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Original scientific paper

Ab initio study of the mechanism of formation of a spiro Si-heterocyclic ring compound involving Ge from H_2Ge=Si: and acetaldehyde

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Abstract: H_2Ge=Si: and its derivatives (X_2Ge=Si:, X = H, Me, F, Cl, Br, Ph, Ar,…) are new species. The cycloaddition reactions of H_2Ge=Si: is a new area for the study of silylene chemistry. The mechanism of the cycloaddition reaction between singlet H_2Ge=Si: and acetaldehyde was investigated using the MP2/6-311++G** method. From the potential energy profile, it could be predicted that the reaction has a dominant reaction pathway. The reaction rule presented is that the two reactants firstly form a four-membered Ge-heterocyclic ring silylene through a [2+2] cycloaddition reaction. As the 3p unoccupied orbital of the Si: atom in the four-membered Ge-heterocyclic ring silylene and the π orbital of acetaldehyde form a π → p donor–acceptor bond, the four-membered Ge-heterocyclic ring silylene further combines with acetaldehyde to form an intermediate. Then the intermediate isomerizes *via* a transition state to a spiro-Si-heterocyclic ring compound involving Ge.

Keywords: H_2Ge=Si:; four-membered Ge-heterocyclic ring silylene; spiro Si-heterocyclic ring compound; potential energy profile.

INTRODUCTION

Unsaturated silylene is a kind of important active intermediate.[1] Its cycloaddition reaction is considered for providing a convenient, short synthesis pathway for the synthesis of tensility cyclotella, silapolycyclic compounds and compounds that are difficult to use with general methods, and is also regarded as an effective method for the synthesis of new bonds and heterocyclic compounds with Si.[2] H_2C=Si: is the simplest unsaturated silylene, which was first observed experimentally by Leclerq and Dubois in 1979.[3] Srinivas *et al.*[4] used neutralization–reionization mass spectrometry to show that H_2C=Si: is a viable molecule in the low-pressure gas phase. A theoretical study indicated that the ground

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state of H_2C=Si: is the singlet state. The energy of H_2C=Si: is 84 kcal* mol^{-1} lower than that of silaacetylide, H_2C=Si: is the lowest energy isomer.[1] Some studies preliminarily were performed on the cycloaddition reaction of unsaturated silylenes,[5–8] but these studies were limited to the cycloaddition reaction of methylene silylene and its derivatives (X_2C=Si:, X = H, Me, F, Cl, Br, Ph, Ar,…). There are no reports on the cycloaddition reaction of H_2Ge=Si: and its derivatives until now and thus, the study of unsaturated cycloaddition reactions of silylene is a new area of research. It is quite difficult to investigate the mechanisms of the cycloaddition reaction directly by experimental methods due to the high reactivity of X_2Ge=Si:, therefore, a theoretical study is more practical. To explore the rules of the cycloaddition reaction between X_2Ge=Si: and asymmetric π-bonded compounds, H_2Ge=Si: and acetaldehyde were selected as model molecules. The cycloaddition reaction mechanism (considering the H and Me transfer simultaneously) was investigated and analyzed theoretically. The results showed that the cycloaddition reaction consists of the five possible pathways given in Scheme 1.

The research results indicated the laws of the cycloaddition reactions between X_2Ge=Si: (X = H, Me, F, Cl, Br, Ph, Ar,…) and asymmetric π-bonded compounds, which are significant for the synthesis of small-ring and spiro Si-heterocyclic ring compound involving Ge. The study extended the research area and enriched the research content of silylene chemistry.

CALCULATION METHOD

MP2/6-311++G**,[9] implemented in the Gaussian 09 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 profile. Zero point energy corrections were included in the energy calculations. In order to establish explicitly the relevant species, the intrinsic reaction coordinate (IRC)[10,11] was also calculated for all the transition states appearing on the energy surface profile of the cycloaddition.

RESULTS AND DISCUSSION

Reaction (1): channel of forming the three-membered ring product (P1)

Theoretical calculations showed that the ground state of H_2Ge=Si: is a singlet state. The geometrical parameters of the intermediate **INT1**, transition state **TS1** and product **P1** that appear in Reaction (1) between H_2Ge=Si: and acetaldehyde 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.

According to Fig. 2, it can be seen that Reaction (1) consists of two steps: *I*) the two reactants **R1** and **R2** form the active intermediate **INT1**, the process of the first step is a barrier-free exothermic reaction of 67.3 kJ mol^{-1}; *II*) inter-

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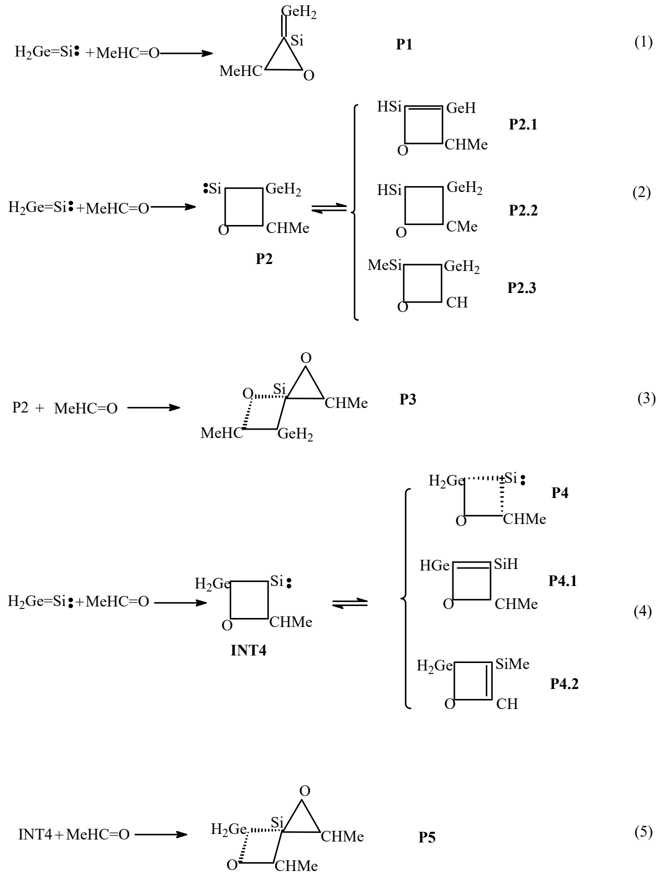
* 1 kcal = 4185 J

mediate **INT1** isomerizes to a three-membered ring product **P1** through the transition state **TS1** with an energy barrier of 90.6 kJ mol^{-1}.



Scheme 1. The possible pathways of the cycloaddition reaction between H_2Ge=Si: and acetaldehyde.

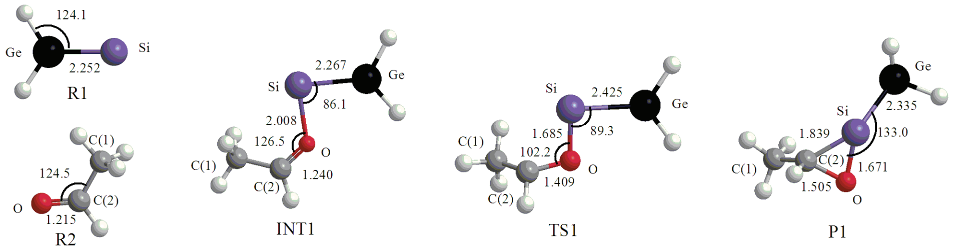
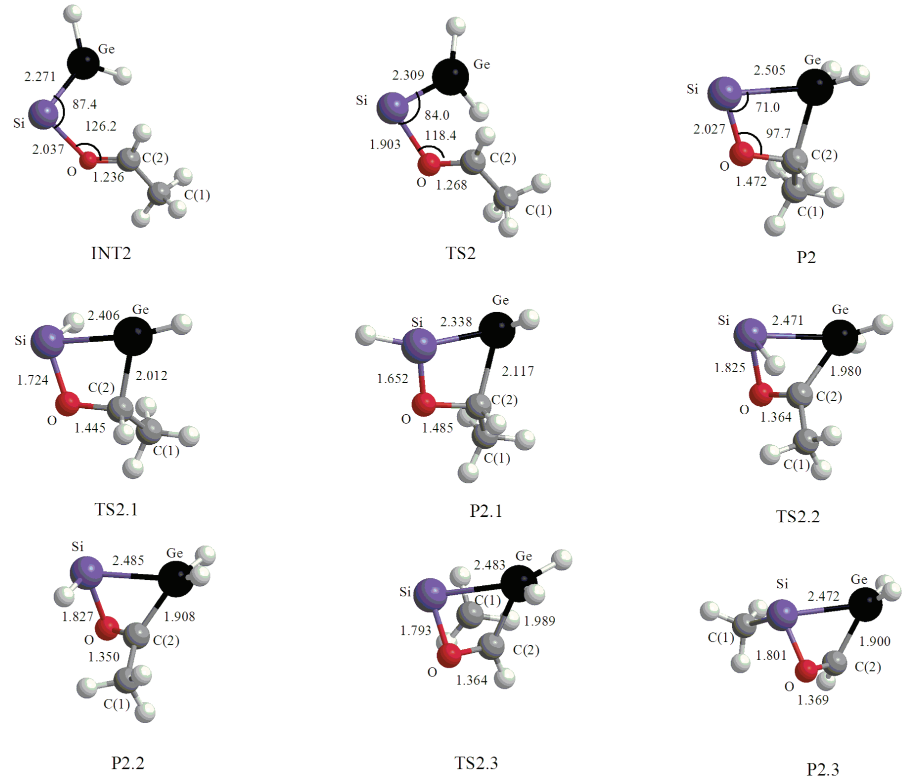


Fig. 1. Optimized MP2/6-311++G** geometrical parameters and the atomic numbering for the species in cycloaddition Reaction (1). Bond lengths and bond angles are in angstroms and degrees, respectively.

*Reaction (2): channels of the formation of the four-membered Ge-heterocyclic ring silylene (**P2**), the H-transfer products (**P2.1** and **P2.2**) and the Me-transfer product (**P2.3**)*

The geometrical parameters for the transition states **TS2**, **TS2.1**, **TS2.2** and **TS2.3** and the products **P2**, **P2.1**, **P2.2** and **P2.3** that appear in Reaction (2) between H_2Ge=Si: and acetaldehyde are given in Fig. 2. The energies are listed in Table I, and the potential energy profile for the cycloaddition reaction is shown in Fig. 3.



INT2 TS2 P2

TS2.1 P2.1 TS2.2

P2.2 TS2.3 P2.3

Fig. 2. Optimized MP2/6-311++G** geometrical parameters of **TS2**, **TS2.1**, **TS2.2**, **TS2.3**, **P2**, **P2.1**, **P2.2** and **P2.3** and the atomic numbering for the cycloaddition Reaction(2). Bond lengths and bond angles are in angstroms and degrees, respectively.

According to Fig. 3, it can be seen that Reaction (2) consists of five steps: the first step is that the two reactants **R1** and **R2** form the intermediate **INT2**, which is a barrier-free exothermic reaction of 76.0 kJ mol^{-1}; the second step is that intermediate **INT2** isomerizes to a four-membered Ge-heterocyclic ring silylene **P2** *via* transition state **TS2** with an energy barrier of 7.3 kJ mol^{-1}; the next three steps are that **P2** undergoes H and Me transfer *via* transition states

TS2.1, **TS2.2** and **TS2.3** with energy barriers of 117.6, 120.7 and 198.2 kJ mol^{-1}, respectively, resulting in the formation of products **P2.1**, **P2.2** and **P2.3**, respectively. The transfer reactions of **P2→P2.1**, **P2→P2.2** and **P2→P2.3** are thermodynamically prohibited at normal temperatures and pressures, because the energies of **P2.1**, P2.2 and **P2.3** are 30.9, 77.6 and 78.1 kJ mol^{-1} higher than that of **P2**, respectively. Comparing Reaction (2) with Reaction (1), the energy barrier of **TS2** is 83.3 kJ mol^{-1} lower than that of **TS1** and therefore, Reaction (2) is the dominant reaction pathway.

TABLE I. Zero point energy (*ZPE* / hartree*), total energies (E_T / hartree) and relative energies (E_R / kJ mol^{-1}) for the species of the cycloaddition reaction between $H_2Ge=Si:$ and acetaldehyde from the MP2/6-311++G** method; $E_T = E(\text{Species})+ZPE$

Reaction	Species	*ZPE*	MP2/6-311++G**	
			E_T	E_R
Reaction (1)[a]	**R1+R2**	0.07018	–2518.87443	0.0
	INT1	0.07320	–2518.90008	–67.3
	TS1(INT1–P1)	0.07267	–2518.86557	23.3
	P1	0.07420	–2518.92589	–135.1
Reaction (2)[a]	**R1+R2**	0.07018	–2518.87443	0.0
	INT2	0.07363	–2158.90339	–76.0
	TS2(INT2–P2)	0.07297	–2158.90061	–68.7
	P2	0.07587	–2158.95515	–211.9
	TS2.1(P2–P2.1)	0.07331	–2518.91033	–94.3
	P2.1	0.07551	–2518.94336	–181.0
	TS2.2(P2–P2.2)	0.07082	–2518.90917	–91.2
	P2.2	0.07169	–2518.92557	–134.3
	TS2.3(P2–P2.3)	0.07251	–2518.87963	–13.7
	P2.3	0.07251	–2518.92539	–133.8
Reaction (3)[b]	**P2+R2**	0.13191	–2672.34877	0.0
	INT3	0.13371	–2672.36326	–38.0
	TS3(INT3–P3)	0.13366	–2672.35132	–6.7
	P3	0.13613	–2627.39877	–131.3
Reaction (4)[a]	**R1+R2**	0.07018	–2518.87443	0.0
	INT4	0.07481	–2518.91810	–114.7
	TS4	0.07484	–2518.91696	–111.7
	P4	0.07553	–2518.93306	–153.9
	TS4.1(INT4–P4.1)	0.07383	–2518.90982	–92.9
	P4.1	0.07501	–2518.92250	–126.2
	TS4.2(INT4–P4.2)	0.07291	–2518.90138	–70.8
	P4.2	0.07350	–2518.93174	–150.5
Reaction(5)[c]	**INT4+R2**	0.13085	–2672.31171	0.0
	INT5	0.13415	–2672.33756	–67.9
	TS5(INT5–P5)	0.13482	–2672.30524	17.0
	P5	0.13589	–2672.37720	–171.9

[a]$E_R=E_T-E_{(\mathbf{R1+R2})}$, [b]$E_R=E_T-E_{(\mathbf{P2+R2})}$, [c]$E_R=E_T-E_{(\mathbf{INT4+R2})}$

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* 1 Hartree = 27.2114 eV

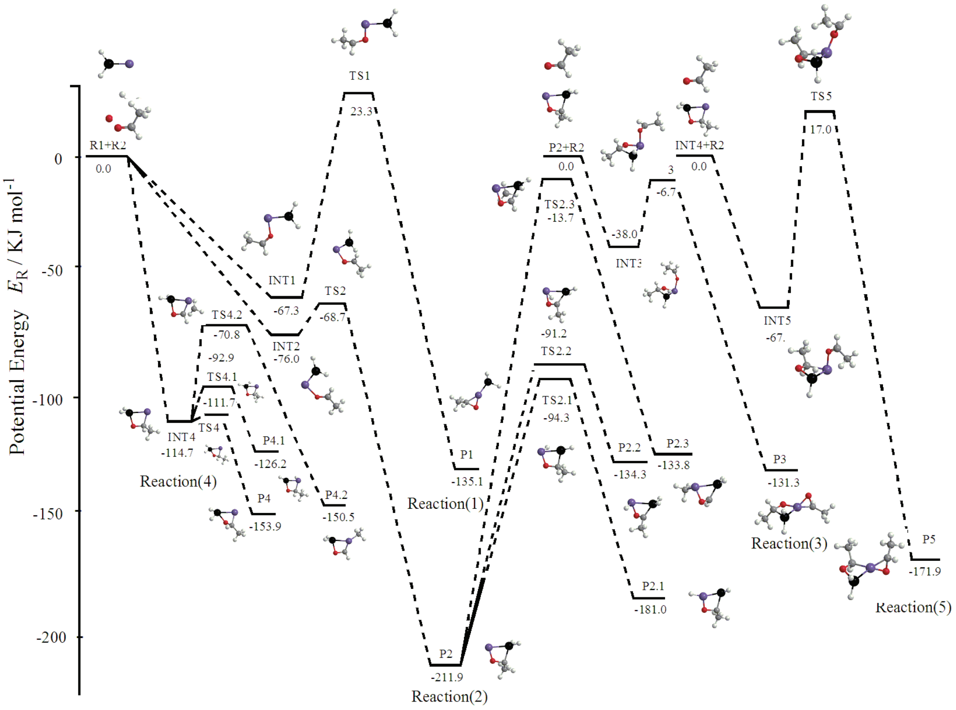
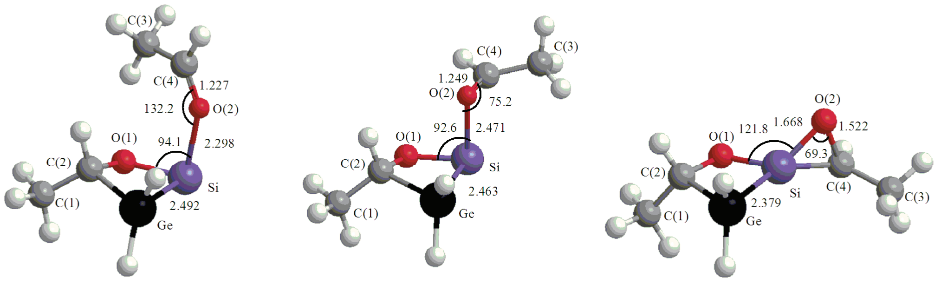


Fig. 3. The potential energy profile for the cycloaddition reactions between $H_2Ge{=}Si$: and acetaldehyde from MP2/6-311++G**.

*Reaction (3): channel of the formation of a spiro Si-heterocyclic ring compound involving Ge (**P3**)*

In Reaction (3), the four-membered Ge-heterocyclic ring silylene (**P2**) further reacts with acetaldehyde (**R2**) to form a spiro Si-heterocyclic ring compound involving Ge (**P3**). The geometrical parameters of intermediate **INT3**, transition state **TS3** and product **P3** that appear in Reaction (3) are given in Fig. 4. The energies are listed in Table I, and the potential energy profile for the cycloaddition reaction is shown in Fig. 3.

According to Fig. 3, it could be seen that Reaction (3) proceeds as follows: on the base of the two reactants (**R1** and **R2**), the four-membered Ge-heterocyclic ring silylene **P2** forms, **P2** further reacts with acetaldehyde to form the intermediate **INT3**, which is a barrier-free exothermic reaction of 38.0 kJ mol^{-1}; and then intermediate **INT3** isomerizes to a spiro-Si-heterocyclic ring compound involving Ge (P3) via a transition state (TS3) with an energy barrier of 31.3 kJ mol^{-1}.

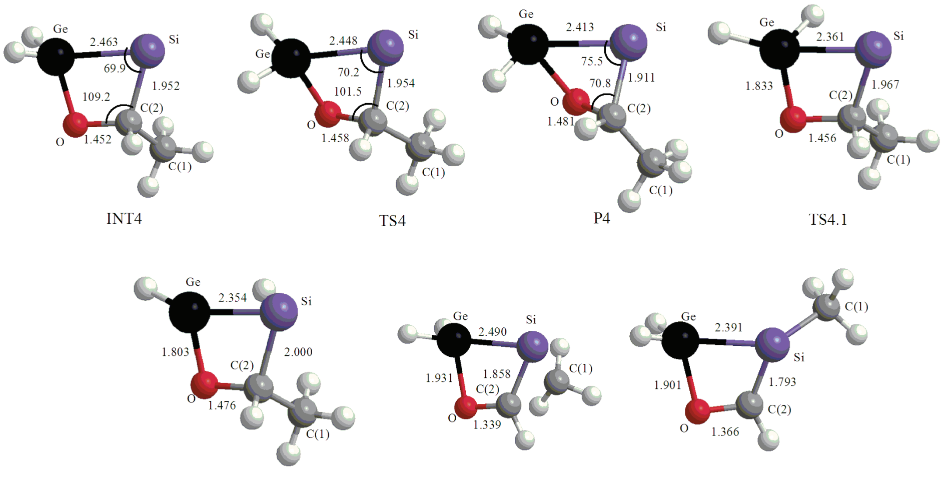


INT3 TS3 P3

Fig. 4. Optimized MP2/6-311++G** geometrical parameters of **INT3**, **TS3** and **P3**, and the atomic numbering for cycloaddition Reaction(3). Bond lengths and bond angles are in angstrom and degree, respectively.

*Reaction (4): channels of the formation of the four-membered Ge-heterocyclic ring silylene **INT4**, the H-transfer product **P4.1**, the CH_3-transfer product **P4.2** and the four-membered ring product **P4***

The geometrical parameters of the four-membered Ge-heterocyclic ring silylene **INT4**, transition states **TS4**, **TS4.1** and **TS4.2**, and products **P4**, **P4.1** and **P4.2** that appear in Reaction (4) between $H_2Ge=Si$: and acetaldehyde are given in Fig. 5. The energies are listed in Table I, and the potential energy profile for the cycloaddition reaction is shown in Fig. 3.



P4.1 TS4.2 P4.2

Fig. 5. Optimized MP2/6-311++G** geometrical parameters of **INT4**, **TS4**, **TS4.1**, **TS4.2**, **P4**, **P4.1** and **P4.2**, and the atomic numbering for the species in cycloaddition Reaction (4). Bond lengths and bond angles are in angstrom and degrees, respectively.

According to Fig. 3, it can be seen that Reaction (4) consists of five steps: *I*) the two reactants (**R1** and **R2**) form the four-membered Ge-heterocyclic ring silylene **INT4**, which is a barrier-free exothermic reaction of 114.7 kJ mol^{-1}; *II*) **INT4** isomerizes to the distorted four-membered ring product **P4** *via* the transition state **TS4** with an energy barrier of 3.0 kJ mol^{-1}; *III*) **INT4** undergoes hydrogen transfer *via* transition state **TS4.1** with an energy barrier of 21.8 kJ mol^{-1}, resulting in the formation of product **P4.1**; *IV*) **INT4** undergoes Me-transfer *via* the transition state **TS4.2** with an energy barrier of 43.9 kJ mol^{-1}, resulting in the formation of product **P4.2**. As the energy barriers of **TS4.1** and **TS4.2** are, respectively, 18.8 and 40.9 kJ mol^{-1} higher than that of **TS4**, **INT4→P4** is the dominant pathway of Reaction (4).

According to Fig. 3, it can be seen that **R1**+**R2→INT1**, **R1**+**R2→INT2** and **R1**+**R2→INT4** are three parallel reactions. The $\Delta_r G_m$ values of **R1**+**R2→INT1**, **R1**+**R2→INT2** and **R1**+**R2→INT4** are –26.1, –31.5 and –67.9 kJ mol^{-1}, respectively. According to the statistical thermodynamics formula[12]:

$$P_T(i) = \frac{e^{-\Delta G_T(i)/RT}}{\sum\limits_i e^{-\Delta G_T(i)/RT}}$$

and $\Delta G_T(i) = -RT\ln K_i$, the equilibrium distributions of **INT1**, **INT2** and **INT4** are, respectively:

$$P_T(\mathbf{INT1}) = K(\mathbf{INT1})/[K(\mathbf{INT1})+K(\mathbf{INT2})+K(\mathbf{INT4})] \approx 0.0,$$
$$P_T(\mathbf{INT2}) = K(\mathbf{INT2})/\,/[K(\mathbf{INT1})+K(\mathbf{INT2})\ +K(\mathbf{INT4})] \approx 0.0$$

and

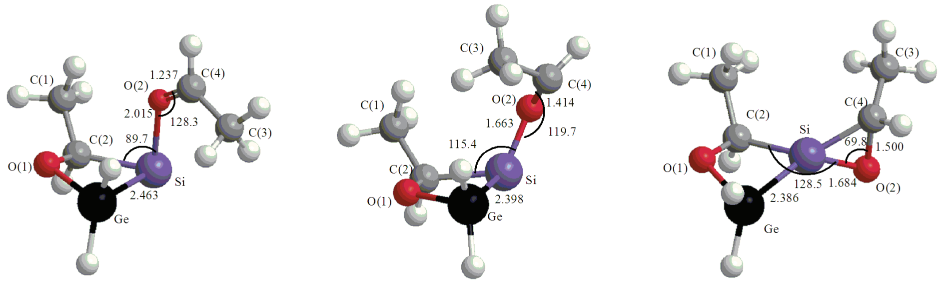
$$P_T(\mathbf{INT4}) = K(\mathbf{INT4})/[K(\mathbf{INT1})+\ +K(\mathbf{INT2})+K(\mathbf{INT4})] \approx 1.0.$$

Hence, **INT4** is the main equilibrium distribution.

*Reaction (5): channel of the formation of a spiro Si-heterocyclic ring compound involving Ge (**P5**)*

In Reaction (5), the four-membered Ge-heterocyclic ring silylene **INT4** further reacts with acetaldehyde (**R2**) to form a spiro Si-heterocyclic ring compound involving Ge (**P5**). The geometrical parameters of intermediate **INT5**, transition state **TS5** and product P5 that appear in Reaction (5) are given in Fig. 6. The energies are listed in Table I, and the potential energy profile for the cycloaddition reaction is shown in Fig. 3.

According to Fig. 2, it can be seen that Reaction (5) proceeds as follows: based on **INT4** formed in Reaction (4), **INT4** further reacts with acetaldehyde (**R2**) to form the intermediate **INT5**, which is a barrier-free exothermic reaction of 67.9 kJ mol^{-1}. Then, intermediate **INT5** isomerizes to a spiro Si-heterocyclic ring compound involving Ge (**P5**) *via* the transition state **TS5** with an energy barrier of 84.9 kJ mol^{-1}. According to Fig. 2, Reactions (4) and (5) are two mutually competitive reactions as they both strive for **INT4**. As **INT4→P4** requires climb over a barrier of 3.0 kJ mol^{-1}, while **INT4+R2→INT5** can directly reduce the system energy by 67.9 kJ mol^{-1} and hence, Reaction (5) should be the main reaction channel.



INT5 TS5 P5

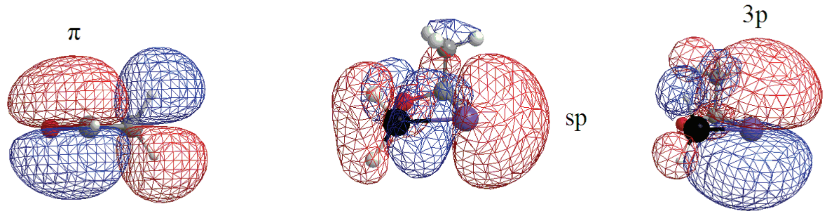
Fig. 6. Optimized MP2/6-311++G** geometrical parameters of **INT5**, **TS5**, **P5** and the atomic numbering for the cycloaddition Reaction (5). Bond lengths and bond angles are in angstroms and degrees, respectively.

Theoretical analysis and explanation of the dominant reaction pathways

According to the above analysis, Reaction (5) should be the dominant reaction channel of the cycloaddition reaction between singlet $H_2Ge{=}Si$: and acetaldehyde. Namely:

$$\mathbf{R1} + \mathbf{R2} \rightarrow \mathbf{INT4} \xrightarrow{+\mathbf{R2}} \mathbf{INT5} \xrightarrow{\mathbf{TS5}} \mathbf{P5}$$

In the three reactions, the frontier molecular orbitals of **R2** and **INT4** are shown in Fig. 7.



HOMO of R2 HOMO of INT4 LUMO of INT4

Fig. 7. The frontier molecular orbitals of **R2** and **INT4**.

According to Fig. 7, the frontier molecular orbitals of **R2** and **INT4** could be expressed as in the schematic diagram in Fig. 8. The mechanism of the dominant reaction channel could be explained with the molecular orbital diagrams (Figs. 1, 5, 6 and 8). According to Figs. 1 and 5, as $H_2Ge{=}Si$: (**R1**) initially interacts with acetaldehyde (**R2**), the [2+2] cycloaddition of the bonding π-orbitals first results in a four-membered Ge-heterocyclic ring silylene (**INT4**). Due to **INT4** still being an active product, it may further react with acetaldehyde (**R2**) to form a spiro Si-heterocyclic ring compound involving Ge (**P5**). The mechanism of this reaction could be explained with Figs. 6 and 8. When **INT4** interacts with acetaldehyde (**R2**), the 3p unoccupied orbital of the Si: atom in **INT4** will insert the π orbital of acetaldehyde from the oxygen side, Then the shift of π-electrons to the p unoccupied orbital gives a π→p donor–acceptor bond, leading to the formation of intermediate **INT5**. As the reaction proceeds, because ∠C(2)–Si–O(2) (**INT5**: 89.7°, **TS5**: 115.4°, **P5**: 231.5°) increases gradually, ∠C(4)–O–(2)Si (**INT5**: 128.3°, **TS5**: 119.7°, **P5**: 69.8°) decreases gradually and the length of the C(4)–O(2) bond (**INT5**: 1.237Å, **TS5**: 1.414Å, **P5**: 1.500 Å) elongates gradually. Finally the Si atom in **INT5** hybridizes to an sp^3 hybrid orbital after the transition state (**TS5**), forming the more stable a spiro-Si-heterocyclic ring compound involving Ge (**P5**).

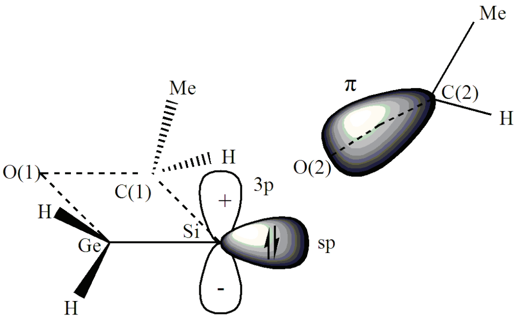


Fig. 8. A schematic diagram for the frontier orbitals of **INT4** and MeHC=O (**R2**).

CONCLUSIONS

Based on the potential energy profile of the cycloaddition reaction between singlet $H_2Ge=Si$: and acetaldehyde obtained using the MP2/6-311++G** method, it could be predicted that Reaction (5) is the dominant reaction pathway of the cycloaddition reaction between singlet $H_2Ge=Si$: and acetaldehyde. The process of Reaction (5) consists of three steps: *I*) the two reactants form a four-membered Ge-heterocyclic ring silylene (**INT4**), which is a barrier-free exothermic reaction of 114.7 kJ mol^{-1}; *II*) **INT4** further reacts with acetaldehyde (**R2**) to form an intermediate (**INT5**), which is a barrier-free exothermic reaction of 67.9 kJ mol^{-1}; *III*) **INT5** isomerizes to a spiro-Si-heterocyclic ring compound involving Ge (**P5**) *via* a transition state (**TS5**) with an energy barrier of 84.9 kJ mol^{-1}.

The π orbital of $X_2Ge=Si$: (X = H, Me, F, Cl, Br, Ph, Ar,…) and the 3p unoccupied orbital of Si: in $X_2Ge=Si$: are involved in cycloaddition reaction of $X_2Ge=Si$: and the asymmetric π-bonded compounds. The [2+2] cycloaddition reaction between the π orbital of $X_2Ge=Si$: and the bonding π orbital of the asymmetric π-bonded compounds leads to the formation of the four-membered Ge-heterocyclic ring silylene. The 3p unoccupied orbital of the Si: atom in the four-membered Ge-heterocyclic ring silylene further reacts with the bonding π orbital of the asymmetric π-bonded compounds to form a spiro-Si-heterocyclic ring compound involving Ge.

ИЗВОД

AB INITIO СТУДИЈА МЕХАНИЗМА НАСТАЈАЊА СПИРО Si-ХЕТЕРОЦИКЛИЧНОГ ЈЕДИЊЕЊА КОЈЕ САДРЖИ Ge ПОЛАЗЕЋИ ИЗ $H_2Ge=Si$: И АЦЕТАЛДЕХИДА

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$H_2Ge=Si$: и његови деривати ($X_2Ge=Si$:, X = H, Me, F, Cl, Br, Ph, Ar,...) су нове молекулске врсте. Његове циклоадиционе реакције су нова област проучавања у хемији силилена. Механизам циклоадиционе реакције између синглетног $H_2Ge=Si$: и ацеталдехида је истраживан MP2/6-311++G** методом. Из профила потенцијалне енергије може се предвидети да реакција има доминантан реакциони пут. Начин реаговања се може представити почетним формирањем четворочланог Ge-хетероцикличног прстена силилена [2+2] циклоадиционом реакцијом. Захваљујући празној 3p орбитали атома Si: у четворочланом Ge-хетероцикличном прстену силилена и π орбитали ацеталдехида формира се π→p донорско-акцепторска веза, а затим се четворочлани Ge-хетероциклични прстен силилена даље комбинује са ацеталдехидом дајући интермедијер. Интермедијер се преко прелазног стања изомеризује у спиро Si-хетероциклично једињење које у прстену садржи Ge.

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