Controversial Effects of Methyl Substitution on the Silaethene to Silanediyl Isomerization. A Theoretical Study

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Ab initio calculations including electron correlation show that the isomerizations of both $H_2Si{=}CH_2$ to $H\ddot{S}i{-}CH_3$ and $CH_3SiH{=}CH_2$ to $CH_3{-}\ddot{S}i{-}CH_3$ are almost thermoneutral and proceed with a sizeable barrier of *ca.* 40 kcal/mol (*ca.* 167 kJ/mol); there is no significant effect of methyl substitution.

Despite recent developments in silaethene chemistry,[1] apparent discrepancies remain between theory and experiment for the barrier height and heat of reaction for the isomerizations (1) and (2) (*via* 1,2-hydrogen shift).

$$H_2Si{=}CH_2 \rightarrow H\ddot{S}i{-}CH_3 \qquad (1)$$

$$CH_3SiH{=}CH_2 \rightarrow CH_3{-}\ddot{S}i{-}CH_3 \qquad (2)$$

A theoretical study[2] predicted the barrier for reaction (1) to be 41.0 kcal/mol,[†] whereas, experimental studies[3,4] indicated that reaction (2) proceeds rapidly. The former experimental data[3] might be interpreted reasonably in terms of a high-temperature process.[5] However, the apparent observation of reaction (2) at 100 K[4] means that its barrier should be less than 5 kcal/mol. The barrier for reaction (1) was recalculated at a higher level of theory,[6] but again a sizeable barrier of 40.6 kcal/mol was obtained. Since the calculations refer strictly to reaction (1), there remains of course the possibility that the presence of the methyl group in reaction (2) is responsible for the discrepancy between theory and experiment.

It has been calculated[2,7–9] at high levels of theory[‡] that reaction (1) is approximately thermoneutral.[10] In contrast, a recent ion cyclotron resonance study[11] provided evidence that $CH_3SiH{=}CH_2$ is 28 kcal/mol more stable than $CH_3{-}\ddot{S}i{-}CH_3$, *i.e.*, reaction (2) is highly endothermic. If this result is indeed true,[12] it may provide indirect support for a significant barrier between $CH_3SiH{=}CH_2$ and $CH_3{-}\ddot{S}i{-}CH_3$. However, the sizeable energy difference favouring $CH_3SiH{=}CH_2$ over $CH_3{-}\ddot{S}i{-}CH_3$ is not compatible with near-degeneracy in energy of $H_2Si{=}CH_2$ and $H\ddot{S}i{-}CH_3$,[2,7–9] unless the additional methyl group has a dramatic effect.

Table 1. Barrier heights and heats of reaction for the isomerizations (1) and (2) in kcal/mol calculated at several levels of theory.[a]

Levels of theory	Barrier height (1)	Barrier height (2)	Heat of reaction (1)	Heat of reaction (2)
HF//3-21G	42.9	45.5	−14.9	−15.7
HF//6-31G	43.4	46.0	−14.1	−14.8
HF//6-31G*	43.5	47.4	−5.8	−5.1
MP3/6-31G*	42.2	43.5	−0.8	−1.9
CISD/6-31G*	41.6	44.9	−3.8	−2.7
CISDQ/6-31G*	39.3	41.4	−3.4	−2.0

[a] Correlation calculations were carried out at the 6-31G* HF optimized geometries.

In view of these apparent conflicts, the effects of methyl substitution must be studied. Thus, we have performed *ab initio* calculations at several levels of theory to provide insight into the difference between reactions (1) and (2). All geometries were fully optimized at the Hartree–Fock (HF) level with three basis sets (3-21G, 6-31G, and 6-31G*),[13] by

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[†] 1 cal = 4.184 J.

[‡] The necessity to include polarization functions and correlation energy correction is well established for calculating heats of reaction correctly.

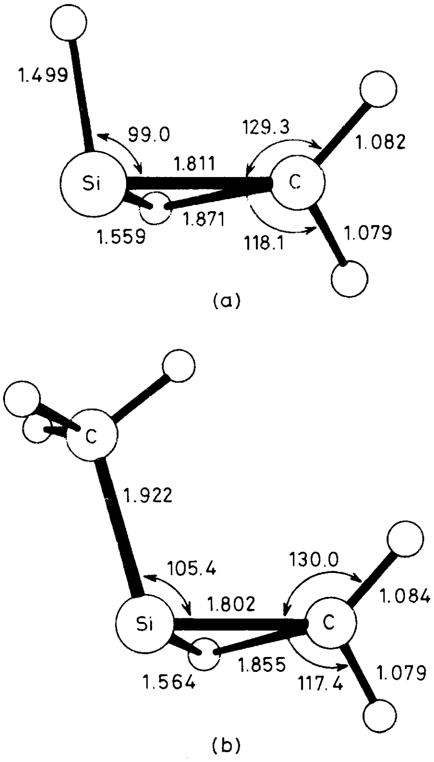

Figure 1. Transition state geometries (Å and degrees) for the isomerizations (1) (a) and (2) (b), obtained at the 6-31G* HF level.

using the analytic energy gradient technique. Electron correlation was incorporated at the 6-31G* HF optimized geometries through third-order Møller-Plesset perturbation (MP3)[14] and configuration interaction (CI). In the correlation calculations, all single (S) and double (D) excitations were included, with the restriction that excitations from core-like orbitals (1s, 2s, 2p for Si and 1s for C) were excluded. The final CI energies (denoted by CISDQ) were obtained by adding the Davidson correction[15] to allow for unlinked quadruple (Q) excitations.

Figure 1 shows the transition states for reactions (1) and (2). It is noteworthy that the two transition state structures are very similar. Probably reflecting the structural similarity, the magnitude of the barrier height for reaction (2) differs little from that for reaction (1), as shown in Table 1. The barriers for reactions (1) and (2) are both sizeable, the latter barrier being rather slightly larger than the former at all levels of theory. Obviously, the present findings exclude a favourable and dramatic effect of methyl substitution on the isomerization barrier height. Moreover, Table 1 reveals that at all levels of theory the energy difference between $H_2Si{=}CH_2$ and $H\ddot{S}i{-}CH_3$ is comparable to that between $CH_3SiH{=}CH_2$ and $CH_3{-}\ddot{S}i{-}CH_3$, and at high levels‡ reactions (1) and (2) are almost thermoneutral (or slightly exothermic), in disagreement with the experimental work.[11]

The present communication confirms that the additional methyl group in reaction (2) can provide no significant difference between reactions (1) and (2). Further experimental work or alternative interpretations seem to be required.§

All calculations were carried out at the Computer Center of the Institute for Molecular Science and at the Computer Center of Tokyo University, using the IMSPAK(WF10—9) and GAUSSIAN80(WF10—25) programs in the IMS Computer Center library program package.

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§ *Note added in proof.* For the interpretation that reaction (2) is catalysed and not unimolecular, see C. A. Arrington, R. West, and J. Michl, *J. Am. Chem. Soc.*, 1983, **105**, 6176.