

Ab Initio Study of Mechanism of Forming Spiro-Ge-Heterocyclic Ring Compound From Cl₂Ge=Ge: and Formaldehyde

Xiuhui Lu,* Yongqing Li, and Jingjing Ming

School of Chemistry and Chemical Engineering, University of Jinan, Jiweilu 106, Jinan, Shandong 250022, P.R. China

*E-mail: lxh@ujn.edu.cn

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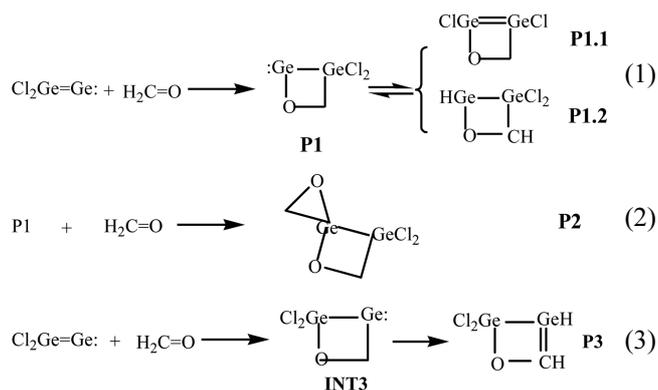
The H₂Ge=Ge: and its derivatives (X₂Ge=Ge:, X = H, Me, F, Cl, Br, Ph, Ar.....) is a new species. Its cycloaddition reactions is a new area for the study of germylene chemistry. The mechanism of the cycloaddition reaction between singlet state Cl₂Ge=Ge: and formaldehyde has been investigated with CCSD(T)//MP2/6-31G* method. From the potential energy profile, it could be predicted that the reaction has only one dominant reaction pathway. The reaction rule presented is that the two reactants first form a four-membered Ge-heterocyclic ring germylene through the [2+2] cycloaddition reaction. Because of the 4p unoccupied orbital of Ge: atom in the four-membered Ge-heterocyclic ring germylene and the π orbital of formaldehyde forming a π→p donor-acceptor bond, the four-membered Ge-heterocyclic ring germylene further combines with formaldehyde to form an intermediate. Because the Ge: atom in intermediate hybridizes to an sp³ hybrid orbital after transition state, then, intermediate isomerizes to a spiro-Ge-heterocyclic ring compound via a transition state. The research result indicates the laws of cycloaddition reaction between H₂Ge=Ge: and formaldehyde, and laid the theory foundation of the cycloaddition reaction between H₂Ge=Ge: and its derivatives (X₂Ge=Ge:, X = H, Me, F, Cl, Br, Ph, Ar.....) and asymmetric π-bonded compounds, which is significant for the synthesis of small-ring and spiro-Ge-heterocyclic compounds. The study extends research area and enriches the research content of germylene chemistry.

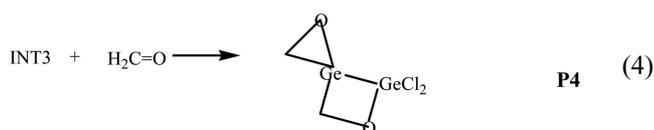
Key Words : Cl₂Ge=Ge: Four-membered Ge-heterocyclic ring germylene, Spiro-Ge-heterocyclic compounds, Potential energy profile

Introduction

Unsaturated germylene is a kind of quite unstable active intermediate. In 1997, Clouthier *et al.*¹ from University of Kentucky observed the first unsaturated germylene-germylidene, which is produced by striking an electric discharge in a high-pressure argon pulse using the tetramethylgermane (TMG) vapor as the precursor. They obtained its molecular structure and the *ab initio* predictions,² electronic spectrum² and oscillatory fluorescence decay² of jet-cooled germylidene (H₂C=Ge:), and learnt the ground state³ of H₂C=Ge: and D₂C=Ge:, the stimulated emission pumping (SEP) spectroscopy⁴ of the first excited singlet state of germylidene. Stogner and Grev⁵ have published the extensive *ab initio* calculations on both germylidene and the trans-bent germylene HCGeH isomer. They found that germylidene is the global minimum on the H₂C=Ge: potential energy surface, with germylene some 43 kcal/mol higher in energy. The barrier to germylene isomerization was predicted to be only 7 kcal/mol and no stable linear germylene structures could be found. Nazari and Chen *et al.*^{6,7} on the compounds of silicon and germanium has been well studied. With regard to the cycloaddition reaction of the unsaturated germylene, we have done some elementary discussion.⁸⁻¹¹ But these studies are limited to the cycloaddition reaction of H₂C=Ge: and its derivatives. There are no reports on the cycloaddition reaction of H₂Ge=Ge: and its derivatives till now, it is a new

branch of unsaturated germylene's cycloaddition reaction. It is quite difficult to investigate mechanisms of cycloaddition reaction directly by experimental methods due to the high activity of H₂Ge=Ge: and its derivatives, therefore, the theoretical study is more practical. To explore the rules of cycloaddition reaction between H₂Ge=Ge: (include its derivatives) and the asymmetric π-bonded compounds, taking into account the diversity of halogenated X₂Ge=Ge: (X=F, Cl, Br), Cl₂Ge=Ge: and formaldehyde were selected as model molecules, the cycloaddition reaction mechanism (considering the H and Cl transfer simultaneously) was investigated and analyzed theoretically. The results show that the cycloaddition reaction consists of four possible pathways, as follows:





Computational Methods

MP2/6-31G*¹² implemented in the Gaussian 03 package is employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis are done for the stationary points on the reaction profile. Zero point energy and CCSD(T) corrections are included for the energy calculations. In order to explicitly establish the relevant species, the intrinsic reaction coordinate (IRC)^{13,14} is also calculated for all the transition states appearing on the cycloaddition energy surface profile.

Results and Discussions

Reaction (1): Channel of Forming the Ge-Heterocyclic Four-Membered Ring Germylene (P1), Cl-Transfer Product (P1.1) and H-Transfer Product (P1.2). Theoretical researches show that the ground state of Cl₂Ge=Ge: is a singlet state. The geometrical parameters of the intermediate (INT1), transition state (TS1, TS1.1, TS1.2) and product (P1, P1.1, P1.2) which appear in reaction (1) between Cl₂Ge=Ge: and formaldehyde are given in Figure 1, the energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Figure 2.

According to Figure 2, it can be seen that the reaction (1) consists of four steps: the first one is that the two reactants (R1, R2) form an intermediate (INT1), which is a barrier-free exothermic reaction of 99.5 kJ/mol; the second step is that the intermediate (INT1) isomerizes to a four-membered Ge-heterocyclic ring germylene (P1) through transition state (TS1) with an energy barrier of 15.4 kJ/mol; the third and

fourth steps are that the P1 undergoes Cl and H transfer *via* transition states TS1.1 and TS1.2 with energy barriers of 36.7 and 177.8 kJ/mol, respectively, resulting in the formation of products P1.1 and P1.2. Because the energies of P1.1 and P1.2 are 6.6 and 96.8 kJ/mol higher than that of P1, so the reactions of P1→P1.1, P1→P1.2 are prohibited in thermodynamics at the normal temperature and pressure, reaction (1) will end in product P1.

Reaction (2): Channel of Forming a Spiro-Ge-Heterocyclic Ring Compound (P2). In reaction (2), the four-membered Ge-heterocyclic ring germylene (P1) further reacts with formaldehyde (R2) to form a spiro-Ge-heterocyclic ring compound (P2). The geometrical parameters of intermediate (INT2), transition state (TS2) and product (P2), which appear in reaction (2) are given in Figure 3. The energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Figure 2.

According to Figure 2, it can be seen that the process of reaction (2) as follows: on the basis of P1 formed from the reaction (1) between R1 and R2, the P1 further reacts with formaldehyde to form an intermediate (INT2), which is a barrier-free exothermic reaction of 81.1 kJ/mol; next, the intermediate (INT2) isomerizes to a spiro-Ge-heterocyclic ring compound (P2) *via* a transition state (TS2) with an energy barrier of 56.9 kJ/mol. Because the energy of P2 is 36.8 kJ/mol higher than that of INT2, so the reaction of INT2→P2 is an endothermic reaction.

Reaction (3): Channels of Forming a Four-Membered Ge-Heterocyclic Ring Germylene (INT3), H-Transfer Product (P3). The geometrical parameters of the four-membered Ge-heterocyclic ring germylene (INT3), transition state (TS3) and product (P3) which appear in reaction (3) between Cl₂Ge=Ge: and formaldehyde are given in Figure 4. The energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Figure 2.

According to Figure 2, it can be seen that reaction (3)

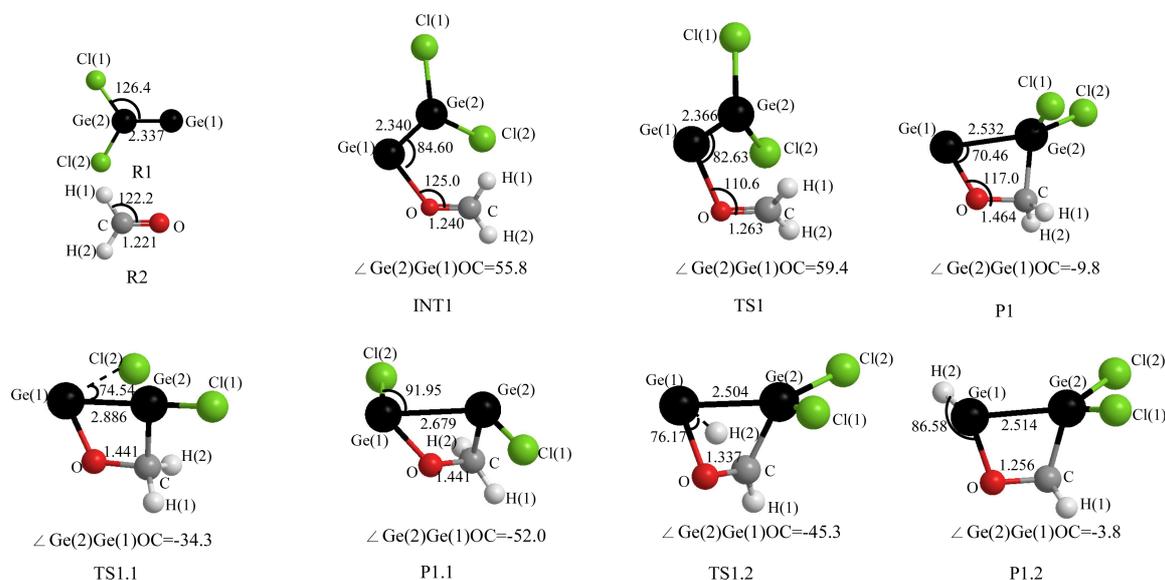
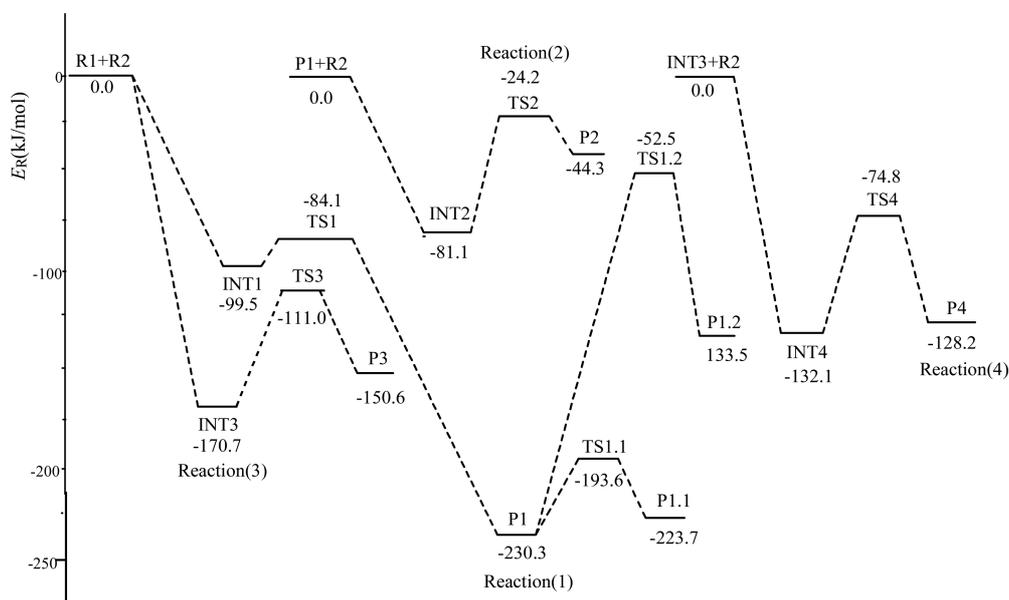


Figure 1. Optimized MP2/6-31G* geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1). Lengths are in Å and angles in degree.

Table 1. Zero point energy (ZPE, hartree), total energies (E_T , hartree) and relative energies (E_R , kJ/mol) for the species from various theoretical methods

Reactio	Species	ZPE	MP2/6-31G*		CCSD(T)//MP2/6-31G*	
			^a E_T	E_R	^a E_T	E_R
^b Reaction (1)	R1+R2	0.03043	-5180.07036	0.0	-5180.15371	0.0
	INT1	0.03376	-5180.11196	-109.2	-5180.19159	-99.5
	TS1(INT1-P1)	0.03283	-5180.10689	-95.9	-5180.18576	-84.1
	P1	0.03516	-5180.16712	-254.0	-5180.24144	-230.3
	TS1.1(P1-P1.1)	0.03410	-5180.15124	-212.4	-5180.22746	-193.6
	P1.1	0.03440	-5180.16688	-253.4	-5180.23891	-223.7
	TS1.2(P1-P1.2)	0.02864	-5180.09783	-65.0	-5180.17369	-52.5
	P1.2	0.02943	-5180.12687	-148.5	-5180.20455	-133.5
^c Reaction (2)	P1+R2	0.06245	-5294.33487	0.0	-5294.43202	0.0
	INT2	0.06565	-5294.36768	-86.1	-5294.46290	-81.1
	TS2(INT2-P2)	0.06465	-5294.34866	-36.2	-5294.44125	-24.2
^b Reaction (3)	P2	0.06628	-5294.36081	-68.1	-5294.44891	-44.3
	R1+R2	0.03043	-5180.07036	0.0	-5180.15371	0.0
	INT3	0.03377	-5180.14409	-193.6	-5180.21872	-170.7
^d Reaction (4)	TS3 (INT3-P3)	0.02872	-5180.11977	-122.6	-5180.19598	-111.0
	P3	0.02963	-5180.13363	-159.0	-5180.21107	-150.6
	INT3+R2	0.06106	-5294.31184	0.0	-5294.39959	0.0
	INT4	0.06529	-5294.35523	-113.9	-5294.44991	-132.1
	TS4(INT4-P4)	0.06337	-5294.33368	-57.3	-5294.42808	-74.8
P4	0.06630	-5294.36017	-126.9	-5294.44843	-128.2	

^a $E_T = E(\text{Species}) + \text{ZPE}$. ^b $E_R = E_T - E_{(R1+R2)}$. ^c $E_R = E_T - E_{(P1+R2)}$. ^d $E_R = E_T - E_{(\text{INT3}+R2)}$

**Figure 2.** The potential energy surface for the cycloaddition reactions between $\text{Cl}_2\text{Ge}=\text{Ge}$: and $\text{H}_2\text{C}=\text{O}$ with CCSD(T)//MP2/6-31G*

consists of two steps: the first step is that the two reactants (R1, R2) form a four-membered Ge-heterocyclic ring germylene (INT3), which is a barrier-free exothermic reaction of 170.7 kJ/mol. The second step is that the INT3 undergoes H-transfer between Ge(1)-C *via* transition state (TS3) with energy barrier of 59.7 kJ/mol, resulting in the formation of product (P3). Because the energy of INT3 is 20.1 kJ/mol higher than that of P3, so the reaction of $\text{INT3} \rightarrow \text{P3}$ is

prohibited in thermodynamics at the normal temperature and pressure, reaction (3) will end in product INT3.

According to Figures 1, 2, 4 and statistical thermodynamics formula: $P_T(i) = e^{-\Delta G_T(i)/RT} / \sum e^{-\Delta G_T(i)/RT}$ and $\Delta G_T(i) = -RT \ln K_i$, it can be seen that INT1 and INT3 are isomerides, $\text{R1}+\text{R2} \rightarrow \text{INT1}$ and $\text{R1}+\text{R2} \rightarrow \text{INT3}$ are two parallel reactions, the equilibrium distributions of INT1 and INT3 are $P_1(\text{INT1}) = K(\text{INT1}) / [K(\text{INT1}) + K(\text{INT3})] \approx 0.0$, $P_1(\text{INT3})$

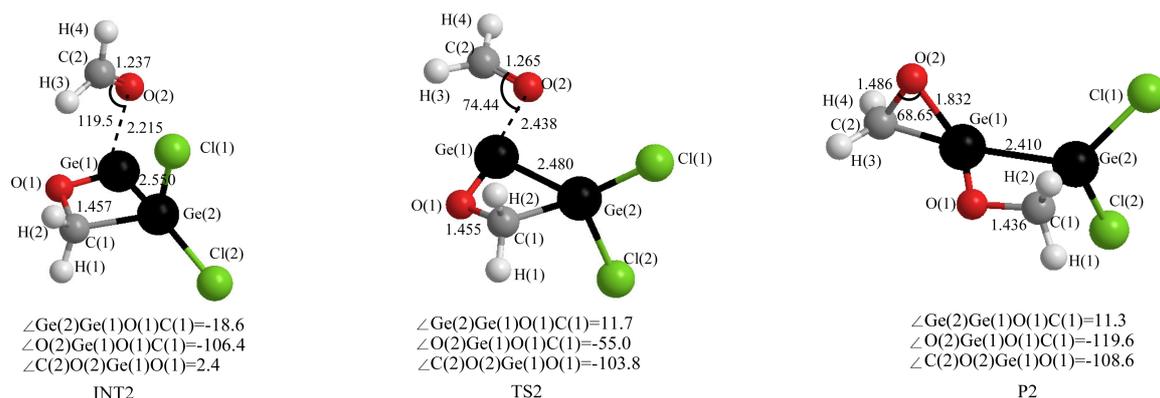


Figure 3. Optimized MP2/6-31G* geometrical parameters of INT2, TS2, P2 and the atomic numbering for cycloaddition reaction (2). Lengths are in Å and angles in degree.

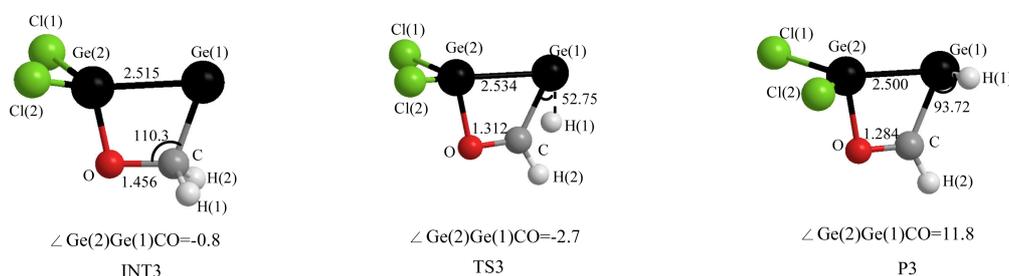


Figure 4. Optimized MP2/6-31G* geometrical parameters of INT3, TS3, P3 and the atomic numbering for cycloaddition reaction (3). Lengths are in Å and angles in degree.

$= K(\text{INT3})/[K(\text{INT1}) + K(\text{INT3})] \approx 1.0$, respectively. So, INT3 is the main distribution.

Reaction (4): Channel of Forming a Spiro-Ge-heterocyclic Ring Compound (P4). In reaction (4), the four-membered Ge-heterocyclic ring germylene (INT3) further reacts with formaldehyde (R2) to form a spiro-Ge-heterocyclic ring compound (P4). The geometrical parameters of intermediate (INT4), transition state (TS4) and product (P4) which appear in reaction (4) are given in Figure 5. The energies are listed in Table 1, and the potential energy surface for the cycloaddition reaction is shown in Figure 2.

According to Figure 2, it can be seen that the process of reaction (4) as follows: on the basis of the two reactants (R1,

R2) to form INT3, it further reacts with formaldehyde (R2) to form an intermediate (INT4), which is a barrier-free exothermic reaction of 132.1kJ/mol. And then intermediate (INT4) isomerizes to a spiro-Ge-heterocyclic ring compound (P4) via a transition state (TS4) with an energy barrier of 57.3 kJ/mol. Because the energy of P4 is 3.9 kJ/mol higher than that of INT4, so INT4→P4 is an endothermic reaction. Compared reaction (4) with reaction (3), In reaction (4), INT3+R2→INT4 can directly reduce the system energy of 132.1 kJ/mol. In reaction (3), the energy barrier of INT3→P3 is 59.7 kJ/mol, therefore, reaction (4) is the dominant reaction pathway.

Theoretical Analysis and Explanation of the Dominant

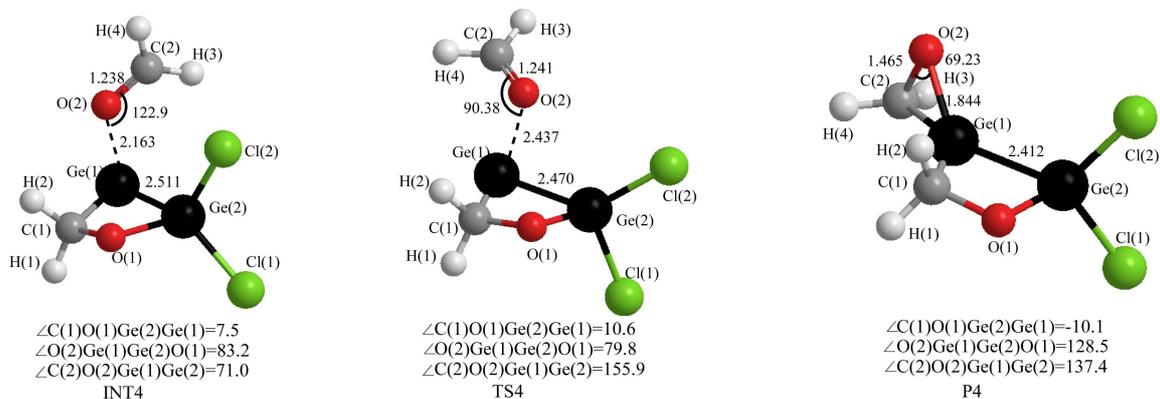


Figure 5. Optimized MP2/6-31G* geometrical parameters of INT4, TS4, P4 and the atomic numbering for cycloaddition reaction (4). Lengths are in Å and angles in degree.

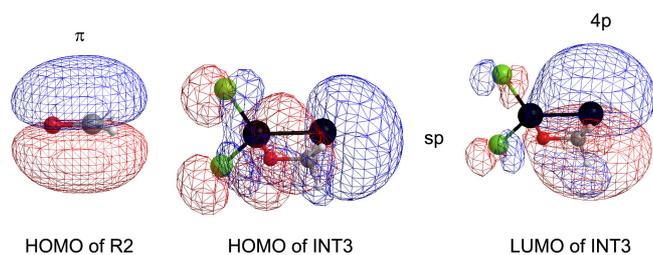


Figure 6. The frontier molecular orbitals of R2, INT3.

Reaction Channel. According to the above analysis, reaction (4) should be the dominant reaction channel of the cycloaddition reaction between singlet $\text{Cl}_2\text{Ge}=\text{Ge}:$ and formaldehyde, as follows:



In the reaction, the frontier molecular orbitals of R2 and INT3 are shown in Figure 6. According Figure 6, the frontier molecular orbitals of R2, INT3 can be expressed in schematic diagram 7. The mechanism of the reaction could be explained with the molecular orbital diagram (Fig. 7) and Figures 1, 4 and 5. According to Figures 1 and 4, as $\text{Cl}_2\text{Ge}=\text{Ge}:$ initially interacts with formaldehyde, the [2+2] cycloaddition of the bonding π -orbitals first results in a four-membered Ge-heterocyclic ring germylene (INT3). Because the four-membered Ge-heterocyclic ring germylene (INT3) is an active intermediate, INT3 further reacts with formaldehyde (R2) to form a spiro-Ge-heterocyclic ring compound (P4). The mechanism of the reaction could be explained with Figures 5 and 7, according to orbital symmetry matching condition, when INT3 interacts with formaldehyde (R2), the 4p unoccupied orbital of the Ge(1) atom in INT3 will insert the π orbital of formaldehyde from oxygen side, then the shift of π -electrons to the p unoccupied orbital gives a $\pi \rightarrow \text{p}$ donor-acceptor bond, leading to the formation of intermediate (INT4). As the reaction goes on, because of $\angle\text{C}(2)\text{O}(2)\text{Ge}(1)\text{C}(1)$ (INT4: 139.4° , TS4: 135.3° , P4: 125.0°) gradually decrease, $\angle\text{C}(2)\text{O}(2)\text{Ge}(1)$ (INT4: 123.1° , TS4: 90.4° , P4: 69.2°) gradually decrease and the C(2)-O(2) bond (INT4: 1.238 Å, TS4: 1.241 Å, P4: 1.465 Å) gradually elongate, the Ge(1) in INT4 hybridizes to sp^3 hybrid orbital after the transition state (TS4), forming a spiro-Ge-heterocyclic ring compound (P4).

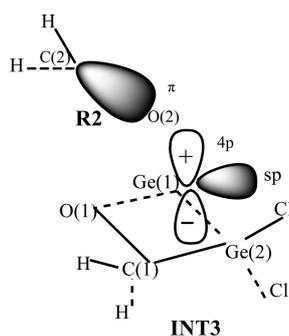


Figure 7. A schematic diagram for the frontier orbitals of INT3 and $\text{H}_2\text{C}=\text{O}(\text{R2})$.

Conclusion

On the basis of the potential energy surface obtained with the CCSD(T)/MP2/6-31G* method for the cycloaddition reaction between singlet $\text{Cl}_2\text{Ge}=\text{Ge}:$ and formaldehyde, it can be predicted that the dominant reaction pathway of the cycloaddition reaction is reaction (4). It consists of three steps, the first step is that the two reactants (R1, R2) form a four-membered Ge-heterocyclic ring germylene (INT3), which is a barrier-free exothermic reaction of 170.7 kJ/mol; the second step is that the INT3 further reacts with formaldehyde (R2) to form an intermediate (INT4), which is also a barrier-free exothermic reaction of 132.1 kJ/mol; the third step is that INT4 isomerizes to a spiro-Ge-heterocyclic ring compound (P4) via a transition state (TS4) with an energy barrier of 57.3 kJ/mol.

The π orbital of $\text{X}_2\text{Ge}=\text{Ge}:$ ($\text{X} = \text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{Ph}, \text{Ar}, \dots$) and the 4p unoccupied orbital of Ge: in $\text{X}_2\text{Ge}=\text{Ge}:$ ($\text{X} = \text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{Ph}, \text{Ar}, \dots$) are the object in cycloaddition reactions of $\text{X}_2\text{Ge}=\text{Ge}:$ ($\text{X} = \text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{Ph}, \text{Ar}, \dots$) and the asymmetric π -bonded compounds. The [2+2] cycloaddition reaction between the π orbital of $\text{X}_2\text{Ge}=\text{Ge}:$ ($\text{X} = \text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}, \text{Ph}, \text{Ar}, \dots$) and the bonding π orbital of the asymmetric π -bonded compounds leads to the formation of the four-membered Ge-heterocyclic ring germylene. The 4p unoccupied orbital of Ge: atom in the four-membered Ge-heterocyclic ring germylene further reacts with the bonding π orbital of the asymmetric π -bonded compound to form an intermediate. Because the Ge atom in the intermediate undergoes sp^3 hybridization after transition state, then, the intermediate isomerizes to a spiro-Ge-heterocyclic ring compound.

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