

Electron-Donating and -Accepting Strength of Enoxysilanes and Allylsilanes in the Reaction with Aldehydes

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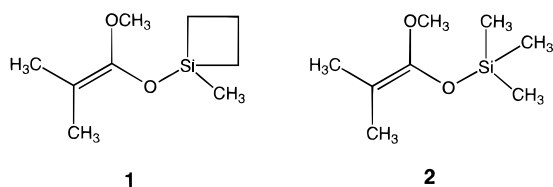
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Abstract: The reactivity of enoxysilanes against aldehydes has been discussed theoretically in terms of the local electron-accepting ability and the Lewis acidic hardness of the silicon center. Those quantities have been evaluated by choosing a Si 3p atomic orbital that will play the major role in the formation of a new bond with the aldehyde oxygen and by projecting out the reactive unoccupied orbital for each enoxysilane molecule that shows the maximum amplitude on that AO. They change significantly depending on the arrangement of bonds around the silicon center. The activation energy calculated for the reaction of enoxysilanes with formaldehyde correlates well with both of the two quantities, showing that 1-enoxysilacyclobutane having a small C–Si–C angle is a stronger Lewis acid than methyl-substituted enoxysilanes. The acidic hardness of silicon in enoxysilane has been found to be very similar in magnitude to that of silicon in the corresponding allylsilane. In contrast, the γ -carbon of an enoxy group has a higher electron-donating ability than that in an allyl group, suggesting that enoxysilanes are more reactive against aldehydes.

Introduction

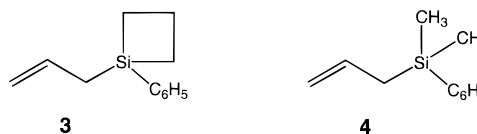
Aldol reaction of enoxysilanes is one of the most useful and familiar transformations for the construction of carbon–carbon bonds.¹ It is carried out usually in the presence of a stoichiometric or catalytic amount of an activator which is most commonly a Lewis acid.² On the other hand, Denmark and collaborators have proposed that the silicon atom constrained in a four-membered ring and attached to an enolate oxygen should behave like a coordinatively unsaturated group III element.³ The proposal was realized by uncatalyzed, room temperature aldol reactions of *O*-(silacyclobut-1-yl) ketene acetals, ketene thioacetals, and ketene amins with aldehydes. For instance, **1** reacts very rapidly with benzaldehyde ($t_{1/2} = 5$ min) at 20 °C in C₆D₆. In contrast, the corresponding enol trimethylsilane **2** has shown no sign of reaction under the same



conditions after 15 days.³ The principle of “ligand-accelerated catalysis” related to the concept of “strain release Lewis acidity” underlies the proposal.^{4,5} Myers also observed dramatic increases in the rate of the reactions of proline-derived *N,O*-ketene silyl acetals with benzaldehyde of 10-fold for silacyclopentane

and around 10⁶ times for silacyclobutane compared to dimethylsilyl derivatives.⁶

Enhancement of reactivity against aldehydes by compressing the tetrahedral silicon atom valency into a four-membered ring has also been reported for the reaction of allylsilanes. Oshima et al. showed recently that 1-phenyl-3-buten-1-ol was obtained in 85% yield by heating a mixture of 1-allyl-1-phenylsilacyclobutane (**3**) and benzaldehyde at 130 °C for 12 h under argon. On the other hand, allylphenyldimethylsilane (**4**) resulted in the



recovery of the starting materials after heating with the aldehyde at 160 °C for 24 h.⁷ Thus, they conjectured that silacyclobutane should be a stronger Lewis acid than the corresponding tetraalkylsilanes.

The reaction of allylsilanes takes place via pentacoordinated trigonal bipyramidal transition states.⁸ An allylsilane molecule serves first as an electron acceptor at the silicon center to form a new bond with the oxygen atom of an attacking aldehyde. The transfer of the silyl group to the aldehyde follows, as the aldehyde carbon and the allylsilane γ -carbon are brought into bonding proximity. The allylic moiety plays the electron-donor part at this stage. The ability of silicon to expand its coordination number is undoubtedly the most important factor of making the aldol reaction of enoxysilanes useful and powerful in synthetic chemistry, and therefore, the reactivity might be argued in terms of angle strain.^{9–11} On the other hand, our theoretical

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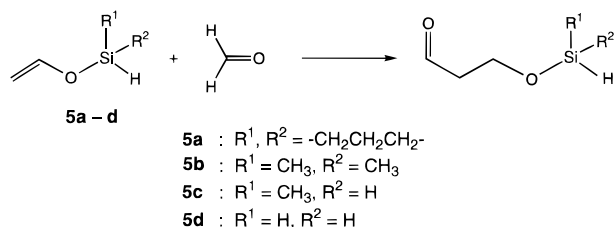
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investigations have demonstrated that the angle of coordination of ligands at the silicon center affects the local electron-accepting ability or the Lewis acidity of the silicon center, making 1-allylsilacyclobutane very reactive against aldehydes relative to methyl-substituted allylsilanes.⁸ This result supports the proposition that the silacyclobutane should be a stronger Lewis acid than tetraalkylsilanes.⁷

Another interesting point to be noted here is that 1-enoxysilacyclobutanes appear to be more reactive than the corresponding 1-allylsilacyclobutanes against aldehydes, though no direct attempt has been made experimentally to determine their relative reactivities under the same reaction conditions. Reactions similar to the one of enoxysilanes or allylsilanes mentioned above have been reported for a variety of compounds involving boron,¹² aluminum,¹³ lithium,¹⁴ zirconium,¹⁵ magnesium,¹⁶ titanium,¹⁷ and other metals, and therefore, an analysis of the reactivity of enoxysilanes and allylsilanes will provide us with a clue to establish the reaction mechanisms of wide applicability. The Lewis acid and base are the basic concepts in chemistry. We examine in this paper why 1-enoxysilacyclobutanes are more reactive than dimethylenoxysilanes against aldehydes and compare the reactivity of γ -carbons in enoxysilanes and in allylsilanes against electrophiles by applying the concept of "acidic and basic hardness" derived by the present authors.^{8,18}

Results and Discussion

Comparison of the Reactivity of Enoxysilanes. To make *ab initio* MO calculations feasible, we set up simplified reaction models which consist of enoxysilanes **5a–d** and formaldehyde.



The structure calculations were made at the restricted Hartree–Fock (RHF) level with the 6-31G* and 6-31G** basis sets and partly at the level of second-order Møller–Plesset perturbation theory with the 6-31G** basis set, by applying the Gaussian 92 program.^{19,20} The stability of the RHF solution was examined with respect to the transition-state structure for the reaction of **5a** by comparing with the unrestricted Hartree–Fock result. The reaction has been reported to be carried out neat or in C₆D₆, THF, and CDCl₃.³ It is difficult to determine any systematic change in solvent effects from experimental results, though aromatic solvents seem to give the fastest rates.

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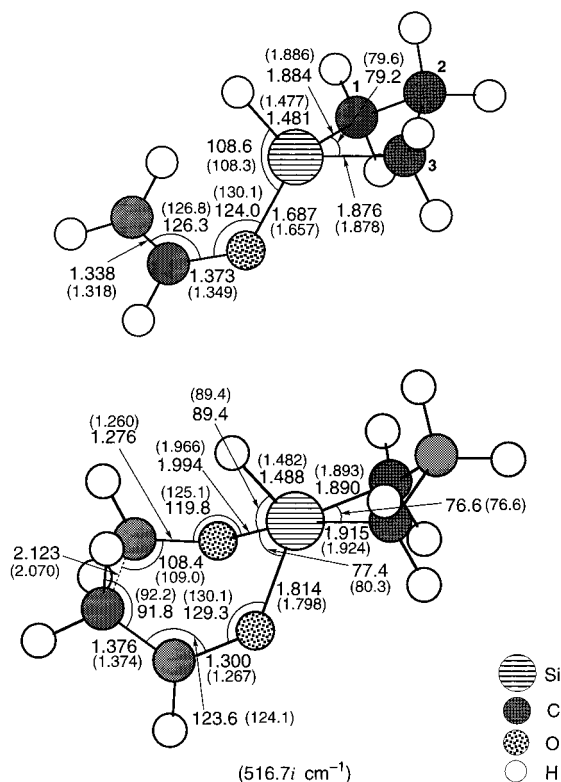


Figure 1. Structures of **5a** (above) and the transition state for the reaction of **5a** with formaldehyde (below) obtained at the MP2/6-31G** level of theory. The results of RHF/6-31G* calculations are given in parentheses.

Thus, we do not take the effect of solvents into account in this study by referring only to the experiments carried out neat or in C₆D₆.

The calculated structure of 1-enoxysilacyclobutane **5a** in an isolated state and that of the transition state for the reaction with formaldehyde are illustrated in Figure 1. The four-membered ring spans one apical and one equatorial position at the transition state. Thus, the C¹–Si–C³ angle is shown to be reduced further by 2.6°, in going from a tetravalent structure in an isolated state to the pentacoordinated transition state. On the other hand, the C³–Si bond spanning an apical site is lengthened from 1.876 Å in an isolated state to 1.915 Å at the transition state to relieve a part of the strain that would be brought into the ring by reducing the C–Si–C angle. The reaction takes a boatlike transition state in accordance with the PM3 calculations reported by Denmark et al.³

The reaction is initiated by an attack of the aldehyde oxygen from the direction as to occupy an apical site at the transition state. The enolate oxygen departs from the silicon center in an equatorial plane, without inducing a pseudorotation of ligands around the pentacoordinated silicon center.^{10,21,22} This is very similar to the reaction of 1-allylsilacyclobutane with aldehyde, as revealed in our previous study.⁸ The incoming carbonyl group and the leaving enoxy group begin to form a new bond at the other ends between two carbon atoms, providing a six-membered ring. It should be more favorable for the enolate oxygen to leave from the silicon center in the equatorial plane to retain the O–Si–O angle in a range suitable for the ring formation.

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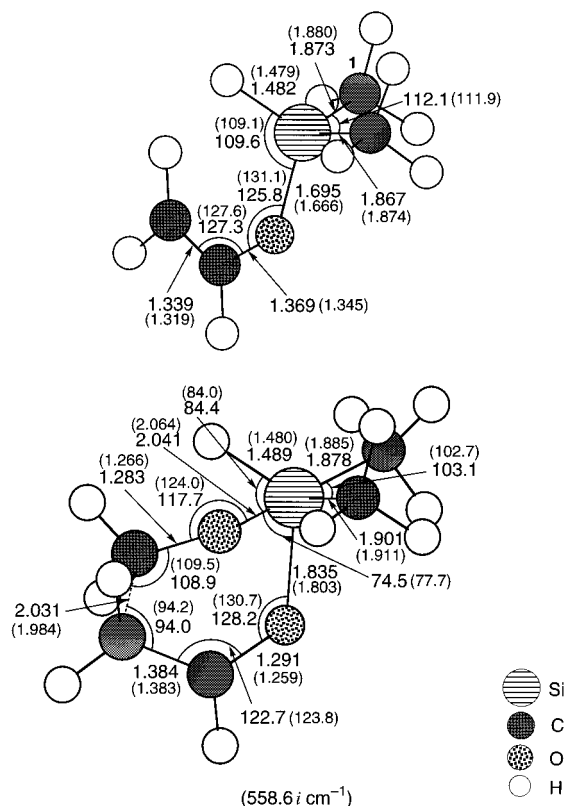


Figure 2. Structures of **5b** (above) and the transition state for the reaction of **5b** with formaldehyde (below) obtained at the MP2/6-31G** level of theory. The results of RHF/6-31G* calculations are given in parentheses.

Table 1. Comparison of the Activation Energies for the Reaction of Enoxysilanes with Formaldehyde^a

species	enoxysilane	formaldehyde	transition state	activation energy ^b	
5a	-558.935 25	-113.866 33	-672.758 83	26.8 ^c	
	-558.952 10	-113.869 74	-672.778 69	27.0 ^d	
	-559.914 98	-114.183 50	-674.083 53	9.4 ^e	
5b	-521.104 88	-113.866 33	-634.915 28	35.1 ^c	
	-521.122 37	-113.869 74	-634.935 51	35.5 ^d	
	-521.957 83	-114.183 50	-636.115 34	16.3 ^e	
	70°	-521.021 08	-113.866 33	-634.852 62	21.8 ^e
	80°	-521.066 19	-113.866 33	-634.892 05	25.4 ^e
90°	-521.089 91	-113.866 33	-634.909 73	29.2 ^e	
100°	-521.101 05	-113.866 33	-634.915 06	32.8 ^e	
5c (R)	-482.055 63	-113.866 33	-595.869 19	33.1 ^c	
5c (S)	-482.054 75	-113.866 33	-595.870 00	32.1 ^c	
5d	-443.005 03	-113.866 33	-556.823 02	30.3 ^c	
	-443.511 98	-114.167 75	-557.657 67	13.8 ^f	
	-443.560 40	-114.183 50	-557.722 78	13.3 ^e	
	-443.568 07	-114.192 02	-557.736 64	14.7 ^g	

^a Total energy is given in hartrees. ^b Activation energy is given in kcal/mol. ^c RHF/6-31G*. ^d RHF/6-31G**. ^e MP2/6-31G**. ^f MP2/6-31G*. ^g MP4/6-31G**/MP2/6-31G*.

The calculated structures of **5b** and the transition state for the reaction with formaldehyde are presented in Figure 2. The mechanism is seen to be essentially the same as that of the reaction of **5a**. It goes through a transition state involving a pentacoordinated silicon and a weak C–C bond. Similar transition-state structures have also been obtained for **5c** and **5d**. Table 1 compares the activation energy of **5a** with those of **5b–d**. It is seen that the barrier height for **5a** having a silacyclobutane structure is 7–9 kcal/mol lower relative to **5b** and also lower than those of **5c** and **5d**. The results agree qualitatively well with the trend observed experimentally for the reactions of enoxysilanes with benzaldehyde.³

The major structural difference between **5a** and **5b** is found in the C–Si–C angle. In order to investigate the effect of the local arrangement of bonds around the silicon center on the reactivity of enoxysilanes, we have also carried out supplemental calculations on imaginary systems in which the C–Si–C angle is frozen at 70°, 80°, 90°, and 100° in **5b** both at the initial state and at the transition state. The activation energies evaluated for the hypothetical process are also presented in Table 1. The results of calculations indicate clearly that the reactivity is related intimately with that angle, as this has been the case in the reaction of allylsilanes.⁸

Acidic Strength of Silicon in Enoxysilanes. A pentacoordinated silicon species is formed at the transition state, and therefore, a certain orbital that extends in the apical direction should play a crucial role in determining the reactivity of enoxysilanes against nucleophiles. The orbital should be localized on the silicon atom. If this orbital is generated by a combination of low-lying unoccupied MOs of an enoxysilane molecule, the silicon center will be a strong electron acceptor. On the contrary, if the components of this localized interacting orbital are found predominantly in the occupied MOs or in the high-lying unoccupied MOs, the silicon center will be a poor electron acceptor in that molecule. To discuss the reactivity of an atom in a molecule, it will be of crucial importance to find the orbital that participates actively in the interaction with the attacking reagent. The frontier orbital would play the dominant role in small molecules, but other MOs should also play significant roles in sizable molecules to give the reactive orbital that is localized on a reaction center.

We have applied then the paired transformations of the MOs of the two fragment species, an enoxysilane molecule and an aldehyde molecule in this case, to find the orbitals that participate in the formation of transient bonds at the transition state.^{23,24} The pair of orbitals that plays a principal role in the interaction between formaldehyde and **5a** is illustrated in Figure 3. The orbital of the aldehyde part consists of the occupied canonical MOs, whereas the orbital of 1-enoxysilacyclobutane is given by a combination of the unoccupied MOs calculated at the 6-31G* level of theory.²⁵ One sees that the orbitals are localized well on the reaction sites to generate the new bond. Pairs of interacting orbitals very similar in shape to those given in Figure 3 have also been obtained for **5b** and for **5b** with the C–Si–C angle frozen at 70°, 80°, 90°, and 100°. A good correlation is shown to exist between the Mulliken overlap population of the orbital pair and the barrier height calculated at the RHF/6-31G* level of theory.²⁶ The population is 0.121 for **5a**, 0.097 for **5b**, and 0.114 for **5b** with the C–Si–C angle fixed at 90°. In this sense, it is possible to interpret the reactivity of the silicon center in various enoxysilanes by calculating these

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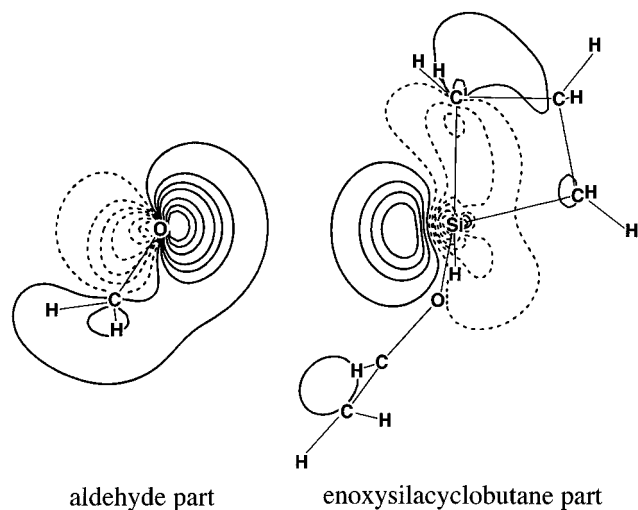


Figure 3. Paired interacting orbitals of formaldehyde and 1-enoxysilacyclobutane. The orbitals have been plotted in the plane defined by the O atom of the former and the Si and C¹ atoms of the latter. Symbols of other atoms and bonds show their projections onto that plane.

interacting orbitals for the transition states.²⁷ But, if a silicon atom constrained in a four-membered ring attached to an enolate oxygen behaves like a coordinatively unsaturated group III element as has been suggested,³ it appears very attractive to somehow trace the origin of differences in reactivity to a certain electronic property of enoxysilane molecules in an isolated state.

The major components of the interacting orbital of the 1-enoxysilacyclobutane part presented above are the p-type AO functions of Si. The contribution of the s-type functions is less than one-third of the p-type functions. In typical pentacoordinated silicon species, the apical ligands are bound to the silicon center principally by the 3p AO having an extension perpendicular to the basal plane.²⁸ Thus, we may take the 3p AO of the silicon having the extension toward the center of a triangle determined by the H, C¹ (H in the case of **5c** (R) and **5d**), and O atoms of an enoxysilane molecule as the orbital that will play a key role in the interaction with an aldehyde. These three atoms come to occupy the equatorial positions at the transition state, and therefore, the AO will be utilized to bind the aldehyde oxygen at the apical site, being freed from the bonding with the atoms at the equatorial positions. Now, by projecting the AO onto the unoccupied canonical MO space of an enoxysilane molecule, we can find the unoccupied reactive orbital that is closest in shape to that AO.²⁹ The orbital obtained in this manner should have the maximum amplitude on that AO, though it will be delocalized to some extent on the neighboring atoms. To generate the AO, this unoccupied orbital should intermix with the occupied counterpart that is obtained simultaneously. This polarization interaction is auxiliary in most reactions,³⁰ and therefore, the reactivity should be determined primarily by the electron-accepting ability of the projected unoccupied orbital.

The level of the unoccupied reactive orbital, denoted here by λ_{unoc} , has been calculated to give the value of 0.27 au for **5a** and 0.32 au for **5b** with the 6-31G** MOs of the MP2/6-31G**

(27) A correlation was also found between the barrier height calculated at the RHF/6-31G level of theory and the energy expectation value of the enoxysilane orbital. It was 0.22 au in **5a** and 0.24 au in **5b**.

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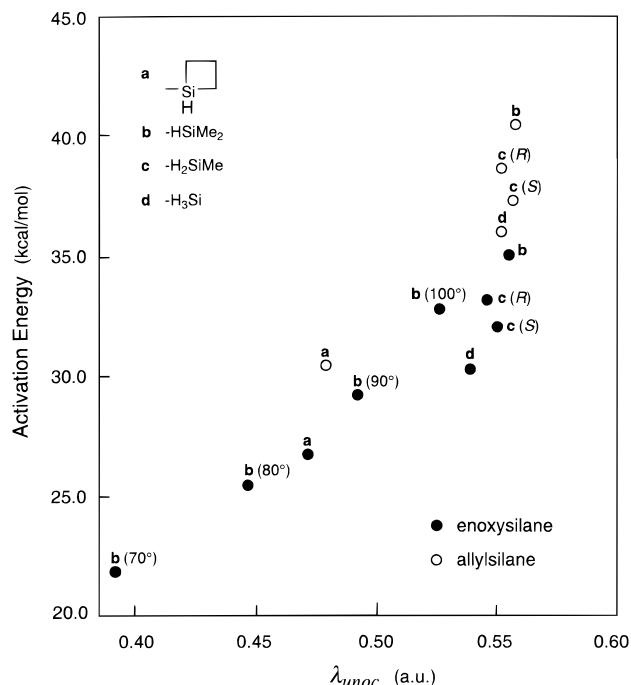
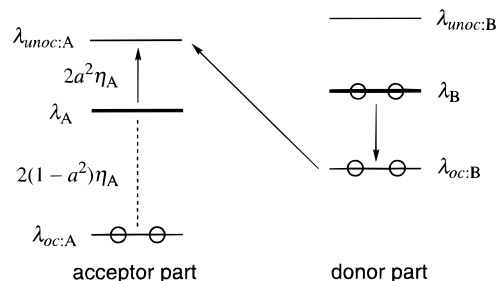


Figure 4. Relation between the calculated activation energy and the electron-accepting strength of the silicon center to give pentacoordinated transition states.

structures.³¹ With the STO-3G MOs, it has been calculated to be 0.47 au for **5a** and 0.55 au for **5b**. Both of these calculations indicate that **5a** should be a stronger electron acceptor than **5b** in the direction in space as specified above in terms of the Si p AO. Figure 4 illustrates the relation between λ_{unoc} values evaluated simply from the STO-3G MOs for the RHF/6-31G* optimized structure of enoxysilane molecules in an isolated state and the barrier heights calculated at the RHF/6-31G* level of theory for **5a–d**. These results, as well as those of additional calculations on imaginary systems in which the C–Si–C angle is frozen at 70°, 80°, 90°, and 100° in **5b**, show clearly that the barrier height correlates well with the electron-accepting strength of the silicon center in enoxysilanes. We have also presented in Figure 4 the results obtained previously for allylsilanes for reference.⁸ It is noticeable that the silicon center exhibits approximately the same electron-accepting ability both in an enoxysilane molecule and in the corresponding allylsilane molecule, although the barrier height for the reaction appears to be significantly lower in the former than in the latter.

As illustrated below, λ_{unoc} depends on two terms, λ and $2a^2\eta$.¹⁸ The former represents the local power of a reaction site or its AO to attract electron density within a reactant molecule. In this sense, $-\lambda$ corresponds to the electronegativity



(31) To obtain the lowest λ_{unoc} value with 6-31G** MOs retaining a large amplitude on the reaction site, we have maximized $\langle \phi_{\text{unoc}} | \delta_r \rangle^2 / |\lambda_{\text{unoc}}|$, where δ_r is the reference orbital (a combination of the inner and outer functions of a Si 3p AO in the present case) and ϕ_{unoc} is the reactive orbital obtained by projecting δ_r onto the unoccupied MO subspace.

defined by Pauling.³² This term is determined primarily by the kind of atom or AO of the reaction site. In order to make the reaction site a good electron acceptor, the electron-accepting capacitance $-\lambda_{\text{unoc}}$ should be as large as possible with $\lambda_{\text{unoc}} \geq \lambda$. That is, λ_{unoc} should be as close as possible to λ . The difference between λ_{unoc} and λ represents the *difficulty* of the reaction site in localizing the interaction on that site. At a very early stage of interaction, the delocalized frontier orbital participates in electron acceptance, since the distances from the constituent atoms of the reactant molecule to the attacking reagent are not so different from each other. In other words, the reaction site is not yet well-defined at a large separation. As the reagent comes closer, the reaction sites participate dominantly in interactions. The bonding interactions between other atoms in the reactant molecule and the reagent should be loosened. This gives rise to a resistance of an enoxysilane molecule against electron acceptance. The localized interacting orbital is brought about by a mixing in of the other unoccupied MOs into the lowest unoccupied MO, elevating the electron-accepting level, λ_{unoc} , above λ .

The gap between λ_{unoc} and λ is given by $2a^2\eta = 2a^2(\lambda_{\text{unoc}} - \lambda_{\text{oc}})/2$, where $-\lambda_{\text{oc}}$ is the electron-donating potential of the reaction site determined for the occupied canonical MOs in a similar manner. The coefficient a^2 ($0 \leq a^2 \leq 1$) measures the *localizability* of the unoccupied reactive orbital on the Si atom. If the projected reactive orbital is not localized well on the reaction site, a^2 will be large. The quantity $(-\lambda_{\text{oc}} + \lambda_{\text{unoc}})/2$ of a reaction site is similar in its form to the *absolute chemical hardness* of a molecule, $(I - A)/2 \approx (-\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$, defined by Parr and Pearson, where I and A signify the ionization potential and the electron affinity of a molecule, respectively, and ϵ_{HOMO} and ϵ_{LUMO} indicate the orbital energies of the highest occupied MO and the lowest unoccupied MO, respectively.^{33,34} It is suggested, therefore, that the $2a^2\eta$ term represents the *acidic hardness* of the reaction site which becomes large when η is large and when the reactant molecule cannot generate the unoccupied reactive orbital that is localized well on the reaction site.¹⁸ It is interesting to see further that $-\lambda = -\{a^2\lambda_{\text{oc}} + (1 - a^2)\lambda_{\text{unoc}}\}$ and we obtain $-\lambda = -\{\lambda_{\text{oc}} + \lambda_{\text{unoc}}\}/2$ by using $a^2 = 1/2$. This is very similar to the *electronegativity* defined by Mulliken, $(I + A)/2$.³⁵ Note, however, that the absolute chemical hardness and the Mulliken electronegativity are the molecular properties, whereas the acidic hardness and basic hardness derived on the basis of a projected reactive orbital represent local properties of a reaction site in a molecule. In typical Lewis acids, a^2 is smaller than 1/2, making λ_{unoc} lie close to λ .¹⁸ Figure 5 illustrates the relation between the calculated barrier height obtained at the 6-31G* level of theory and the acidic hardness of the Si center represented by the 3p AO. It is seen that **5a** is softer as an acid than **5b**.

There is a depletion of electrons at the silicon center in silane molecules, being attracted by the neighboring more negative atoms. When the C-Si-C angle is squeezed in a dimethyl-enoxysilane molecule, the Si p AO which has its extension perpendicular to the plane bisecting the C-Si-C angle is freed

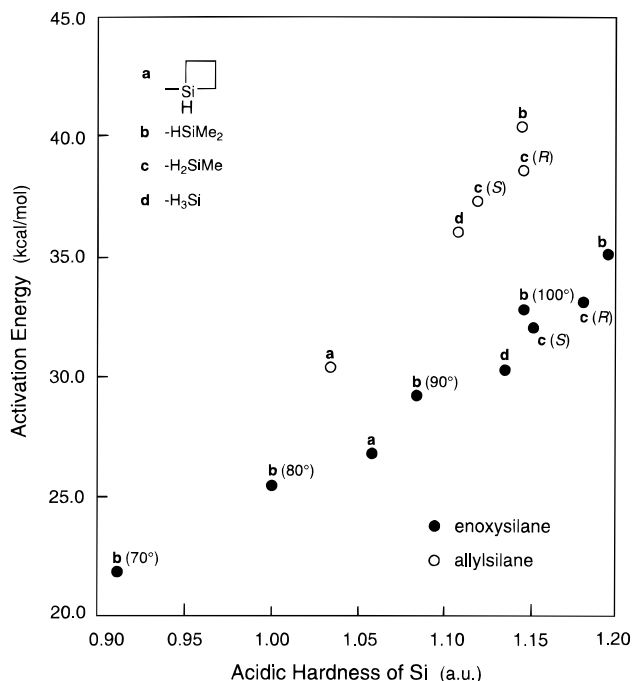
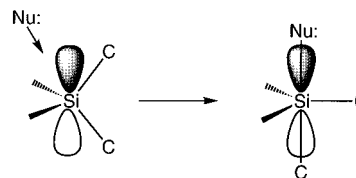


Figure 5. Relation between the calculated activation energy and the acidic hardness of the silicon center.

from the Si-C bonds and will appear predominantly in the unoccupied MO space.



Thus, **5b** with the C-Si-C angle fixed at a smaller value should have a stronger electron-accepting ability than that with the normal bond angle. It is natural then that the lowering of the lowest unoccupied MO having this p AO as the major component correlates with the relative reactivity of silacyclobutanes in the nucleophilic cleavage of the Si-C bond, as reported.³⁶ The higher reactivity of **5a** is also attributed to this evacuated orbital. Incidentally, inclusion of the Si 3s AO does not change the argument discussed above. For example, by mixing the s AO of the Si center into the p-type reference of the reacting orbital with a 1:3 ratio in weight, we have obtained $\lambda_{\text{unoc}} = 0.46$ au for **5a** and 0.54 au for **5b** at the STO-3G level, in place of 0.47 and 0.55 au, respectively, as given above for the pure p-type reference orbital. The silicon center in **5a** is shown again to be softer as a Lewis acid than that in **5b**.³⁷

The transition state appears at an earlier stage of the reaction in **5a**, as depicted by the shorter bond length, 1.814 Å, between the Si center and the enolate oxygen at the transition state compared to that in **5b**, 1.835 Å.³⁸ A similar trend has also been observed in the reaction models of allylsilanes.⁸ The important role of the reaction center in these reactions is to circulate electron population from the aldehyde oxygen to the aldehyde carbon through the enolate or allyl group, giving rise to a new C-C bond at the other termini. The pentacoordinated

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(34) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6801. (c) Pearson, R. G. *Acc. Chem. Res.* **1993**, *26*, 250.

(35) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782.

(36) Krapivin, A. M.; Mägi, M.; Svergun, V. I.; Zaharjan, R. Z.; Babich, E. D.; Ushakov, N. V. *J. Organomet. Chem.* **1980**, *190*, 9.

(37) The acidic hardness term has been calculated to be 1.18 au for **5a** and 1.31 au for **5b** with the s and p hybrid reference orbital.

(38) The Si-O bond has also been calculated to be shorter in **5b** with C-Si-C fixed at 70° (1.645 Å) than in **5b** with C-Si-C fixed at 100° (1.661 Å) at the 6-31G* level of theory.

silicon is suitable for binding both the attacking aldehyde and the leaving enolate or allyl at the transition state. The simple Mulliken population analysis shows that the positive net charge on the silyl group is significantly smaller in **5a** than in **5b** at the transition state, being 0.452 and 0.499, respectively.²⁶ The electronic charge has been transmitted more efficiently in **5a**.

The C–Si–C angle is 80° in silacyclobutane, and the strain energy has been calculated to be comparable to that in cyclobutane.³⁹ Thus, the enhanced reactivity of silacyclobutanes has been ascribed to the ability of silicon to rehybridize from tetrahedral to trigonal bipyramidal, allowing for relief of the strain energy.³ The effect of strain has also been invoked in nucleophilic substitution reactions at silicon.^{10,11} It has been revealed, however, that the silacyclobutane ring spans one apical and one equatorial position at the pentacoordinated transition state,³ and therefore, the C–Si–C angle is not expanded in the present systems. It is now clear that the strong ability of tetravalent silicon to expand its valency and the strong ability of silicon constrained in a four-membered ring to attract electrons are the most important factors that make 1-enoxysilanes very reactive.

Basic Strength of the α -Carbon in Enoxy- and Allylsilanes.

An enoxysilane molecule serves as an electron acceptor at the silicon atom, but it should play an electron donor part at the enoxy unit. It is supposed, therefore, that the lower activation energy calculated for the reaction of an enoxysilane with an aldehyde compared to the corresponding allylsilane is related to the stronger reactivity of the terminal carbon in the former. We have estimated the electron-donating potential $-\lambda_{oc}$ of the carbon, by taking the 2p AO which has the extension perpendicular to the enoxy or allylic plane as the reactive orbital and by projecting it onto the occupied MO space of some of the species studied above. The λ_{oc} values obtained have suggested that enoxysilanes should be stronger electron donors than allylsilanes.

To make the comparison more distinct, we have examined the reactivity of the terminal carbons in enoxysilanes having the structure $\text{CH}_2=\text{CX}-\text{O}-\text{SiH}_3$ and in allylsilanes having the structure $\text{CH}_2=\text{CX}-\text{CH}_2-\text{SiH}_3$. A good correlation is seen to exist between the λ_{oc} values estimated with the STO-3G MOs and the activation energy calculated at the 6-31G* level of theory for several electron-attracting and electron-releasing substituent groups, X, as illustrated in Figure 6.⁴⁰ The difference between the two species is nice and systematic. In the case of X = H, λ_{oc} is -0.31 au for enoxysilane and -0.32 au for allylsilane, the activation energy being 5.7 kcal/mol lower in the former. It is suggested, therefore, that enoxysilanes should be more reactive against aldehydes than the corresponding allylsilanes owing to the higher electron-donating abilities at the terminal carbon atom.

The electron-donating potential $-\lambda_{oc}$ consists of two parts, the electronegativity term $-\lambda$ of the reaction site and the *basic hardness* term, $2(1 - a^2)\eta$, which measures the difficulty that a reaction site would experience in electron donation. The first term should be similar in magnitude, since the reacting orbital is the carbon $2p\pi$ AO in all the cases. Then, the γ -carbon will be a strong electron donor when η is small and when the localizability of the projected orbital on the C $2p\pi$ AO is large, i.e., $2(1 - a^2)$ is small. Figure 7 illustrates the relation between the basic hardness of the terminal carbon and the calculated activation energy with respect to the substituted enoxysilanes

(39) Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 352.

(40) The dominant component is the highest occupied MO in most of the substituted silanes studied here. Projection of the $2p\pi$ AO onto the occupied MO space of ethylene gives rise to the highest occupied π MO.

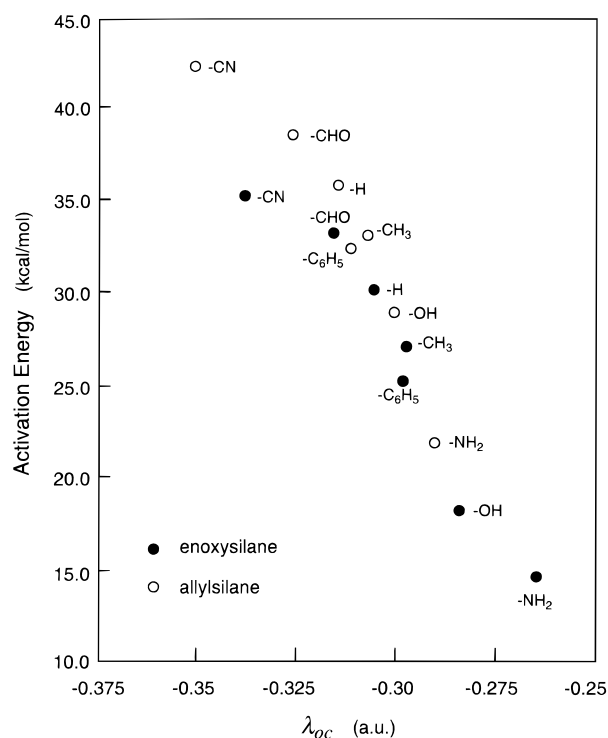


Figure 6. Relation between the reactivities of enoxy- and allylsilanes against formaldehyde and the electron-donating potential of the terminal carbon.

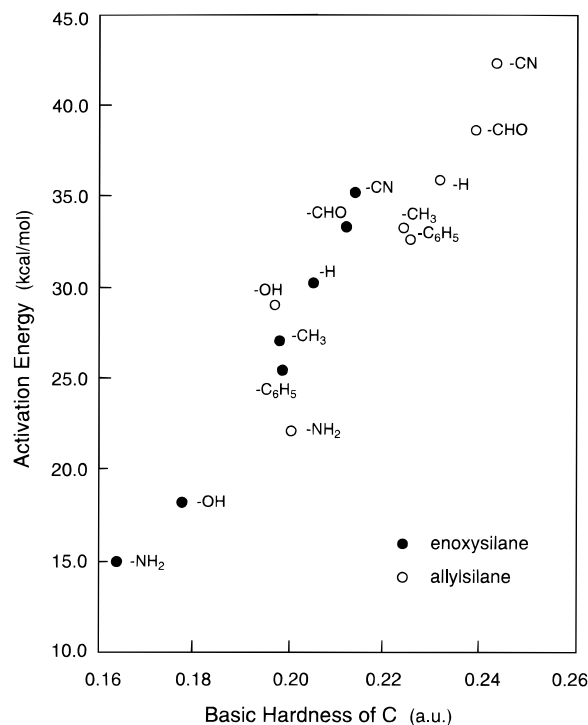


Figure 7. Relation between the reactivity of enoxy- and allylsilanes against formaldehyde and the basic hardness of the terminal carbon.

and allylsilanes. Enoxysilanes are demonstrated here to be stronger electron donors than the corresponding allylsilanes, in accordance with the reactivity trend suggested by Mayr.⁴¹ This difference obtained for isolated reactant molecules will emerge in the course of the reactions to bring the difference in barrier height.

A consideration of local activity of molecules has led us to a more generalized scheme of orbital interactions which includes

(41) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938.

all the important MOs as well as the frontier orbitals and is related more intimately with the basic notions in chemistry. One may notice that the present treatment coincides with the frontier orbital theory at the limit of the smallest reactant molecule for a given type of reaction. It is now clear that a charge-controlled interaction between a hard acid and a hard base is nothing but an outcome of a weak electron delocalization.⁴² The weak electron delocalization should be reasoned in terms of the acidic and basic hardness of the reaction sites in the electron-accepting and -donating parts. In any event, electron delocalization is the driving force of chemical reactions, bringing about the formation of new bonds and the breaking of old bonds along the reaction paths.⁴³ Electrostatic interactions between atomic charges do not lead to the interchange of covalent bonds.

Reactions similar to the one discussed above have been investigated extensively for allylic and enoxy compounds with a variety of metals.^{12-17,44} We find a considerable variation in the size and structure of reactant molecules. The reaction paths and the energetics of those reactions will be clarified by sophisticated *ab initio* MO calculations. Then, the analysis based on the concept of a composite of an acid and a base will be of use as a simple way of connecting the results of calculations with our chemical intuition in discussing the mechanisms of the reactions and looking for the origin of differences in reactivity of those systems.

Conclusion

At the transition state of the reaction between enoxysilanes and aldehydes, a certain orbital of an enoxysilane molecule forms a transient bond with the attacking aldehyde. By tracing

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(43) Fujimoto, H.; Inagaki, S.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 2670.

(44) Yamamoto, Y.; Asano, N. *Chem. Rev.* **1993**, *93*, 2207.

the origin of this orbital back to a reactant molecule in an isolated state, it has been shown that the difference in reactivity among enoxysilanes arises from a property that is inherent to those molecules. The silicon center in 1-enoxysilacyclobutane should be a stronger Lewis acid in an isolated state due to its smaller C-Si-C angle than those in methyl-substituted enoxysilanes. Experimental observations that some 1-enoxysilacyclobutanes react with aldehydes in the absence of an activator are understandable in this context. Relief of strain at the transition state may not necessarily be invoked to differentiate the reactivity in this case. The proposal that a silicon atom constrained in a four-membered ring behaves like a coordinatively unsaturated element appears to be reasonable.³ The ligands at the silicon center control the direction of an attack of aldehydes by producing an orbital that has a large amplitude in a specific region in space around the silicon center. The reactivity is governed predominantly by the electron-accepting ability of that orbital.

It has been demonstrated also that the electron-accepting ability of the silicon center is similar in enoxysilanes and in the corresponding allylsilanes. In contrast, enoxysilanes show stronger electron-donating abilities at the γ -carbon of the enoxy unit than that of the allylic unit in allylsilanes. It is suggested, therefore, that enoxysilanes are more reactive than the corresponding allylsilanes against aldehydes, though direct comparison does not seem to be attempted so far in a vast amount of experiments.

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