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***Ab initio* study of the mechanism of the formation of a bis-heterocyclic compound containing Si and Ge by reaction of germylene silylene (H₂Ge=Si:) and ethene**

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Abstract: The mechanism of the cycloaddition reaction between singlet state germylene silylene (H₂Ge=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 only 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 with Ge (INT1). Due to sp³ hybridization of the Si atom in four-membered ring silylene with Ge (INT1), INT1 further reacts with ethene to form a bis-heterocyclic compound with Si and Ge (P2).

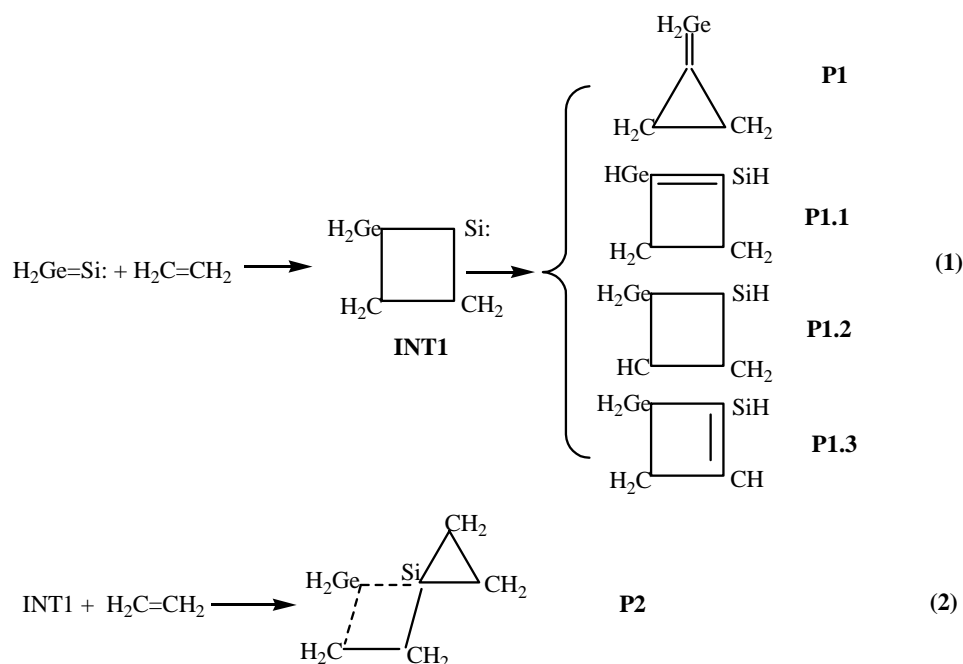
Keywords: germylene silylene; reaction mechanism; potential energy profile.

INTRODUCTION

Unsaturated silylenes are an important type of active intermediates. Their cycloaddition reactions are considered as providing a convenient, short synthesis pathway for the synthesis of tensility cyclotella, silapolycyclic compounds and compounds that are difficult to synthesize by other methods, and are also regarded as an effective method for the syntheses of new bonds and heterocyclic compounds containing Si. H₂C=Si: is the simplest unsaturated silylene, which was first observed experimentally by Leclercq and Dubois in 1979.¹ Srinivas *et al.*² employed neutralization–reionization mass spectrometry to show that H₂C=Si: is a viable molecule in a low-pressure gas phase. A theoretical study indicated that the ground state of H₂C=Si: is a singlet state.³ The energy of H₂C=Si: is 84 kcal mol⁻¹ lower than that of silacetylide; thus, H₂C=Si: is the lowest energy isomer.⁴ Preliminary studies on the cycloaddition reactions of unsaturated silylenes were performed,^{5–9} but these studies were limited to the cycloaddition re-

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action of methylene silylene and its derivatives ($X_2C=Si:$, $X=H, F, Cl, CH_3$, *etc.*). Hitherto, no reports on the cycloaddition reaction of germylene silylene and its derivatives ($X_2Ge=Si:$, $X=H, F, Cl, CH_3$, *etc.*) exist; it is a new area of research on the cycloaddition reaction of unsaturated silylenes. It is quite difficult to investigate the mechanisms of the cycloaddition reaction directly by experimental methods due to the high activity of germylene silylene, therefore, a theoretical study is more practical. To explore the rules of the cycloaddition reaction between germylene silylene (including its derivatives) and symmetric π -bonded compounds, germylene silylene ($H_2Ge=Si:$) and ethene were selected as model molecules, and the mechanism of the cycloaddition reaction between germylene silylene and ethene was investigated and analyzed theoretically. The results showed that there are two possible pathways for the cycloaddition reaction (considering the H transfer simultaneously) as follows:



CALCULATION METHOD

MP2/6-31G^{*10} implemented in the Gaussian 98 package was employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis were performed for the stationary points on the reaction potential energy 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 coordinates (IRC)^{11,12} were also calculated for all the transition states appearing on the potential energy profile of the cycloaddition.

RESULTS AND DISCUSSION

Reaction (1): The pathways of the formation of a four-membered ring silylene with Ge (INT1), H-transfer products (P1.1, P1.2 and P1.3) and a three-membered ring product (P1)

Theoretical investigations showed that the ground state of germylene silylene ($\text{H}_2\text{Ge}=\text{Si}$) is the singlet state. The geometric parameters of the intermediate (INT1), transition states (TS1, TS1.1, TS1.2 and TS1.3) and products (P1, P1.1, P1.2 and P1.3), which appear in reaction (1) between germylene silylene and ethane, 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 unique imaginary frequencies of the transition states TS1, TS1.1, TS1.2 and TS1.3 are 196.4 , 600.2 , 1037.0 and 985.6 cm^{-1} , respectively, and, consequently, these transition states can be affirmed as real ones. According to the calculations of the IRC of TS1, TS1.1, TS1.2 and TS1.3, further optimization of the primary IRC results, TS1 connects INT1 with P1, TS1.1 connects INT1 with P1.1, TS1.2 connects INT1 with P1.2 and TS1.3 connects INT1 with P1.3.

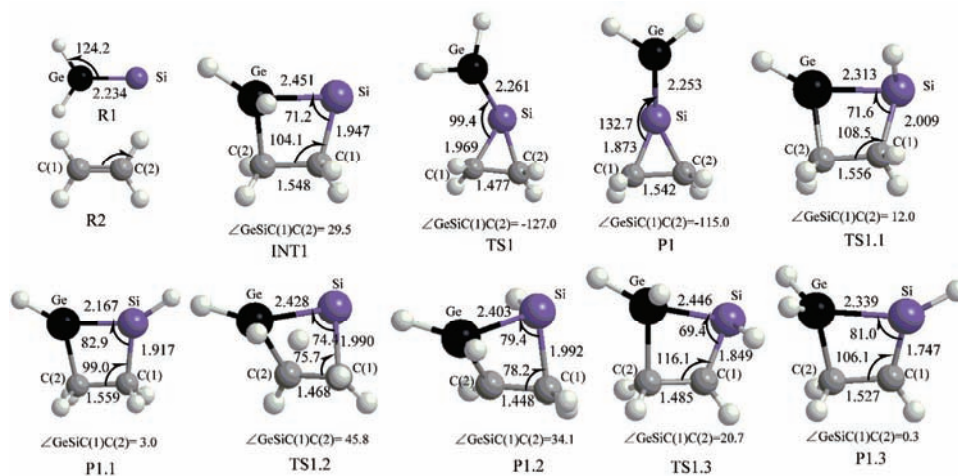


Fig. 1. Optimized MP2/6-31G* geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1). Bond lengths and bond angles are in Å and °, respectively.

According to Fig. 2, it can be seen that reaction (1) consists of five steps: the first step is that the two reactants (R1 and R2) form a four-membered ring silylene (INT1), which is a barrier-free exothermic reaction of $127.9 \text{ kJ mol}^{-1}$; the second step is that INT1 isomerizes to a three-membered ring product (P1) via the transition state TS1 with an energy barrier of 56.7 kJ mol^{-1} ; the following three steps are that INT1 undergoes H-transfer via transition states TS1.1, TS1.2

and TS1.3 with energy barriers of 42.4, 66.2 and 118.6 kJ mol⁻¹, respectively, resulting in the formation of products P1.1, P1.2 and P1.3. As the energy of P1 is 39.7 kJ mol⁻¹ higher than that of INT1, the reaction INT1→P1 is thermodynamically prohibited at normal temperature and pressure. The energy barriers of TS1.2 and TS1.3 are 14.3 and 23.8 kJ mol⁻¹ higher than that of TS1.1; therefore, INT1→P1.1 is the dominant reaction pathway of the reaction (1).

TABLE 1. Zero point energy (*ZPE* / hartree), total energies (*E_T* / hartree) and relative energies (*E_R* / kJ·mol⁻¹) for the species from various theoretical methods (*E_T* = *E*(Species) + *ZPE*; *E_R* = *E_T* - *E*(R1+R2); *E_R* = *E_T* - *E*(INT1+R2))

Reaction	Species	<i>ZPE</i>	MP2/6-31G*		CCSD(T)/MP2/6-31G*	
			<i>E_T</i>	<i>E_R</i>	<i>E_T</i>	<i>E_R</i>
(1)	R1+R2	0.06544	-2441.59424	0.0	-2441.67589	0.0
	INT1	0.07079	-2441.65402	-157.0	-2441.72461	-127.9
	TS1(INT1-P1)	0.06938	-2441.63161	-98.1	-2441.70301	-71.2
	P1	0.06962	-2441.63776	-114.3	-2441.70947	-88.2
	TS1.1(INT1-P1.1)	0.06935	-2441.63740	-113.3	-2441.70845	-85.5
	P1.1	0.07197	-2441.66161	-176.9	-2441.72835	-137.7
	TS1.2(INT1-P1.2)	0.06714	-2441.63285	-101.4	-2441.69939	-61.7
	P1.2	0.06805	-2441.66461	-184.8	-2441.72831	-137.6
	TS1.3(INT1-P1.3)	0.06492	-2441.60500	-28.3	-2441.67945	-9.3
	P1.3	0.06734	-2441.66052	-174.0	-2441.72664	-133.2
(2)	INT1+R2	0.12283	-2519.88701	0.0	-2519.99449	0.0
	P2	0.12720	-2519.95156	-169.5	-2520.04690	-137.6

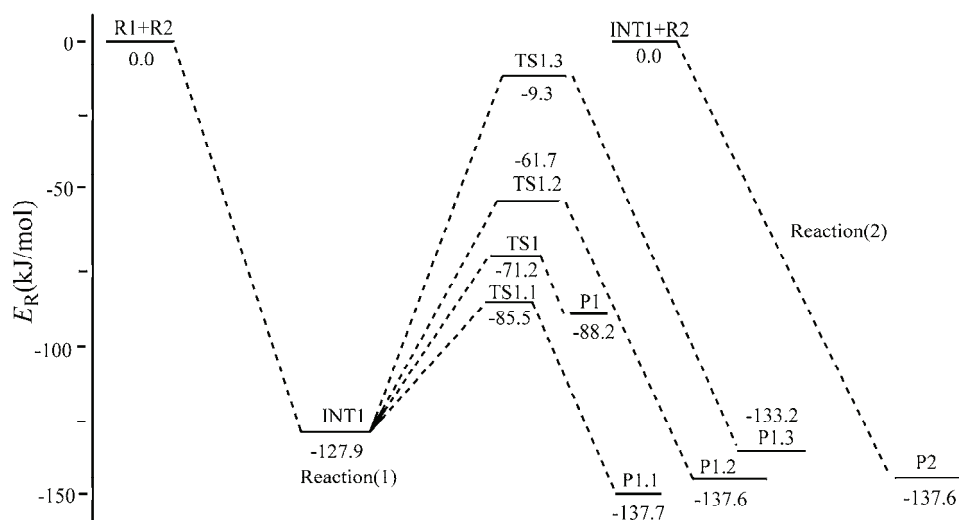


Fig. 2. The potential energy profile for the cycloaddition reactions between H₂Ge=Si: and H₂C=CH₂ with CCSD (T)/MP2/6-31G*.

Reaction (2): The formation pathway of a bis-heterocyclic compound with Si and Ge (P2)

In reaction (2), INT1 further reacts with ethene (R2) to form a bis-heterocyclic compound with Si and Ge (P2). The geometrical parameters of product (P2) which appear in reaction (2) are given in Fig. 3. The energies are listed in Table I, and the potential energy profile for the cycloaddition reaction is shown in Fig. 2. According to Fig. 2, reaction (2) is a barrier-free exothermic reaction of $137.6 \text{ kJ mol}^{-1}$. A careful and detailed study of this reaction, for which no intermediates or transition states exist, was performed. It is believed that due to the large radius of the Si atom before an intermediate or transition state could be formed, sp^3 hybridization of the Si atom in INT1 occurred and INT1 combined with the ethene to form a bis-heterocyclic compound with Si and Ge (P2).

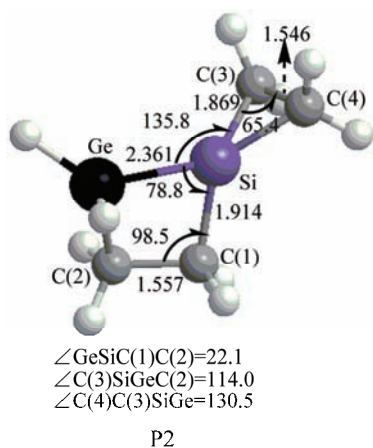


Fig. 3. Optimized MP2/6-31G* geometrical parameters of P2 and the atomic numbering for the species in cycloaddition reaction (2). Bond lengths and bond angles are in Å and °, respectively.

According to Fig. 2, $\text{INT1} \rightarrow \text{P1.1}$ and reaction (2) are two mutually competitive reactions but because $\text{INT1} \rightarrow \text{P1.1}$ requires a barrier of 42.4 kJ mol^{-1} be surmounted, while $\text{INT1} + \text{R2} \rightarrow \text{P2}$ directly reduces the system energy by $137.6 \text{ kJ mol}^{-1}$, reaction (2) should be the main reaction pathway.

Theoretical analysis and explanation of the dominant reaction pathway

According to the above analysis, the dominant reaction pathway of the cycloaddition reaction between singlet state germylene silylene and ethene is as follows:



In this reaction, the frontier molecular orbitals of R1, R2, and INT1 are shown in Fig. 4. According to Fig. 4, the frontier molecular orbitals of R1, R2 and INT1 can be expressed as in the schematic diagram given in Figs. 5 and 6. The mechanism of the dominant reaction channel can be explained with the mo-

lecular orbital diagrams (Figs. 5 and 6) and Figs. 1 and 3. According to Figs. 1 and 5, when germylene silylene and ethene approach each other, due to the [2+2] cycloaddition effect of the two π -bonds in germylene silylene and ethene, a four-membered ring silylene with Ge is formed (INT1). As INT1 is an active intermediate, it may further react with ethene to form a bis-heterocyclic compound with Si and Ge (P2). The mechanism of this reaction can be explained with Figs. 3 and 6. As INT1 and ethene approach each other, due to the large radius of the Si atom in INT1, sp^3 hybridization of the Si atom in INT1 occurs before the formation of any intermediate or transition state between INT1 and ethane and then INT1 combines with the ethene to form a bis-heterocyclic compound with Si and Ge (P2).

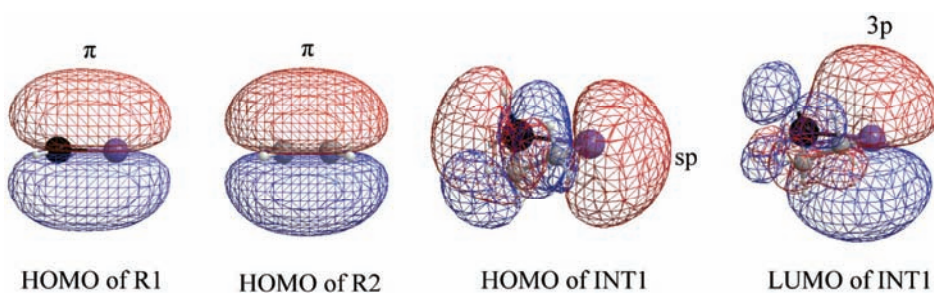


Fig. 4. The frontier molecular orbital of R1, R2 and INT1.

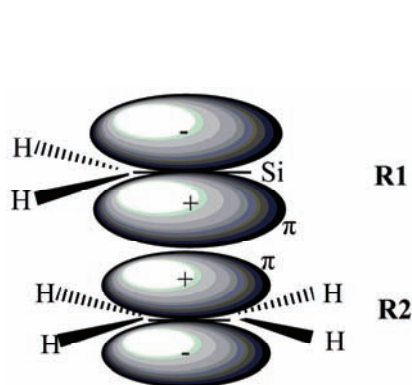


Fig. 5. A schematic interaction diagram for the frontier orbitals of $H_2Ge=Si:$ (R1) and $H_2C=CH_2$ (R2).

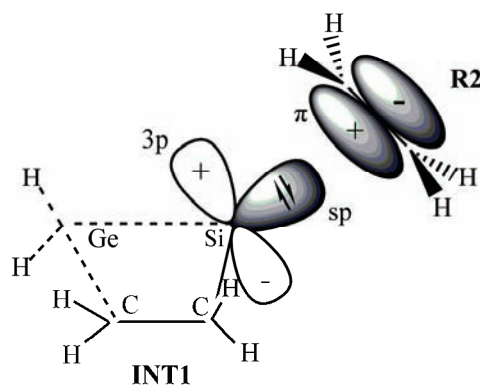


Fig. 6. A schematic interaction diagram for the frontier orbitals of INT1 and $H_2C=CH_2$ (R2).

CONCLUSIONS

From the potential energy profile of the cycloaddition reaction between singlet state germylene silylene and ethene obtained by the CCSD(T)//MP2/6-31G* method, it can be predicted that the reaction has a dominant reaction pathway. The dominant reaction pathway consists of two steps: first the two reactants form

a four-membered ring silylene with Ge (INT1) through a barrier-free exothermic reaction of $127.9 \text{ kJ mol}^{-1}$ and then INT1 further reacts with ethene (R2) to form a bis-heterocyclic compound with Si and Ge (P2), which is also a barrier-free exothermic reaction of $137.6 \text{ kJ mol}^{-1}$.

ИЗВОД

AB INITIO ИСПИТИВАЊЕ МЕХАНИЗМА РЕАКЦИЈЕ ФОРМИРАЊА
БИС-ХЕТЕРОЦИКЛИЧНИХ ЈЕДИЊЕЊА СА Si И Ge ИЗМЕЂУ
ГЕРМИЛЕН-СИЛЕНА ($\text{H}_2\text{Ge}=\text{Si}$) И ЕТЕНА

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Механизам цикло-оксидационе реакције између гермилен-силена ($\text{H}_2\text{Ge}=\text{Si}$) у синглетном стању и етена је био испитиван CCSD(T)//MP2/6-31G* методом из профила потенцијалне енергије уз претпоставку да реакција има само један доминантни реакциони пут. Приказано правило о једном реакционом путу је да [2+2] циклоадиција проузрокује да два реактанта доводе до формирања четворочланог прстена силена са Ge (INT1). Због sp^3 хибридизације Si атома у четворочланом прстену силена са Ge (INT1), INT1 надаље реагује са етеном градећи бис-хетероциклично једињење са Si и Ge (P2).

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