



## Theoretical study on the mechanism of cycloaddition reaction between dimethyl germylidene and formaldehyde

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### ABSTRACT

The cycloaddition mechanism of the reaction between singlet dimethyl germylidene and formaldehyde has been investigated with MP2/6-31G\* method, including geometry optimization and vibrational analysis for the involved stationary points on the potential energy surface. The energies of the different conformations are calculated with CCSD (T)//MP2/6-31G\* method. From the potential energy profile, we predict that the cycloaddition reaction between singlet dimethyl germylidene and formaldehyde has two dominant reaction pathways. First dominant reaction pathway consists of three steps: (1) the two reactants (R1, R2) firstly form an intermediate INT1a through a barrier-free exothermic reaction of 43.0 kJ/mol; (2) INT1a then isomerizes to a four-membered ring compound P1 via a transition state TS1a with an energy barrier of 24.5 kJ/mol; (3) P1 further reacts with formaldehyde(R2) to form a germanic heterocyclic compound INT3, which is also a barrier-free exothermic reaction of 52.7 kJ/mol; Second dominant reaction pathway is as following: (1) the two reactants (R1, R2) firstly form a planar four-membered ring intermediate INT1b through a barrier-free exothermic reaction of 50.8 kJ/mol; (2) INT1b then isomerizes to a twist four-membered ring intermediate INT1.1b via a transition state TS1b with an energy barrier of 4.3 kJ/mol; (3) INT1.1b further reacts with formaldehyde(R2) to form an intermediate INT4, which is also a barrier-free exothermic reaction of 46.9 kJ/mol; (4) INT4 isomerizes to a germanic bis-heterocyclic product P4 via a transition state TS4 with an energy barrier of 54.1 kJ/mol.

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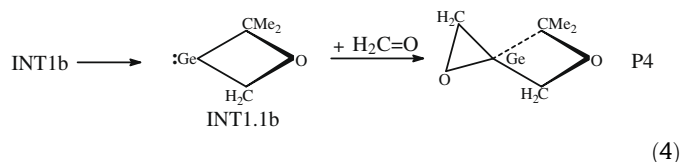
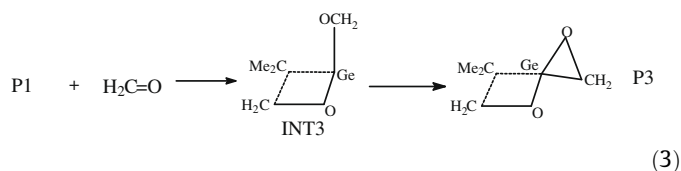
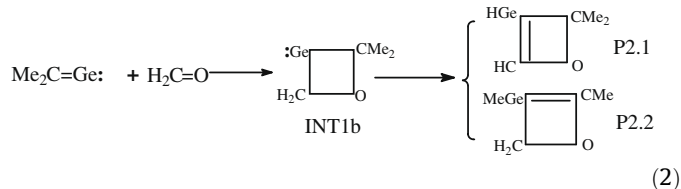
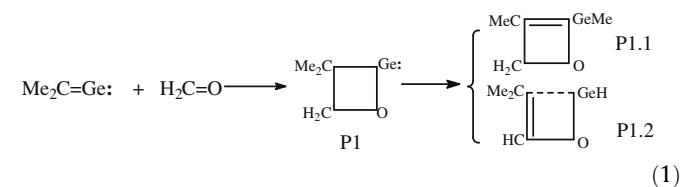
### 1. Introduction

Germylene is a kind of quite unstable active intermediate [1]. Germylene reactions are regarded as the effective method in the synthesis of new bonds and heterocyclic compounds with Ge [2–5], which is a very active research field in organo-Ge chemistry. Especially since many organo-Ge compounds had been reported to possess biological activity, the reactions concerning germylenes became the focus of the research. It was also reported that Herrmann et al. [6] had separated two kinds of stable germylenes, which could be used as the original body to prepare Ge-film by chemical vapor deposition (CVD). Therefore, the research on germylenes and germylene reactions has important theoretical and practical significances. Many cycloaddition reaction [7,8] and insertion reactions [9] about the saturated germylene had been studied theoretically hitherto known. The study on unsaturated germylenes is still on the initial stage. In 1997, Clouthier et al. [10] 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 tetram-

ethylgermane (TMG) vapor as the precursor. They obtained its molecular structure and the ab initio predictions [11], electronic spectrum [11] and oscillatory fluorescence decay [11] of jet-cooled germylidene( $\text{H}_2\text{C}=\text{Ge}:$ ), and learnt the ground state [12] of  $\text{H}_2\text{C}=\text{Ge}:$  and  $\text{D}_2\text{C}=\text{Ge}:$  the stimulated emission pumping(SEP) spectroscopy [13] of the first excited singlet state of germylidene. Stogner and Grev have published the extensive ab initio calculations [14] on both germylidene and the trans-bent germyne  $\text{HC}\equiv\text{GeH}$  isomer. They found that germylidene is the global minimum on the  $\text{H}_2\text{C}=\text{Ge}:$  potential energy surface, with germyne some 43 kcal/mol higher in energy. The barrier to germyne isomerization was predicted to be only 7 kcal/mol and no stable linear germyne structures could be found. With regard to the cycloaddition reaction of the unsaturated germylene, we have done some elementary discussion on the mechanism of the cycloaddition reaction between unsaturated germylenes and symmetric  $\pi$ -bonded compounds [15]. In order to further explore the rules of cycloaddition reaction between unsaturated germylenes and asymmetric  $\pi$ -bonded compounds, dimethyl germylidene [ $(\text{CH}_3)_2\text{C}=\text{Ge}:$ ] and formaldehyde were selected as model molecules, and its mechanism was investigated and analyzed theoretically in terms of the four possible pathways of cycloaddition reaction (considering the hydrogen and methyl transfer simultaneously) as follows:

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## 2. Calculation methods

MP2/6-31G\* [16] implemented in the Gaussian03 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 further confirm the correctness of the relevant species, vibration analysis is included, and the intrinsic reaction coordinate (IRC) [17,18] was also calculated for all the transition states appearing on the potential energy profile.

## 3. Results and discussion

### 3.1. Reaction (1): channels of forming four-membered ring product P1, CH<sub>3</sub>-transfer product P1.1 and H-transfer product P1.2

Theoretical calculations show that the ground state of dimethyl germylidene is singlet. The geometrical parameters for the intermediates (INT1a, INT1b, INT1.1b), transition states (TS1a, TS1b, TS1.1b, TS1.1, TS1.2) and products (P1, P1.1, P1.2) appearing in reaction (1) between dimethyl germylidene and formaldehyde are given in Fig. 1. The energies are listed in Table 1, and the potential energy surfaces for the cycloaddition reaction are shown in Fig. 2.

The unique imaginary frequencies of the transition states TS1a, TS1b, TS1.1b, TS1.1 and TS1.2 are 138.0i, 159.9i, 224.8i, 268.9i and 998.0i, respectively. Therefore, these transition states can be affirmed as the real ones. Their IRC (with the step-length of 0.1 amu<sup>-1/2</sup>bohr) analysis confirms that TS1a connects INT1a and P1; TS1b connects INT1b and INT1.1b, TS1.1b connects INT1.1b and P1, and TS1.1 connects P1 and P1.1, TS1.2 connects P1 and P1.2.

It can be intuitively observed from Fig. 2 that reaction (1) has two reaction pathways a and b. Path a consists of four steps, the first one is a barrier-free exothermic reaction with  $\Delta E$  of 43.0 kJ/mol,

leading to an intermediate INT1a, which then isomerizes to a four-membered ring product P1 via a transition state TS1a. Subsequently, the product P1 isomerizes to CH<sub>3</sub>-transfer product P1.1 and H-transfer product P1.2 via transition states TS1.1 and TS1.2 with energy barriers of 197.5 and 132.3 kJ/mol, respectively. Path b consists of five steps, the first step is a barrier-free exothermic reaction with  $\Delta E$  of 50.8 kJ/mol, leading to a four-membered ring intermediate INT1b. The second step is INT1b isomerizes to a twist four-membered ring intermediate INT1.1b via a transition state TS1b. Subsequently, the third step is INT1.1b isomerizes to a planar four-membered ring product P1 via transition state TS1.1b with energy barrier of 141.7 kJ/mol. The fourth and fifth steps are the product P1 isomerizes to CH<sub>3</sub>-transfer product P1.1 and H-transfer product P1.2 via transition states TS1.1 and TS1.2 with energy barriers of 197.5 and 132.3 kJ/mol, respectively. The energy of P1.1 and P1.2 are 123.0 and 43.1 kJ/mol higher than P1, so, the reaction P1 → P1.1 and P1 → P1.2 are forbidden in thermodynamics, reaction (1) will end in P1. According to the comparison of path a with path b in reaction (1), the energy of TS1.1b of path b is 117.2 kJ/mol higher than that of TS1a of path a, so path a is the dominant channel of forming P1.

### 3.2. Reaction (2): channels of forming four-membered ring intermediate INT1b, H-transfer product P2.1 and CH<sub>3</sub>-transfer product P2.2

The geometrical parameters for the transition states (TS2.1, TS2.2) and products (P2.1, P2.2) appearing in reaction (2) between dimethyl germylidene and formaldehyde are given in Fig. 3. The energies are listed in Table 1, and the potential energy surfaces for the cycloaddition reaction are shown in Fig. 2.

The unique imaginary frequencies of the transition states TS2.1 and TS2.2 are 692.0i and 311.2i, respectively. Therefore, these transition states can be affirmed as the real ones. Their IRC (with the step-length of 0.1 amu<sup>-1/2</sup>bohr) analysis confirms that TS2.1 connects INT1b and P2.1; and TS2.2 connects INT1b and P2.2. It can be observed from Fig. 2 that reaction (2) consists of three steps. The first one is a barrier-free exothermic reaction with  $\Delta E$  of 50.8 kJ/mol, leading to an intermediate INT1b, subsequently, INT1b isomerizes to H-transfer product P2.1 and CH<sub>3</sub>-transfer product P2.2 via transition states TS2.1 and TS2.2 with energy barriers of 71.6 and 82.4 kJ/mol, respectively. The energy of P2.1 and P2.2 is 49.4 and 22.9 kJ/mol higher than INT1b, so, the reaction INT1b → P2.1 and INT1b → P2.2 are forbidden in thermodynamics, reaction (2) will end in INT1b.

### 3.3. Reaction (3): channels of forming germanic bis-heterocyclic product P3

In reaction (3), the active four-membered ring product P1 further reacts with formaldehyde (R2) to form the germanic bis-heterocyclic compound P3. The geometric parameters for the intermediate INT3, the transition state TS3 and the product P3 appearing in reaction (3) are given in Fig. 4. The energies are listed in Table 1. The potential energy surface for reaction (3) is illustrated in Fig. 2.

The unique imaginary frequency of the transition state TS3 is 203.4i, and therefore the transition state can be affirmed as the real one. IRC (with the step-length of 0.1 amu<sup>-1/2</sup>bohr) analysis confirms that TS3 connects INT3 and P3. According to Fig. 2, the process of reaction (3) is as following: on the basis of P1 formed from the reaction (1) between R1 and R2, P1 further reacts with formaldehyde (R2) to form an intermediate INT3 through a barrier-free exothermic reaction of 52.7 kJ/mol. Then, INT3 isomerizes to a germanic bis-heterocyclic product P3 via a transition state TS3, for which the energy barrier is 168.8 kJ/mol. The energy of P3 is

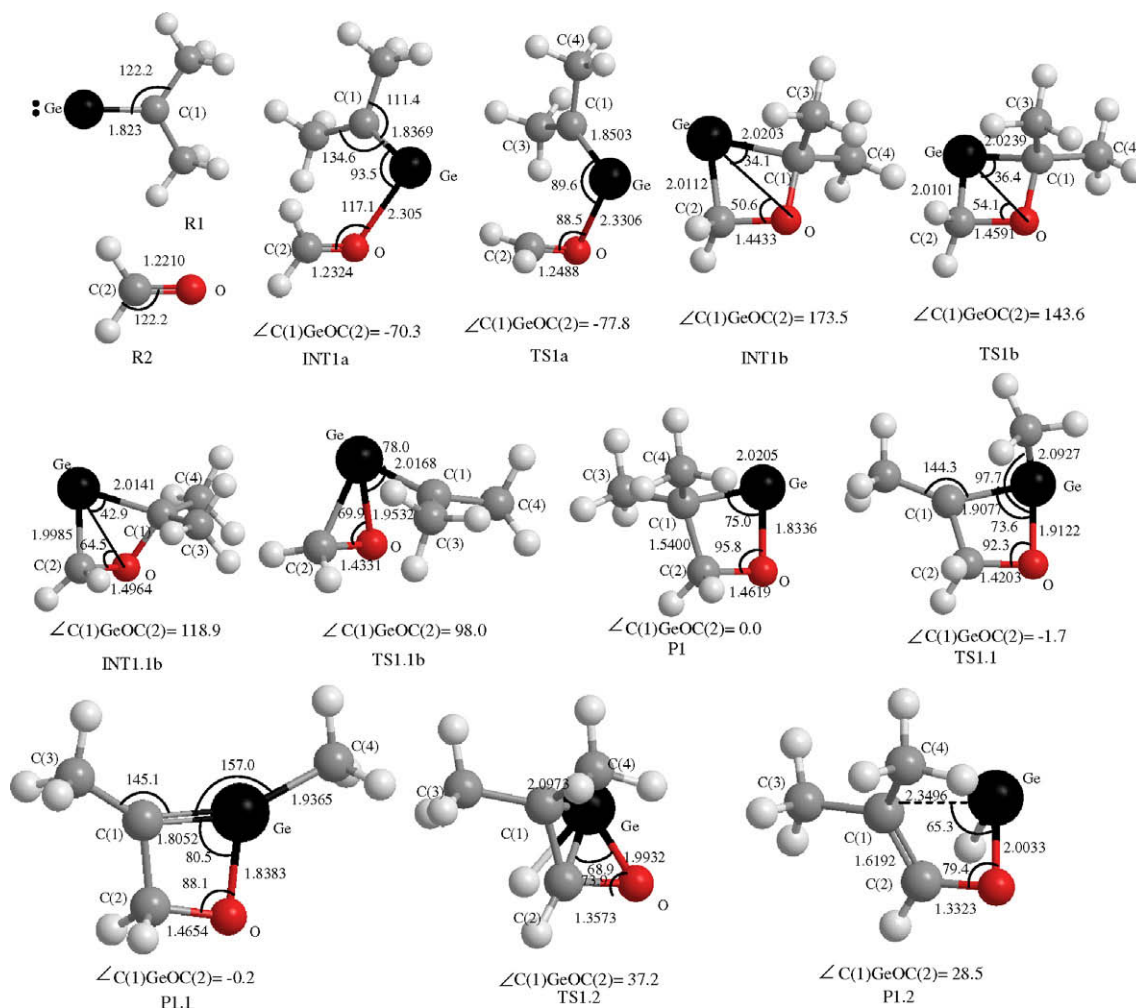


Fig. 1. Optimized MP2/6-31G\* geometrical parameters and the atomic numbering for the species in cycloaddition reaction (1). Bond lengths (Å) and angles (°).

22.1 kJ/mol higher than INT3, so, the reaction  $\text{INT3} \rightarrow \text{P3}$  is forbidden in thermodynamics, reaction will end in INT3.

#### 3.4. Reaction (4): channels of forming germanic bis-heterocyclic product P4

In reaction (4), the active four-membered ring intermediate INT1.1b further reacts with formaldehyde (R2) to form the germanic bis-heterocyclic product P4. The geometric parameters for the intermediate INT4, the transition state TS4 and the product P4 appearing in reaction (4) are given in Fig. 5.

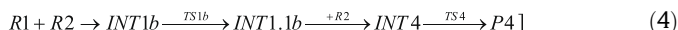
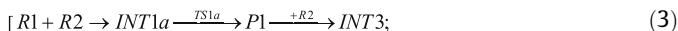
The energies are listed in Table 1. And the potential energy surface for reaction (4) is illustrated in Fig. 2. The unique imaginary frequency of the transition state TS4 is 261.7i, and the transition state can therefore be affirmed as the real one. IRC (with the step-length of  $0.1 \text{ amu}^{-1/2} \text{ bohr}$ ) analysis of TS4 confirms that TS4 connects INT4 and P4.

According to Fig. 2, the process of reaction (4) is as following: on the basis of INT1.1b created from the reaction (1) between R1 and R2, INT1.1b further reacts with formaldehyde (R2) to form the intermediate INT4 through a barrier-free exothermic reaction with  $\Delta E$  of 46.9 kJ/mol. Then, INT4 isomerizes to a germanic bis-heterocyclic product P4 via a transition state TS4, for which the barrier is 54.1 kJ/mol. According to Fig. 2, it is realizing that reaction (4) and  $\text{INT1.1b} \rightarrow \text{P1}$  in reaction (1) form a mutual competition reaction due to scrambling for INT1.1b together. In reaction (4), INT1.1b

and R2 form an intermediate INT4 just through a barrier-free exothermic reaction of 46.9 kJ/mol. However, INT1.1b isomerizes to P1 with an energy barrier of 141.7 kJ/mol. Compared the two reactions, it can be known that reaction (4) will be the dominant reaction channel.

#### 3.5. Theoretical analysis and explanation of the dominant reaction channels

According to the above analysis, reactions (3) and (4) should be the two dominant reaction channels of the cycloaddition reaction between singlet dimethyl germylidene and formaldehyde. namely:



Mulliken atomic charges of the species in the two dominant reaction channels are given in Fig. 6.

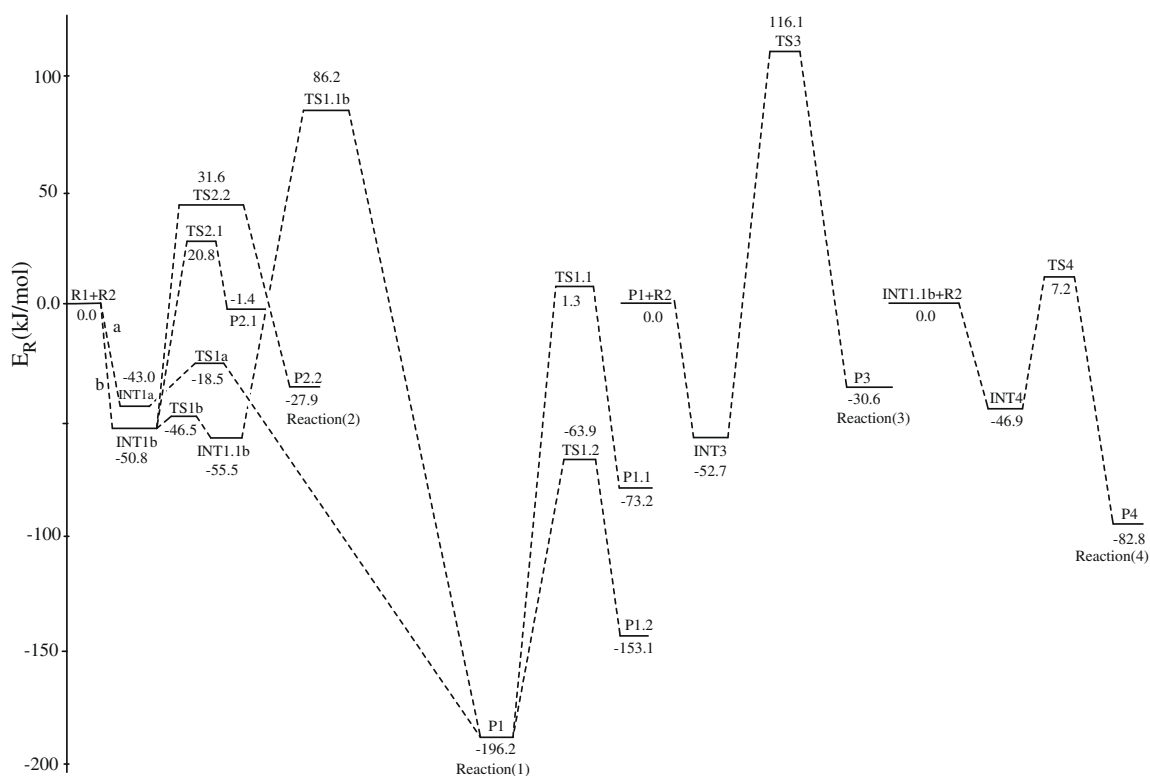
The mechanism of reaction (3) could be explained with the molecular orbital diagram (Figs. 7 and 8) and Figs. 1 and 4. According to Figs. 7 and 1, the carbonyl in formaldehyde is a polar group, and the electron clouds of the  $\pi$ -bond gather around the side of oxygen, when the dimethyl germylidene interacts with formaldehyde, the 4p unoccupied orbital of the Ge atom of dimethyl germylidene can react with the  $\pi$ -bond from the side of oxygen. Then the shift of  $\pi$ -electrons to the p unoccupied orbital gives a  $\pi \rightarrow \text{p}$

**Table 1**  
Total energies ( $E_T$ , a.u.) and relative energies ( $E_R$ , kJ/mol) for the species from various methods.

Reactions	Species	MP2/6-31G <sup>*</sup>		CCSD(T)//MP2/6-31G <sup>*</sup>	
		<sup>a</sup> $E_T$	<sup>b</sup> $E_R$	<sup>a</sup> $E_T$	<sup>b</sup> $E_R$
Reaction (1)	R1 + R2	-2304.80004	0.0	-2304.88846	0.0
	INT1a	-2304.81932	-50.6	-2304.90485	-43.0
	TS1a(INT1a-P1)	-2304.81081	-28.3	-2304.89551	-18.5
	INT1b	-2304.82213	-58.0	-2304.90782	-50.8
	TS1b(INT1b-INT1.1b)	-2304.82046	-53.6	-2304.90619	-46.5
	INT1.1b	-2304.82621	-68.7	-2304.90960	-55.5
	TS1.1b(INT1.1b-P1)	-2304.76576	90.0	-2304.85563	86.2
	P1	-2304.88104	-212.6	-2304.96320	-196.2
	TS1.1(P1-P1.1)	-2304.79575	11.3	-2304.88795	1.3
	P1.1	-2304.83842	-100.8	-2304.91634	-73.2
	TS1.2(P1-P1.2)	-2304.83189	-83.6	-2304.91278	-63.9
	P1.2	-2304.86606	-173.3	-2304.94677	-153.1
Reaction (2)	R1 + R2	-2304.80004	0.0	-2304.88846	0.0
	TS2.1	-2304.79172	21.8	-2304.88054	20.8
	P2.1	-2304.80244	-6.3	-2304.88897	-1.4
	TS2.2	-2304.79117	23.3	-2304.87642	31.6
	P2.2	-2304.81395	-36.5	-2304.89908	-27.9
Reaction (3)	P1 + R2	-2419.02150	0.0	-2419.12649	0.0
	INT3	-2419.04350	-57.8	-2419.14656	-52.7
	TS3(INT3-P3)	-2419.02366	-5.7	-2419.08229	116.1
	P3	-2419.04187	-53.5	-2419.13816	-30.6
Reaction (4)	INT1.1b + R2	-2418.96667	0.0	-2419.07289	0.0
	INT4	-2418.98467	-47.3	-2419.09075	-46.9
	TS4(INT4-P4)	-2418.96555	2.9	-2419.07015	7.2
	P4	-2419.00497	-100.6	-2419.10443	-82.8

<sup>a</sup>  $E_T = E$  (energy of electronic structure for the species) + ZPE (zero-point energy correction).

<sup>b</sup>  $E_R = E_T - E_{(R1+R2)}$ ,  $E_R = E_T - E_{(P1+R2)}$ ,  $E_R = E_T - E_{(INT1.1b+R2)}$ .



**Fig. 2.** The potential energy surface for the cycloaddition reactions between dimethyl germylidene and formaldehyde with CCSD(T)//MP2/6-31G<sup>\*</sup>.

donor–acceptor bond, leading to the formation of INT1a. As the reaction goes on, the  $\angle C(1)GeO$ (INT1a: 93.5°, TS1a: 89.6°, P1: 75.0°) gradually decrease, the Ge–C(1)(INT1a: 1.8369 Å, TS1a: 1.8503 Å, P1: 2.0205 Å) and C(2)–O(INT1a: 1.2324 Å, TS1a:

1.2488 Å, P1: 1.4619 Å) bond gradually elongate, which finally transforms the INT1a into the four-membered ring product P1 via the transition state TS1a. In the conformation of P1, Ge atom is unsaturated, so P1 may further react with formaldehyde(R2) to



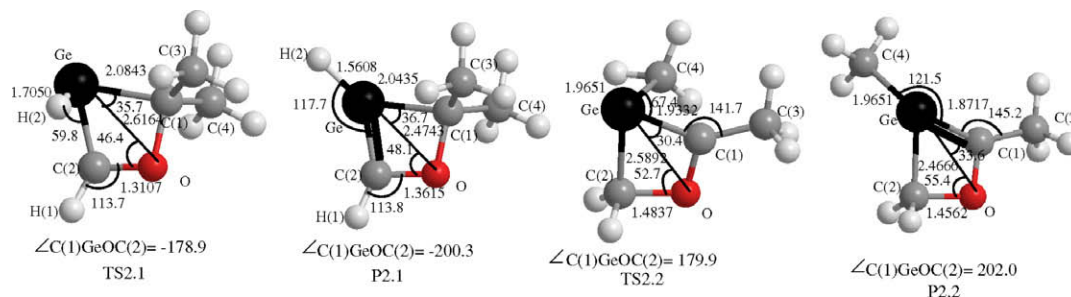


Fig. 3. Optimized MP2/6-31G\* geometrical parameters of TS2.1, P2.1, TS2.2, P2.2 and the atomic numbering for cycloaddition reaction (2). Bond lengths (Å) and angles ( $^\circ$ ).

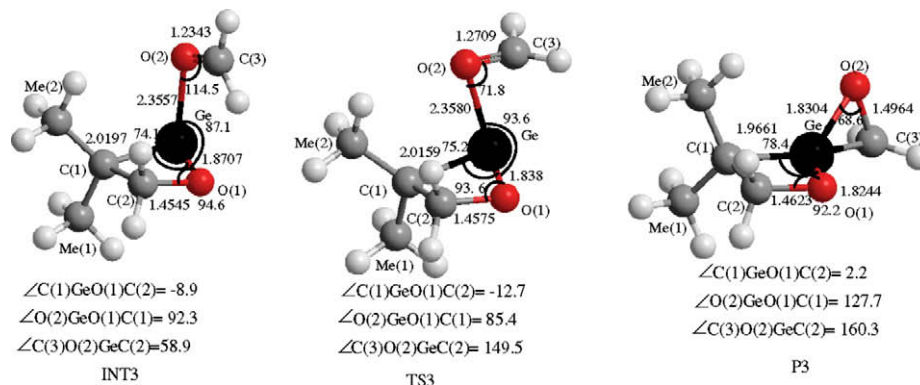


Fig. 4. Optimized MP2/6-31G\* geometrical parameters of INT3, TS3, P3 and the atomic numbering for cycloaddition reaction (3). Bond lengths (Å) and angles ( $^\circ$ ).

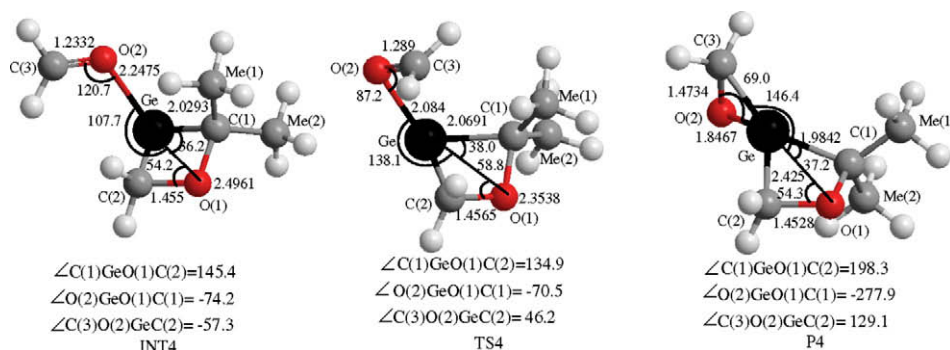


Fig. 5. Optimized MP2/6-31G\* geometrical parameters of INT4, TS4, P4 and the atomic numbering for cycloaddition reaction (4). Bond lengths (Å) and angles ( $^\circ$ ).

form germanic heterocyclic compound INT3. The mechanism of this reaction could be explained with the molecular orbital diagram (Fig. 8) and Fig. 4. According to orbital symmetry matching condition, when the P1 interacts with formaldehyde (R2), the 4p unoccupied orbital of the Ge atom of P1 can react with the  $\pi$ -bond from the side of oxygen, then the shift of  $\pi$ -electrons to the p unoccupied orbital gives a  $\pi \rightarrow p$  donor-acceptor bond, leading to the formation of germanic heterocyclic compound INT3.

The mechanism of reaction (4) could be explained with the molecular orbital diagram (Figs. 9 and 10) and Figs. 1 and 5. According to Figs. 9 and 1, as dimethyl germylidene initially interacts with formaldehyde, the [2+2] cycloaddition of the bonding  $\pi$ -orbitals firstly results in a planar four-membered ring intermediate INT1b. Due to the larger ring tension in INT1b, INT1b stores high energy, because of such energy, INT1b isomerizes to a twist four-membered ring intermediate INT1.1b via a transition state TS1b. In the conformation of INT1.1b, atom Ge is unsaturated. So, INT1.1b may further reacts with formaldehyde (R2) to form the germanic bis-heterocyclic product P4. The mechanism of this reac-

tion could be explained with the molecular orbital diagram (Fig. 10) and Fig. 5. According to orbital symmetry matching condition, when the active intermediate INT1.1b initially interacts with formaldehyde (R2), the 4p unoccupied orbital of the Ge atom of INT1.1b can react with the  $\pi$ -bond from the side of oxygen, then the shift of  $\pi$ -electrons to the p unoccupied orbital gives a  $\pi \rightarrow p$  donor-acceptor bond, leading to the formation of INT4. As the reaction goes on,  $\angle O(2)GeO(1)$  (INT4:  $107.7^\circ$ , TS4:  $138.1^\circ$ ),  $\angle C(3)O(2)GeC(2)$  (INT4:  $-57.3^\circ$ , TS4:  $46.2^\circ$ ) gradually increase, and  $\angle C(3)O(2)Ge$  (INT4:  $120.7^\circ$ , TS4:  $87.2^\circ$ ) gradually decrease, the O(2)–Ge (INT4: 2.248 Å, TS4: 2.084 Å) bond gradually shorten, and C(3)–O(2) (INT4: 1.233 Å, TS4: 1.289 Å) bond gradually elongate, the Ge in INT4 hybridizes to  $sp^3$  hybrid orbital after TS4, forming the germanic bis-heterocyclic product P5.

Compared the cycloaddition reaction between dimethyl germylidene and formaldehyde with the cycloaddition reaction [15] between germylidene and ethylene, we can know that, because of asymmetry of  $\pi$  bond in formaldehyde, the cycloaddition reaction between dimethyl germylidene and formaldehyde is more complex

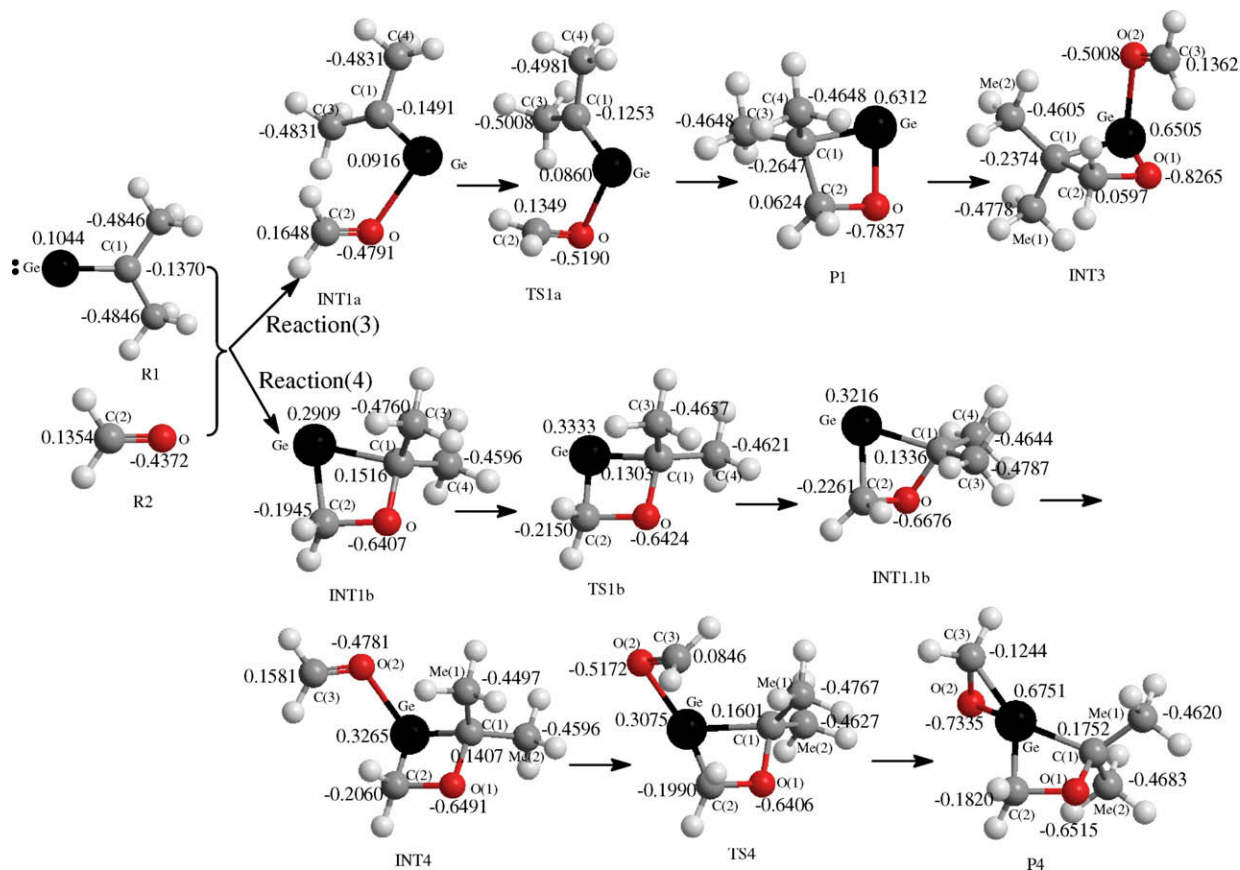


Fig. 6. Mulliken atomic charges of the species in the two dominant reaction channels of the cycloaddition reaction between singlet dimethyl germylidene and formaldehyde.

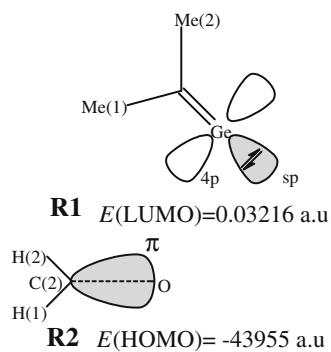


Fig. 7. MO symmetry-adaptation of  $\text{Me}_2\text{C}=\text{Ge}$ : and  $\text{H}_2\text{C}=\text{O}$  (R2).

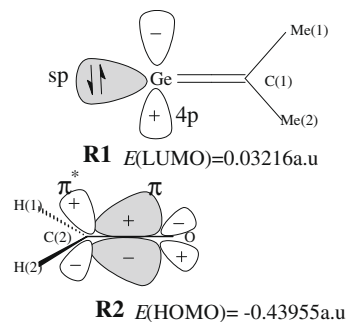


Fig. 9. MO symmetry-adaptation of  $\text{Me}_2\text{C}=\text{Ge}$ : and  $\text{H}_2\text{C}=\text{O}$  (R2).

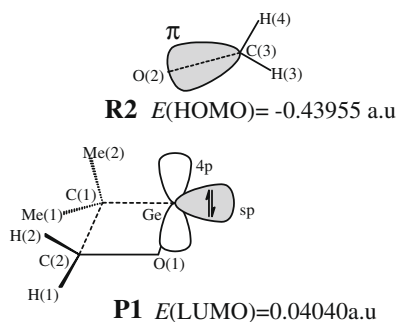


Fig. 8. Molecule orbital symmetry-adaptation of P1 and  $\text{H}_2\text{C}=\text{O}$  (R2).

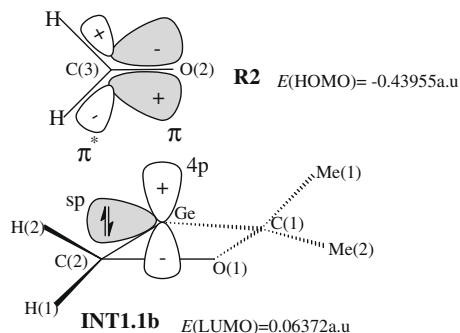


Fig. 10. Molecule orbital symmetry-adaptation of INT1.1b and  $\text{H}_2\text{C}=\text{O}$  (R2).

than the cycloaddition reaction between germylidene and ethylene. Only in terms of the dominant reaction channel, the cycloaddition reaction between dimethyl germylidene and formaldehyde has two dominant reaction channels, while the cycloaddition reaction between germylidene and ethylene has only one. The same point of the two reactions is that, whether it is the initial monocyclic intermediate or bicyclic intermediate, they are formed by that the 4p unoccupied orbital of the Ge atom in corresponding reactants insert into  $\pi$  orbit of formaldehyde (or ethylene). Further isomerization of these intermediates leads to the formation of the corresponding monocyclic and bicyclic products.

#### 4. Conclusion

On the basis of the potential energy surface obtained with the CCSD (T)//MP2/6-31G\* method for the cycloaddition reaction between singlet dimethyl germylidene and formaldehyde, it can be predicted that the two dominant reaction pathways of the cycloaddition reaction are reactions (3) and (4). Reaction (3) consists of three steps: (1) the two reactants (R1, R2) firstly form an intermediate INT1a through a barrier-free exothermic reaction of 43.0 kJ/mol; (2) INT1a then isomerizes to a four-membered ring compound P1 via a transition state TS1a with an energy barrier of 24.5 kJ/mol; (3) P1 further reacts with formaldehyde(R2) to form a germanic heterocyclic compound INT3, which is also a barrier-free exothermic reaction of 52.7 kJ/mol; The process of reaction (4) is as following: (1) the two reactants (R1, R2) firstly form a planar four-membered ring intermediate INT1b through

a barrier-free exothermic reaction of 50.8 kJ/mol; (2) INT1b then isomerizes to a twist four-membered ring intermediate INT1.1b via a transition state TS1b with an energy barrier of 4.3 kJ/mol; (3) INT1.1b further reacts with formaldehyde(R2) to form an intermediate INT4, which is also a barrier-free exothermic reaction of 46.9 kJ/mol; (4) INT4 isomerizes to a germanic bis-heterocyclic product P4 via a transition state TS4 with an energy barrier of 54.1 kJ/mol.

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