Ab Initio Study on the Mechanism of Forming a Germanic Hetero-Polycyclic Compound between Alkylidenegermylene and Ethylene

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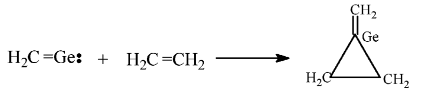
The mechanism of the cycloaddition reaction of forming a germanic hetero-polycyclic compound between singlet alkylidenegermylene and ethylene has been investigated with MP2/6-31G* method, including geometry optimization and vibrational analysis for the involved stationary points on the potential energy surface. The energies of the different conformations are calculated by CCSD(T)//MP2/6-31G* method. From the surface energy profile, it can be predicted that the dominant reaction pathway for this reaction consists of three steps: the two reactants first form a three-membered ring intermediate INT1 through a barrier-free exothermic reaction of 35.4 kJ/mol; this intermediate then isomerizes to an active four-membered ring product $P_{2.1}$ via a transition-state TS2.1 with a barrier of 57.6 kJ/mol; finally, $P_{2.1}$ further reacts with ethylene to form the germanic hetero-polycyclic compound P_3, for which the barrier is only 0.8 kJ/mol. The rate of this reaction path considerably differs from other competitive reaction paths, indicating that the cycloaddition reaction has an excellent selectivity.

1. Introduction

Germylene is a kind of quite unstable active intermediate.[1] A germylene reaction, which is a very active research field in organo-Ge chemistry, is regarded as an effective method in the synthesis of new bond and heterocyclic compounds with Ge.[2−5] Especially since many organo-Ge compounds are biochemically active, the reactions concerning germylenes have been the focus of research. In addition, it was reported that Herrmann et al.[6] had separated two kinds of stable germylenes, which can 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. We have done some research on the cycloaddition reaction between saturated germylenes and symmetric or asymmetric π-bonded compounds.[7,8] However, there is still no report on the cycloaddition reaction of unsaturated germylenes. To explore the rules of cycloaddition reaction between unsaturated germylenes and symmetric π-bonded compounds, alkylidenegermylene and ethylene were selected as model molecules, and its mechanism was investigated and analyzed theoretically in terms of the three possible pathways of cycloaddition reaction (considering the hydrogen transfer simultaneously) as follows:



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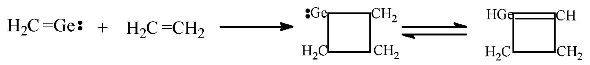

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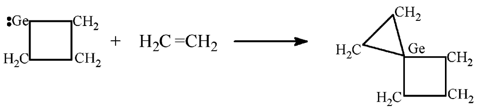

(3)

2. Calculation Methods

MP2/6-31G*[9] implemented in the Gaussian98 package is employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis is done for the stationary points on the reaction profile. Zero-point energy and CCSD(T) corrections are included for the energy calculations. To explicitly establish the relevant species, the intrinsic reaction coordinate (IRC)[10,11] was also calculated for all the transition states appearing on the cycloaddition energy surface profile.

3. Results and Discussions

3.1. Reaction 1: Three-Membered Ring Product Channel. The theoretical calculations indicate that the ground state of alkylidenegermylene is a singlet. The geometrical parameters for the intermediate INT1, transition-state TS1, and product P_1 appearing in reaction 1 between alkylidenegermylene (R_1) and ethylene (R_2) are given in Figure 1. The energies are listed in Table 1, and the potential energy surfaces for the cycloaddition reaction are given in Figure 2. The unique imaginary frequency of the transition-state TS1 is -312.2 cm^{-1} and the transition state can therefore be affirmed as the real one. According to the calculation of the IRC of TS1 and further optimization for the primary IRC results, TS1 connects INT1 and P_1.

According to Figure 2, it can be directly seen that reaction 1 consists of two steps: the first one is a barrier-free exothermic reaction of 35.4 kJ/mol, resulting in an intermediate INT1; then, INT1 isomerizes to a three-membered ring product P_1 with a barrier of 87.0 kJ/mol.

3.2. Reaction 2: Four-Membered Ring Product Channel. The geometric parameters for the transition-states (TS2.1, TS2.2) and products ($P_{2.1}$, $P_{2.2}$) appearing in reaction 2 between alkylidenegermylene and ethylene are given in Figure 3. The energies are listed in Table 1. The potential energy surface for reaction 2 is illustrated in Figure 2.

The unique imaginary frequencies of the transition-states TS2.1 and T S2.2 are -422.0 and -984.7 cm^{-1}, respectively,

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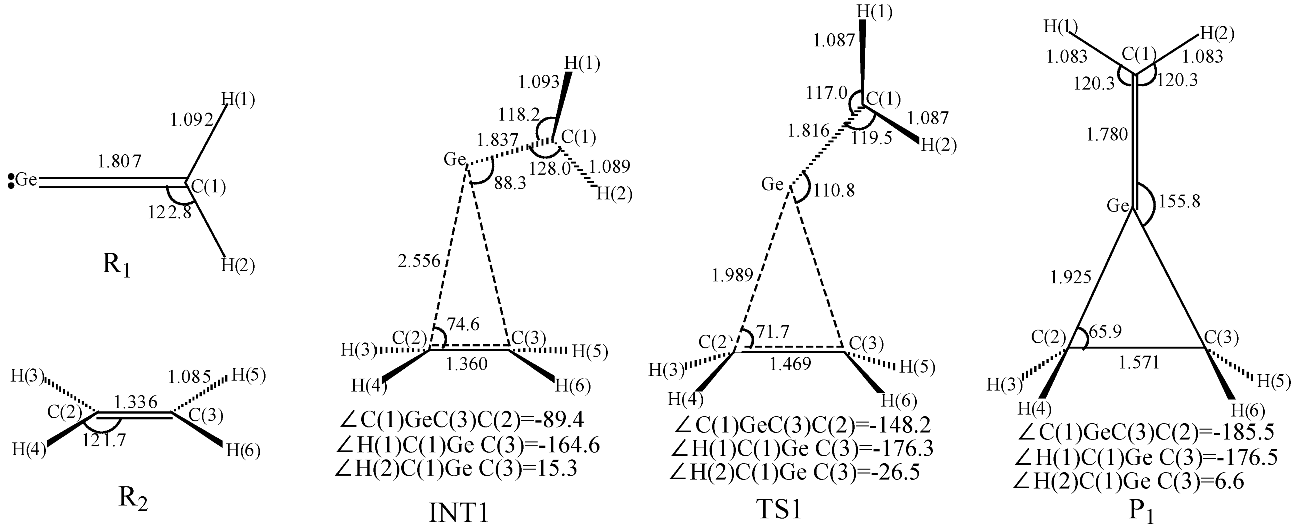

Figure 1. Optimized MP2/6-31G* geometrical parameters and atomic numbering for the species in cycloaddition reaction 1. Bond lengths and angles are in Å and in deg.

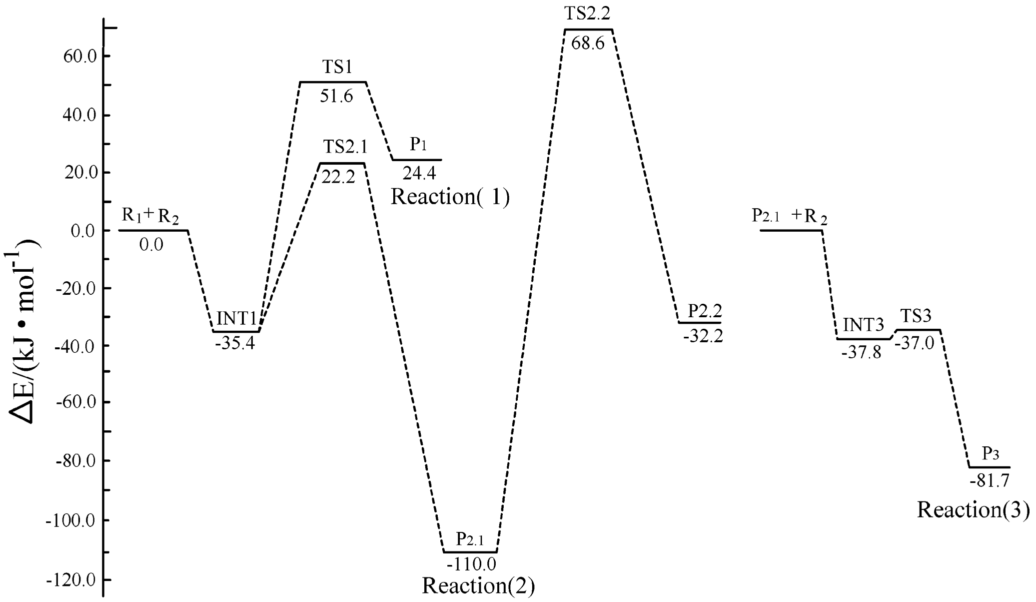

Figure 2. The potential energy surface for the cycloaddition reactions between alkylidenegermylene and ethylene with CCSD(T)//MP2/6-31G*.

and therefore the two transition states can be affirmed as the real ones. According to the calculations of the IRC of TS2.1 and TS2.2 and the further optimization of the primary IRC results, TS2.1 connects INT1 and $P_{2.1}$, and TS2.2 connects $P_{2.1}$ and $P_{2.2}$.

It can be directly seen from Figure 2 that reaction 2 consists of three steps: the first one is a barrier-free exothermic reaction of 35.4 kJ/mol, leading to an intermediate INT1, which then isomerizes to a four-membered ring product $P_{2.1}$ via a transition-state TS2.1 with a barrier of 57.6 kJ/mol, and finally the product $P_{2.1}$ isomerizes to product $P_{2.2}$ via a transition-state TS2.2 with a barrier of 178.6 kJ/mol, which results from the hydrogen transfer. With so high a barrier and the energy of TS2.2 being 68.6 kJ/mol higher than that of the two reactants, the third step of reaction 2 is quite difficult to achieve at room temperature, and the reaction 2 in fact ends in the product $P_{2.1}$. The reason is the quite long separation between C(1) and Ge (2.016 Å) and short separation between C(1) and H(2) (1.100 Å) in P2.1, which makes it quite difficult for H(2) to transfer from C(1) to Ge.

TABLE 1: Total Energies (E_T, au) and Relative Energies (E_R, kj·mol^{-1}) for the Species Obtained with Different Theoretical Methods

	MP2/6-31G*		CCSD(T)//MP2/6-31G*	
species	E_T[a]	E_R[b]	E_T	E_R
	Reaction 1 and Reaction 2			
$R_1 + R_2$	−2190.61361	0.0	−2190.68634	0.0
INT1	−2190.63214	−48.7	−2190.69984	−35.4
TS1(INT1−P_1)	−2190.60079	33.7	−2190.66667	51.6
P_1	−2190.61407	−1.2	−2190.67705	24.4
TS2.1(INT1−$P_{2.1}$)	−2190.61413	−1.4	−2190.67790	22.2
$P_{2.1}$	−2190.66403	−132.4	−2190.72822	−110.0
TS2.2($P_{2.1}$−$P_{2.2}$)	−2190.58667	70.7	−2190.66020	68.6
$P_{2.2}$	−2190.63695	−61.3	−2190.69861	−32.2
	Reaction 3			
$P_{2.1}$ + ethylene (R_2)	−2268.89702	0.0	−2268.99811	0.0
INT3	−2268.91562	−48.8	−2269.01250	−37.8
TS3(INT3−P_3)	−2268.91532	−48.0	−2269.01220	−37.0
P_3	−2268.93884	−109.8	−2269.02923	−81.7

[a] $E_T = E$energy electronic structure for the species+ ZPE (zero-point energy correction). [b] $E_R = E_T - E(R_1 + R_2)$.

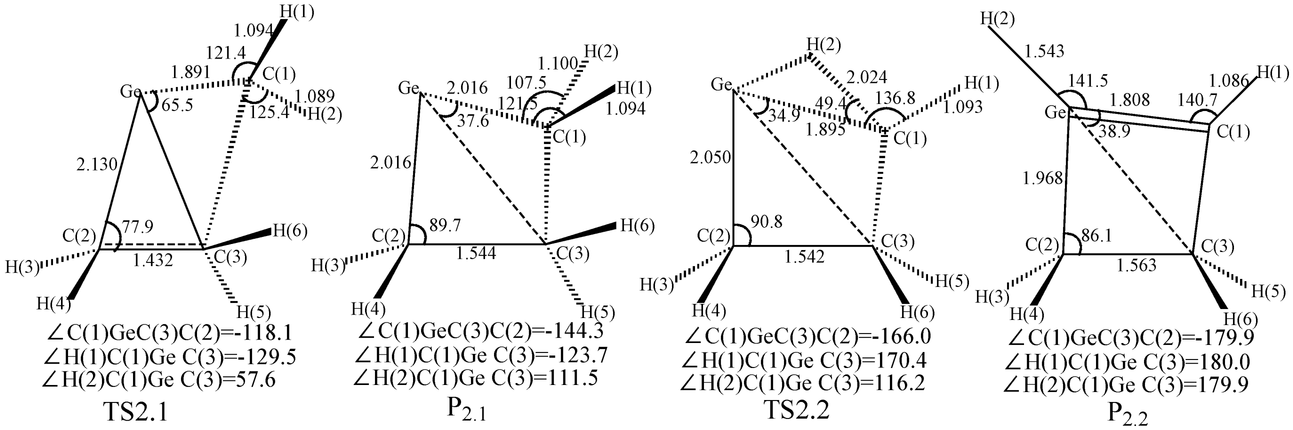

Figure 3. Optimized MP2/6-31G* geometrical parameters of TS2.1, $P_{2.1}$, TS2.2, $P_{2.2}$, and atomic numbering for cycloaddition reaction 2. Bond lengths and angles are in Å and in deg.

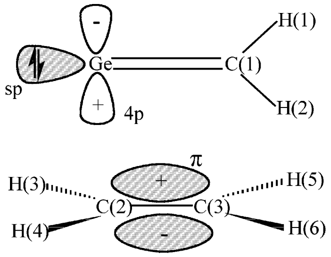

Figure 4. Frontier molecular orbital (MO) symmetry adaption of $H_2C{=}Ge$ and C_2H_4.

Reactions 1 and 2 compete with each other. Figure 2 shows that the energy of the transition-state TS1 in reaction 1 is 29.4 kJ/mol higher than that of the transition-state TS2.1 in reaction 2. According to the exponential law of reaction rate [$k = A\exp(-E_a/RT)$] (A is assumed to be approximately equal), the reaction rate from TS2.1 to $P_{2.1}$ is approximately 1.4×10^5 times as fast as that from TS1 to P_1 at room temperature (298 K), and thus, reaction 2 will be the dominant reaction. In other words, the dominant reaction is in fact a reaction of forming an active four-membered ring product $P_{2.1}$. The mechanism of reaction can be explained with the frontier molecular orbitals (Figure 4) and Figures 1 and 3. The combination of the unoccupied 4p orbital of the Ge atom of alkylidenegermylene with the π orbital of ethylene gives a $\pi \rightarrow$ P donor−acceptor bond, forming a three-membered ring intermediate INT1 as alkylidenegermylene initially interacts with ethylene. We have done careful potential energy surface scan for the formation of INT1. The results show that the formation of INT1 is a barrier-free exothermic reaction, which is probably due to the strong bonding effect of the 4p unoccupied orbital of Ge atom of alkylidenegermylene with the π-bonded electron cloud of ethylene. With the reaction going on, the dihedral angles ∠C(1)GeC(3)C(2) (INT1: −89.4°, TS2.1: −118.1°, $P_{2.1}$: −144.3°) and ∠C(3)C(2)Ge (INT1: 74.6°, TS2.1: 77.9°, $P_{2.1}$: 89.7°) gradually increase and the ∠C(1)GeC(3) (INT1: 88.3°, TS2.1: 65.5°, $P_{2.1}$: 37.6°) gradually decreases, which finally transforms the INT1 into the twisted four-membered ring product $P_{2.1}$ via the transition-state TS2.1. In the conformation of $P_{2.1}$, the combination between alkylidenegermylene and ethylene mainly depends on the [2+2] cycloaddition of the two π bonds. Since the sp lone electron pair and the 4p unoccupied orbital on Ge atom do not participate in bond formation, $P_{2.1}$ is still an active intermediate. It is not difficult to predict that $P_{2.1}$ can further react with ethylene to form a polycyclic compound.

3.3. Reaction 3: Polycyclic Product Channel. In reaction 3, the active four-membered ring compound $P_{2.1}$ further reacts with ethylene to form the germanic hetero-polycyclic product P_3. The geometric parameters for the intermediate INT3, transition-state TS3, and product P_3 appearing in reaction 3 are given in Figure 5. The energies are listed in Table 1. The potential energy surface for reaction 3 is illustrated in Figure 2.

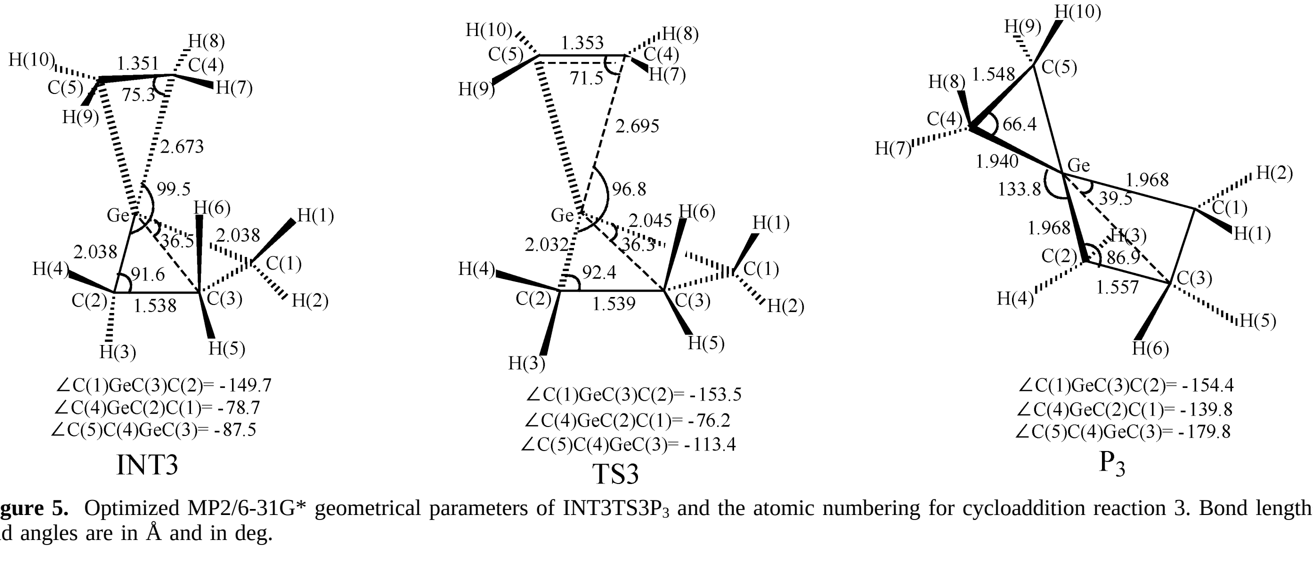

Figure 5. Optimized MP2/6-31G* geometrical parameters of INT3TS3P_3 and the atomic numbering for cycloaddition reaction 3. Bond lengths and angles are in Å and in deg.

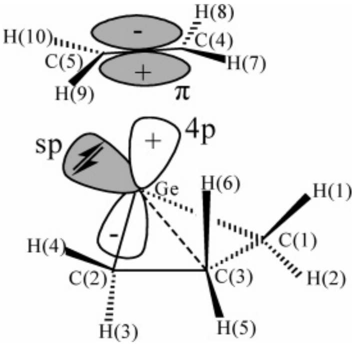

Figure 6. MO symmetry adaption of $P_{2.1}$ and $H_2C{=}CH_2$.

The unique imaginary frequency of the transition-state TS3 is $-67.6\ cm^{-1}$, and the transition state can therefore be affirmed as the real one. According to the calculation of the IRC of TS3 and further optimization for the primary IRC results, TS3 connects INT3 and P_3.

According to Figure 2, reaction 3 consists of two steps: the first one is a barrier-free exothermic reaction of 37.8 kJ/mol, resulting in an intermediate INT3; the second one is the isomerization of INT3 to a polycyclic product P_3 via a transition-state TS3 with a quite small barrier of 0.8 kJ/mol. With so small a barrier and the energy of P_3 being 81.7 kJ/mol lower than that of the total energy of $P_{2.1}$ and R2, it is obvious that reaction 3 is very easy to achieve. The mechanism of reaction 3 can be explained with the frontier molecular orbital (Figure 6) and Figures 3 and 5. The combination of the unoccupied 4p orbital of the Ge atom of $P_{2.1}$ with the π orbital of ethylene gives a $\pi \rightarrow$ P donor−acceptor bond, forming an intermediate INT3 as $P_{2.1}$ initially interacts with ethylene. The formation of INT3 is similar to that of INT1, which mainly results from the strong bonding effect of 4p unoccupied orbital of Ge atom of $P_{2.1}$ with the π-bonded electron cloud of ethylene. In the conformation of INT3, the sp lone electron pair on Ge does not participate in bond formation, which makes INT3 to be in the state of quite high energy. With the reaction going on, the bond length of C(4)−Ge (INT3: 2.673 Å, P3: 1.940 Å) gradually shortens, the dihedral angle ∠C(5)C(4)GeC(3) (INT3: −87.5°, TS3: −113.4°, P_3: −179.8°) gradually increases and the bond length of C(4)−C(5) (INT3: 1.351 Å, TS3: 1.353 Å, P_3: 1.548 Å) gradually stretches, which transforms INT3 into more stable polycyclic product P_3. In the conformation of P_3, the sp lone electron pair and unoccupied p orbital on Ge atom react with the antibonding unoccupied π^* orbital on C(5) end and the π-bonded electron cloud on C(4) end, respectively, forming the circular donor−acceptor bonds of SP $\rightarrow \pi^*$ and $\pi \rightarrow$ P [bond order value of C(4)−Ge: 0.32362, bond order value of C(5)−Ge: 0.31759]. According to the molecular orbital theory, this kind of bonding effect can be shown in Figure 7. In the conformation of P_3, there are no longer any sp lone pair electrons and unoccupied p orbital on the Ge, which is also the original driving force for $P_{2.1}$ further reacting with ethylene to form the product P_3.

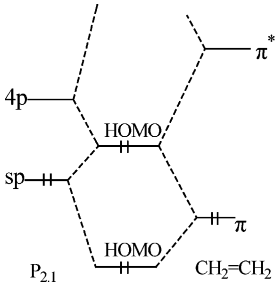

Figure 7. A schematic interaction diagram for the frontier orbitals of $P_{2.1}$ and $H_2C{=}CH_2$.

4. Conclusion

On the basis of the surface energy profile obtained with the CCSD(T)//MP2/6-31G* method for the cycloaddition reaction between singlet alkylidenegermylene and ethylene, it can be predicted that the dominant reaction pathway of this reaction consists of three steps: the two reactants first form a three-membered ring intermediate INT1 through a barrier-free exothermic reaction of 35.4 kJ/mol; this intermediate then isomerizes to an active four-membered ring product $P_{2.1}$ via a transition-state TS2.1 with a barrier of 57.6 kJ/mol; finally, $P_{2.1}$ further reacts with ethylene to form the germanic hetero-polycyclic product P_3, for which the barrier is only 0.8 kJ/mol. The rate of this reaction path considerably differs from other competitive reaction paths, indicating that the cycloaddition reaction has an excellent selectivity.

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