to investigate the effect of the C−Si−C angle on the reactivity, we have carried out calculations on an imaginary system in which the C−Si−C angle of

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[34] When the phenyl group was not replaced by a hydrogen in allylsilanes, **1c** would be optically active.

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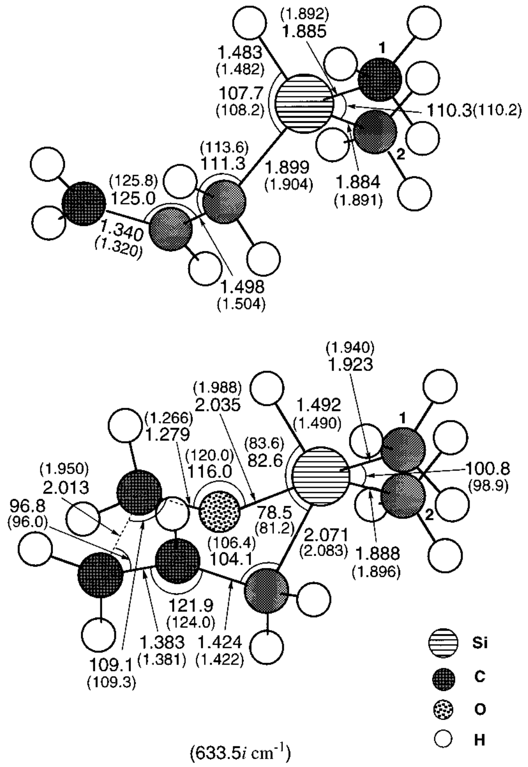

Figure 2. The structures of **1b** (above) and the transition state for the reaction of **1b** with formaldehyde (below) optimized at the MP2/6-31G** level of theory. Values in parentheses indicate the results obtained by RHF/6-31G* calculations.

Table 1. Total Energy of Allylsilanes and of Transition States for the Reaction with Formaldehyde[a]

species	allylsilane	formaldehyde	transition state	activation energy[b]
1a	−523.07287	−113.86633	−636.89064	30.5[c] (33.3)[d]
	−523.09293	−113.86974	−636.91374	30.7[e]
	−523.09165	−113.86727	−636.91239	29.2[f]
1b	−485.24181	−113.86633	−599.04371	40.4[c] (43.6)[d]
	−485.26245	−113.86974	−599.06718	40.8[e]
	−485.26154	−113.86727	−599.06522	39.9[f]
1c (*R*)	−446.19489	−113.86633	−559.99977	38.6[c]
1c (*S*)	−446.19461	−113.86633	−560.00150	37.3[c]
1d	−407.14757	−113.86633	−520.95646	36.0[c]

[a] Total energy is given in hartrees. [b] Activation energy is given in kcal/mol. [c] RHF/6-31G*. [d] Corrected for the zero-point vibration energy.[35b] [e] RHF/6-31G**. [f] MP2/6-31G**.

Table 2. Effect of the C−Si−C Angle on the Reactivity of Allyldimethylsilane with Formaldehyde

C−Si−C angle (deg)	activation energy (kcal/mol)[a]	C−Si−C angle (deg)	activation energy (kcal/mol)[a]
70.0	26.5	90.0	34.5
(78.0)	(30.5)[b]	100.0	38.6
80.0	30.4	(110.2)	(40.4)[c]

[a] RHF/6-31G*. [b] Allylsilacyclobutane. [c] C−Si−C angle not frozen.

1b is fixed at an angle both in the initial state and in the transition state. The activation energy calculated in this manner is presented in Table 2. Those values are only for the purpose of understanding the reactivity trend of allylsilanes, but one sees that the barrier height becomes lower as the C−Si−C bond angle is made smaller. The barrier height for the reaction of **1a** is located very close to that of **1b** with the C−Si−C angle frozen at 80°. The result of calculations suggests that the reactivity of allylsilanes against nucleophiles is related intimately with the local arrangement of bonds around the silicon center.

Lewis Acidic Strength of the Reaction Site. It has been suggested experimentally that the high reactivity of allylsilacyclobutanes against aldehydes should originate from a strong Lewis acidic nature of the silicon center.[32,33,39,40] It is interesting then to find a way of estimating the electrophilicity or Lewis acidic strength of the silicon center by MO calculations. It is necessary to estimate the strength in a particular direction in the three-dimensional space from which the oxygen of the aldehyde would attack.

The transition states presented in Figures 1 and 2 tell us the direction from which the oxygen of formaldehyde attacks the silicon center. An orbital of the silicon that extends in that direction should play a crucial role. It is generated by combining the 3s, 3p (and 3d) AO's of the silicon atom. If the orbital consists mainly of low-lying unoccupied MO's of an allylsilane molecule, the silicon center will be a strong electron acceptor. On the contrary, if the orbital is found for the most part in the occupied MO's or in the high-lying unoccupied MO's of an allylsilane molecule, the silicon center will be a poor electron acceptor. In order to discuss the electrophilicity of the silicon center, we should find out for each allylsilane molecule an *unoccupied orbital* that is closest in shape and in energy to the *reference orbital* of silicon, having the maximum amplitude in the direction of the oxygen attack.[41] To make the present application clearer, we may mention briefly the procedure.

The reference orbital denoted here by δ_r can be expanded in terms of the occupied canonical MO's ϕ_i and the unoccupied canonical MO's ϕ_j of an allylsilane molecule.[41]

$$\delta_r = \sum_i^{\mathrm{oc}} d_{i,r}\,\phi_i + \sum_j^{\mathrm{unoc}} d_{j,r}\,\phi_j \tag{1}$$

Then, the unoccupied orbital that is the closest to δ_r is defined simply by[41]

$$\phi_{\mathrm{unoc}}(\delta_r) = \left(\sum_j^{\mathrm{unoc}} d_{j,r}\,\phi_j\right)\Big/\left(\sum_j^{\mathrm{unoc}} d_{j,r}^2\right)^{1/2} \tag{2}$$

The orbital is given by a linear combination of the unoccupied canonical MO's and, therefore, the *electron-accepting capacitance* of the orbital δ_r is evaluated by[41]

$$\lambda_{\mathrm{unoc}}(\delta_r) = \left(\sum_j^{\mathrm{unoc}} d_{j,r}^2\,\epsilon_j\right)\Big/\left(\sum_j^{\mathrm{unoc}} d_{j,r}^2\right) \tag{3}$$

where ϵ_j is the orbital energy of the component unoccupied MO ϕ_j. The denominator in eq 2 is the normalization factor which allows us to compare *local* strengths of reaction sites as electron acceptors within a molecule and between molecules in a unified manner. A stronger electron acceptor should have a lower λ_{unoc} value.

In order to discuss the reactivity trend of allylsilanes, it may be more useful to evaluate such a quantity for molecules in an isolated state than to make a comparison at the transition states. In the present case, the carbonyl oxygen attacks an apical site of the silicon center at the transition state. It has been shown in our previous study that p-type AO functions play the dominant role in binding the ligands at the apical sites in pentacoordinated silicon species.[21] Then, the orbital δ_r may be

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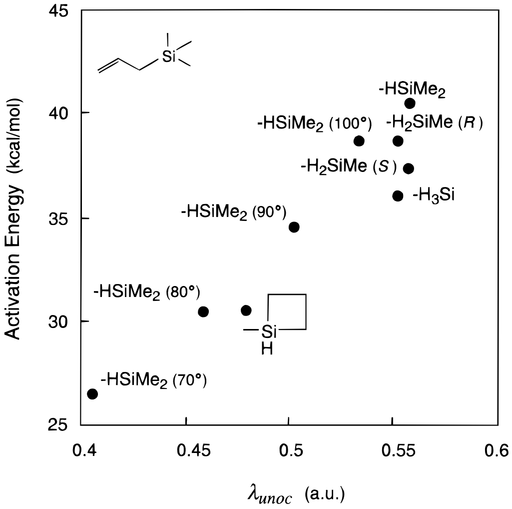
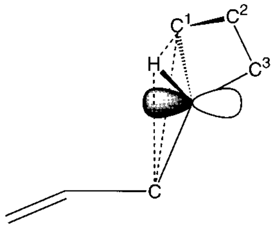


Figure 3. Relation between the calculated activation energies and the electron-accepting strengths of the silicon center calculated by taking the 3p AO which will interact with the oxygen of formaldehyde to give a pentacoordinated transition state.

taken simply as a combination of the $3p_x$, $3p_y$, and $3p_z$ AO's of the silicon pointing at the center of the triangle defined by the three adjacent atoms, a hydrogen atom, C^1 of the silacyclobutane ring, and an allylic carbon.[42]



We attempted first to find a combination of the inner and outer parts of Si 3p functions that gives the lowest value of λ_{unoc} for the 6-31G** calculations. It was 0.233 au for **1a** and 0.287 au for **1b**, indicating that the former had a low-lying unoccupied reactive orbital relative to the latter. Allylsilacyclobutane should be a stronger electron acceptor than allyldimethylsilane. The participation of the inner function of the Si 3p AO's was found to be small, 14% in weight in **1a** and 9% in weight in **1b**. The inner functions might not have been utilized effectively in **1a** to form Si−C bonds in such a strained bond arrangement around the silicon center.

The concept of bonds or orbitals may be easier to imagine in the minimal basis calculations. By using the STO-3G MO's,[43] λ_{unoc} was evaluated to be 0.480 au for **1a** and 0.557 au for **1b**. Unfortunately, we do not have the rate constants of the reactions observed for a variety of allylsilanes at the same reaction condition. Then, we have plotted λ_{unoc} against the calculated activation energies for **1a**−**1d** and for **1b** with the C−Si−C angle fixed at several values in Figure 3. One finds a good correlation between the two theoretical quantities. Now, the high reactivity of allylsilacyclobutane is attributed to its strong electron-accepting ability of the silicon center originating mainly from its small C−Si−C angle. The second lowest unoccupied MO, as shown in Figure 4 for **1a**, has been found to be the major component of ϕ_{unoc} at the STO-3G level MO calculations in the molecules studied here. Reactivities of molecules are often discussed in terms of the frontier MO.[44] One looks at the amplitude of the MO on some particular AO or AO's of the reaction site, as well as its energy level. Then, the present approach provides a simple alternative which evaluates the contributions of all the MO's relevant for an interaction. Incidentally, the methyl-substituted and dimethyl-substituted allylsilanes, **1b** and **1c**, have λ_{unoc} values similar to that of allylsilane, **1d**. Thus, the higher activation energy calculated for **1b** or for **1c** relative to **1d** may be ascribed to steric repulsion.

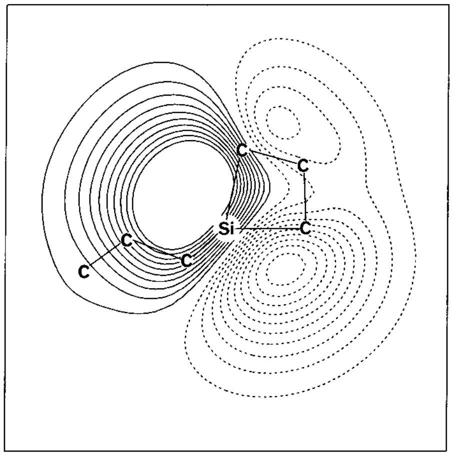


Figure 4. The second lowest unoccupied MO of **1a**. The orbital was plotted in the plane which is determined by the Si, C^1, and C^3 atoms.

The *electron-donating potential* $-\lambda_{\text{oc}}$ of the reference orbital can be estimated in a similar manner by examining the occupied MO space.[41] Then, the orbital δ_r is placed in energy between λ_{oc} and λ_{unoc}:[45]

$$\begin{aligned}\lambda(\delta_r) &= \sum_i^{\text{oc}} d_{i,r}^2\, \lambda_{\text{oc}}(\delta_r) + \sum_j^{\text{unoc}} d_{j,r}^2\, \lambda_{\text{unoc}}(\delta_r) \\ &= a^2\lambda_{\text{oc}}(\delta_r) + (1-a^2)\lambda_{\text{unoc}}(\delta_r) \qquad (4)\end{aligned}$$

The 3p AO of the silicon center chosen as δ_r is partially filled in allylsilane molecules, being composed of the occupied canonical MO's and unoccupied MO's, as given by eq 1. Then, the coefficients $|a|$ $(1 \le a^2 \le 1)$ and $(1 - a^2)^{1/2}$ measure the contributions from the occupied MO space and from the unoccupied MO space to the orbital δ_r, respectively. When the reaction site serves as an electron acceptor, $|a|$ indicates the fraction of the projected orbital ϕ_{unoc} that is not utilized for the interaction. Accordingly, a^2 should be smaller in order to give the reaction site a stronger electron-accepting ability.

Parr and collaborators have suggested that the *global chemical hardness* of a molecule is estimated in terms of ionization potential and electron affinity by $(I - A)/2$ or $(-\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$.[46,47] This should be a *molecular* property analogous to the electronegativity given by Mulliken.[48] The quantities $-\lambda_{\text{oc}}$ and $-\lambda_{\text{unoc}}$ defined above correspond respectively to the *local* ionization potential and *local* electron affinity of a reaction

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[42] It is also possible to take an atomic hybrid orbital or a combination of several AO's delocalized over the reaction site and nearby atoms as the orbital δ_r.

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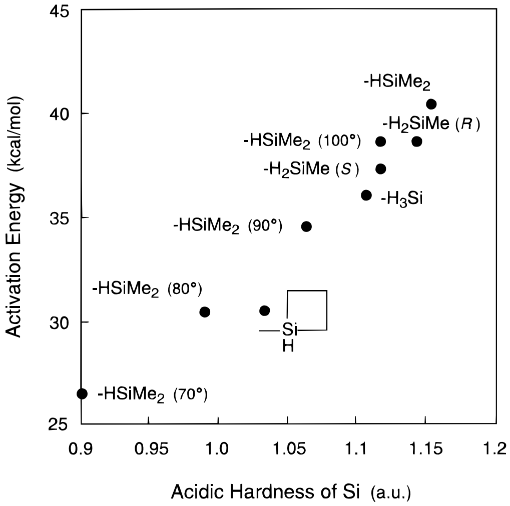

Figure 5. Relation between the calculated activation energies and acidic hardness of the 3p AO of the silicon having the extension in the direction of the oxygen attack.

site in a molecule. Similarly, λ is a measure of chemical potential (or electronegativity) of an atom or a group which stands for its power to attract electrons in a molecule. Thus, we may define the *local hardness* of the silicon center in the direction of the attacking nucleophile by[45]

$$\eta(\delta_r) = \{-\lambda_{oc}(\delta_r) + \lambda_{unoc}(\delta_r)\}/2 \qquad (5)$$

Now, we have

$$\lambda_{unoc}(\delta_r) = \lambda(\delta_r) + 2a^2\eta(\delta_r) \qquad (6)$$

The reactive orbital ϕ_{unoc} is elevated in energy by $2a^2\eta$ relative to the orbital δ_r. Since $|a|$ is the inactive fraction of ϕ_{unoc}, the second term is regarded as indicating a resistance of the orbital δ_r against electron acceptance. Hence, it may be called the *acidic hardness* of the reaction site. The relation between λ and λ_{unoc} is illustrated schematically as follows:[45]

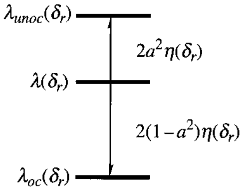

Figure 5 illustrates the relation between the acidic hardness of the silicon center and the calculated activation energies. Again, we find a good correlation between the two calculated quantities. The acidic hardness is shown to be considerably smaller in allylsilacyclobutane, 1.03 au, than in allyldimethylsilane, 1.15 au, with the normal C−Si−C angle.[49] In addition, the acidic hardness becomes smaller as the C−Si−C angle is made smaller in the dimethyl-substituted model, **1b**.

The Lewis acidic strength used by experimental chemists seems to be slightly different from the acidic hardness introduced above. The strength may be closer to the local electron-accepting capacitance itself. As shown above, the capacitance depends both on the local chemical potential λ and the acidic hardness of a reaction site, $2a^2\eta$. It should be noted that acidic hardness in the present treatment can evaluate the ability of a molecule to localize the interaction on the reaction site. The localizability will change from one site to the other site within a molecule to determine the most reactive position in a large molecule. In any case, the strength of the silicon center as an electron acceptor is demonstrated in the present analysis to govern the reactivity of allylsilanes against carbonyl compounds.

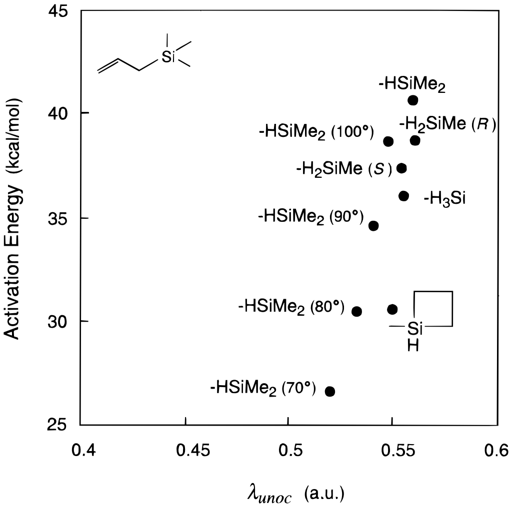

Figure 6. Relation between the calculated activation energies and the electron-accepting strengths of the 3p AO of the silicon center calculated by assuming an attack of aldehyde from the back side of a Si−CH_3 or Si−H bond.

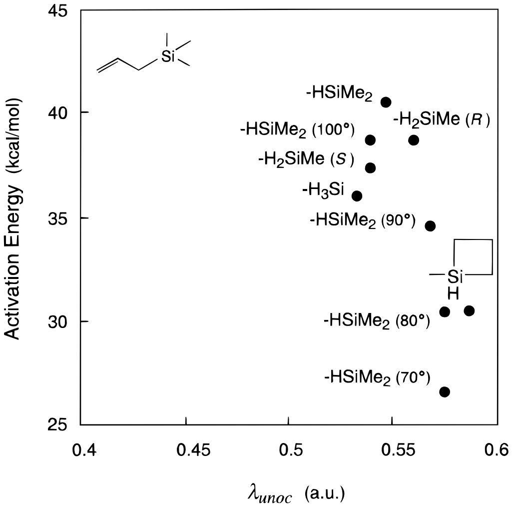

Figure 7. Relation between the calculated activation energies and the electron-accepting strengths of the 3p AO of the silicon obtained by assuming an S_N2 type substitution mechanism.

By assuming an attack of the carbonyl oxygen directly from the back side of Si−C^3 bond in **1a** and Si−C^2 bond in **1b**, we tested another 3p AO that was oriented along the Si−C bond. The orbital was taken also along the Si−CH_3 bond in the case of **1c** (*S*), but along a Si−H bond in the case of **1c** (*R*) and in **1d**. The λ_{unoc} values obtained from the STO-3G MO's correlate with the calculated barrier heights as illustrated in Figure 6, but do not differ significantly among the molecules studied. The acidic hardness term has been calculated to be 1.16 au for **1a** and 1.15 au for **1b**. Another reaction mechanism we have examined is an S_N2 type substitution of the allyl group by the carbonyl oxygen. By taking a 3p AO having the direction along the Si−C (allyl) bond as the reference orbital, we have obtained the electron-accepting capacitance of the silicon center presented in Figure 7. We do not find any significant correlation between the two calculated quantities in this case. The silicon center in **1a** does not show a stronger electron-accepting ability than that

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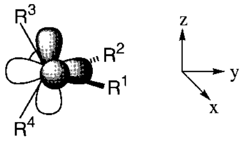
(49) The acidic hardness has been calculated to be 0.748 au for **1a** and 0.883 au for **1b** in the MO calculation at the 6-31G** level of theory. Relative magnitudes are of significance.

in **1b**. These results indicate that the aldehyde is most likely to attack the silicon center from the least-hindered direction which is also the direction of the strongest electron-accepting ability of allylsilacyclobutane. Then, the reaction goes through a six-membered cyclic transition state involving a pentacoordinated silicon center, as depicted in Figure 1. An important conclusion derived here is that allylsilacyclobutane shows a strong acidic property when a nucleophile attacks the silicon center within a certain solid angle. That is, the reactivity of the silicon center is very directional in the space.

The difference in reactivity of allylsilanes may be understood in a naive way by considering hybridization around the silicon center. Chemical bonds in tetravalent silicon species may be represented by means of the hybrids of 3s AO and three 3p AO's of Si and the AO's of ligands. Then, if the $R^1{-}Si{-}R^2$ angle is squeezed, the $R^3{-}Si{-}R^4$ angle is made wider and the Si−R bonds come to be represented mainly by the 3s, $3p_y$, and $3p_z$ AO's. The ligands $R^1{-}R^4$ are more electronegative and, accordingly, there is a depletion of electrons in the silicon center. Thus, the $3p_x$ AO should be found predominantly in the unoccupied MO's and will be utilized effectively to form a bond with an attacking nucleophile. The high reactivity of allylsilacyclobutane relative to allyldimethylsilane is interpreted in this manner. The reason why acidic strength of the silicon center in allylsilanes is related to its C−Si−C angle is given in the same context. The acidic hardness presented above provides a numerical scale of estimating the strength of acids.



An alternative interpretation of the reactivity trend might be given on the basis of the relaxation of angle strain. In the reaction of **1b**, the C−Si−C angle is reduced from 110.3° to 100.8° on going from an isolated tetravalent state to the pentacoordinated transition state. This change may destabilize the reacting system. In contrast, the C−Si−C angle is reduced only by a small margin in **1a**, from 78.0° to 75.7°, on going from an isolated state to the transition state. As mentioned above, the strain in the ring in **1a** should be reduced by stretching a C−Si bond. The calculations on an imaginary system **1b** with fixed C−Si−C angles have shown, however, that the system with a smaller angle gives a lower activation energy. This strongly supports the proposition that the Lewis acidic strength of silicon center is a key to understanding the reactivity trend of allylsilanes.[28,33,34]

Conclusion

The present study of the reaction of allylsilanes with formaldehyde has shown that the reaction takes place via a pentacoordinated transition state. The oxygen of aldehyde attacks the apical site of the silicon center, while the allyl group departs from the silicon center in the equatorial plane without causing pseudorotation. The reaction of allylsilacyclobutane has been shown to have a considerably lower activation energy than the reaction of allyldimethylsilane. Calculations on an imaginary model system have revealed that the barrier height is related to the arrangement of bonds at the silicon center. To find the effect of local structure of allylsilanes on reactivities, electron-accepting ability and acidic hardness of the silicon center have been evaluated by projecting the 3p AO of the silicon atom extending in the direction of the nucleophilic attack onto the unoccupied MO space of allylsilane molecules. These quantities have been found to correlate well with the calculated activation energies of the reaction.

Sizable molecules are multifunctional in chemical reactions, having several reaction sites. It is not easy to interpret those reactivities in terms of an MO or to find out the MO's that participate actively in interactions of large reactant molecules with a reagent. Chemical interactions are local by nature and are very directional in the three-dimensional space. Some reagents will attack the reactant from the preferred direction in the space to yield a product selectively, whereas some others will not, being hindered, for example, by steric repulsion. Examination of local electron-accepting ability of a site in a particular direction allows us a comparison of molecules that are different in size and structure and, hence, will be of use in discussing the reactivity of silicon species and other organometallic compounds.

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