CHEMISTRY LETTERS, pp. 387-390, 1991.

Ab Initio MO Study of the Reaction of Pentacoordinate Allylsilicates with Aldehydes[1)]

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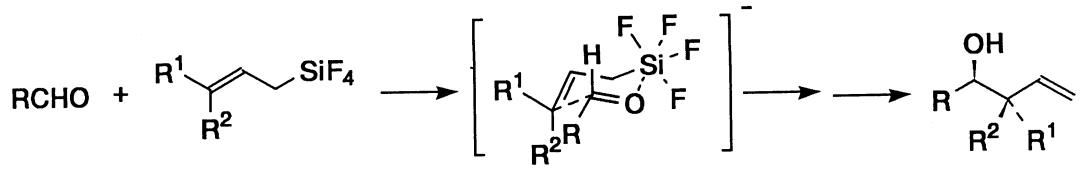
Transition state structures for the reaction of allyltetrafluorosilicate with formaldehyde as well as structures of the silicate and related compounds were located with ab initio MO calculations. The origin of the unique reactivity of pentacoordinate allylsilicates observed experimentally is discussed on this basis.

Much attention has been focused on the enhanced reactivity of pentacoordinate organosilicon compounds. We wish herein to report the first ab initio MO study on the transition state structure of a reaction of pentacoordinate organosilicon compounds.

We have recently found that pentacoordinate allyltetrafluorosilicates react with various aldehydes in a regiospecific and highly diastereoselective manner.[2)] The high reactivity and the unique stereochemistry of the reaction of pentacoordinate allylsilicates have been ascribed to the following two factors. One is the significant Lewis acidity of the silicon center to give hexacoordinate silicates. The other is the enhanced nucleophilicity of the γ-carbon of the allylsilicates due to the enhanced σ – π conjugation. The cyclic transition state structure may be favored since the hexacoordination at silicon may further increase the electron-donating ability of the silyl group and in turn the nucleophilicity of the allylic γ-carbon due to σ – π conjugation.



Ab initio molecular orbital calculations were carried out with the GAUSSIAN 82[3)] and HONDO[4)] programs. The structures of reactants and products were optimized with the MIDI-4*[5)] basis set including d orbitals for C, O, and Si atoms and anion p orbitals for F atoms. Transition state structures were located with the MIDI-4(*) basis set, which is the standard MIDI-4 basis set augmented with d orbitals for Si. The analytical energy gradient with respect to atomic coordinates was used to optimize structures. Each structure was fully optimized and characterized according to the number of negative eigenvalues of the force constant

Table 1. Structures for $CH_2=CHCH_2SiF_n^{3-n}$ Calculated with MIDI-4* Basis Set

	1 (n = 3)	**2** (n = 4)	**3** (n = 5)
Bond length (Å)			
Si–F	1.63	1.67 – 1.74	1.74 – 1.76
$Si–C_\alpha$	1.85	1.90	1.99
$C_\alpha–C_\beta$	1.51	1.50	1.49
$C_\beta–C_\gamma$	1.32	1.33	1.33
C–H	1.08–1.09	1.09	1.09 – 1.10
Bond angle (deg)			
$C_\alpha SiF$	112.6 (av.)	117.8, 123.6	88.5, 93.0
		93.1, 90.8	91.3, 90.3
			177.6
$SiC_\alpha C_\beta$	112.7	113.7	117.5
$C_\alpha C_\beta C_\gamma$	124.6	126.0	128.3
Dihedral angle (deg)			
$SiC_\alpha C_\beta C_\gamma$	–104.3	–121.3	–125.6
Mulliken charge			
C_α	–0.40	–0.37	–0.38
C_β	–0.25	–0.22	–0.11
C_γ	–0.26	–0.31	–0.38
Si	1.37	1.38	1.51
Total energy (hartrees)	–703.12465	–802.55797	–901.81852

matrix (Hessian). The Hessians of reactants and products should have no negative eigenvalues, while that of the transition state structure should have only one negative eigenvalue.

Selected parameters for the structure of (allyl)SiF_n^{3-n} (**1**, n = 3; **2**, n = 4; **3**, n = 5) optimized with the MIDI-4* basis set are shown in Table 1. Geometry around the silicon atom is approximated by tetrahedral, trigonal bipyramidal (TBP), and octahedral arrangement for **1**, **2**, and **3**, respectively. The allyl group in the pentacoordinate allylsilicate **2** occupies the equatorial position of the TBP structure as expected. The Si–C bond lengths of this series of compounds increase with increasing number of ligands at silicon. Dihedral angles between the Si–C and C=C bonds are 14.3 , 31.3 , and 35.6 for **1**, **2**, and **3**, respectively, suggesting that, in addition to hyperconjugative stabilization between the Si–C bond and the vinyl π bond, the steric effect may be an important factor to determine the preferred conformation.

Mulliken atomic charges as calculated by subtraction of Mulliken gross atomic population from the nuclear charge at allylic α–, β–, and γ–carbons as well as the silicon atom for **1**, **2**, and **3** are summarized in Table 1. The atomic charge of the allylic γ–carbon increases in the order of **1**< **2**< **3**, being suggestive of the increasing nucleophilicity at the γ–carbon in this order. On the other hand, the atomic charge of the silicon atom is positive among all the compounds **1–3** and increases as the coordination number of silicon atom increases. The present calculations indicate that the reaction of **1** with F^- gives the stable pentacoordinate species **2**, while the formation of **3** from **2** and F^- is endothermic. This result suggests that the Lewis acidity of **2** is significantly lower than that of **1** at least in a gas phase.

$$\underset{\mathbf{1}}{CH_2{=}CHCH_2SiF_3} \xrightarrow[\Delta E = -72.5\ kcal/mol]{F^-} \underset{\mathbf{2}}{CH_2{=}CHCH_2SiF_4^-} \xrightarrow[\Delta E = 35.8\ kcal/mol]{F^-} \underset{\mathbf{3}}{CH_2{=}CHCH_2SiF_5^{2-}}$$

The reaction of **2** with formaldehyde was investigated theoretically by using MIDI-4(*) basis set. First, the possibility of the formation of a hexacoordinate silicate complex was examined. Although **2** was stabilized by the complexation with formaldehyde at the initial stage of the reaction, the complex did not involve the coordination of carbonyl oxygen to silicon but a weak hydrogen-bonding between a fluorine atom at silicon and a hydrogen of the aldehyde. Among various transition state structures, a cyclic chair, three cyclic boat, and a linear forms were searched. Although no boat form of the transition state structure has been located yet, the hexacoordinate chair form was found to be 50.2 kcal/mol lower in energy than a linear pentacoordinate one. Thus it was theoretically concluded that the cyclic chair form is a more favorable transition state structure than the chain form, being in accord with our empirical model.

Table 2. Bond Lengths for the Chair and Linear Transition State Structures

Bond	Length /Å	
	Chair form	Linear form
Si–C_α	2.134	2.783
C_α–C_β	1.422	1.351
C_β–C_γ	1.376	1.481
C–C(carbonyl)	2.224	1.616
Si–O	1.902	–
O–C(carbonyl)	1.267	1.340
Si–F	1.686–1.732	1.625–1.634

The cyclic chair and linear transition state structures are shown in Fig. 1 and Table 2. A forming C–C bond length of 2.22 Å in the chair form is comparable to that for the allylation of formaldehyde with allylborane (2.28 Å) and allylboronic acid (2.18 Å) calculated with the 3-21G basis set.[6] The chair transition state structure is an early (reactant-like) one with the Si–O, Si–C, C_α–C_β, and C_β–C_γ bond lengths which are 1.90, 2.13, 1.42, and 1.38 Å, respectively. In comparison with the chair structure, the linear transition state structure is a late (product-like) one, which has the Si–C length of 2.78 Å, the C_α–C_β length of 1.35 Å, and the C_β–C_γ length of 1.48 Å.

Next, given the chair transition state structure, the relative energies of axial and equatorial conformations of alkyl groups were assessed theoretically by replacing an appropriate hydrogen with a standard methyl group (R_{CC} = 1.54 Å, R_{CH} = 1.08 Å, <CCH = 109.5°). Single point calculations with the MIDI-4(*) level indicate that a methyl group attached to the carbonyl carbon prefers the equatorial position over the axial position by 18.7 kcal/mol, which corresponds to the value for the similar reaction of allylborane (5.5 kcal/mol with the 3-21G basis set). The larger relative energy of the allylsilicate suggests its higher stereoselectivity compared

with the allylborane.

The present results are consistent with the experimental observations qualitatively as a whole and support our model of the cyclic transition state structure for the reaction of allyltetrafluorosilicate with formaldehyde. Further calculations taking account of electron correlation at the transition state structures are in progress.

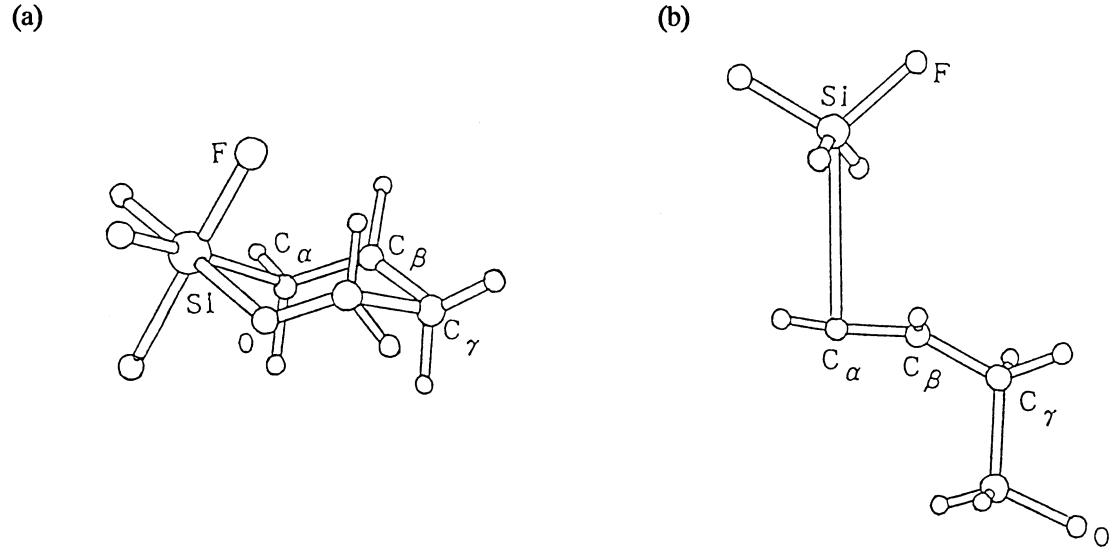


Fig. 1. Cyclic-chair (a) and acyclic (b) transition state structures for the reaction of **2** with $H_2C=O$ determined with MIDI-4(*) basis set.

References

1) Chemistry of Organosilicon Compounds. 282.

2) M. Kira, K. Sato, and H. Sakurai, *J. Am. Chem. Soc.*, **110**, 4599 (1988); **112**, 257 (1990); K. Sato, M. Kira, and H. Sakurai, *ibid.*, **111**, 6429 (1989); M. Kira, M. Kobayashi, and H. Sakurai, *Tetrahedron Lett.*, **28**, 4081 (1987); M. Kira, T. Hino, *ibid.*, **30**, 1099 (1989). For a review, H. Sakurai, *Synlett*, **1989**, 1.

3) GAUSSIAN 82, J. S. Binkley, M. J. Frisch, R. A. Whiteside, D. J. DeFrees, K. Rahgavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

4) HONDO (Version 7.0), M. Dupuis, J. D. Watts, H. O. Villar, and G. J. B. Hurst, IBM Corporation, Scientific Engineering Computations, Kingston, New York 12401, QCPE #544, Indiana University, Bloomington, IN.

5) H. Tatewaki and S. Huzinaga, *J. Comput. Chem.*, **1**, 205 (1980); Y. Sakai, H. Tatewaki, and S. Huzinaga, *ibid.*, **2**, 100 (1981).

6) Y. Li and K. N. Houk, *J. Am. Chem. Soc.*, **111**, 1236 (1989).

(Received November 26, 1990)