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Photoreaction dynamics of permethylcyclohexasilane $(Me_2Si)_6$ via triplet state surface: A direct MO dynamics study

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Abstract

The photoreaction mechanism of permethylcyclohexasilane via the excited triplet state potential energy surface, $(Me_2Si)_6$ $(T_1) \rightarrow (Me_2Si)_5 + Me_2Si$:, has been studied by means of direct MO dynamics method with a full dimensional potential energy surface. In order to test the possibility of triplet state channel, we considered the reaction path on the triplet state surface in the present study. The total energy and energy gradient on each atom were calculated at each time step during the reaction by the PM3-MO method. The dynamics calculations suggested that the six-membered Si-ring is spontaneously changed to five-membered one and methylsilylene radical on the T_1 surface. The reaction was completed within 1.0 ps. The present calculations strongly indicated that the photochemical extrusion of silylene Me_2Si from the Si-ring compounds is possible on the triplet energy surface as well as on the S_1 surface. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Polysilanes; Triplet state; Direct MO dynamics

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1. Introduction

Photochemical behavior of polysilanes and its derivatives plays an important role in the photoresistant process of the polymers [1]. Photo-irradiation on cyclic-silane compound $(R_2Si)_n$ ($n = 5$, 6 and 7 where R is alkyl group) leads to silylene radical (R_2Si) and the lower-membered Si ring compound $(R_2Si)_{n-1}$. For example, the six-membered ring $(Me_2Si)_6$ is dramatically changed to a five-membered ring $(Me_2Si)_5$ by UV irradiation with 254 nm [2–4].

$$(Me_2Si)_6 \rightarrow (Me_2Si)_5 + Me_2Si: \qquad (1)$$

In 1979, Drahnak, Michl and West found that irradiation of permethylcyclosilane trapped in a rigid glass of 3-methylpentane or methylcyclohexane at 77 K, yielded both $(Me_2Si)_5$ and dimethyl-silylene radical Me_2Si by a photochemical extrusion reaction {i.e. reaction 1 (Eq. (1)) [2]. A similar reaction was observed in argon matrices at 10 K [3]. The products of reaction 1 were characterized by comparison of its UV–vis and IR spectra with those of an authentic sample of this stable compound. Ishikawa and Kumada observed that reaction 1 proceeds easily by UV-light irradiation with $\lambda = 254$ nm in cyclohexane at 330 K [4].

From the experimental point of view, it is suggested that reaction 1 proceeds on singlet (S_1) state potential energy surface (PES) [2]. However, Ramsey suggested on the basis of Woodward–Hoffmann selection rule that both $^1(\sigma-\sigma^*)$ and $^3(\sigma-\sigma^*)$ excited states correlate to silylene radical R_2Si dissociation channel rather than $(\sigma-\pi)$ excited state [5]. This means that the elimination reaction is possible on T_1 surface (triplet channel) as well as on S_1 surface (singlet channel), if intersystem crossing (surface hopping process) is occurred. Although the triplet channel is expected to be minor, studying the dynamics for the triplet channel is important not only for elucidating the detailed photoreaction mechanism in cyclic-Si compounds and but also for planing future experiment.

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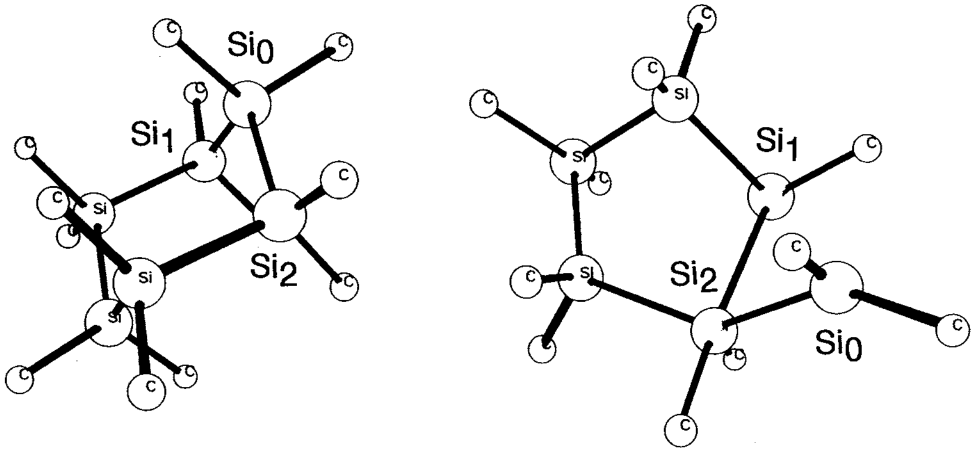

$(Me_2Si)_6$
1

$(Me_2Si)_5\cdots Me_2Si:$
2

Fig. 1. Optimized structures of $(Me_2Si)_6$ at ground (**1**) and triplet (**2**) states calculated by PM3-MO method.

In the present study, the reaction dynamics of $(Me_2Si)_6$ on the triplet state surface is investigated by means of the direct MO dynamics method. Primary aim of this study is to predict theoretically the dynamics of $(Me_2Si)_6$ on triplet state surface, such as the reaction time and lifetime of the unstable state on the triplet state. The results show that the photochemical extrusion reaction of silylene from the Si-ring compound is possible on triplet state surface as well as on S_1 surface.

2. Method of calculations

In general, the classical trajectory is performed on an analytically fitted potential energy surface as previously carried out by us [6]. However, it is not appropriate to predetermine the reaction surface of reaction 1 due to the large number of degrees of freedom ($3N-6=156$ where N is number of atoms in the reaction system). Therefore, in the present study, we applied the direct trajectory calculation with all degrees of freedom [7]. The energy gradients on all atoms were calculated at the PM3-MO level at each time step.

In the trajectory calculation, we used optimized geometry of $(Me_2Si)_6$ as an initial structure. At a starting point of the trajectory calculation, atomic velocities for all atoms were adjusted to give a temperature of 300 K. The potential energy (total energy) and energy gradients at each time step was calculated at the PM3-MO level [8]. The program code to calculate the trajectory was made by our group [7].

In the calculation of the classical trajectory, we assumed that each atom moves as a classical particle on the PM3 multi-dimensional potential energy surfaces. The equations of motion for **n** atoms in a molecule are given by

$$m_i\, dv_{\mu i}/dt = F_{\mu i}$$

$$dx_{\mu i}/dt = v_{\mu i}$$

where $x_{\mu i}$ ($\mu = 1, 2, 3$) are the three Cartesian coordinates of the i-th atom with mass m_i, $F_{\mu i}$'s are the three components of the force acting on the i-th atom. These equations were numerically solved by the Runge–Kutta method. No symmetry restriction was applied in the calculation of the gradients in the Runge–Kutta method. The time step size was chosen by 0.1 fs.

3. Results

3.1. Structure of $(Me_2Si)_6$ at the ground state

The structure of permethylcyclohexasilane $(Me_2Si)_6$ at the ground state is fully optimized by means of the PM3-MO method. The distance of Si–Si bond in $(Me_2Si)_6$ is calculated to be 2.4285 Å. Note that Si_1–Si_2 distance (3.8746 Å) is much longer than that of Si_0–Si_1 distance (2.4286 Å), where the numbering of Si atom is indicated in Fig. 1. The angle of Si_1–Si_0–Si_2 is calculated to be 105.8° which is close to a normal angle in Si compound.

3.2. Structure at the first excited triplet (T_1) state

The structure for $(Me_2Si)_6$ at the triplet state is fully optimized by means of the energy gradient method with no-symmetry restriction. An initial structure in the optimization procedure is chosen as that of the ground state. The PM3 calculation suggests that the first excited triplet state is composed of σ–σ^* excited state, so that the T_1 state correlates to the dissociation channel of the triplet silylene radical Me_2Si:. An illustration of the fully optimized structure is given in Fig. 1. The Z-matrices of all optimized structures (the ground and first excited states) are available upon request. The most stable structure for T_1 state is much different from that of the ground state: the distance between Si_1 and Si_2 is much shortened at the excited T_1 state (3.8746 vs. 2.5337 Å). In addition, the bond length of Si_0–Si_1 atoms is elongated from that of the ground state (2.5400 vs. 2.4285 Å). This means that the six-membered Si ring would be deformed at the excited state and formed both five-membered ring and silylene radical, i.e. reaction 1 proceeds on the T_1 state. As will be seen in latter section, population analysis also indicates that the bond of Si_1–Si_2 is newly formed by the reaction at the excited state.

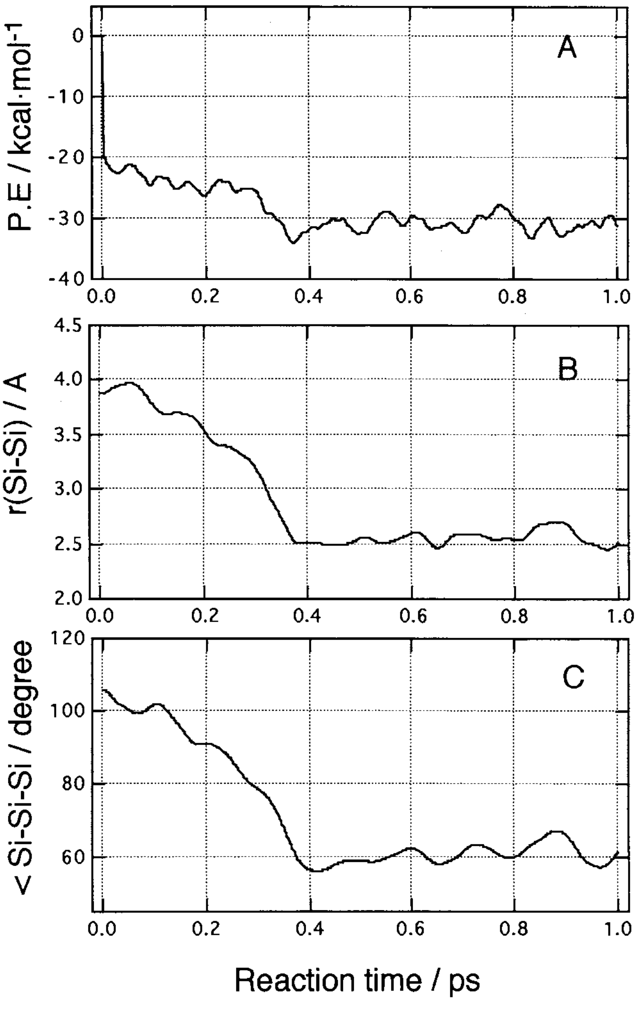

Fig. 2. Sample trajectory calculated by the direct PM3-MO dynamics method with T_1 potential energy surface. (A) potential energy, (B) interatomic distance of Si_1–Si_2, and (C) angle of Si_1–Si_0–Si_2 versus reaction time.

3.3. Dynamics of reaction 1

As shown in previous section, the geometry optimization of T_1 state indicated that the initial geometry chosen as the ground state structure is drastically changed to the large distorted structure which corresponds to the five-membered Si ring. In addition, Me_2Si radical is dissociated by the photodissociation of $(Me_2Si)_6$. In this section, the time-dependent reaction dynamics of reaction 1 is studied by the direct MO dynamics calculation in order to elucidate photochemical behavior of $(Me_2Si)_6$.

In the direct dynamics calculation, the optimized geometry obtained at the ground state is chosen as an initial geometry. The potential energy (PE), the distance between Si_1 and Si_2 (denoted by r(Si–Si) in Fig. 2) and the angle of Si_1–Si_0–Si_2 are monitored as a function of reaction time. The results are plotted in Fig. 2. At time zero, the Si skeleton has a regular six-membered ring structure. The time dependence of PE indicates that the structure of six-membered Si-ring is spontaneously changed at the excited state to the five-membered ring without activation barrier. The lowering of energy level at first stage (0 ∼ 0.01 ps) is due to the fact that the Si–Si bond elongation (structural relaxation of whole molecule) is immediately occurred after the electronic excitation. After the first relaxation, the energy is gradually lowering as a function time. According to this energy lowering, the interatomic distance between Si_1 and Si_2 atoms is shortened by the reaction from 3.8746 to 2.5340 Å. In contrast, Si_0–Si_j; distances ($j = 1, 2$) are elongated. The final Si_1–Si_2 distance (2.5340 Å) is strictly dose to that of normal Si–Si single bond. In addition, the angle of Si_1–Si_0–Si_2 is largely changed from 105.8 to 60.1° and electronic state of moiety of Me_2Si_0 is significantly dose to silylene radical SiR_2 at triplet state. These results imply that the six-membered ring is changed to the five-membered ring at T_1 state.

Table 1
Bond populations calculated as a reaction time

Time (ps)	Bond population	
	Si_1–Si_2	Si_0–Si_1
0.0	0.000	0.351
0.2	0.147	−0.652
0.4	0.378	−0.408
0.6	0.032	−0.640
0.8	0.090	−0.538

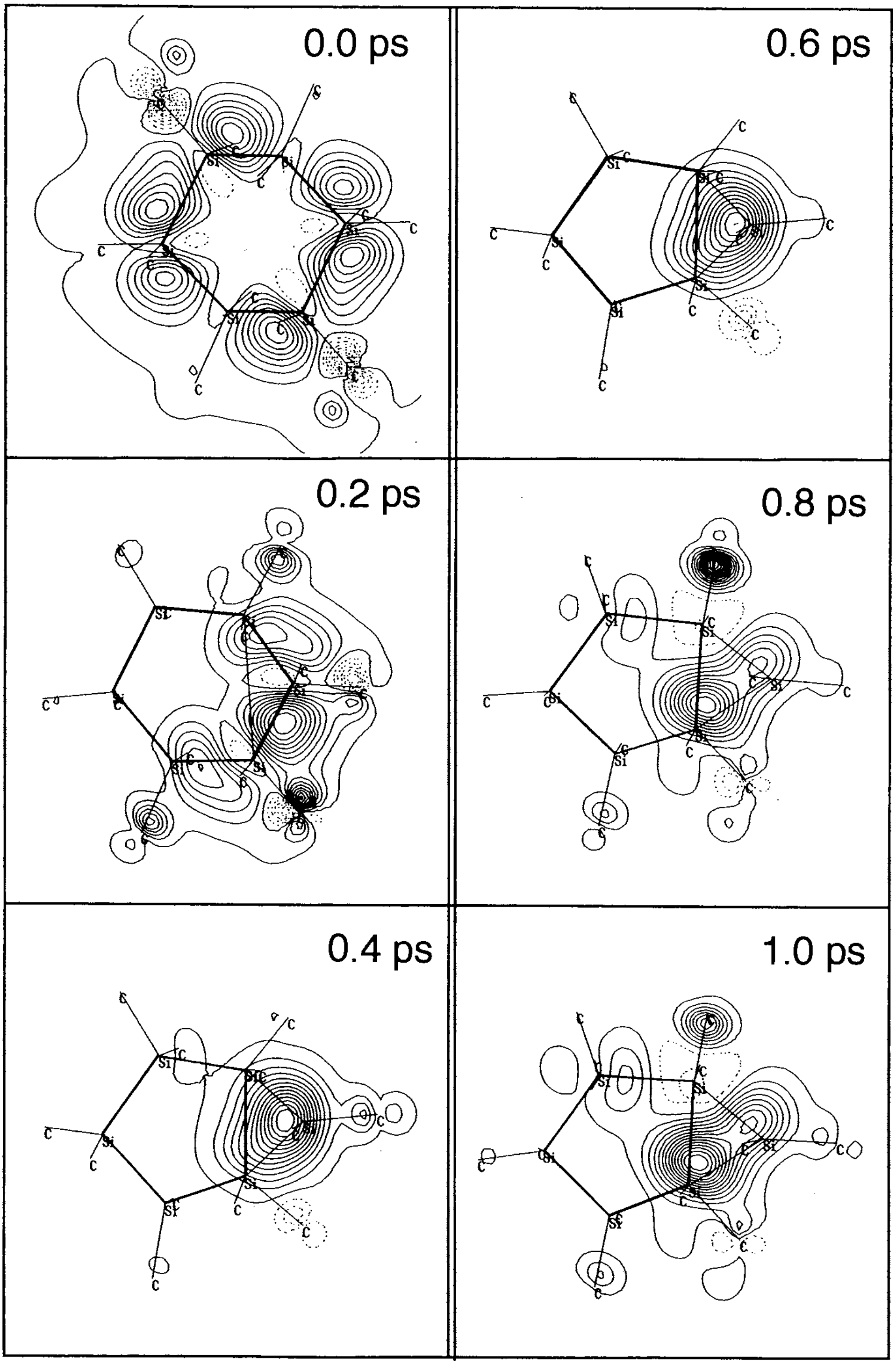

Fig. 3. Snapshots of the geometry and contour maps of spin density on $(Me_2Si)_6$ as a function reaction time on the T_1 potential energy surface. Bold line indicates the Si–Si skeleton. Real and dot lines show positive and negative spin densities, respectively.

3.4. Bond populations during the reaction

In order to elucidate the bond broken/formation processes as a function of reaction time, the bond populations between Si–Si bonds are calculated at selected reaction time. The results are summarized in Table 1. At time zero, the bond population between Si_1 and Si_2 is zero, meaning that there is no interaction between Si_1 and Si_2 atoms. On the other hand, bond population of Si_0–Si_1 bond is obtained by 0.351 which is as large as a normal bond population of Si–Si single bond. After 0.2 ps, the bond population of Si_0–Si_1 bond becomes a negative sign, whereas the one for Si_1–Si_2 bond has a positive value (0.147). After 0.4 ps,

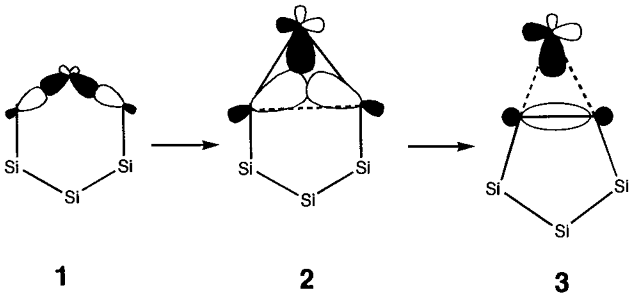

Fig. 4. Schematic representation of orbital interactions of the Si atoms at the T_1 excited state along the reaction coordinate.

the population of Si_1–Si_2 bond is 0.378 which corresponds to a normal bond population in Si–Si single bond, suggesting that the five-membered ring is completely formed at 0.4 ps. In addition, the population of Si_0–Si_2 is still negative at 0.4 ps.

Since an excess energy yielded as a reaction enthalpy converts mainly to the internal energy of five-membered ring, the vibrational and deformation modes of Si–Si skeleton are fully excited. Hence the population at sampling points (0.6 and 0.8 ps) were accidentally small. Time averaged population would give a normal Si–Si bond population.

3.5. Spin densities during the reaction

Contour plots of the spin density on $(Me_2Si)_6$ at selected reaction times are illustrated in Fig. 3. At the initial point of the photoreaction (0.0 ps), the unpaired electrons are fully delocalized over the Si-ring whose Si skeleton is a regular chair form. Methyl carbons have a negative spin density. It should be noted that there is no interaction between Si_1–Si_2 at time zero. The structure of ring-skeleton is deformed by accompanying with molecular vibration. At 0.2 ps, the unpaired electrons are distributed over four Si atoms and the Si skeleton is deformed by the structural relaxation. In this time, distance of Si_1–Si_2 is as long as 3.5 Å which is 0.5 Å shorter than the initial structure. After 0.4 ps, the unpaired electrons are extensively localized on Si_0 atom as clearly seen in Fig. 3 (0.4 ps). The electronic state and structure of the moiety of Me_2Si_0 are dose to those of silylene radical. At 0.6 ps, the unpaired electrons are fully localized on the Me_2Si_0 moiety and the chemical bond of Si_1–Si_0 is completely formed.

Table 2
Relative energies (in eV) in $(R_2Si)_6$ photo-reaction system ($R = CH_3$ and H)

R			UHF/3-21G[a]	UMP2/3-21G[a,b]
CH_3	$(Me_2Si)_6$	(S_0)	0.0	
		(T_1)	6.82	
	$(Me_2Si)_5+Me_2Si$	(T_1)	1.78	
	$(Me_2Si)_5+Me_2Si$	(S_0)	1.40	
H	$(H_2Si)_6$	(S_0)	0.0	0.0
		(T_1)	8.02	7.35
	$(H_2Si)_5+H_2Si$	(T_1)	2.32	2.86
	$(H_2Si)_5+H_2Si$	(S_0)	2.23	2.54

The values are calculasted by ab-initio UHF and UMP2 methods with 3-21G basis set.

[a] Closed shell molecules (S_0) were calculated by the RHF and MP2 methods.

[b] Geometries are optimized at the UHF/3-21G level.

4. Discussion

The previous studies have been considered only singlet energy surface (S_1) for reaction 1. However, it is important to elucidate the dynamics via the triplet state surface for deeper understanding the photoreaction of cyclic-Si compounds. From this point of view, the dynamics of the elimination reaction on the triplet state (T_1) surface have been investigated in the present study. The dynamics calculation strongly indicated that the photochemical extrusion reaction of Me_2Si: proceeds on T_1 surface as well as S_1 surface, if intersystem crossing (surface hopping process) between S_1 and T_1 occurred on the reaction. This theoretical prediction can be confirmed by an experiment that triplet quencher is added to the reaction system and concentration dependency on the yield of Me_2Si: is examined.

Photoreaction mechanism of $(Me_2Si)_6$ is qualitatively discussed in terms of the orbital interaction. Schematic representation of the orbital interaction on the Si_1–Si_0–Si_2 moiety during the photoreaction process is illustrated in Fig. 4. At the ground state, the highest occupied molecular orbital (HOMO) shows that all Si–Si bonds have a bonding nature, suggesting that the regular cyclic structure is most stable. At the first excited state, the orbital interaction of Si–Si bonds changes to all anti-bonding type and the unpaired electrons are widely delocalized on Si–Si skeleton. After the electronic and vibrational coupling (this is composed of a symmetric Si_0–Si_j ($j = 1$ and 2) stretching mode), the unpaired electrons are localized on the Si atom which dissociates as the silylene radical. The interaction between Si_0 and Si_j ($j = 1$ and 2) is composed of strong anti-bonding interaction (**1**). Magnitude of the anti-bonding interaction may be enough to occur the elongation of Si_0–Si_j bonds. Accompanying with the slight elongation of Si_0–Si_j bonds, the Si_1–Si_2 bond is newly formed because of the same orbital phase (**2**). After more elongation of the Si–Si bond, the Si_1–Si_2 bond is completely generated (**3**) and silylene radical is dissociated from five-membered ring.

We considered only the reaction system composed of six-membered ring $(Me_2Si)_6$ in the present study. Our preliminary calculation [9] indicates that the silylene radical is also generated from the five-membered ring $(Me_2Si)_5$ at the T_1 state and this reaction proceeds in terms of the same mechanism as reaction 1. Hence the present mechanism would be general in photoreaction of the cyclic-Si compounds.

Several approximations to calculate the potential energy surface and to treat the reaction dynamics were introduced in the present study. We assumed PM3 multi-dimensional potential energy surface in the trajectory calculations throughout. The rapid geometry change occurred at the short time region because the initial structure at T_1 surface is much unstable. In order to ascertain this point, a preliminary ab-initio MO calculation was carried out at the UHF/3-21G and UMP2/3-21G levels of theory. In all UHF calculations for the open-shell triplet (T_1) state, $\langle S^2 \rangle$ values were < 2.040 throughout. The relative energies calculated are given in Table 2. Both ab-initio calculations showed that the energy level of triplet state is much higher than that of product states (singlet and triplet). This result implies that reaction 1 occurs spontaneously from T_1 state. It can be expected from the energetics (Table 2) that ab-initio dynamics calculation would give larger reaction rate for reaction 1. More accurate wave function (such as MP2/6-31G*) may provide deeper insight in the dynamics. Despite several assumptions are introduced here, the results enable us to obtain valuable information on the photoreaction process in $(Me_2Si)_6$.

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References

[1] R.D. Miller, J. Miehl, Chem. Rev. 89 (1989) 1359.

[2] T.J. Drahnak, J. Miehl, R. West, J. Am. Chem. Soc. 101 (1979) 5427.

[3] A.S. Nazran, J.A. Hawari, D. Griller, I.S. Alnaimi, W.P. Weber, J. Am. Chem. Soc. 106 (1984) 7267.

[4] M. Ishikawa, M. Kumada, J. Organometal. Chem. 42 (1972) 325.

[5] B.G. Ramsey, J. Organometal. Chem. 67 (1974) C67.

[6] (a) H. Tachikawa, Chem. Phys. 211 (1996) 305. (b) H. Tachikawa, J. Phys. Chem. 99 (1995) 255. (c) H. Tachikawa, T. Hamabayashi, H. Yoshida, J. Phys. Chem. 99 (1995) 16630. (d) H. Tachikawa, H. Takamura, H. Yoshida, J. Phys. Chem. 98 (1994) 5298. (e) H. Tachikawa, N. Ohta, Chem. Phys. Lett. 224 (1994) 465. (f) H. Tachikawa, A. Ohtake, H. Yoshida, J. Phys. Chem. 97 (1993) 11944. (g) H. Tachikawa, N. Hokari, H. Yoshida, J. Phys. Chem. 97 (1993) 10035.

[7] (a) H. Tachikawa, J. Phys. Chem. A 101 (1997) 7454. (b) H. Tachikawa, J. Phys. Chem. 100 (1996) 17090. (c) H. Tachikawa, K. Komaguehi, Int. J. Mass Spectrom. Ion Process 164 (1997) 39.

[8] (a) J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209. (b) J.J.P. Stewart, J. Comput. Chem. 10 (1989) 221. (c) M.J. Friseh, G.W. Trucks, M. Head-Gordon, et al., An ab-initio molecular orbital calculation program; Gaussian 92, Revision F.3, Gaussian, Pittsburgh, PA, 1992. (d) Program for the dynamics calculation was made by our group.

[9] Y. Yamada, H. Tachikawa, (to be published).