Ab initio study of mechanism of the formation of a silicic bis-heterocyclic compound in the reaction of silylenesilylene (H₂Si=Si:) with ethene

XIUHUI LU*, LEYI SHI, YONGQING LI and ZHINA WANG

School of Chemistry and Chemical Engineering, University of Jinan, Jinan, Shandong, 250022, People's Republic of China

Abstract: The mechanism of the cycloaddition reaction of the formation of a silicic bis-heterocyclic compound between singlet state silylenesilylene (H₂Si=Si:) and ethene was investigated by the CCSD(T)//MP2/6-31G* method. From the potential energy profile, it can be predicted that the reaction has one dominant reaction pathway. The presented rule of the dominant reaction pathway is that the [2+2] cycloaddition effect of the two reactants leads to the formation of a four-membered ring silylene (INT1). When the four-membered ring silylene (INT1) interacts with ethene, due to sp^3 hybridization of the Si: atom in four-membered ring silylene (INT1), the four-membered ring silylene (INT1) further combines with ethene to form a silicic bis-heterocyclic compound (P2).

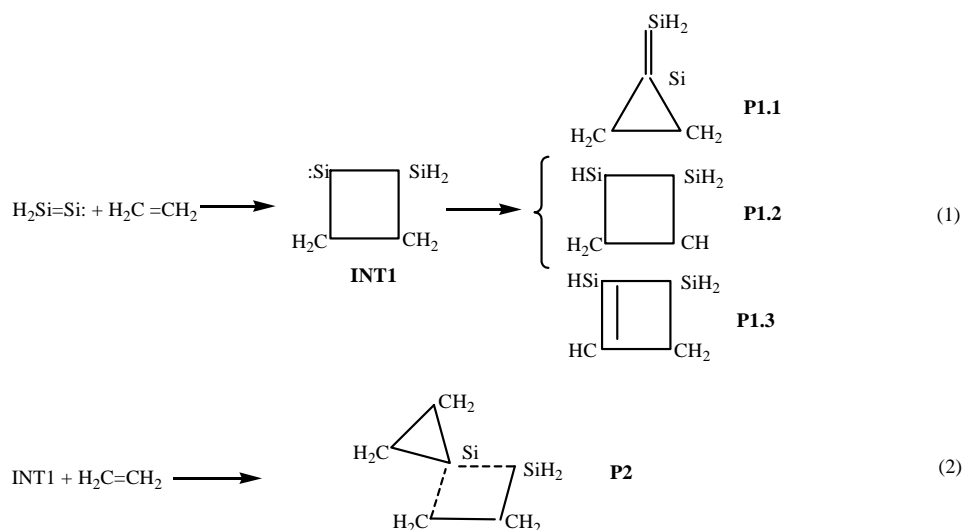*Keywords*: silylenesilylene (H₂Si=Si:); cycloaddition reaction; potential energy profile.

INTRODUCTION

In recent years, silylene as an important active intermediate has attracted much attention in various fields of chemistry[1,2] and has led to a varied chemistry concerning silylenes. Reactions of silylene are regarded as an effective method in the synthesis of new bonds and heterocyclic compounds containing Si, which have long been some of the most interesting topics for organo–silicon chemists. There have been many theoretical and experimental investigations on addition reactions to saturated silylene.[3–9] For example, the rate constant for the reaction of SiH_2 ($\tilde{X}^1A$) and C_2H_4 is 9.7×10^{-11} cm³ mol⁻¹ s⁻¹, measured by Inoue and Suzuki using the laser photolysis–laser-induced fluorescence method at 298 K and 1 Torr.[6]

Becerra *et al.*[9] obtained the following Arrhenius parameters: log (*A* / cm³ mol⁻¹ s⁻¹) = –10.10±0.06, E_a = –3.91±0.47 kJ mol⁻¹, and the Arrhenius Equa-

---

tion: log $(k$ / cm^3 mol^{-1} s$^{-1}) = (-10.10\pm0.06) + (3.91\pm0.47$ kJ mol$^{-1})$ / RTln 10, by using laser flash photolysis to generate SiH$_2$ and monitoring the reaction of SiH$_2$ with acetaldehyde over the pressure range 1–100 Torr and temperature range 297–599 K. Some studies were performed on the cycloaddition reaction of saturated silylene.[10–13] In addition, the cycloaddition reaction of unsaturated silylenes were preliminarily studied,[14–18] but these studies were always limited to the cycloaddition reaction of silylidene and its derivatives (R$_1$R$_2$C=Si: (R$_1$, R$_2$ = = H, Me, F, Cl, Br, Ph, Ar, *etc.*)). Hitherto, there are no reports on the cycloaddition reaction of silylene silylene and its derivatives (R$_1$R$_2$ Si=Si: (R$_1$, R$_2$ = H, Me, F, Cl, Br, Ph, Ar, *etc.*)); hence, this is a new study field of the cycloaddition reaction of unsaturated silylene. In order to explore the rules of the cycloaddition reactions between silylenesilylene or its derivatives and symmetric π-bonded compounds, silylenesilylene (H$_2$Si=Si:) and ethene were chosen as model molecules, and it's the mechanism of their reaction was investigated and analyzed theoretically. The results showed that this cycloaddition reaction has two possible pathways (considering the hydrogen transfer simultaneously) as follows:

(1)

(2)

The research result indicates the laws of the cycloaddition reaction between silylenesilylene (H$_2$Si=Si:) and its derivatives and symmetric π-bonded compounds, which are significant for the synthesis of small-ring and bis-heterocyclic compounds with Si. This study extends the research area of the reactions of ethene with R$_2$C=C:[19,20] and heteroatom substituted ylenes (Si and Ge)[14,17,21–25], and especially enriches the research knowledge of silylene chemistry.

CALCULATION METHOD

MP2/6-31G^{*26} implemented in the Gaussian 98 package was employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis were realized for the stationary points on the reaction profile. Zero point energy and CCSD(T) corrections were included in the energy calculations. In order to explicitly establish the relevant species, the intrinsic reaction coordinate (IRC)[27,28] was also calculated for all the transition states appearing on the cycloaddition energy profile.

RESULTS AND DISCUSSION

The geometric parameters of the four-membered ring silylene (INT1), the transition states (TS1.1, TS1.2 and TS1.3) and the products (P1.1, P1.2, P1.3 and P2) which appear in the cycloaddition reactions (1) and (2) between silylene-silylene (R1) and ethene (R2) are given in Fig. 1. The energies are listed in Table I, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. The results of the IRC calculation for TS1.1, TS1.2 and TS1.3 are given in Fig. 3. According to the calculations of the IRC of TS1.1, TS1.2 and TS1.3 and further optimization for the primary IRC results, TS1.1 connects INT1 with P1.1; TS1.2 connects INT1 with P1.2 and TS1.3 connects INT1 with P1.3. According to Fig. 2, it can be seen that reaction (1) consists of four steps: 1) the two reactants (R1 and R2) form a four-membered ring silylene (INT1), which is a barrier-free exothermic reaction of 509.6 kJ mol^{-1}; 2) INT1 isomerizes to a three-membered ring product (P1.1) through transition state (TS1.1) with an energy barrier of 72.7 kJ mol^{-1}; 3) and 4) INT1 undergoes hydrogen transfer, *via* either transition state TS1.2 and TS1.3 with energy barriers of 60.1 and 116.0 kJ mol^{-1}, resulting in the formation of product P1.2 and P1.3, respectively. According to Fig. 2, because the energy of P1.1 is 51.5 kJ mol^{-1} higher than that of INT1, the reaction of INT1→P1.1 is thermodynamically prohibited at normal temperatures and pressure. INT1→P1.2 and INT1→P1.3 are mutually competing reactions but because the energy of TS1.3 is 55.9 kJ mol^{-1} higher than that of TS1.2, P1.2 is the main product of reaction (1).

In reaction (2), INT1 further reacts with ethene (R2) to form a silicic bis-heterocyclic compound (P2). According to Fig. 2, this reaction is a barrier-free exothermic reaction of 141.7 kJ mol^{-1}. A careful and detailed study of this reaction, for which no intermediates or transition states exist, was performed. It was believed that when INT1 interacts with ethene, due to the large radius of the Si atom, sp^3 hybridization the Si(2) atom in INT1 occurs before INT1 and ethene could form intermediate and transition states, and thus INT1 combines with ethene to form the silicic bis-heterocyclic compound (P2).

According to Fig. 2, INT1→P1.2 and reaction (2) are two mutually competitive reactions and as the reaction INT1→P1.2 has a barrier of 60.1 kJ mol^{-1} while the reaction INT1+R2→P2 directly reduces the system energy by 141.7 kJ mol^{-1}, reaction (2) should be the main reaction pathway.

According to the above analysis, the dominant reaction channel of the cyclo-addition reaction between singlet silylenesilylene and ethene is as follows:
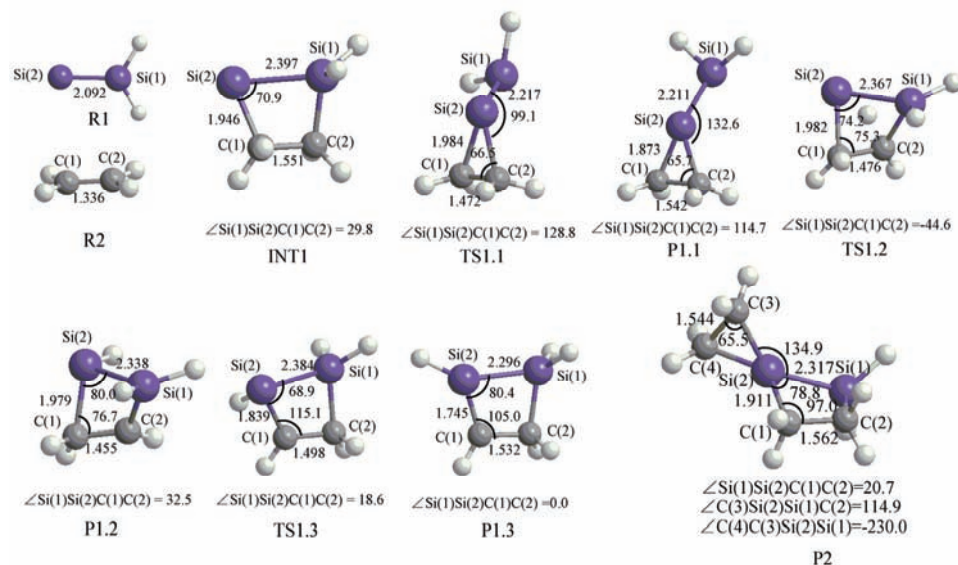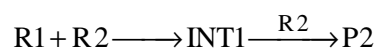
$$R1 + R2 \longrightarrow INT1 \xrightarrow{\ R2\ } P2$$

Fig.1. Optimized MP2/6-31G* geometrical parameters and the atomic numbering for the species in cycloaddition reactions (1) and (2). Bond lengths and bond angles are in angstroms and degrees, respectively.
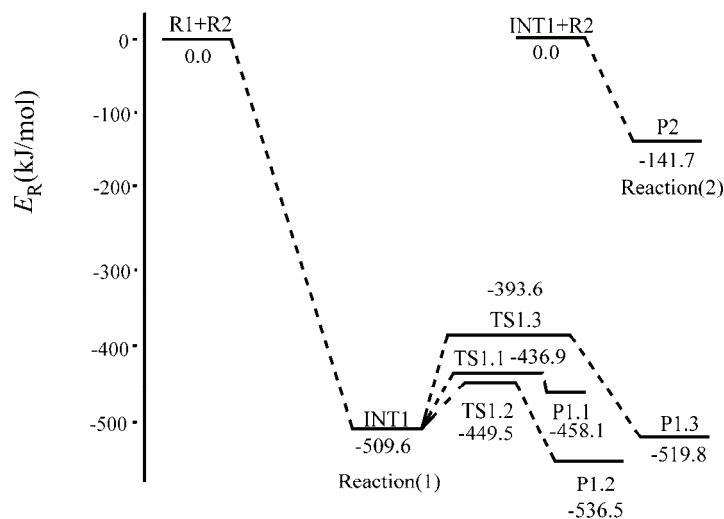

Fig. 2. The potential energy profile for the cycloaddition reactions between H$_2$Si=Si: and ethene with CCSD (T)//MP2/6-31G*.

The mechanism of the dominant reaction pathway can be explained by the molecular orbital diagrams (Figs. 4 and 5) and Fig. 1. According to the NBO analysis of INT1, the natural electron configuration of the Si(2) atom in INT1 is [core] $3s(1.69)\ 3p(1.62)\ 3d(0.02)$. Hence, it is certain that the hybridization of Si(2) atom in INT1 is sp (Fig. 5). According to Figs. 1 and 4, when the silylenesilylene (R1) interacts with ethane (R2), due to the [2+2] cycloaddition effect of the two π-bonds in silylenesilylene (R1) and ethene, a four-membered ring silylene (INT1) is formed. As INT1 is still an active intermediate, INT1 may further react with ethene to form a silicic bis-heterocyclic compound (P2). The mechanism of this reaction can be explained with Figs. 1 and 5. When INT1 interacts with ethene, due to the large radius of the Si atom, sp^3 hybridization of the Si(2) atom in INT1 occurs before any intermediate or transition states could be formed. Thus INT1 combined with ethene to form a silicic bis-heterocyclic compound (P2). According to the NBO analysis of P2, the Si(2) atom is $sp^{2.53}$ in the Si(2)–C(1) bond, the Si(2) atom is $sp^{2.54}$ in the Si(2)–Si(1) bond, the Si(2) atom is $sp^{3.81}$ in the Si(2)–C(3) bond, the Si(2) atom is $sp^{3.24}$ in the Si(2)–C(4) bond. Thus, it is certain that the Si(2) atom in INT1 undergoes sp^3 hybridization, when INT1 interacts with ethene.
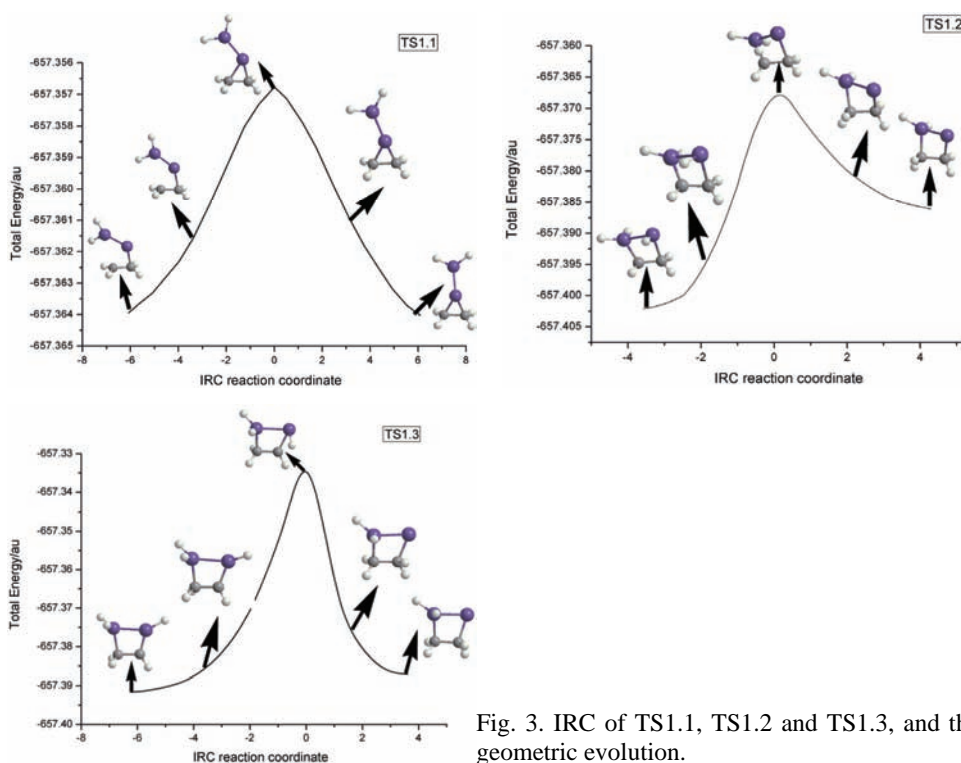

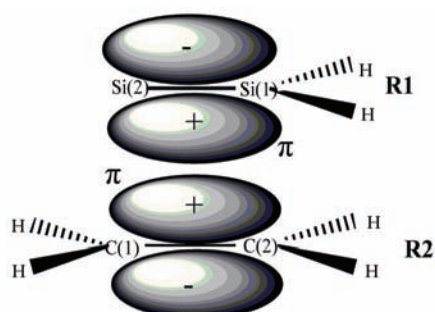Fig. 3. IRC of TS1.1, TS1.2 and TS1.3, and their geometric evolution.

Fig. 4. A schematic interaction diagram for the frontier orbitals of H₂Si=Si: (R1) and H₂C=CH₂ (R2).
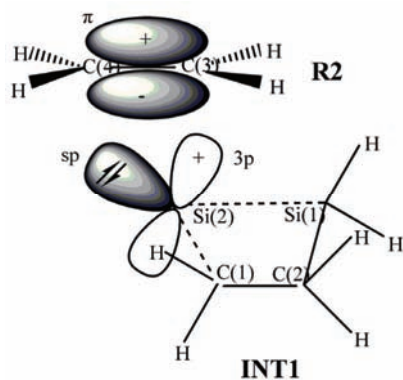

Fig. 5. A schematic interaction diagram for the frontier orbitals of INT1 and H₂C= CH₂ (R2).

CONCLUSIONS

From the potential energy profile of the cycloaddition reaction between singlet silylenesilylene and ethene obtained by the CCSD(T)//MP2/6-31G* method, it can be predicted that the dominant channel of this reaction consists of two steps: I) the two reactants first form a four-membered ring silylene (INT1) through a barrier-free exothermic reaction of 509.6 kJ mol^{-1} and (II) INT1 further reacts with ethene (R2) to form a silicic bis-heterocyclic compound (P2), which is also a barrier-free exothermic reaction of 141.7 kJ mol^{-1}.

ИЗВОД

AB INICIO ПРОУЧАВАЊЕ МЕХАНИЗМА НАСТАЈАЊА БИС-ХЕТЕРОЦИКЛИЧНОГ ЈЕДИЊЕЊА РЕАКЦИЈОМ СИЛИЛЕНСИЛИЛЕНА (H₂Si=Si:) И ЕТЕНА

XIUHUI LU, LEYI SHI, YONGQING LI и ZHINA WANG

School of Chemistry and Chemical Engineering, University of Jinan, Jinan, Shandong, 250022, People's Republic of China

Механизам циклоадицијске реакције између синглетног силиленесилилена (H₂Si=Si:) и етена, у којој настаје једно бис-хетероциклично једињење, истраживан је методом CCSD(T)//MP2/6-31G*. На основу профила потенцијалне енергије, предвиђа се да реакција има један доминантни реакциони пут. То је [2+2] циклоадиција која доводи до формирања

силилена са четворочланим прстеном (INT1). Када четворочлани прстен силилена (INT1) интерагује са етеном, услед sp3 хибридизације Si: атома у прстену, овај прстен се комбинује са етеном градећи једно бис-хетероциклично силицијумово једињење (P2).

REFERENCES

1. a) M. Jones Jr., R. A. Moss, *Reactive Intermediates*, Vol. 1, Wiley Interscience, New York, 1978, p. 229; b) M. Jones Jr., R. A. Moss, *Reactive Intermediates*, Vol. 2, Wiley Interscience, New York, 1981, p. 335; c) M. Jones Jr., R. A. Moss, *Reactive Intermediates*, Vol. 3, Wiley Interscience, New York, 1985, p. 333
2. R. A. Abramovitch, *Reactive Intermediates*, Vol. 2, Plenum Press, New York, 1982, p. 297
3. D. S. Rogers, K. L. Walker, M. A. Ring, E. O'Neal, *Organometallics* **6** (1987) 2313
4. J. A. Boatz, S. Gordon, *J. Phys. Chem.* **93** (1989) 3025
5. D. A. Horner, R. S. Grev, F. Schaefer, *J. Am. Chem. Soc.* **114** (1992) 2093
6. G. Inoue, M. Suzuki, *Chem. Phys. Lett.* **122** (1985) 361
7. A. Al-Rubaiey, R. Walsh, *J. Phys. Chem.* **98** (1994) 5303
8. R. Becerra, J. P. Cannady, R. Walsh, *J. Phys. Chem., A* **103** (1999) 4457
9. R. Becerra, J. P. Cannady, R. Walsh, *Phys. Chem. Chem. Phys.* **3** (2001) 2343
10. X. H. Lu, Y. X. Wang, C. B. Liu, C. H. Deng, *Acta Chim. Sinica* **56** (1998) 1075
11. X. H. Lu, Y. X. Wang, C. B. Liu, *Chem. J. Chin. Univ.* **20** (1999) 612
12. X. H. Lu, Y. X. Wang, C. H. Deng, *Acta Phys. Chem. Sinica* **14** (1998) 309
13. X. H. Lu, Y. X. Wang, C. B. Liu, *Chin. J. Chem. Phys.* **12** (1999) 460
14. X. H. Lu, H. B. Yu, W. R. Wu, *New J. Chem.* **29** (2005) 332
15. X. H. Lu, H. B. Yu, Y. H. Xu, P. P. Xiang, Y. D. Liu, *J. Mol. Struct. (Theochem)* **770** (2006) 185
16. X. H. Lu, H. B. Yu, Y. H. Xu, P. P. Xiang, X. Che, *Mol. Phys.* **105** (2007) 1961
17. X. H. Lu, X. Che, H. B. Yu, P. P. Xiang, Y. H. Xu, *J. Mol. Struct. (Theochem)* **821** (2007) 53
18. X. H. Lu, H. B. Yu, X. Che, P. P. Xiang, *Int. J. Quant. Chem.* **108** (2008) 1114
19. X. H. Lu, P. P. Xiang, R. Wei, X. Che, *J. Mol. Struct. (Theochem)* **853** (2008) 82
20. X. H. Lu, Z. X. Lian, Y. Q. Li, *J. Serb. Chem. Soc.* **76** (2011) 743
21. X. H. Lu, J. F. Han*;* H. B. Yu*;* Z. X. Lian, *Chin. J. Chem. Phys.* **23** (2010) 533
22. X. H. Lu, Y. Hua Xu, H. B Yu, W. R. Wu, *J. Phys. Chem., A* 109 (2005) 6970
23. X. H. Lu, Y. H. Xu, H. B. Yu, H. Lin, *Chin. J. Chem,* **23** (2005) 1339
24. C. L. Tian, Y. H. Xu, X. H. Lu, *Int. J. Quantum Chem.* **110** (2010) 1675
25. X. H. Lu, J. F. Han, Z. X. Lian, Y. Q. Li, *J. Serb. Chem. Soc.* **76** (2011) 1395
26. L. A. Curtis, K. Raghavachari, J. A. Pople, *J. Chem. Phys.* **98** (1993) 1293
27. K. Fukui, *J. Phys. Chem.* **74** (1970) 4161
28. K. Ishida, K. Morokuma, A. Komornicki, *J. Chem. Phys.* **66** (1981) 2153.